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DEVELOPMENT AND EVALUATION OF HETEROGENEOUS CATALYSTS FOR THE REFORMING OF METHANE-RICH GASES TO SYNTHESIS GAS

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Abstract

Through the Dry Reforming of Methane (DRM), two abundant greenhouse gases ($\text{CH}_4 + \text{CO}_2$) are transformed into syngas ($\text{H}_2 + \text{CO}$). This syngas ($+ \text{H}_2$) could be utilized to produce key chemicals like methanol and ammonia, disclosing the potential of the DRM to solve current environmental concerns. Despite being promising, DRM still faces challenges to overcome, mostly related to catalyst deactivation over time via coking, sintering of the active sites and oxidation of these under the high operation temperatures needed. The previous relates to the high stability of both reactants, the transformation of which is highly-energy demanding. Thus, the appropriate implementation of DRM would only be possible through the development of cost-effective catalysts, which also display high activity and stability. For this purpose, several low-loading Ni formulations (2.5 wt.% Ni) supported on $\text{MgO-Al}_2\text{O}_3$ mixed oxides were investigated throughout this work, focusing on enhancing their catalytic performance and preventing deactivation via the different mechanisms. The prepared catalysts were thoroughly studied using solid-state characterization techniques to identify structure-activity relationships.

Specific physicochemical properties of the catalysts were finely tuned by the selection of the preparation and activation conditions. For example, the metal-support interaction (MSI), the distribution of Ni particles on the catalysts' surface, and the catalysts' redox properties were in the spotlight during catalyst development, aiming to enhance their performance and to prevent their deactivation. Specifically, the impacts of the support's MgO content of commercial $\text{MgO-Al}_2\text{O}_3$ supports on the catalysts' activity and coke deposition properties were firstly investigated. By next, and as a follow up to previous work performed in our group [1], the impregnation pH of citric acid-assisted preparations was tuned to enhance the catalysts' physicochemical properties, and by doing so, their activity and stability. Then, different chelating agents (citric, diethylenetriaminepentaacetic and tartaric acids, the same as glycine) were used to assist the wet impregnation of Ni precursors, aiming to promote a finer distribution of the Ni active sites and to strengthen their MSI, and thus, the catalysts' activity and stability. Finally, different bi-/trimetallic formulations were investigated (bimetallic: Ga^{3+} , Ce^{4+} ; trimetallic: $\text{La}^{3+} + \text{Ga}^{3+}$ and $\text{Gd}^{3+} + \text{Sc}^{3+}$), aiming to tune the chemical (and electronic) properties of the catalysts both at their surface and bulk, and to modify MSI, distribution of Ni species and to improve the catalysts' performance.

Despite the improvements made on commercial supports, coke deposition, particle sintering, and oxidation of the active sites were hardly avoided. To enhance catalyst performance and to prevent their deactivation over time, an enhanced home-made $\text{MgO-Al}_2\text{O}_3$ support was developed, which improved the activity of selected catalysts, but most importantly, these displayed exceptional resistance against deactivation. Such improvements were rationalized through rigorous catalyst characterization.

Afterwards, CH_4 -rich feeds ($\text{CH}_4/\text{CO}_2 = 2:1$) were reformed to evaluate the feasibility of using the developed catalysts to valorize biogas as alternative feedstock via reforming reactions. The significance of the latter lies with the simultaneous mitigation of greenhouse gas emissions, and the transformation of renewable carbon sources (i.e., waste-derived biogas) into valuable syngas for downstream applications. Deeper investigations on the valorization of CH_4 -rich feeds were done via other oxidative reforming reactions: the Bi- and Tri-Reforming of Methane (BRM and TRM), which utilize $\text{CO}_2 + \text{H}_2\text{O}$, or $\text{CO}_2 + \text{H}_2\text{O} + \text{O}_2$ as oxidants, respectively. The latter focused on enhancing the produced H_2/CO ratio by means of process variants, without injecting external H_2 to the syngas produced via DRM. The obtained H_2 -rich syngas could then be used, e.g., in the production of fuels via Fischer-Tropsch synthesis.

Finally, reforming CH_4 -rich feeds with the main catalysts' poisons present in biogas (i.e., NH_3 or H_2S) was investigated using the developed catalyst, to work under conditions closer to real applications. The latter was accompanied by the development of regeneration strategies after catalyst deactivation. All the previous was done to develop non-noble and low-Ni loading catalysts for the industrialization of the reforming of waste-derived biogas, and to contribute to a circular carbon economy and to provide sustainable energy solutions.

Zusammenfassung

Durch Trockenreformierung von Methan (DRM) werden die Treibhausgase $\text{CH}_4 + \text{CO}_2$ in Synthesegas ($\text{H}_2 + \text{CO}$) umgewandelt. Letzteres ($+ \text{H}_2$) könnte zur Herstellung von Basischemikalien wie Methanol und Ammoniak verwendet werden, und zeigt das Potenzial der DRM zur Lösung aktueller Umweltprobleme. Dennoch gibt es noch einige Herausforderungen zu bewältigen, die hauptsächlich mit der Deaktivierung des Katalysators durch Verkokung, Versinterung der aktiven Stellen und deren Oxidation bei den erforderlichen hohen Betriebstemperaturen zusammenhängen, die wegen der hohen Stabilität der beiden Reaktanten sehr energieaufwendig ist. Die angemessene Umsetzung von DRM wäre daher nur durch die Entwicklung kostengünstiger Katalysatoren möglich, die zudem eine hohe Aktivität und Stabilität aufweisen. Hierzu wurden in dieser Arbeit mehrere Ni-Formulierungen mit geringer Beladung (2,5 Gew.-% Ni) auf $\text{MgO-Al}_2\text{O}_3$ -Mischoxiden untersucht, wobei der Schwerpunkt auf der Verbesserung der katalytischen Leistung und der Verhinderung der Deaktivierung lag. Die hergestellten Katalysatoren wurden mithilfe von Festkörpercharakterisierung gründlich untersucht, um Struktur-Aktivitäts-Beziehungen zu ermitteln.

Die physikalisch-chemischen Eigenschaften der Katalysatoren wurden durch Wahl der Herstellungs- und Aktivierungsbedingungen abgestimmt. So standen beispielsweise die Metall-Träger-Wechselwirkung (MSI), die Verteilung der Ni-Partikel auf der Oberfläche der Katalysatoren und die Redox-Eigenschaften im Mittelpunkt der Katalysatorentwicklung, um ihre Leistung zu verbessern und ihre Deaktivierung zu verhindern. Insbesondere wurden zunächst die Auswirkungen des MgO -Gehalts des Trägers von handelsüblichen $\text{MgO-Al}_2\text{O}_3$ -Trägern auf die Aktivität der Katalysatoren und die Eigenschaften der Koksabscheidung untersucht. In Anlehnung an frühere Arbeiten unserer Gruppe [1] wurde der pH-Wert der Imprägnierung mit Zitronensäure eingestellt, um die physikochemischen Eigenschaften der Katalysatoren und damit ihre Aktivität und Stabilität zu verbessern. Anschließend wurden weitere Chelatbildner (Diethylentriaminpentaessigsäure und Weinsäure, ebenso wie Glycin) zur Unterstützung der Nassimprägnierung von Ni-Vorläufern verwendet, um eine feinere Verteilung der aktiven Ni-Stellen zu fördern und deren MSI und damit die Aktivität und Stabilität der Katalysatoren zu stärken. Schließlich wurden verschiedene bi-/trimetallische Formulierungen untersucht (bimetallisch: Ga^{3+} , Ce^{4+} ; trimetallisch: $\text{La}^{3+}+\text{Ga}^{3+}$ und $\text{Gd}^{3+}+\text{Sc}^{3+}$), um die chemischen und elektronischen Eigenschaften der Katalysatoren sowohl an der Oberfläche als auch in der Masse abzustimmen.

Trotz der Verbesserungen, die an kommerziellen Trägern vorgenommen wurden, konnten Koksablagerungen, Partikelsinterung und Oxidation der aktiven Stellen kaum vermieden werden. Um die Leistung der Katalysatoren zu erhöhen und ihre Deaktivierung im Laufe der Zeit zu verhindern, wurde ein selbst hergestellter $\text{MgO-Al}_2\text{O}_3$ -Träger entwickelt, der zu aktiveren Katalysatoren führte, vor allem aber eine außergewöhnliche Resistenz gegen Deaktivierung aufwies. Diese Verbesserungen wurden durch eine rigorose Charakterisierung des Katalysators interpretiert. Anschließend wurden CH_4 -reiche Modellgase ($\text{CH}_4/\text{CO}_2 = 2:1$) verwendet, um die Effizienz der entwickelten Katalysatoren zur Veredelung von Biogas als alternativem Einsatzstoff für das DRM zu bewerten.

Vertiefende Untersuchungen zur Veredelung CH_4 -reicher Gase wurden über andere Reformierungs-Varianten durchgeführt: das Bi- und Tri-Reforming von Methan (BRM und TRM) mit $\text{CO}_2+\text{H}_2\text{O}$ bzw. $\text{CO}_2+\text{H}_2\text{O}+\text{O}_2$ als Oxidationsmittel. Letzteres konzentrierte sich auf die Erhöhung des erzeugten H_2/CO -Verhältnisses, ohne dass externes H_2 zu dem mittels DRM erzeugte Synthesegas beigemischt wird. Das erhaltene H_2 -reiche Synthesegas könnte z. B. bei der Herstellung von Kraftstoffen verwendet werden.

Schließlich wurde die Reformierung von CH_4 -reichen Gasen mit den wichtigsten Katalysatorgiften in Biogas (NH_3 , H_2S) am besten Katalysator unter anwendungsnahen Bedingungen untersucht. Dabei wurden Regenerationsstrategien nach der Deaktivierung des Katalysators verglichen.

All dies geschah mit dem Ziel, unedle Katalysatoren mit niedriger Ni-Beladung zu entwickeln, um die Reformierung von aus Abfällen gewonnenem Biogas zu industrialisieren und einen Beitrag zu einer kreislauforientierten Kohlenstoffwirtschaft und zu nachhaltigen Energielösungen zu leisten.

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List of abbreviations

(S)TEM: (Scanning) Transmission Electronic Microscopy

ATR: Autothermal Reforming of Methane

BET: Brunauer-Emmet-Teller (Isothermal N₂ Adsorption at Low Temperature)

BF: Bright-Field

BID: Barrier Discharge Ionization Detector

BRM: Bi-Reforming of Methane

c.a.: Complexing Agent

CA: Citric Acid

CCS(U): CO₂ Capture and Storage (and Utilization)

CHNS: Quantification of Carbon, Hydrogen, Nitrogen and Sulfur (via Oxidation)

CNT: Carbon Nanotube

COS: Carbonyl Sulfide

CO₂-TPD: CO₂ Temperature-Programmed Desorption

CP: Home-made MgO-Al₂O₃ Prepared Using the Co-Precipitation Method Calcined at 550 °C

DME: Dimethyl Ether

DRM: Dry Reforming of Methane

DTPA: Diethylenetriaminepentaacetic Acid

EDTA: Ethylenediaminetetraacetic Acid

EPR: Electronic Paramagnetic Resonance Spectroscopy

Eq.: Equation

FA: Formic Acid

FT: Fischer-Tropsch

GC: Gas Chromatography

GHG: Greenhouse Gas

GHSV: Gas Hourly Space Velocity

Gly: Glycine

H₂-TPR: H₂ Temperature-Programmed Reduction

HAADF: High-Angle Annular Dark-Field

HAc: Acetic Acid

HOMO: Highest Occupied Molecular Orbital

HPLC: High Performance Liquid Chromatography

HT: Home-made MgO-Al₂O₃ Prepared Using the Hydrothermal Method Calcined at 550 °C

HTC: Hydrotalcite

ICDD: International Center for Diffraction Data

ICP-OES: Inductively Coupled Plasma – Optical Emission Spectroscopy

L: Ligand

MeOH: Methanol

MS: Mass Spectrometry

MSI: Metal-Support Interaction

O₂-TPO: O₂ Temperature-Programmed Oxidation

p: Pressure

POM: Partial Oxidation of Methane

PZC: Point of Zero Charge

RDS: Rate-Determining Step

REM: Rare-Earth Metal

RWGS: Reverse Water Gas Shift Reaction

S1: Calcined Commercial Pural MG30 (Sasol, GmbH) at 550 °C

S2: Calcined Commercial Pural MG50 (Sasol, GmbH) at 550 °C

S2.800: Calcined Commercial Pural MG50 (Sasol, GmbH) at 800 °C

S3: Calcined Commercial Pural MG63 (Sasol, GmbH) at 550 °C

S4: Calcined Commercial Pural MG70 (Sasol, GmbH) at 550 °C

S/C: Steam-to-Carbon Ratio

SCC: Synthetic Carbon Cycle

SEA: Strong Electrostatic Adsorption

SMSI: Strong Metal-Support Interaction

SRM: Steam Reforming of Methane

Syngas: Synthesis Gas

T: Temperature

TA: Tartaric Acid

TOS: Time on Stream

T_{ox}: Oxidation Temperature

T_{red}: Reduction Temperature

TRM: Tri-Reforming of Methane

UH: Home-made MgO-Al₂O₃ Prepared Using Urea-Assisted Hydrothermal Method Calcined at 550 °C

vol.%: Volume Percentage

WI.800: Home-made MgO-Al₂O₃ Prepared Using Wet Impregnation Calcined at 800 °C

wt.%: Weight Percentage

X_i: Conversion of Component 'i'

XPS: X-Ray Photoelectron Spectroscopy

XRD: X-Ray Diffraction

1. Introduction, Motivation and Objectives

1.1 Introduction

One of the central challenges of our era is redesigning established processes based on conventional hydrocarbons to produce energy and added-value chemicals, while decreasing the environmental deterioration. Besides, these alternative processes should also ensure the food, energy, and environmental security at the same time. Historically, fossil fuels (coal, oil and natural gas) have been used to produce energy (both on industrial and household scales) and high added-value products (fuels, plastics, etc.), which consequently emit greenhouse gases (GHG), predominantly CO_2 , CH_4 , NO_x , among others [2]. These GHG are mostly released into the atmosphere without adequate disposal treatment, causing environmental pollution, the impacts of which have been thoroughly discussed in the literature [3]. Apart from the contamination, the intensive exploitation is causing the depletion of the reserves of fossil fuels, which is another growing concern. Currently, the proposed approaches towards a ‘greener’ and more sustainable economy are mostly focusing on alternative and renewable carbon (such as biomass, bioethanol, biomethanol, etc.) and energy (wind, solar, geothermal, H_2 , etc.) sources to reduce the overall environmental impacts [4]. Thus, the vast availability of CH_4 and CO_2 and their potential to be transformed into versatile syngas (mixture of $\text{H}_2 + \text{CO}$) enables them to be used for the production of chemicals and fuels through alternative processes [5-7]. Therefore, their economic and environmental potential is clearly unveiled.

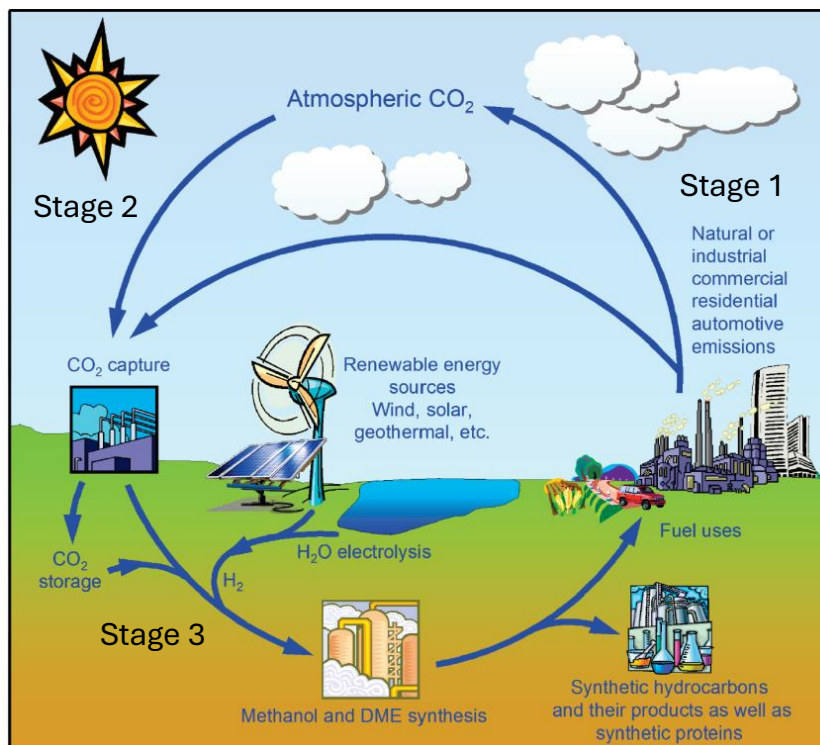


Figure 1-1. Schematic representation of the Synthetic Carbon Cycle (SCC). Reprinted with permission from [4]. Copyright 2011 American Chemical Society.

The whole picture contemplating the emission (Stage 1), capture (Stage 2) and reutilization (Stage 3) of these C-sources (especially CO_2) based on renewable and low carbon footprint energy is known as the Synthetic Carbon Cycle (SCC), which is depicted in Figure 1-1. Obviously, as there is accumulation of the GHG in the atmosphere, a disbalance between the emission rates and reutilization of these GHG exists. The previous suggests that new technological approaches should be developed to compensate the emissions of GHG with their reutilization, i.e., to close the SCC, although it is still challenging [4].

On the first place, the emission of both CO₂ and CH₄ are discussed to be the core of the problem. In this sense, the most abundant GHG is the CO₂, the concentration of which has increased historically along the economic development (atmospheric CO₂ concentration ~ 420 ppm in August, 2024) [8]. The main anthropogenic emitters of CO₂ are classified in static and mobile sources, being the first ones: the combustion plants of fossil fuels to produce energy and heat, the so-called ‘heavy industry’ (production of cement, aluminum, etc.) and the agriculture and housing sectors, while the transportation sector is considered as the only mobile source, which toxic emissions are due to the combustion of conventional fuels [9, 10]. On the other hand, the main emitters of anthropogenic CH₄ are mostly static, being intensive animal farming (fermentative digestion of ruminants), anaerobic decomposition of organic matter (for example, biomass or organic waste) and the intensive application of fertilizers the predominant ones [11, 12]. The same as for CO₂, the environmental CH₄ concentration has also increased over the course of the human industrial history (atmospheric CH₄ concentration ~ 1921 ppb in July, 2024) [13]. Besides, large amounts of CH₄ can be found in natural gas deposits or occluded within CH₄-containing clathrates (natural gas hydrate deposits in the sea floor or arctic regions) [14]. Thus, large volumes of CO₂ and CH₄ of natural and anthropogenic origin are, in principle, available, but unfortunately, their obtention with adequate concentration for further use is generally deficient and/or causes further environmental damage.

The origin of these molecules determines the success of the second stage of the cycle, as the efficient capture from the environment mostly depends on the type of emitting source. In this sense, on-site CO₂ capture systems are considered as feasible approaches for recovering high CO₂ fractions when installed at the exhaust of industrial stationary emitters, for example, cement or steel production plants [15, 16]. However, this approach completely disregards the emissions coming from mobile sources. To reutilize this GHG fraction, the direct CO₂ capture and storage (CCS) from the environment using chemical sorbents/membranes has been proposed, but it is still an intensive energy demanding process, as large volumes of air are processed to concentrate the atmospheric ‘low’ CO₂ concentrations (~ 400 ppm). In addition to that, the sorbents used for CO₂ removal/storage usually require regeneration (for example, via electric heating) between cycles of use, which adds to the process’ energy demand and complexity [17, 18]. Summed to the inorganic sorbents, CO₂ is also naturally captured from the air by photosynthetic organisms like plants, (micro)algae and by autotrophic non-photosynthetic bacteria on land and in the oceans and metabolized into biomolecules [19]. Some of these metabolic byproducts, like vitamins, biopolymers or biofuels are economically attractive, thus, the rational exploitation of these organisms has been proposed for CCS and utilization (CCSU) [20]. For example, microalgae raceway ponds are a promising technology used for CO₂ mitigation and production of biofuels. However, and despite the arguable benefits, this approach requires high energy inputs for compressing and feeding air to the growth media, and for the separation and harvesting of algal biomass, which consecutively worsen the process carbon footprint [21].

Lastly, the reutilization of C-building blocks into added-value products (stage 3 in Figure 1-1) is considered the center of the carbon cycle. In terms of CO₂ utilization, several processes have been proposed, such as the catalytic hydrogenation of CO₂ to produce methanol (MeOH), dimethyl ether (DME) and formic acid (FA), the methanation of CO₂, the partial reduction of CO₂ to form CO, among others [4, 22]. Equally important is the valorization of CH₄ for the modern era. CH₄ can be combusted to produce energy in gas power plants (for example, the combustion of natural or landfill gases) and in different reforming and/or oxidation reactions (steam reforming (SRM, Eq. 1), partial oxidation (POM, Eq. 2) and dry reforming (DRM, Eq. 3) of methane, or their combinations: bi-reforming of methane (BRM, Eq. 4), autothermal reforming of methane (ATR, Eq. 5) or tri-reforming of methane (TRM, Eq. 6)) to produce syngas for the synthesis of methanol and hydrocarbons, among others [23].



As displayed in Eqs. 1-6, any adequate CH₄-containing source could be used to feed the reformers for syngas production. Thus, considering their chemical composition (see Table 1-1), biogas, landfill gas and agricultural waste could be used as feedstocks for the reforming reactions. These alternative sources of CH₄ are produced by the anaerobic decomposition of organic matter using methanogenic microorganisms under controlled conditions [24, 25]. Interestingly, the production of biogas admits organic residues like manure, sludge and biomass from industry and households as raw material, thus, the end point of these wastes is simultaneously addressed. The composition of the resulting gases depends on the organic matter used to feed the digester and the operation conditions chosen for its processing. Unfortunately, these waste-derived feeds are richer in CH₄ (compared to CO₂) and contain trace impurities (such as NH₃ and H₂S), which generally inhibits the reforming catalysts. Therefore, the direct valorization of these gases using the reforming reactions could potentially close the SCC, but still needs to be optimized for its successful implementation.

Table 1-1. Averaged chemical compositions of CH₄-rich feedstocks produced by anaerobic decomposition of organic waste [24, 25].

Component	Biogas	Landfill gas	Agricultural waste
CH ₄	53 – 58 vol.%	35 – 65 vol.%	60 – 75 vol.%
CO ₂	39 – 43 vol.%	15 – 50 vol.%	19 – 33 vol.%
N ₂	1 – 5 vol.%	5 – 40 vol.%	0 – 1 vol.%
O ₂	0.2 – 0.9 vol.%	0 – 5 vol.%	< 0.5 vol.%
H ₂ S	2 – 1000 ppm	0 – 100 ppm	3000 – 10000 mg/m ³
NH ₃	0.25 – 70 ppm	5 ppm	50 – 100 mg/m ³

1.2 Conversion of methane to produce syngas: SRM, POM and DRM

The main differences between the individual reforming/oxidation reactions (which only use one type of oxidant) are the type of molecule used to oxidize the CH₄ (H₂O for SRM, O₂ for POM, and CO₂ for DRM) with different product H₂/CO ratio and the related kinetic and thermodynamic aspects (both SRM and DRM are endothermic reactions, while POM is an exothermic reaction) [26]. Firstly, the SRM is a mature industrial process, which is used worldwide to transform CH₄ into H₂-rich syngas.

The SRM reaction is typically operated at 800 – 950 °C and 15 – 40 bar using Ni catalysts [27]. As described in Eq. 1, a theoretical H_2/CO ratio = 3 is predicted for SRM, which is usually higher than the H_2/CO ratio $\approx 2 - 2.2$ required for other downstream processes [28], like methanol and Fischer-Tropsch (FT) synthesis to produce hydrocarbons and fuels [27]. Thus, the composition of the syngas obtained using SRM might need adjustment to optimize the production of high-added value compounds through coupled downstream processes, as mentioned before. Additionally, the SRM is an intensive energy consuming technology, both due to its endothermicity and the need of large volumes of steam, which represents high operation costs and potentially, the emission of more GHG (mostly CO_2) [27, 29]. Apart from that, the catalysts used for SRM usually deactivate due to particle growth and re-oxidation of the active phases with H_2O , however, coke deposition is not a major concern under appropriate operation conditions (steam-to-carbon ratio (S/C) ≥ 2.5 , $T > 800$ °C).

Regarding the CH_4 partial oxidation (POM, Eq. 2), it utilizes O_2 to oxidize CH_4 to produce a theoretical ratio $H_2/CO = 2$. Unfortunately, H_2/CO ratios ≤ 2 are generally obtained using POM, thus, the as-produced syngas needs enrichment steps to tune the produced syngas for successful downstream applications [26]. This process is operated at 950 – 1100 °C and 100 bar [29]. Due to its exothermicity, the energy input required is comparatively lower to SRM and DRM, which outstands among the endothermic reforming reactions. However, the formation of hot spots throughout the catalyst bed is difficult to control (which deteriorates the catalyst activity and lifespan), summed to the risks of explosion on using high temperatures and O_2 [30]. In this case, catalyst deactivation is also consequence of particle growth and metal re-oxidation (due to O_2 molecule), while the formation of coke is reported to play a minor role in this regard.

Finally, the DRM is considered as a promising route to process the most abundant GHG (CO_2 and CH_4) simultaneously into valuable syngas. Based on Eq. 3, DRM produces a H_2/CO ratio = 1, which can be coupled with the production of chemicals, such as acetic acid (HAc), DME, among others [31, 32]. Obviously, such low H_2/CO does not meet the requirements for direct methanol and/or Fischer-Tropsch synthesis, thus, the produced syngas must be enriched with external H_2 accordingly. The DRM is frequently operated at 650 – 850 °C and 1 bar [29]. Despite its environmental attractiveness, the DRM faces catalyst deactivation via particle agglomeration, metal oxidation (CO_2 and/or *in situ* produced H_2O might oxidize the active metal) and especially, coke deposition. Thus, as the feed is richer in carbon compared to SRM and POM, summed to a thermodynamic preference to form coke at the regular DRM reaction conditions, coke deposition is difficult to be avoided [33]. A detailed discussion regarding thermodynamic aspects of DRM (BRM, TRM and undesired side reactions) is provided in the following chapter.

1.3 Combined reforming processes: BRM, ATR and TRM

As a way to tackle the disadvantages associated with each individual reforming reaction and prevent catalyst deactivation, the combination of the individual reforming reactions has been proposed [34]. By following this approach, new reaction pathways are enabled with their respective thermodynamic and kinetic aspects, which are more complex than the individual reactions and must be contemplated during the process design. The most interesting remark about these combined reactions is that the resulting H_2/CO ratio can be easily tuned by changing the feed composition and the operation conditions (temperature, pressure, etc.) [35]. As displayed in Eq. 4, the BRM combines DRM and SRM to produce a H_2/CO ratio = 2, which theoretically allows the coupling of the obtained syngas with the production of chemicals and fuels without downstream H_2 enrichment steps. Moreover, BRM could be argued as a safer process than POM in terms of explosive reaction mixtures, as no external O_2 is fed at high temperatures. On the other hand, the ATR (Eq. 5) combines an endothermic and an exothermic reaction (SRM and POM, respectively), which of course brings versatility to the heat management of the system, while targeting a H_2/CO ratio = 2. By this approach, a marked decrease in the energy consumption is reported (some reports even argue thermoneutrality), while the amount of O_2 fed is comparatively lower than POM [36]. Finally, the TRM (Eq. 6) is the combination of the three individual oxidation reactions:

DRM, SRM and POM. Thus, the syngas composition obtained with TRM can be easily tuned by fixing the fractions of the different oxidants in the feed, turning the TRM into the most versatile reforming system among the combined reforming reactions.

However, and despite seeming advantageous compared to the individual reforming reactions, operating BRM, ATR and/or TRM is markedly more complex, but most importantly, these processes are not exempt of catalyst deactivation. Based on previous literature [34, 35], the deactivation mechanisms for the individual and combined reforming reactions are arguably similar, which might rise from common features/requirements between reactions, such as: similar catalyst formulations, operation at high temperature in the presence of oxidizing agents, comparable reaction mechanisms, among others. Therefore, the efficient control of the different deactivation mechanisms existing in the reforming reactions is considered as the core problem to solve before these catalytic systems can be efficiently implemented.

1.4 Reforming catalysts: overview and remarks

As previously stated, the deactivation of reforming catalysts is one of the main hurdles for their appropriate application. Certain points are argued as key to enhance the catalysts' efficiency and prevent their deactivation, namely: i) the catalysts' composition, particle size of active metal and optimization of the preparation method, ii) enhancing the adsorption of the reactants, iii) the catalysts' structure, iv) the support's type and physicochemical properties and v) strengthening the metal support interaction (MSI) effect, among others [37]. All the previous points are depicted in Figure 1-2.

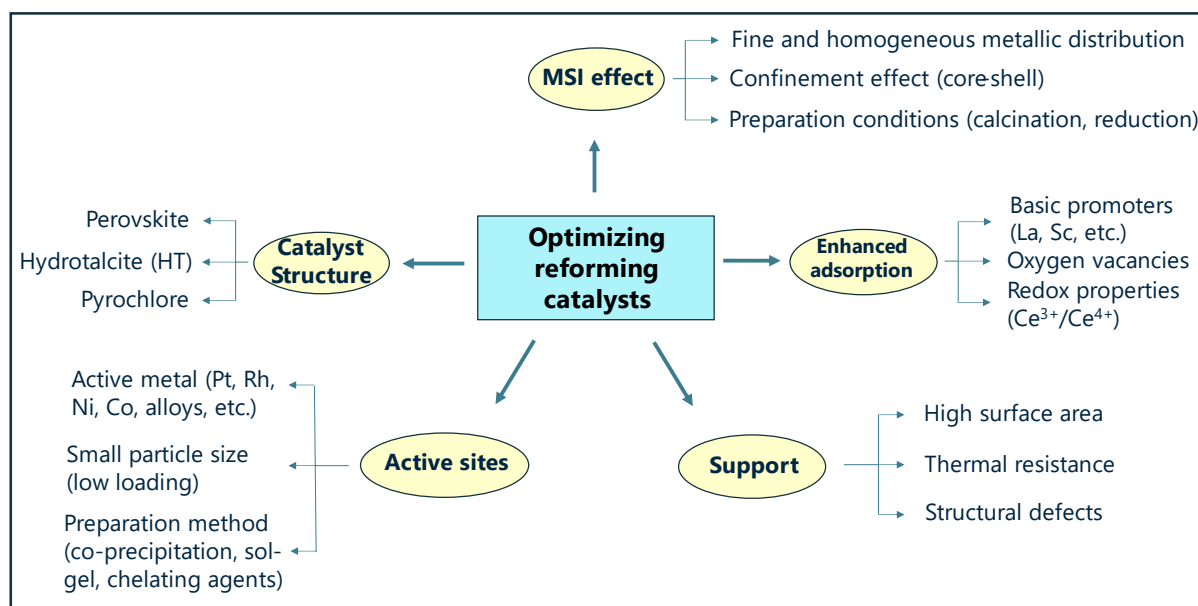


Figure 1-2. Strategies for the optimization of reforming catalysts.

Firstly, catalysts based on noble (Pt, Pd, Rh, etc.) and non-noble transition (Ni, Co) metals have been identified as active species for the different reforming reactions [38-41]. Regardless of the type of metal chosen for a reforming catalyst, the metal precursors are generally reduced *in situ* before reaction, as the reduced (metallic) form is regarded as the catalysts' active sites. On the one hand, catalysts based on noble metals are tendentiously more active and robust against specific deactivation mechanisms (for example, formation of coke and re-oxidation of the metallic species under operation conditions) compared to the non-noble metals. However, their high prices, questionable availability and expensive recycling usually make them unattractive, especially when targeting catalyst upscaling. On the contrary, the non-noble metals are usually preferred as active components, mostly due to their comparatively lower costs, higher availability and most importantly, their competitive reforming activity vs. their noble metal counterparts [42]. However, non-noble metals tend to deactivate fast under the typical reforming

conditions, mostly due to coke accumulation, metal particle growth and/or the re-oxidation of the active phases.

Obviously, the development of non-noble based catalysts is highly desired, but catalyst deactivation is the core problem. In this sense, the selection and optimization of the preparation methods are powerful tools to tune the catalysts' final physicochemical properties and thus, their performance and resistance against deactivation [43]. For example, preparation methods such as the co-precipitation, sol-gel, hydrothermal deposition-precipitation (with or without assisting by urea hydrolysis) and wet impregnation have been thoroughly studied for preparing non-noble based reforming catalysts [44, 45]. These methods of catalyst preparation impact on the catalysts' surface area, pore volume, and the size of the active sites, their spatial distribution (i.e., depositing the particles on the surface or embedded within the support's structure, among others) and how these are stabilized throughout the support via MSI, the targeted materials' structure (for example, hydrotalcite, perovskites, spinels, pyrochlore, mixed oxides, among others) and the number of structural defects [46]. The big picture suggests that simple, economical, reproducible, scalable, but (still) impactful preparation methods are preferred, especially to bridge the progress made in the academy towards more realistic applications [29, 47].

Moreover, the activity and stability of the active sites strongly depend on the catalyst composition and their size. For example, non-noble metals can be stabilized with additional noble or non-noble metals by forming alloys (for example, NiPt or NiCo alloys [48, 49]), intermetallic compounds (Ni_3Al , $\text{Ni}_3\text{GaCo}_{0.25}$ [50, 51]), or via strong Ni^0 -promoter interaction (for example, Ni^0 -Rh or Ni^0 -B stabilized sites [52]). Therefore, the chemical, electronic and coordination local environment of the Ni active sites is modified, and thus, their reactivity and stability against deactivation [53, 54]. Moreover, including rare-earth elements (REM; like La, Gd, Sc) to non-noble catalysts fosters the adsorption of the reforming reactants by enhancing the catalyst's basicity (i.e., improve the adsorption of acidic CO_2 by formation of labile $\text{REM}_2\text{O}_2\text{CO}_3$ species) or creating defects in the catalysts' structure [38]. On the other hand, the alkali metals (Na, K, Cs) have been reported to bind to the most active coke-forming sites of the Ni particles, which alters their electron density and increase the catalyst basicity [55]. Thus, the previous approach enhances the catalyst stability by decreasing the coke deposition rate, but unfortunately, at expenses of catalyst activity due to the partial coverage of these active sites [56]. Another point relates to the size of the active particles. Generally, small sized particles are desired, as these are finely distributed over the support material and are generally more resistant against agglomeration and coke formation during operation under severe reforming conditions (compared to large particle agglomerates). In this sense, dispersing low loads of precursors species over high surface area supports generally leads to catalysts with finely distributed particles over the support [57, 58].

As can be anticipated, the support material also contributes to the catalysts' physicochemical features. Generally, thermally stable, and versatile supports (in terms of their chemical composition and the ease with which it can be tuned) with basic character, high surface area and with a certain number of structural defects are preferred in reforming reactions, as they promote the adsorption of the oxidizing reforming reactants and improve the overall catalyst activity and stability [59-61]. One clear example of a material which meets all the previous requirements is the $\text{MgO-Al}_2\text{O}_3$ mixed oxide. Such mixture is reported to be advantageous compared to the parental oxides (MgO or $\gamma\text{-Al}_2\text{O}_3$), as it keeps most of the good attributes of its constitutive oxides, while possessing a remarkable (and tunable) basic character and strong interaction with the Ni active species [62]. When $\text{MgO-Al}_2\text{O}_3$ mixed oxides are used as support for reforming catalysts (for $\text{Ni/MgO-Al}_2\text{O}_3$), the resulting materials generally show improved activity and stability (compared to $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ or Ni/MgO) [63].

Another important fact relates to the stabilization of the active sites with the support material through MSI, which shapes the stability of the reforming catalysts. Understandably, strong metal support interactions (SMSI) are generally desired for reforming catalysts, as they can prevent particle agglomeration during operation at severe reaction conditions, which ultimately leads to coke formation [64]. Different approaches can be used to strengthen the MSI, namely: i) optimizing the preparation conditions, such as the pH, preparation and calcination temperatures and/or calcination atmosphere, ii)

choosing support materials which can efficiently stabilize the active particles, iii) decreasing the active particle size and/or using adequate promoters, among others [65]. Other alternative approaches to strengthen the MSI are protecting the active sites with permeable oxidic layers, (as it is the case for Ni@SiO₂ core-shell or yolk-shell particles, or Ni particles covered with ZrO₂ oxidic layers deposited using atomic layer deposition (ALD) [66, 67]), or depositing the active particles within ordered structures inside the support (for example, inside the channels of SBA-15 or SBA-16 [68-70]). Evidently, there is an intricate interplay between the preparation methods and the catalyst composition and structure, which in the end, defines the catalysts' physicochemical features and their performance [37].

1.5 Effect of changing the operation conditions in the reforming of CH₄

The operation conditions chosen for catalyst pre-treatment and for the reforming reactions impact on the catalyst activity, selectivity, and stability, thus, these must be rationally adjusted during process optimization.

Generally, higher reduction degrees of metal precursor and conversion of the reactants are obtained at higher temperatures ($T > 700\text{ }^{\circ}\text{C}$), but unfortunately, these regimes promote the deactivation of the catalysts via particle agglomeration, formation of coke deposits and/or oxidation of the active sites. To understand the previous point better, a thermodynamic analysis of the reforming reactions and deactivating phenomena can be found in the following chapter. For example, DRM is generally studied using low flow rates of diluted and stoichiometric ($\text{CH}_4/\text{CO}_2 = 1:1$) feeds at high temperatures. Consequently, these reaction conditions increase the probability of the reaction to occur, thus, these regimes increase the conversion of reactants. However, those reaction conditions might not provide useful knowledge for the reforming of waste-derived feedstocks (as those listed in Table 1-1). In this sense, if the valorization of CH₄-rich biogases is pursued to close the SCC, CH₄-rich feeds ($\text{CH}_4/\text{CO}_2 > 1$) must be intensively investigated. As already mentioned, molar ratios $\text{CH}_4/\text{CO}_2 > 1$ are more challenging reaction conditions for the catalysts, as less CO₂ is available to transform the CH₄, while the excess of CH₄ and low CO₂ content promote coke accumulation and accelerate catalyst deactivation.

Summed to the previous, the trace impurities present in these CH₄-rich gases (mostly NH₃ and/or H₂S; see Table 1-1) provoke rapid catalyst deactivation during reforming operation. These poisonous compounds generally block the active sites and impede them to catalyze the reaction [71]. Unfortunately, these molecules are difficult to remove from the catalysts' structure during operation. Therefore, catalyst reactivation using high temperature regeneration treatments are generally required to restore the catalysts' activity, which generally impact on the morphology and stability of the active sites for subsequent catalytic cycles. For example, oxidation of the Ni⁰ active sites via oxidative treatments and/or particle sintering generally take place simultaneously, which impact on the catalytic performance further.

Despite the importance of valorizing these waste-derived gases to establish a more sustainable economy, only few reports have studied the dry reforming of CH₄-rich gases including deactivating trace compounds [72-77]. Besides, little has been done regarding the development of successful regeneration strategies after severe catalyst deactivation, followed by catalytic evaluation in consecutive cycles. The previous could be crucial to succeed in the reforming of real biogas. Therefore, developing active and stable catalysts for the reforming of CH₄-rich feeds in presence of poisonous trace compounds (to mimic biogas) and their successful regeneration after deactivation is still a central milestone to reach.

1.6 Motivation of the work

The direct valorization of real CH₄-rich waste-derived feeds still represents a major challenge for the different CH₄ reforming reactions, mostly due to the lack of active catalysts, able to operate during long times under these highly deactivating regimes. Thus, basing on the discussion presented within this chapter and previous knowledge obtained in our group regarding DRM catalysts [1, 78-80], the main motivation of this work was the development of active and resistant low loading (2.5 wt.% Ni) Ni-based catalysts supported on MgO-Al₂O₃ mixed oxides for the reforming of CH₄-rich gases. Different

knowledge-based formulations were investigated, aiming to enhance the activity of the catalysts and to minimize their deactivation over time on stream using different reforming regimes. Another motivation of this work was gaining a deep understanding of the MgO-Al₂O₃ support material on the reforming activity and stability. Consecutively, different preparation methods were investigated to develop an improved MgO-Al₂O₃ support material compared to commercial ones, targeting enhanced catalytic performance and minimized catalyst deactivation. Investigating the physicochemical features of the developed and spent catalysts (after various regimes) was another motivation of this work, as it would enable the identification of structure-activity relationships and the causes of catalyst deactivation. Additionally, the feasibility of valorizing synthetic waste-derived biogas was another core motivation of this work. Recalling the economic and technological potential of valorizing biogas using Ni-based catalysts, intensive catalytic testing in biogas-like reaction regimes, followed by developing efficient regeneration strategies after severe coke accumulation, and/or poisoning with NH₃ and H₂S was another motivation of this work. Finally, developing versatile catalysts able to operate in the combined BRM and TRM to tune the product ratio H₂/CO to produce syngas with adequate composition motivated this work further. Therefore, studying all the previous points would contribute to build a more complete picture regarding the applicability and robustness of the developed materials and potentially, aid in closing the SCC.

1.7 Objectives

To accomplish the motivations previously described, 6 specific objectives were identified:

- 1) To develop and screen several low-loading (2.5 wt.%) Ni-based catalysts supported on commercial MgO-Al₂O₃ mixed oxides, using reaction feeds with high carbon content and only 10% N₂ dilution.
- 2) To tune the physicochemical properties of the MgO-Al₂O₃ support by using different preparation methods, aiming to enhance the catalytic activity, selectivity, and stability.
- 3) To investigate the physicochemical properties of the fresh, *ex situ* reduced, and spent materials after different reaction regimes with advanced solid-state characterization techniques, to correlate these with their catalytic performance, the same as for the identification of deactivation causes.
- 4) To understand the impacts of changing the reaction conditions in the catalytic activity and stability, aiming to improve the catalysts' performance and to identify outstanding samples for the valorization of biogas.
- 5) To develop regeneration strategies for the elimination of coke, NH₃, or H₂S species after catalyst deactivation during reforming of model biogas.
- 6) To investigate the outperforming catalysts in combined reforming reactions (BRM and TRM) to understand the effects of H₂O and/or O₂ addition in the feed and to tune the product H₂/CO syngas ratio by means of process variants.

2. State-of-the-Art

This chapter discusses the theory behind the reforming systems. In the first part of this chapter, the thermodynamics, reaction, and deactivating mechanisms of the reforming reactions are firstly described. The DRM system was mainly discussed, but continuous comparison was done throughout this chapter between the different reforming reactions (DRM, BRM and TRM). ATR was not discussed as it was outside the scope of this work. Finally, this chapter reports on the physicochemical impacts caused by specific parameters fixed during catalyst preparation, the same as catalysts' formulation and reaction conditions, to advance the optimization of both reforming catalysts and overall process.

2.1 Thermodynamic aspects

The DRM is an endothermic and reversible reaction, which usually requires high temperatures ($T > 700$ °C) to shift the equilibrium from reactants to products, i.e., to convert CH_4 and CO_2 into syngas. It is crucial to understand the thermodynamics behind the processes to find optimum reaction conditions and to understand the thermodynamic limits imposed for these reactions. The following discussion does not contemplate how the changes in the reaction pressure impacts on the thermodynamic calculations, as all the reforming reactions in this work were performed at atmospheric pressure. The reader is referred to the following reports [81, 82] for thermodynamic analysis at different reaction pressures.

Thermodynamic analysis of DRM (see Figure 2-1 a) predicts that the equilibrium concentration of CH_4 and CO_2 generally decreases with the increase of the reaction temperature (a lower equilibrium concentration indicates a higher conversion). This relates to the high amount of energy required to activate and dissociate the reactants' bonds: 435 kJ/mol are required to dissociate one C-H bond of CH_4 and 526 kJ/mol are required to dissociate one C=O bond of CO_2 [83]. The enthalpies of bond dissociation for each molecule demonstrate the robustness of the reactants, and for this reason, they are usually referred as 'thermodynamic sinks' in the literature, especially the CO_2 . Under conventional DRM conditions (i.e., $\text{CH}_4/\text{CO}_2 = 1$ and $p = 1$ bar), the conversions of CH_4 and CO_2 are comparable and prevail at $T > 650$ °C (vs. other side reactions), reaching full conversions at $T > 800$ °C. By contrast, using methane-rich feeds (for example, $\text{CH}_4/\text{CO}_2 \geq 1.5$) generally leads to lower CH_4 conversions compared to that of CO_2 at all temperatures, as the CO_2 is considered as the limiting reactant [84]. Independently of the feed composition, one could think to operate the catalytic process at $T > 800$ °C, but such regimes are: i) highly energy consuming and ii) promote the sintering of the active metal particles, which consequently leads to severe coke deposition (further discussed in section 2.3.2).

The sintering of the active particles decreases the availability/number of the Ni active sites and promotes coke accumulation, which ultimately impacts on the catalysts' activity. In connection to the previous, the Ni Tammann temperature ($T_{\text{Tammann}} = 691$ °C) indicates that the mobility of the Ni nanoparticles throughout the catalysts' structure during operation at optimum DRM temperatures is difficult to avoid [85]. Therefore, strengthening the MSI has been reported as an efficient approach to anchor the Ni particles to the support, and to prevent the Ni migration and agglomeration at the required DRM temperatures [63]. Moreover, the deposition of coke was found to be favored over large Ni particles (sized > 15 nm), as coke formation seems to be structure sensitive, i.e., the nucleation of carbon structures is favored over surface step sites (compared to edge, terrace sites, among others) [86]. Thus, large Ni agglomerates are statistically more likely to possess surface step sites, thus, they promote coke deposition.

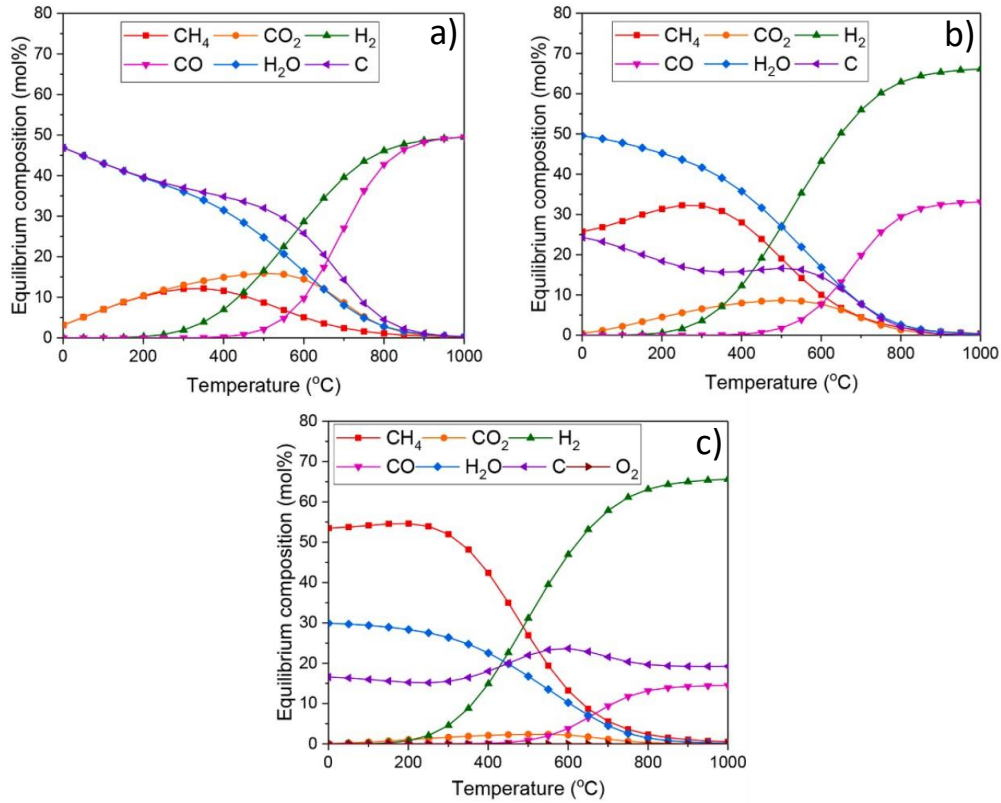


Figure 2-1. a) DRM, b) BRM and c) TRM equilibrium compositions predicted using thermodynamic calculations at $p = 1$ bar and stoichiometric feeds ($\text{CH}_4/\text{CO}_2 = 1:1$ for a), $\text{CH}_4/\text{CO}_2 = 3:1$ for b) and $\text{CH}_4/\text{CO}_2 = 20:1$ for c)). Reprinted with permission from [26]. Copyright 2022 Elsevier.

As depicted in Figure 2-1 a, the formation of H_2O is observed under typical DRM conditions ($T < 820$ °C) via the reverse water-gas shift reaction (RWGS: Eq. 7), while increasing $T > 820$ °C inhibits its occurrence. The RWGS reaction shifts the process selectivity (i.e., decrease $\text{H}_2/\text{CO} < 1$) and lowers the CH_4 conversion (X_{CH_4}) compared to that of CO_2 (X_{CO_2}). Moreover, the incidence of the RWGS is also reported for CH_4 -rich feeds $\text{CH}_4/\text{CO}_2 \geq 1$ [84], however, its impacts on catalyst performance are less profound due to the lower amount of CO_2 available for this reaction [87, 88].



Going one step forward, the thermodynamic calculations also determine almost complete CH_4 and CO_2 conversions at $T > 800$ °C for BRM and TRM, the thermodynamic analysis and calculation conditions of which are depicted in Figure 2-1 b and c, respectively. Regarding the products, including H_2O and O_2 in the feed increases preferentially the equilibrium H_2 content, which consequently increases the H_2/CO ratio as predicted by Eqs. 4 and 6, respectively. Naturally, both BRM and TRM reactions consume H_2O as main reactant, however, the selectivity of these reactions is also affected by the occurrence of RWGS, as it was previously described for DRM [26]. The equilibrium concentration of H_2O tends to zero for both BRM and TRM when $T > 800$ °C, i.e., high H_2O conversions are expected at high reaction temperatures. The previous suggests that the production of H_2O via the RWGS (Eq. 7) is also disfavored at high temperatures, similar to what is observed for DRM. Particularly in TRM, and by only considering its thermodynamic aspects, a O_2 content close to zero is predicted at all analyzed temperatures, which is attributed to its high reactivity and selectivity towards CH_4 oxidation. Finally, the three reforming reactions inevitably form coke at $T < 800$ °C, the formation of which decreases when steam is included in the reaction feeds (BRM and TRM). The exothermic Boudouard reaction (Eq. 8) is favored at $T < 700$ °C, while the endothermic CH_4 decomposition (Eq. 9) predominates at $T > 700$ °C. Generally, the formation of coke is thermodynamically favored at higher CH_4/CO_2 ratios, as the excess of CH_4 can undergo cracking (as described by Eq. 9) [84]. Thermodynamically, increasing the temperatures further

($T > 700\text{ }^{\circ}\text{C}$) would limit the formation of coke, being $T > 870\text{ }^{\circ}\text{C}$ considered as (theoretically) DRM coke-free regimes, as can be observed in Figure 2-1 a [89]. A deeper analysis regarding coke formation and oxidation can be found in section 2.3.1.



2.2 Reaction mechanisms

There is still no consensus regarding the DRM reaction mechanisms, as these are thought to depend on the catalysts' physicochemical properties, especially on their chemical composition, particle size and support's nature [90]. However, two different reaction mechanisms are frequently reported for temperature-activated DRM, which include formate or carbonate intermediates (both depicted in Figure 2-2 a-b, respectively) [26, 27]. Moreover, alternative reaction mechanisms have been reported for plasma-assisted DRM, but as only thermal DRM was studied in this work, only a brief discussion of plasma-driven mechanisms is given below.

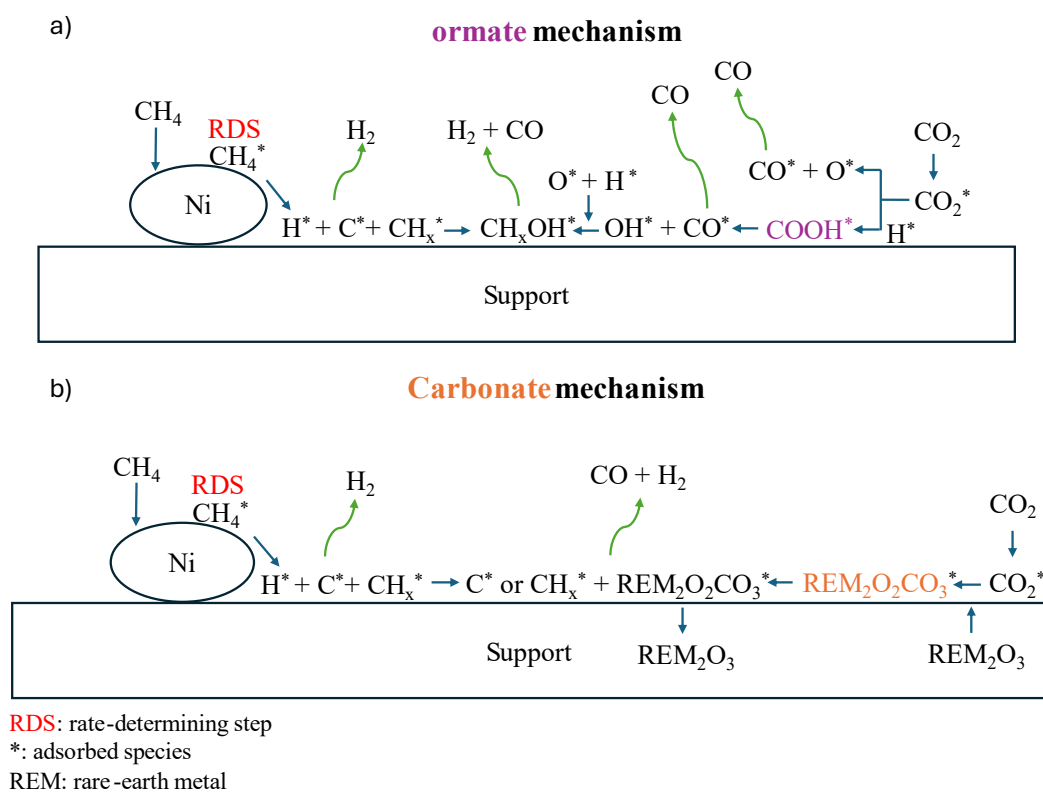


Figure 2-2. Schematic representation of the: a) formate and b) carbonate reaction mechanisms [38]. RDS: rate-determining step, *: adsorbed species, REM: rare-earth metal.

Both formate and carbonate thermal reaction pathways start similarly with the CH_4 dissociation. Firstly, CH_4 is adsorbed on the reduced metal sites (CH_4^*), where the C-H bonds are dissociated, leading to CH_x^* species ($0 \leq x \leq 3$), H_2^* (which rapidly desorbs from the surface as H_2) and/or $\text{C}^* + \text{H}^*$ atoms (adsorbed over the metal surface). The previous is regarded as the rate-determining step (RDS; i.e., it determines how fast the overall reaction can proceed), thus, efficient control of the first step generally determines the efficiency of the entire process. Secondly, CO_2 is adsorbed preferentially at the interface between the metal and the support, but adsorption on the support's surface or metal surface is also reported for both mechanisms. As the area of metal-support interface is limited due to a finite number of adsorption metallic sites, the CO_2 adsorption greatly depends on the metal load and its dispersion [91]. It is reported that the pathway followed by the adsorption and dissociation of CO_2 molecule determines the final

reaction pathway [92]. The carbonate mechanism is favored in catalysts with basic character, for example, catalysts containing La_2O_3 might form $\text{La}_2\text{O}_2\text{CO}_3$ oxy-carbonates during CO_2 adsorption [93-95].

During the formate mechanism (depicted in Figure 2-2 a) [27], CO_2 is firstly adsorbed on the catalyst surface (CO_2^*) and can then follow two possible pathways: it can be dissociated to form $\text{CO}^* + \text{O}^*$ adsorbed species, which can then release CO and leave reactive O^* on the surface, or it can react with H^* species (formed during CH_4 dissociation and might spillover from the Ni active sites) and be transformed into formate (COOH^*) intermediates. These formates can dissociate into adsorbed CO^* and OH^* (hydroxyl) species. The latter oxidize the C^* and/or CH_x^* to produce H_2^* and CO^* , which are finally desorbed as H_2 and CO. Besides, O^* species (formed during CO_2 dissociation) can also oxidize the C^* and/or CH_x^* to produce CO and/or H_2 .

Contrarily, the carbonate mechanism strongly depends on the catalyst composition [96, 97]. In this case, CO_2 is adsorbed and reacts with the oxidic REM (La_2O_3 , for example), to produce carbonate-derived species (for example, lanthanum oxycarbonate $\text{La}_2\text{O}_2\text{CO}_3^*$). The latter species then react with the C^* and/or CH_x^* to produce CO^* and/or H_2^* (which are subsequently desorbed as H_2 and CO) and/or La_2O_3 . As a general remark, both mechanisms require CH_4 adsorption and dissociation on the reduced active sites, however, the role of the oxidized Ni species ($\text{Ni}^{2+}/\text{Ni}^{\delta+}$, especially neighboring the reduced Ni sites) is sometimes discussed in the literature. It is argued that these cationic Ni species might aid in withdrawing the electron density (at least partially) of the C-H bond of CH_4 , thus making its cleavage less energy demanding [98].

The plasma-assisted DRM reaction mechanisms [99] are reported as more complex than those activated by thermal energy due to the highly reacting atmosphere created under plasma conditions, i.e., formation of multiple high energy reactive particles and high energy provided by the plasma itself. Some of these species are free electrons, intermediate radicals derived from the reactants or products, and cationic or anionic particles, which exist in the gaseous phase and/or on the catalyst surface. During operation, the plasma activates the produced particles, which then combine in different chemical reactions to produce not only syngas, but also other hydrocarbons like C_2H_4 , C_2H_6 , among others. The latter are formed during radical recombination reactions [100]. The formation of hydrocarbons with more than one C atom has been frequently reported under non-thermal plasma-assisted DRM, as the low reaction temperature inhibits the decomposition of polymerized long chain hydrocarbons [101]. Thus, the poorer selectivity towards syngas for the plasma-assisted DRM usually shades its application. However, plasma technology is gaining interest due to a potential decrease in energy consumption (compared to thermal DRM), but this process still requires optimization to obtain sufficient conversion degrees of reactants with adequate selectivity towards syngas.

Regarding the thermal BRM and TRM [34, 35], it is argued that their reaction mechanisms share similitudes with those of DRM. In both combined reactions, it is considered that the mechanisms contemplate four steps. The first one is the same as in DRM: CH_4 surface adsorption and dissociation. Secondly, the oxidizing agents ($\text{CO}_2 + \text{H}_2\text{O}$ or $\text{CO}_2 + \text{H}_2\text{O} + \text{O}_2$, for BRM and TRM, respectively) are adsorbed preferentially at the interface Ni-support and dissociate into the different reactive intermediates (H^* , O^* , C^* , CO^* , depending on the feed composition). Then, the surface intermediates combine with C/ CH_x species to produce and desorb syngas in the last reaction step.

2.3 Mechanisms of catalyst deactivation

Once the thermodynamics and reaction mechanism of the reforming reactions have been discussed, different phenomena regarding catalyst deactivation become evident. Understanding them is crucial to find ways to reduce and/or eliminate their negative impacts on reforming catalysts' activity and stability. In this sense, coke deposition, particle growth, re-oxidation of the active phases and catalyst poisoning are the main responsible for catalyst deactivation.

2.3.1 formation of carbonaceous structures

The proposed reforming reactions mechanisms contemplate the formation of C fragments (with or without H) on the catalysts' surface via CO disproportionation (Eq. 8) and/or CH₄ dissociation (Eq. 9) at high temperature [102]. These C species can combine through polymerization reactions under operation conditions, leading to carbonaceous intermediates characterized by their structure (i.e., chain length) and H/C ratio [27, 71, 103]. Generally, highly ordered carbonaceous assemblies expose low H/C ratio and are difficult to gasify during reforming operation [102]. Therefore, these generally accumulate throughout the catalysts' structure over time on stream, which affects the catalytic performance negatively (this discussion is deepened below). A scheme modelling the accumulation of coke via CH₄ dehydrogenation is displayed in Figure 2-3.

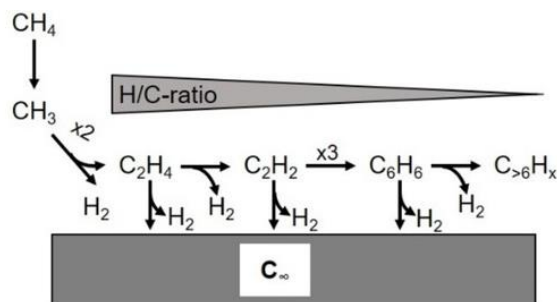


Figure 2-3. Pathway for CH₄ dehydrogenation, including polymerization of carbon intermediates, and accumulation of coke according to the authors in [103, 104]. Reprinted with permission from [27]. Copyright 2022 Wiley.

Focusing on Ni catalysts, it is argued that the surface of the Ni sites acts as template for the growth of the different carbonaceous structures, ordered from higher to lower H/C ratios: amorphous coke, carbon nanotubes (CNT), carbon whiskers and graphitic coke [105]. For example, the first type is described as reactive carbon structures with high H/C ratio and low degree of structural order, which are generally oxidized during reforming operation and therefore, they are not considered deactivating C species.

Secondly, the CNT have a lower H/C ratio and higher degree of structural order (compared to the amorphous species), and these might cause catalyst deactivation. Three different types of CNTs are mostly described in the literature [106]. For example, if the CNT grows from the bottom of a Ni particle outwards, they generally detach the Ni from the support, leading to a CNT with the (still) active Ni site at its tip (the carbon nanotube might act as a different support material), thus ensuring that the activity is unaffected. The same occurs when the CNTs grow from the surface of the Ni particles outwards, leaving the Ni partially accessible to the reactants but still attached to the parental support. On the contrary, when the carbon nanotube encloses a Ni particle during its growth, the latter will be completely or totally deactivated as the accessibility of the reactants to the Ni nanoparticle will be obstructed [86]. Thirdly, carbon whiskers are a hard type of coke with high degree of structural order and low H/C ratio, and thus, they are difficult to oxidize during catalyst operation. Such type of carbonaceous growth is undesired, as it generally blocks the catalysts' pores (decreasing the surface area and affecting the diffusion of reactants), causes reactor plugging (and pressure drop problems) and might even destroy the support material. Finally, the graphitic coke is a highly crystalline carbonaceous structure with low (to none) H content and high degree of C density/order, which generally leads to irreversible coverage of the surface of the Ni active sites. The latter ones block completely the surface active particles, thus, this type of coke causes catalyst deactivation [106].

Generally, the selectivity of a catalyst towards the oxidation of the carbonaceous species during operation (compared to the rate of C formation) determines if coke will accumulate. For example, non-gasified amorphous carbon species usually evolve during the reaction into ordered graphitic structures, which promotes catalyst deactivation [106]. Thus, non-deactivating coke structures can turn into deactivating ones if not gasified. The efficiency of coke gasification is linked to both the catalysts'

physicochemical properties (for example: basicity, particle size, MSI, among others) and to the operation conditions (temperature, pressure, contact times, feed compositions, among others). For example, catalysts with acidic character show higher rate of the CH₄ cracking (Eq. 9), thus, these promote the deposition of coke [107]. The link between the catalysts' physicochemical properties and the formation of coke will be discussed later in this chapter. Regarding the operation conditions, generally low temperatures ($T \approx 600 - 650$ °C), high pressures ($p > 1$ bar), short contact times (high GHSV) and high amount of carbon in the feed ($\text{CH}_4/\text{CO}_2 > 1$ in DRM) favor the formation of coke.

Regarding the feed composition, DRM uses a feed comparatively richer in carbon compared to the other reforming processes, which turns this reaction more susceptible to deposit coke during operation [81]. The previous is further enhanced when feeds with $\text{CH}_4/\text{CO}_2 > 1$ are used, and therefore, these are more prone to form coke, i.e., they are regarded as more 'severe' reaction regimes. By contrast, both BRM and TRM have other C oxidants in their feeds (besides having CO₂), which can participate in carbon oxidation. The previous processes can be described with the inverse of Eq. 8, or Eq. 10 and Eq. 11, for the oxidation of C with CO₂, H₂O and O₂, respectively [84].



2.3.2 Particle growth mechanisms and oxidation of the active sites

Active Ni catalysts for the reforming reactions generally display numerous active sites which are accessible to catalyze the reaction. Generally, such catalysts possess small (< 15 nm) Ni particles finely distributed throughout a porous support material with high surface area. Unfortunately, very small metallic nanoparticles are generally unstable under the required high temperatures ($T > 700$ °C), thus, particle migration and agglomeration are difficultly avoided. Two mechanisms mainly describe these growing processes, which are the nanoparticle migration and coalescence, and the Ostwald ripening [26]. The first one is described by a Brownian-motion-like mechanism, in which the small particles move throughout the support due to the increase in their energy (provided by the high temperature) and eventually collide and combine, leading to particles with increased size. The second mechanism contemplates the migration of neighboring Ni adatoms willing to minimize their surface energy. Thus, larger particles tend to grow faster than smaller ones due to the difference in their surface energy. Metallic particles which strongly interact with the support usually discourage the particle migration mechanisms. Obviously, the latter evidences the importance of the MSI effect in the formulation of stable reforming catalysts.

Another common deactivation mechanism considers the oxidation of the reduced metal particles. It is argued that metallic Ni centers are the active sites for the CH₄ adsorption and dissociation, thus, these are considered crucial for the reforming reactions. Therefore, intensive Ni oxidation leads to decreased catalyst activity, while complete activity loss is observed in fully oxidized Ni catalysts. The presence of the different oxidizing agents (CO₂, H₂O and O₂) and the high reaction temperatures used in the reforming reactions are responsible for such deactivating oxidation [108, 109]. However, despite having a higher fraction of oxidizing molecules in their feeds, both BRM and TRM generally produce more H₂ (compared to DRM), thus, *in situ* reduction of oxidized Ni species also occurs in the combined reforming reactions. Therefore, simultaneous processes which involve oxidation-reduction steps occur during reforming operation, thus, the resulting catalysts' activity and stability depend on how these redox reactions counterbalance themselves.

2.3.3 Catalyst poisoning

As previously introduced, the direct valorization of biogas using reforming reactions is obstructed not only by severe coke accumulation, but also by catalyst poisoning caused by the trace gases present in the different CH₄-rich alternative feedstocks, especially for Ni systems. Catalyst poisoning generally refers to an irreversible chemical transformation of the active metal into inactive species, or strong adsorption and obstruction of the active sites with undesired molecules [71]. On the one hand, H₂S is considered as the main deactivating molecule in biogas for reforming catalysts based on transition metals. The S²⁻ anion has its highest occupied molecular orbital (HOMO) (p orbitals) filled with 3 lone electron pairs, and combination with available (non-fully occupied) d orbitals of most of the transition metals acts as driving force for the formation of metal sulfides (known as sulfidation) [110]. These sulfides can be bulk or surficial species, being the surface S-species very stable at high T. Thus, H₂S (or other S-containing compounds present in some waste-derived CH₄-rich feedstocks like SO₂ or carbonyl sulfide (COS), which can be transformed into H₂S during reaction at high temperature [75]) strongly adsorb/chemisorb on the active sites. Consequently, inactive Ni-S phases ((a) in Figure 2-4) cause irreversible catalyst deactivation during reforming of untreated S-containing feeds at high temperature [73].

Besides, the strongly chemisorbed S-species on Ni sites alter their electronic properties, which can impact on their stability at high temperatures and/or on their capacity to adsorb the reactants for catalysis [71, 111]. For example, the Ni-Ni bonds are debilitated in presence of S, which weakens the interaction of these active sites with the support, promoting particle migration on the catalysts' surface and agglomeration at high temperatures ((b) in Figure 2-4) [112]. Consequently, less active sites would be available to adsorb the reactants (i.e., lower activity and less coke gasification), while the deposition of carbon is simultaneously accelerated on the larger Ni sites ((c) in Figure 2-4).

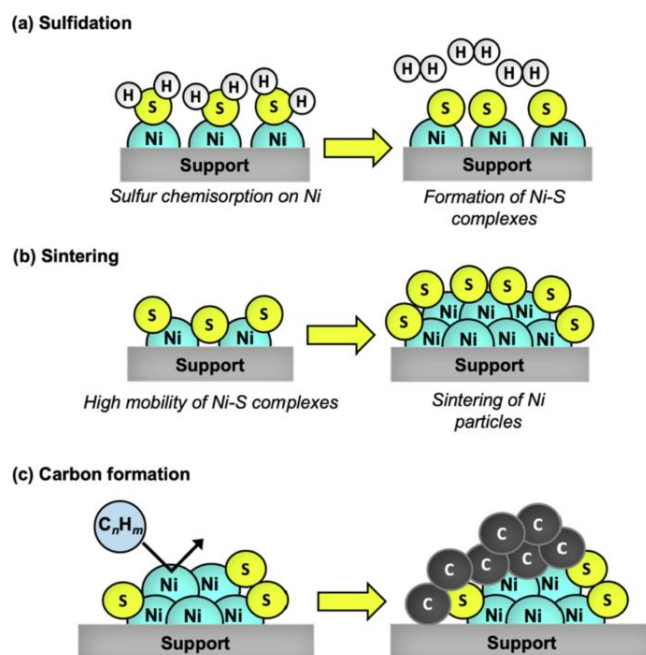


Figure 2-4. Sulfur poisoning pathway of dry reforming of S-containing tar according to the authors in [111]. Reprinted with permission from [111]. Copyright 2022 Elsevier.

According to the authors in [113], a notorious increase in coke deposition has been reported in the dry reforming of methane including H₂S in the reaction feed using Ni/SiO₂ catalysts. The latter was attributed to the progressive poisoning of the Ni active sites with S, summed to accelerated agglomeration of the remaining unpoisoned Ni⁰ sites, which seemed to be somehow promoted under these reaction conditions. Thus, the structural changes most likely dropped the activity to almost zero in less than 2 hours on stream at temperatures ranging between 700 – 800 °C. Moreover, the authors

hypothesized that the lower conversion rates might have also fostered the occurrence of side reactions, like the RWGS and the Boudouard and CH₄-cracking (described by Eqs. 7, 8, and 9, respectively), as the H₂/CO ratio followed the same deactivating trend as that of X_{CH₄}.

On the other hand, NH₃ can adsorb (reversibly or irreversibly) and dissociate (into NH_x^{*} + H^{*}) on the Ni sites, which blocks them to adsorb and transform the reforming reactants, decreasing the catalytic performance [73]. Additionally, the adsorption of NH₃ could also accelerate the deposition of coke, as adsorbed N-compounds block some CO₂-adsorption sites, which obstructs the gasification of C species via the inverse of the Boudouard reaction (Eq. 8). Generally, the deactivation of Ni-based catalysts due to NH₃ poisoning (at least, at levels resembling those present in biogas ~ 100 ppm) requires longer exposure times compared to S. Other compounds, such as siloxanes with different number of carbon atoms or chain lengths (for example, decamethyl-cyclopenta-siloxane) can transform during operation at high temperature into SiO₂ (s) and crystallize over the Ni active sites [114, 115]. Thus, the accessibility of the latter to the reactants is reduced, which leads to catalyst deactivation.

Unfortunately, poisoning of Ni-based reforming catalysts is very difficult to avoid, and the regeneration of these generally requires aggressive treatments, which ultimately depends on how strongly the poison bonds to the Ni sites and alters the physicochemical properties of the catalyst [71]. For example, T > 900 °C in the absence of deactivating compounds and/or oxidation-reduction cycles at high temperatures (T > 850 °C) [116] would be necessary to reactivate S-poisoned catalysts. Needless to say that these types of procedures might provoke particle agglomeration and/or structural collapse of the catalytic systems (decrease the surface area, pore blockage, among others).

All the previous suggests that the reforming of real biogas deactivates the catalysts in complex ways, and even co-dependencies/synergies between different deactivation mechanisms seems to exist. Thus, overcoming catalyst deactivation under such reaction mixtures is clearly a complex task. Thus, the direct valorization of these waste-derived gases using reforming reactions would require one or combinations of the following approaches: i) upstream treatments to remove these trace gases, ii) establishing efficient regeneration strategies for deactivated Ni catalysts and/or iii) the development of active and poisoning-resistant materials, especially against sulfur. The effects of some promoters on sulfur resistance are further discussed in section 2.4.2.

2.4 Optimization of Ni-based reforming catalysts

The rational design of catalysts for reforming reactions is crucial for maximizing the process efficiency and catalyst lifespan. This section discusses the central points related to the optimization of Ni-based catalyst in DRM, but this discussion might apply for Ni-based catalysts for BRM and TRM as well.

2.4.1 The active sites: effect of Ni loading, Ni particle size, and its dispersion

As mentioned in the introduction of this work, the use of noble metals was not investigated in this work, and therefore, these were no longer considered for the discussion. This work focused on Ni-based catalysts instead.

Generally, Ni catalysts show high reforming activity at reasonable prices, but unfortunately, their stability at high operation temperatures (T > 800 °C) is arguably their weakest point, as previously discussed. Under these conditions, Ni is prone to sinter and to deposit coke during reforming operation. Thus, the development of highly active and stable Ni catalysts might push the application of the reforming technologies further. In this regard, not only the preparation procedure and load of Ni are crucial for determining the catalyst activity and stability, but also the Ni particle size and the approach followed to disperse the precursors during catalyst preparation.

Firstly, several physicochemical features such as the basicity, redox properties, and morphology, size and distribution of the Ni particles (bulk and surface composition) throughout the support are largely defined by the preparation method [117]. Particularly, the deposition of Ni precursors on Mg-Al mixed oxides was done using the wet impregnation method throughout this dissertation, as it is a facile,

efficient, environmentally friendly (water was used as solvent) and potentially up-scalable preparation route for preparing supported Ni catalysts [118]. It is also argued that this preparation method generally produces catalysts with a high fraction of deposited particles over the catalyst surface [118]. The latter is of outmost importance, as the reforming reactions are generally sensitive to the surface composition, especially benefited on catalysts with high surface Ni content [119, 120]. However, the wet impregnation might generate differences between the catalysts' bulk and surface compositions, which can lead to mass transport problems in heterogeneous reactions or to the formation of active sites with very different activities and stabilities during reaction. Thus, the preparation must be properly adjusted. On the other hand, preparation methods like the co-precipitation, sol-gel and hydrothermal methods generally produce materials with more homogeneous compositions (surface vs. bulk). However, these methods are generally more difficult to up-scale, and might be more expensive and toxic (require more sophisticated and/or corrosive chemicals) [118]. But most importantly, a higher fraction of active particles might be occluded within the support's structure, especially when the metal and support precursors are added simultaneously.

The calcination temperature is also decisive for shaping the catalysts' physicochemical features. Firstly, thermal treatments ($T > 500\text{ }^{\circ}\text{C}$) using static air are generally chosen to transform the metal precursors into the catalyst oxidic species [118]. Secondly, the support's phases (and their crystallinity) are also modified through solid state transformations during calcination [121]. The previous two phenomena can lead to other solid state changes, i.e., the diffusion of these new oxidic Ni species within the support's matrix (for example, formation of $\text{Ni}_x\text{Mg}_{(1-x)}\text{Al}_2\text{O}_4$ with $0 \leq x \leq 1$, by calcination of the precursors at $1000\text{ }^{\circ}\text{C}$), which can define the stability of the final Ni sites. Apart from the previous, the formation of the active sites in some catalytic systems require high calcination temperature under reductive atmospheres, as it is the case for some Ni-based perovskites [122]. In such cases, the metal precursor cations migrate from the support's bulk structure towards the surface, thus, the resulting metallic nanoparticles are finely distributed and strongly anchored to the support, which makes them resistant against agglomeration [123]. Other properties, such as the sulfur tolerance in DRM, have been reported to be enhanced by calcination at high temperatures ($T = 1500\text{ }^{\circ}\text{C}$). The latter seems to be linked to the production of more oxygen vacancies in the catalysts' structure which improves CO_2 adsorption, which might provide a more oxidative atmosphere for removing the deposited S-species via oxidation. However, large and ordered Ni agglomerates (up to 100 nm) were consequently formed, which promotes the deactivation by coke formation. Unfortunately, the removal mechanism of S-species from the catalyst's structure is not well understood and needs to be further investigated [77].

Regarding the metallic loading, discrepancies exist between the reported catalysts' Ni load and how this parameter shapes the catalyst performance in reforming systems. On the one hand, some authors claim that high Ni loads ($> 10\text{ wt.\% Ni}$) are essential to get highly reducible and active reforming catalysts [58, 124, 125]. With this approach, the formation of the reduced active sites occurs at lower temperatures, thus, higher activities are supposedly achieved. However, some factors are to be considered for this type of catalytic systems. Firstly, obtaining a fine and homogeneous distribution of a high amount of Ni precursor ions over a support material with finite number of adsorbing sites is challenging, especially when impregnation methods are chosen for catalyst preparation. The previous generally leads to large particle agglomerates after preparation. Secondly, high Ni reducibility generally implicates that the Ni particles do not expose strong interaction with the support, thus, particle sintering is hardly avoidable during catalyst operation at high temperature. Consequently, using high Ni loads usually leads to catalysts with large particles which expose mild MSI, thus, these are prone to agglomerate and deactivate.

In connection to the latter, the Ni particle size and shape plays a crucial role in the CH_4 dissociation and carbon deposition processes. It is argued that the dissociative CH_4 adsorption is energetically favored at Ni step sites (compared to terrace Ni sites), thus, smaller Ni nanoparticles show tendentially higher catalytic activity compared to larger Ni agglomerates. The latter type is argued to have less amount of step Ni sites at fixed Ni content [126]. Additionally, it has been demonstrated that Ni catalysts with

particles < 15 nm generally discourage the formation of coke, as the CH₄ decomposition (Eq. 9) is argued as size sensitive [86]. On the other hand, other authors report better reforming performance and stability at lower Ni contents (< 5 wt.% Ni), as finely distributed Ni particles exposing strong interaction with the support material are mostly formed, which also discourage coke deposition [79, 127]. Unavoidably, these catalytic systems also face drawbacks, such as the formation of a fraction of small Ni nanoparticles exposing very strong MSI difficult to reduce, which shades the formation of the metallic active sites during activation and affects the catalyst performance negatively [128].

Another route towards fine and homogeneous Ni distribution over a support material is adding complexing agents (c.a., or ligands: L) during catalyst preparation. Most of the investigated L are organic acids, thus, their degree of ionization in solution is strongly affected by the preparation conditions, and therefore, how they bind the Ni ions. In this sense, previous reports have already investigated the impacts of using complexing agents such as CA, glycine (Gly) and ethylenediaminetetraacetic acid (EDTA) on Ni-based reforming catalysts [129-132]. It has been found that these Ls decrease the catalysts' Ni particle size and promote a finer distribution of the particles throughout the support material. Their promotional effect lies with the formation of Ni-organic complexes in the early preparation stages (solution) that impede them to form large particle agglomerates over the support's surface [133].

Generally, the efficiency with which the complexing agents bind with Ni is determined by the type of complexing agent (molecular structure and size, number and nature of binding sites like -COOH, -NH₃, lone electron pairs, double bonds, etc.), their concentration (compared to the amount of Ni to disperse) and the preparation conditions (as the preparation pH, the solution's ionic strength, preparation temperature, time for complex formation, etc.) used [134]. Apart from the chemistry occurring in solution, the subsequent deposition of the Ni complexes over the support during preparation and their impacts after catalyst calcination are equally important. The deposition of the Ni-complexes over the support is generally considered as an exchange reaction between the molecules (i.e., the ligands, water molecules, among others) in the coordination sphere of the Ni ions in solution with the OH-groups exposed (to the impregnating solution) by the support [135]. The previous is favored when the charge of the support and the metal complexes in solution are opposite. A deeper discussion of this phenomenon can be found in section 2.4.3. Finally, besides the decrease in the catalysts' Ni particle size, the thermal decomposition of these organic molecules during calcination generally increases the catalysts' surface area and pore volume, which is generally beneficial for the catalysts' specific activity [129].

2.4.2 Bi-/trimetallic Ni-based catalysts' formulations

Apart from the Ni load, particle size and distribution throughout the support material, including additional elements into the catalyst formulation is an efficient route to tune Ni reforming catalysts. In this sense, specific elements can cause alterations in the chemical and electronic properties of the Ni active sites, which define the catalysts' activity and stability. Particularly, several benefits can be mentioned, such as i) changing the catalysts' basicity, ii) stabilizing small Ni nanoparticles, iii) modifying the reducibility of Ni species, iv) promoting the gasification of coke or the elimination of sulfur, among others [83, 105, 136].

One group of efficient promoters for Ni-based reforming catalyst are the REM (such as Sc, Ce, La, Gd) [94]. These usually improve the catalysts' basicity, induce a high degree of structural defects (oxygen vacancies) due to a mismatch between the atomic sizes in the host-guest structures. They can also impart an improved oxygen storage-release capacity due to reversible redox mechanisms (for example, oxidation/reduction of Ce³⁺/Ce⁴⁺), and these can even determine the reaction mechanism by formation of REM₂O₂CO₃, as previously discussed in section 2.2 [137]. Consequently, all these modifications enhance the adsorption of the reforming reactants (CO₂, H₂O and/or O₂) as these processes are promoted in catalysts with basic character and/or exposing certain degree of structural defects, as already mentioned. Therefore, including these REM enhance the catalysts' activity and stability. Additionally, promoters like La have been shown to improve the Ni reducibility, which promotes the formation of the

Ni active sites [138]. On the contrary, elements like Sc and Gd have been proved to strengthen the MSI effect, thus, these prevent the sintering of Ni particles during operation at high temperatures [139, 140].

Including other elements in the formulations such as transition metals (Co, Cu) usually leads to different types of Ni species, for example, small and stabilized pure Ni particles surrounded by transition metal-rich domains (resistant to oxidation and agglomeration during reforming), bimetallic clusters made of combination between Ni-transition metal in close contact and/or robust solid state alloys (including random solid-solution alloys, surface alloys, alloys with core-shell structures, among others) [141]. These transition metals, especially those from the first period, share electronic and structural similarities with the Ni element and are easier to blend: most of these have available d electrons in their outer electron shells and similar atomic sizes. For example, Ni-Co alloys generally expose very strong MSI, which binds the particles strongly to the support and prevent particle sintering, while these sites generally expose high catalytic performance. Moreover, an alloyed NiCo/CeZr catalysts showed improved sulfur tolerance (compared to only Ni catalysts over same ceria-zirconia support [142]), possibly due to the strong MSI (which prevents formation of NiS), unique electronic properties (which impeded the adsorption of H₂S during operation) and due to high number of oxygen vacancies (which might have oxidized the Ni-S sites into SO₂ at T = 775 °C). On the other hand, Ni-Cu alloys are usually endowed with improved reducibility (thus, milder MSI) and discouraged coke formation [141, 143]. Despite that these elements are arguably similar with Ni, they can also impart certain degree of structural defects, which might improve the adsorption of CO₂.

Summed to the previous metals, another interesting promoter which can improve reforming catalysts is Ga. Thus, Ga is known for forming low-melting point alloys with Ni, improving the dispersion of the Ni particles and strengthening the MSI, increasing the availability of O species to oxidize the carbon deposits and also to tune the acidity of the Ni-based catalysts [144, 145]. Apart from the individual effects imparted by each promoter, using combinations of the promoters might enable new beneficial effects in the catalysts' physicochemical properties and efficiency. The previous approach was considered during the formulation of some of the catalysts reported in this work.

2.4.3 Effect of support composition and metal-support interactions (MSI)

The support material also contributes to the efficiency of reforming catalyst due to its intrinsic physicochemical properties, but most importantly, due to its interaction with the active metal species. As previously mentioned, the MSI effect is fundamental in shaping the performance of reforming catalysts. Generally, strong MSI are desired, as this effect tunes the reducibility of the catalysts and protects their activity during operation at high temperatures [146]. However, when the MSI is excessively strong, the reduction of the metal species might be disfavored, and therefore, a medium point should be reached to endow the catalyst with a balanced resistance against deactivation and sufficient reducibility [147]. Regarding the origin of the MSI effect, it is argued to arise from any (or combinations) of the following phenomena: charge transfer between the nanoparticles and the support, the morphology (and size) of the nanoparticles and the chemical composition and electronic environment of the metal nanoparticles and the support [148].

Up to date, several metal oxides have been investigated as carrier materials for Ni reforming catalysts, such as: γ -Al₂O₃, MgO, MgAl₂O₄, TiO₂, SiO₂, among others [149, 150]. Generally, supports with basic character are preferred as they promote the adsorption of acidic CO₂, which can improve the overall catalyst activity and stability by improving the adsorption of one reforming reactant and the gasification of coke deposits (inverse of Eq. 8), as previously mentioned. However, other properties such as their surface area, thermal and physical resistance, chemical composition and structure, among others, are also crucial [151]. For example, γ -Al₂O₃ is a widely studied material, which is chemically and mechanically stable (even at high temperatures), has high surface area and interacts strongly with Ni. Unfortunately, when γ -Al₂O₃ is used as support for DRM (for example: Ni/ γ -Al₂O₃), it tends to deactivate fast under typical DRM conditions, mostly due to the formation of carbonaceous deposits (enhanced by its mild acidic character) and the transformation of the Ni active species into the inactive

NiAl₂O₄ spinel phase [152, 153]. On the other hand, MgO has been reported to be another cost-effective material, which possesses strong basic character, remarkable abrasion resistance and textural properties. However, due to the inconvenient strong interaction between the NiO and MgO phases (as they display similar crystallographic features, they can form solid solutions in a wide range of concentrations, both cations have same charge (2+) and similar cationic radii 0.69 nm and 0.72 nm for Ni²⁺ and Mg²⁺, respectively [154]), Ni/MgO catalysts might require $T > 1000\text{ }^{\circ}\text{C}$ to form the Ni active sites [155]. Fortunately, the previous disadvantages can be controlled by combining γ -Al₂O₃ and MgO in adequate fractions. For example, adding MgO into γ -Al₂O₃ prevents the formation of the inactive NiAl₂O₄ spinel during operation (forming Ni_xMg_(1-x)Al₂O₄ ($0 \leq x \leq 1$) instead), increases the catalysts' basicity and strengthens the MSI effect [63]. As already discussed, the previous aspects are important for the stability of reforming catalysts. However, the MgO content is critical in determining the Ni reducibility mediated by MSI, CO₂ adsorption and coke gasification properties, and thus, it must be optimized [156].

Finally, the MSI effect deserves a deeper discussion. For example, some factors which strengthen it are: i) small and dispersed metal particles supported over a metal oxide with high surface area, ii) interaction mediated via electrostatic forces between the support and the metal (benefitted when both counterparts expose opposite charge sign, known as strong electrostatic adsorption: SEA), and iii) combinations of the previous points, among others. Some authors argue that the MSI effect can be traced back to early preparation stages, as benefitted interaction between the metal precursors and the carrier materials during preparation shapes the final catalysts' MSI [157]. This evidences that the choice of the preparation conditions (impregnation temperature, pressure, ionic strength, pH, among others) is crucial for shaping this effect. For example, changing the preparation pH not only modifies the precursor formation, but also the surface charge of a solid material. In this sense, metal oxides are populated with hydroxyl groups on their surface, the ionization degree of which depends on the media's pH [158, 159]. Therefore, the selected pH during the preparation determines the surface charge of the support. For example, for most of the oxides used as support in DRM (Al₂O₃, MgO, TiO₂, etc.), using acidic preparation conditions will protonate their surface hydroxyl groups and expose an overall positive charge (under these specific conditions), while deprotonated hydroxyl groups predominate on the surface at higher pH values (thus leading to a negatively charged surface). The pH at which the net charge of the support is balanced (zero) is called point of zero charge (PZC). With the previous in mind, it is then expected that a support at preparation pH < PZC (positive charged support) would preferentially adsorb anions, while the adsorption of cations is expected at pH > PZC (negative charged support) [160].

2.4.4 Impacts of changing the reaction conditions on the reforming activity and stability

The catalyst efficiency, stability and the incidence of the deactivation mechanisms not only depend on the physicochemical properties of the catalytic system *per se*, but also on the selection of the reaction conditions (such as the feed composition, temperature, contact time, etc.). Moreover, even the thermodynamics of the system strongly depends on the feed composition, thus, the reaction conditions must be properly chosen. If the valorization of CH₄-rich waste-derived feedstocks via reforming reactions is required to close the SCC, deeper investigations using alternative reaction feeds are necessary. Unfortunately, these regimes are highly deactivating for Ni-based catalysts. Following the discussion made in sections 2.1 and 2.3, the excess of methane in the feed causes lower methane conversion at all temperatures, a higher CO₂ conversion, an enhanced formation of coke deposits promoted by the CH₄ cracking (Eq. 9) and poisoning of the active phases with highly deactivating trace compounds.

Additionally, the reaction temperature is also a critical point for the reforming reactions, as addressed during the discussion of the thermodynamics of the reforming processes (section 2.1). Summarizing, high temperatures usually promote high conversion and selectivity towards H₂, but they also favor catalysts' deactivation via sintering and represent high energy costs, which represents trade-offs to contemplate during process design. With the previous in mind and focusing on DRM, performing tests at 600 – 650 °C and using CH₄/CO₂ > 1 (to mimic biogas sources) would be essential to identify selective, active and coke resistant catalysts, as these regimes strongly promote the formation of coke.

Lastly, the dilution of the feed and the applied flow rates impact on the conversion of reforming catalysts due to kinetic effects. Generally, high flow rates decrease the conversions due to a short contact time between the Ni active sites and the reactants [161]. Despite seeming challenging, through appropriate process optimization, high flow rates might also represent regimes in which higher H₂ productivities can be achieved, and therefore, these are also interesting [162].

The dependence of the reforming productivity and the feed composition is also evident for the combined reforming reactions. According to the CH₄ and CO₂ contents in biogas (see Table 1-1), both BRM and TRM could reform such CH₄-rich feed (free of impurities), but of course, proper amounts of H₂O and/or O₂ need to be externally fed. As a general trend, increasing the amount of water in the feed (compared to CO₂) tends to shift the equilibrium towards the SRM, thus, there is an increase in the H₂ production. On the other hand, increasing the O₂ content (in TRM) generally shifts the equilibrium towards the POM, which might affect the thermal management due to the combination of endothermic and exothermic reactions. Finally, the H₂/CO can be tuned by fixing the reaction feed composition, evidencing the importance of this parameter in process design.

Lastly, a short discussion on the uses of syngas is provided due to its economic and technological significance. Thus, the downstream application of the produced syngas via reforming reactions strongly depends on the resulting H₂/CO ratio. For example, syngas with low H₂ content (for example, derived from DRM: $H_2/CO \leq 1$) could be used to produce higher alcohols (than MeOH), DME and HAc, and/or for the reduction of iron ore (Fe₂O₃) in steel mills [163, 164]. Furthermore, a H₂-richer syngas (for example, derived from BRM or TRM: $1.8 \leq H_2/CO \leq 2.2$) could be used to produce MeOH or hydrocarbons via FT synthesis [4]. Finally, a H₂-rich syngas (for example, derived from SRM: $H_2/CO = 3$) could be used after CO + CO₂ separation for the synthesis of ammonia via the Haber-Bosch process [164]. Thus, producing syngas of adequate composition through reforming reactions and without needing to inject external H₂ to adjust the H₂/CO ratio could, in principle, simplify the coupling of different chemical processes, while reducing the environmental footprint simultaneously.

3. Materials and Methods

3.1 Preparation of catalysts

For the preparation of the catalysts, the following chemicals were used without further purification: deionized water prepared with an in-house filtering system (conductivity $< 5 \mu\text{S}/\text{cm}$), hydrotalcite (HTC)-derived Mg-Al oxides (Pural MG30, 50, 63 and 70, Sasol GmbH, Germany), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, Germany, $> 98\%$), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, India, $\geq 99\%$), MgO light (Merck, Germany, $> 95\%$), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma Aldrich, Germany, ACS reagent $\geq 98\%$), $\text{Al}(\text{OH})_3$ (Sigma Aldrich, Germany, $< 98\%$), NaHCO_3 (Sigma Aldrich, Germany $< 95\%$), $\text{CO}(\text{NH}_2)_2$ (urea, Merck, Germany, $\geq 99\%$), $\text{C}_6\text{H}_8\text{O}_7$ (citric acid, CA, Roth, Germany, $> 99.5\%$), $\text{C}_4\text{H}_6\text{O}_6$ ((2R, 3R)-(+)-tartaric acid, TA, Merck, Germany, $> 99.0\%$), $\text{C}_2\text{H}_5\text{NO}_2$ (glycine, Gly, Alfa Aesar, Germany, $> 99\%$), $\text{C}_{14}\text{H}_{23}\text{N}_3\text{O}_{10}$ (diethylenetriaminepentaacetic acid, DTPA, Fluka, Switzerland, $> 99.0\%$ purity), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, Germany, 99.9%), $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Acros Organics, USA, 99.9%), $\text{Sc}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Fischer Scientific, Germany, 99.9%), $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Sigma Aldrich, USA, 99.9%), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, Germany, 99.99%), solutions of 1.0 M HNO_3 (prepared by dilution of concentrated HNO_3 : ThermoFisher, United Kingdom, 65%) and standardized solution of $1.0 \text{ M NH}_4\text{OH}$ (Alfa Aesar, Germany).

All the catalysts discussed in chapters 4.1 – 4.3 had low-Ni loading (target $2.5 \text{ wt.}\%$ Ni) and were prepared using the wet impregnation method. The low metal load was mainly chosen as a follow-up to previous work done in our group [1, 78-80]. Such catalysts displayed exceptional activity, stability and selectivity under severe reforming conditions (i.e., $\text{GHSV} = 170 \text{ L}/(\text{g}_{\text{cat}} \cdot \text{h})$ with only $10 \text{ vol.}\%$ dilution of the reforming feed with internal standard) at comparatively lower Ni content to what is generally reported in the literature [58, 124, 125]. The reader is also referred to section 2.4.1 for a deeper discussion regarding the effect of the Ni load on catalyst performance and physicochemical properties. These samples are listed in Table 3-1. The detailed preparation methods can be found within this chapter, while the argumentation regarding the selection of the different modifications is found in the following chapters. The different calcination treatments used for catalysts preparation were done using a muffle furnace with venting port under static air.

Table 3-1. Description of the materials used throughout this work.

Material name	Prep. method ^a	Calcination program	Remark ^b	Preparation described in section	Discussion in chapter
NiO	Calc.	800°C (6 h)	-	3.1.1	4.1
S1 ^c	Calc.	550°C (6 h)	$30 \text{ wt.}\%$ MgO	3.1.1	4.1
S2 ^c	Calc.	550°C (6 h)	$50 \text{ wt.}\%$ MgO	3.1.1	4.1
S2.800 ^c	Calc.	400°C (3 h) + 800°C (6 h)	$50 \text{ wt.}\%$ MgO	3.1.1	4.1
S3 ^c	Calc.	550°C (6 h)	63% MgO	3.1.1	4.1
S4 ^c	Calc.	550°C (6 h)	70% MgO		4.1
MgO	Calc.	550°C (6 h)	-	3.1.1	4.1
Ni/MgO	WI	400°C (3 h) + 800°C (6 h)	-	3.1.2	4.1
Ni(CA)/S1	WI	400°C (3 h) + 800°C (6 h)	CA	3.1.2	4.1
Ni(CA)/S2	WI	400°C (3 h) + 800°C (6 h)	CA	3.1.2	4.1
Ni(CA)/S3	WI	400°C (3 h) + 800°C (6 h)	CA	3.1.2	4.1, 4.2
Ni(CA)/S4	WI	400°C (3 h) + 800°C (6 h)	CA	3.1.2	4.1

Ni/S2	WI	400 °C (3 h) + 800 °C (6 h)	-	3.1.2	4.1
Ni(CA-1)/S2	WI	400 °C (3 h) + 800 °C (6 h)	CA (pH < 1)	3.1.2	4.1
Ni(CA-2)/S2	WI	400 °C (3 h) + 800 °C (6 h)	CA (pH = 2)	3.1.2	4.1
Ni(CA-4)/S2	WI	400 °C (3 h) + 800 °C (6 h)	CA (pH = 4)	3.1.2	4.1
Ni(CA-5.5)/S2	WI	400 °C (3 h) + 800 °C (6 h)	CA (pH = 5.5)	3.1.2	4.1, 4.2
Ni(CA-9)/S2	WI	400 °C (3 h) + 800 °C (6 h)	CA (pH = 9)	3.1.2	4.1
Ni(TA)/S2	WI	400 °C (3 h) + 800 °C (6 h)	TA	3.1.2	4.1, 4.2
Ni(Gly)/S2	WI	400 °C (3 h) + 800 °C (6 h)	Gly	3.1.2	4.1
Ni(DTPA)/S2	WI	400 °C (3 h) + 800 °C (6 h)	DTPA	3.1.2	4.1
NiCe/S2	WI	400 °C (3 h) + 800 °C (6 h)	-	3.1.2	4.1
NiGa/S2	WI	400 °C (3 h) + 800 °C (6 h)	-	3.1.2	4.1
NiLaGa/S2	WI	400 °C (3 h) + 800 °C (6 h)	-	3.1.2	4.1, 4.2
NiGdSc/S2	WI	400 °C (3 h) + 800 °C (6 h)	-	3.1.2	4.1, 4.2
CP	CP	550 °C (6 h)	-	3.1.3.1	4.2
HT	HT	550 °C (6 h)	-	3.1.3.2	4.2
UH	UH	550 °C (6 h)	-	3.1.3.3	4.2
WI.800	WI	800 °C (6 h)	-	3.1.3.4	4.2
Ni(CA-5.5)/CP	WI	400 °C (3 h) + 800 °C (6 h)	CA (pH = 5.5)	3.1.4	4.2
Ni(CA-5.5)/HT	WI	400 °C (3 h) + 800 °C (6 h)	CA (pH = 5.5)	3.1.4	4.2
Ni(CA-5.5)/UH	WI	400 °C (3 h) + 800 °C (6 h)	CA (pH = 5.5)	3.1.4	4.2
Ni(CA-5.5)/WI.800	WI	400 °C (3 h) + 800 °C (6 h)	CA (pH = 5.5)	3.1.4	4.2, 4.3
Ni(CA-4)/WI.800	WI	400 °C (3 h) + 800 °C (6 h)	CA (pH = 4)	3.1.4	4.2
Ni(TA)/WI.800	WI	400 °C (3 h) + 800 °C (6 h)	TA	3.1.4	4.2
Ni(Gly)/WI.800	WI	400 °C (3 h) + 800 °C (6 h)	Gly	3.1.4	4.2
NiLaGa/WI.800	WI	400 °C (3 h) + 800 °C (6 h)	-	3.1.4	4.2, 4.3
NiGdSc/WI.800	WI	400 °C (3 h) + 800 °C (6 h)	-	3.1.4	4.2, 4.3

^a: Prep. method: preparation method. Calc.: calcination. WI: wet impregnation. CP: co-precipitation at fixed pH. HT: hydrothermal deposition-precipitation. UH: HT using urea for hydrolysis. ^b: molar ratio: c.a./Ni = 1.5. When no pH value is indicated between brackets, no change in the pH was done during the preparation. ^c: commercial materials.

3.1.1 Commercial Mg-Al supports (S1, S2, S3, S4 and S2.800), MgO and NiO

Firstly, commercial Mg-Al hydrotalcite-derived materials with different wt.% of MgO (30, 50, 63 and 70 wt.%, for Pural MG30, 50, 63 and 70, Sasol GmbH, respectively) were calcined under static air in a muffle furnace from room temperature to 550 °C (2 K/min) for 6 h. The as-obtained supports were nomenclated as S1, S2, S3 and S4 for calcined Pural MG30, 50, 63 and 70, respectively. Additionally, S2.800 refers to the support Pural MG50 calcined at 400 °C (2K/min) for 3 h, followed by calcination at 800 °C for 6 h (2 K/min) under static air. NiO and MgO were used as reference materials. NiO was

prepared by calcining $\text{Ni}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 800 °C for 6 h (2 K/min) under static air, while MgO was calcined in the same way as the different commercial supports (550 °C).

3.1.2 Preparation of low-loading Ni catalysts supported on calcined $\text{MgO-Al}_2\text{O}_3$

The first pool of catalysts was classified in four groups I-IV, each of them focusing on the effects of: changing the support's Mg content (Group I), using CA at specific pH values (Group II), using different chelating agents (Group III), and incorporating additional metals in the catalysts' formulation (Group IV).

The catalysts of groups I-IV were prepared using the wet impregnation method. Basically, for the preparation of 5 g of calcined catalyst, 0.619 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 150 mL of distilled water in a round bottom flask (to get 2.5 wt.% Ni in the calcined catalyst), placed on a heating mantle and magnetically stirred at 480 rpm for 15 min at 50 °C. Afterwards, different formulations were used during the impregnation, which are detailed below:

- For catalysts of Group I: 'Ni(CA)/Si' (*i*: 1, 2, 3 and 4; detailed in section 3.1.1). After dissolution of Ni precursors, 0.603 g of CA were added to each solution (CA/Ni molar ratio = 1.5). After stirring for 4 h, 4.875 g of the different supports were added (S1, S2, S3 or S4).
- For catalysts of Group II: 'Ni(CA-Z)/S2' (Z: <1, 2, 4, 5.5 and 9). After complete Ni dissolution, 0.603 g of CA were added to each solution (CA/Ni molar ratio = 1.5) and the pH was adjusted using solutions of 1.0 M HNO_3 or 1.0 M NH_4OH . Thus, 2 mL of HNO_3 were added to get pH < 1, unmodified solution of Ni + CA had a pH = 2, while 4.2, 6.3 and 8.5 mL of NH_4OH were added to attain pH = 4, 5.5 and 9, respectively. After stirring for 4 h, 4.875 g of support S2 were added.
- For catalysts of Group III: 'Ni(L)/S2' (L: CA, TA, Gly or DTPA). After Ni dissolution, different amounts of complexing agents were added to the solution (CA: 0.604 g, TA: 0.478 g, Gly: 0.239 g and DTPA: 1.256 g; c.a./Ni molar ratio = 1.5). After stirring for 4 h, 4.875 g of support S2 were added.
- For catalysts of Group IV: 'NiM/S2' (M: Ce, Ga, LaGa or GdSc). After Ni dissolution, different amounts of promoters were added to the solution at constant molar ratio (bimetallic: metal/Ni = 0.8, while trimetallic: sum of promoters/Ni = 0.8; 0.736 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.435 g of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 0.369 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.218 g $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ or 0.306 g $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.218 g $\text{Sc}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, respectively. After stirring for 4 h, 4.875 g of support S2 were added.
- Finally, as reference materials, Ni/S2 and Ni/MgO were prepared following a similar impregnation method than that used to prepare catalysts of Groups I-IV, but without including c.a., changing the pH or adding promoters in the preparation (for Ni/S2) and by changing the support to MgO (for Ni/MgO).

After addition of the support, each dispersion was stirred at 480 rpm for 16 h at 60 °C. Then, the liquid was removed stepwise using rotavapor at 60 °C and ~ 150 mbar. The samples were then dried in a furnace at 120 °C for 16 h under static air. The dried solids were ground, sieved (size < 180 μm) and calcined under static air from room temperature to 400 °C (2 K/min) for 3 h, then to 800 °C (2 K/min) for 6 h.

3.1.3 Development of an improved $\text{MgO-Al}_2\text{O}_3$ mixed oxide support

Different preparation methods were investigated to develop a home-made material which displays improved physicochemical properties and leads to better catalytic performance vs. those supported on commercial S2.

3.1.3.1 Co-precipitation method (CP)

The procedure was adapted from [165]. For the preparation of ~ 20 g of calcined Mg-Al mixed oxide, 15.897 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 18.383 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 300 mL of deionized water (solution A) and 6.262 g of NaOH and 13.147 g of Na_2CO_3 were dissolved in 300 mL of deionized water (solution B). Solutions A and B were added dropwise simultaneously into a round bottom flask containing 50 mL of deionized water. A white precipitate was immediately formed. The addition of the reagents was adjusted to get a constant pH = 8.5 during the preparation (measured every 5 min during the addition of the reagents). The dispersion was stirred (320 rpm) at 50 °C and the resulting solid was aged under the same conditions for 30 min. Finally, the white precipitate was filtered (using vacuum pump) and washed 5 times with deionized water at room temperature, until the eluting mother liquor had a pH of 7. The mother liquor after the fifth (last) wash was collected and analyzed by ICP and the Na^+ content was < 50 ppm. The solid was dried overnight under the fume hood at room temperature, then 2 h at 120 °C in an oven under static air, ground to particles sized < 180 μm and finally calcined at 550 °C (2 K/min) for 6 h.

3.1.3.2 Hydrothermal dissolution-precipitation method (HT)

The procedure was adapted from [166]. For the preparation of ~ 2.5 g of calcined Mg-Al mixed oxide, 1.574 g of MgO light, 1.727 g of $\text{Al}(\text{OH})_3$ and 1.1761 g of NaHCO_3 were dispersed in 20 g of deionized water in a 50 mL Teflon-lined stainless steel autoclave and heated in an oven at 180 °C for 20 h. The closed autoclave was then cooled down under water flow, the resulting dispersion was filtered (vacuum pump), and the white solid was washed 5 times using deionized water at room temperature until the pH of the eluting mother liquor was 7. The mother liquor after the fifth (last) wash was collected and analyzed by ICP, and the Na^+ content was < 20 ppm. The solid was finally treated as in section 3.1.3.1.

3.1.3.3 Hydrothermal dissolution-precipitation method using urea for hydrolysis (UH)

An adjusted procedure to that described in [167] was used. For the preparation of ~ 7.5 g of calcined MgAl mixed oxide, 9.542 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 11.0362 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 23.64 g of urea (molar ratio of urea/Mg = 10.5) were dissolved in 250 mL of deionized water in a 400 mL beaker and stirred at 480 rpm at room temperature for 30 min. Then, the solution was transferred into a 500 mL Teflon lined stainless steel autoclave and heated to 180 °C in an oven for 20 h. The closed autoclave was cooled down under water flow, the precipitate was vacuum filtered, washed 5 times with deionized water at room temperature until the pH of the mother liquor was 7. The obtained white precipitate was then dried, ground, and calcined as in section 3.1.3.1.

3.1.3.4 Wet impregnation of commercial Pural MG63 (S3) with $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (WI.800)

For the preparation of ~ 7.5 g of calcined Mg-Al mixed oxide, 5.163 g of commercial Pural MG63 and 7.587 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dispersed in 80 mL of deionized water in a 250 mL beaker. The dispersion was mixed using a high-performance dispersing device (Ultra Turrax, IKA devices) at 13500 rpm for 2 min and then the suspension was transferred into a 250 mL round bottom flask. Approximately 20 mL of deionized water were used to transfer the remaining solids from the beaker into the round bottom flask. The suspension was then evaporated using rotavapor at 60 °C and ~ 150 mbar. The white solid was heated in an oven at 120 °C overnight (under static air), then it was ground < 180 μm and calcined at different temperatures. The dried solid was calcined under static air at 800 °C (2 K/min) for 6 h.

3.1.4 Preparation of selected catalysts using home-made MgO-Al₂O₃ supports

The catalyst Ni(CA-5.5)/S2 was used as benchmark material due to its physicochemical properties and competitive performance. Thus, the support materials developed in sections 3.1.3.1-4 were used to prepare again the CA-assisted catalyst at fixed pH = 5.5, and then evaluated in DRM.

For the preparation of 3 g of the calcined Ni(CA-5.5)/P catalyst (P: CP, HT, UH and WI.800), 0.372 g of Ni(NO₃)₂·6H₂O were dissolved in 90 mL of distilled water in a 250 mL round bottom flask, placed on a heating mantle and magnetically stirred for 15 min at 50 °C and 480 rpm. After complete dissolution of the Ni precursor, 0.368 g of CA were added to the solution (CA/Ni molar ratio = 1.5) and the pH was adjusted to pH = 5.5 using 3.5 mL of 1.0 M NH₄OH solution, stirred at 480 rpm at 50 °C for 4 h. Afterwards, 2.95 g of calcined home-made support sized < 180 µm were added, and the dispersion was stirred at 480 rpm for 16 h at 60 °C. The synthesis was finished by removing the liquid in rotavapor, drying, grinding, and calcining the solid, as described in section 3.1.2. Finally, the catalysts Ni(CA-4)/WI.800, Ni(TA)/WI.800, NiLaGa/WI.800 and NiGdSc/WI.800 were prepared a second time following the method described in section 3.1.2, but using WI.800 (prepared in section 3.1.3.4) as support material.

3.2 Characterization of solid materials

Different instrumental characterization techniques were used for fresh, *ex situ* reduced and spent catalysts, such as: chemical analysis using inductively coupled plasma-optical emission spectroscopy (ICP-OES) for metals, and oxidation of deposited coke and sulfur for spent catalysts (CHNS analysis), surface charge determination (using zeta potentiometry and salt addition method), isothermal N₂ adsorption at low temperature (BET), X-Ray diffraction (XRD), temperature-programmed reduction using H₂ (H₂-TPR), temperature programmed desorption of CO₂ (CO₂-TPD), temperature-programmed oxidation using O₂ (O₂-TPO), (scanning) transmission electron microscopy ((S)TEM), X-Ray photoelectron spectroscopy (XPS) and electronic paramagnetic resonance (EPR). The basics of the different characterization techniques used to analyze the prepared and spent catalysts are described in the Appendix (see sections 7.1.1-9).

3.3 Catalytic reforming tests

The gases used for the catalyst pre-treatment and different reforming and regeneration tests were dosed using calibrated mass flow controllers (MFC, Brooks and Bronkhorst High-Tec), while deionized water was fed using a calibrated Shimadzu HPLC pump (model LC-20AT). The following gases were utilized: Ar, N₂, and H₂ (Air Liquide, Germany, 99.999% purity), CH₄ (Air Liquide, Germany, 99.95% purity), CO₂ (Linde, Germany, 99.995% purity), synthetic air (Air Liquide, Germany, 99.999% purity) and O₂ (Air Liquide, Germany, 99.9995% purity). Additionally, the following test gases were used for the experiments with deactivating molecules (impurities) present in biogas: 0.5 vol.% NH₃/He (Linde, Germany, 99.99%) and a certified gas mixture (Air Liquide, Germany) containing: 400 ppm H₂S (98%), 58 vol.% CH₄ (99.5%), 40 vol.% CO₂ (99.995%) and ~ 2 % N₂ (99.999%).

All the catalytic activity tests were performed in fixed-bed quartz reactors (length = 20.2 cm, volume = 14.1 mL, inner diameter = 9.6 mm) using an isolated electrical furnace (Applied Tests Systems Inc., max. temperature 1000 °C). The temperature was monitored using a thermocouple embedded in a quartz guided tube placed in the middle of the catalyst bed, which consisted of 50 mg of catalyst powder (sized < 180 µm) diluted with 2 g (1:40) of inert quartz sized between 0.5 – 0.8 mm. Two quartz wool plugs (20 mg each) sandwiched each extreme of the catalyst bed.

The setup was connected to an on-line Shimadzu GC-2030 (previously calibrated for all reactants using test gases and H₂O) to analyze feed and product gases during operation in real time. The GC was equipped with two analytical lines, two barrier discharge ionization detectors (BID) and three columns: Shimadzu RT-Plot-U-BOND (30 m × 0.53 mm × 20 µm) and a switchable combination of Shimadzu RT-Molsieve 5A (30 m × 0.53 mm × 50 µm) to separate H₂, N₂, H₂S, Ar, O₂, N₂, CH₄ and CO in line 1,

and Shimadzu Volatile Amine (30 m × 0.32 mm × 5 µm) to separate CO₂, NH₃, H₂O in line 2. Helium was used as a carrier gas. Sampling was performed every 15 min during the tests without H₂O or NH₃, while sampling every 29 min was done during tests with these 2 compounds. The gas lines, GC in- and outlet, valves, sample loop, etc., were heated to T > 120 °C using additional heating devices (heating bands and oven in the GC sample loop chamber) to avoid water condensation. A diagram of the setup used for the different reforming experiments, the same as representative chromatograms obtained using the developed separation method are found in Figure A 1 a-b, respectively.

The carbon balance was monitored for all experiments and ranged between 96 – 105 %. For calculations of the CH₄, CO₂, O₂ and H₂O conversions, H₂/CO ratio and H₂ productivity, Eqs. 12 – 17 were used, respectively.

$$X_{\text{CH}_4} (\%) = \frac{\dot{n}_{\text{CH}_4,\text{in}} - \dot{n}_{\text{CH}_4,\text{out}}}{\dot{n}_{\text{CH}_4,\text{in}}} \times 100 \quad (\text{Eq. 12})$$

$$X_{\text{CO}_2} (\%) = \frac{\dot{n}_{\text{CO}_2,\text{in}} - \dot{n}_{\text{CO}_2,\text{out}}}{\dot{n}_{\text{CO}_2,\text{in}}} \times 100 \quad (\text{Eq. 13})$$

$$X_{\text{O}_2} (\%) = \frac{\dot{n}_{\text{O}_2,\text{in}} - \dot{n}_{\text{O}_2,\text{out}}}{\dot{n}_{\text{O}_2,\text{in}}} \times 100 \quad (\text{Eq. 14})$$

$$X_{\text{H}_2\text{O}} (\%) = \frac{\dot{n}_{\text{H}_2\text{O},\text{in}} - \dot{n}_{\text{H}_2\text{O},\text{out}}}{\dot{n}_{\text{H}_2\text{O},\text{in}}} \times 100 \quad (\text{Eq. 15})$$

$$\text{H}_2/\text{CO ratio} = \frac{\dot{n}_{\text{H}_2,\text{out}}}{\dot{n}_{\text{CO},\text{out}}} \quad (\text{Eq. 16})$$

$$\text{H}_2 \text{ productivity} = \frac{2 \times X_{\text{CH}_4} \times F_{\text{CH}_4}}{g_{\text{cat}}} \quad (\text{Eq. 17})$$

Being: $\dot{n}_{\text{in}}$ and $\dot{n}_{\text{out}}$ the mole streams of the reactants at the inlet and outlet, respectively, and F_{CH_4} : the volumetric flow of methane.

3.3.1 DRM screening and stability tests in CH₄/CO₂ = 1:1

The catalysts were firstly reduced *in situ* at 700 °C using 50 mL/min of pure H₂ for 1.5 h before the screening DRM tests. The selected reduction temperature was lower compared to those needed according to the catalysts' H₂-TPR profiles. The reasons for this are described in sections 4.1.1.2 and 4.1.2.2, while relevant catalytic results are displayed in Figure A 1 c-d. Afterwards, the catalyst bed was flushed using 100 mL/min Ar for 15 min until no H₂ peak was detected in the chromatograms and heated to the first reaction temperature (750 °C). Meanwhile, the feed composition (pre-mixed for 30 min in by-pass mode) was determined via 5 consecutive GC injections until obtaining reproducible peak areas of the gas mixture used for the reaction. Afterwards, these gases were fed into the reactor, and the experiment was performed at 5 consecutive temperature steps ranging from T = 600 – 750 °C (the T order was as follows: 750, 700, 650, 600 and back to 750 °C, each step lasting for 5 h: 1 h for thermal equilibration and 4 h of isothermal hold and GC sampling). The following conditions were used during the tests: CH₄/CO₂/N₂ = 45:45:10 vol.%, p = 1 bar and Gas Hourly Space Velocity (GHSV) = 170 L/(g_{cat}·h). The temperature was increased/decreased at 2 K/min (accordingly) under the reaction conditions. N₂ was used as internal standard for calculating volumetric changes during reaction.

For the long-term stability tests, selected catalysts were pre-reduced at 750 °C (instead of 700 °C), which will be further discussed in chapter 4.1. After reduction, the temperature was decreased to 600 °C (at 2 K/min) to perform the long-term runs under the following conditions: CH₄/CO₂/N₂ = 45:45:10 vol.%, p = 1 bar and GHSV = 170 L/(g_{cat}·h).

3.3.2 Impacts of changing the reaction conditions

Generally, sufficient conversions rates and high H₂ productivity are desirable for reforming catalysts, as higher fractions of reactants are converted towards syngas with appropriate H₂ content (per unit of mass of catalyst and time), which is of outmost importance for further downstream applications. The previous

points depend on the operation conditions chosen, especially on the GHSV and CH₄/CO₂ ratio. As discussed in section 2.4.4, high GHSV and CH₄/CO₂ ratios are severe reaction conditions for the reforming catalysts, but these could also represent regimes in which high fractions of H₂ can be obtained per unit of time, while considering more application-related feedstocks. Therefore, the impacts of these reaction conditions were investigated through different GHSV (42.5 – 190 L/(g_{cat}·h)) and by increasing the CH₄ content in the feed (CH₄/CO₂ = 2:1). Focus was set on the catalyst stability under CH₄ excess conditions and high GHSV = 170 L/(g_{cat}·h), to resemble biogas sources and to highlight the catalytic activity, coking resistance and H₂ productivity of the prepared catalysts.

3.3.2.1 Effect of GHSV (CH₄/CO₂ = 1:1)

The effect of changing the GHSV was studied for Ni(CA-5.5)/WI.800 and NiLaGa/WI.800 after *in situ* reduction at 750 °C for 1.5 h. These tests were performed at 600 °C using CH₄/CO₂/N₂ = 45:45:10 vol.%, p = 1 bar, and changing the GHSV from 42.5 to 190 L/(g_{cat}·h) (the following order was used: 42.5, 85.0, 127.5, 170, 190 and back to 42.5 L/(g_{cat}·h) (3 h each step)).

3.3.2.2 Screening and long-term tests in CH₄/CO₂ = 2:1

Selected catalysts were also evaluated using CH₄/CO₂ = 2:1. Firstly, the samples were *in situ* reduced at 700 °C, and then tested under the following conditions: CH₄/CO₂/N₂ = 60:30:10 vol.%, p = 1 bar and GHSV = 170 L/(g_{cat}·h), while changing the temperature from T = 600 – 750 °C (as done in section 3.3.1).

For the stability tests, selected catalysts were pre-reduced at different temperatures (700, 750 or 800 °C) using 50 mL/min of H₂ for 1.5 h, followed by flushing with 100 mL/min of Ar for 15 min. The reactions were carried out at 750 °C and under the following conditions: feed composition CH₄/CO₂/N₂ = 60:30:10 vol.%, p = 1 bar and GHSV = 170 L/(g_{cat}·h).

3.3.2.3 Process variants: BRM and TRM

Selected catalysts were pre-reduced at the optimum conditions (identified through experiments described in section 3.3.2.2). Both BRM and TRM reactions were carried out using increasing consecutive temperatures (750, 800, 850 and back to 750 °C) at p = 1 bar and theoretical GHSV = 170 L/(g_{cat}·h). The flow rates of the gases (CH₄, CO₂, N₂, O₂) were measured before feeding vaporized water, while the water fed was tracked by the weight loss before and after reaction and GC. With regards to BRM, each temperature was held for 18 h using feeds of CH₄/H₂O/CO₂/N₂ = 45:30:15:10 vol.%. On the other hand, each temperature was held for 5 h for TRM, while feeds of CH₄/H₂O/CO₂/O₂/N₂ = 55:20:5:10:10 vol.% were used.

3.3.3 Development of regeneration strategies

Summed to the catalysts' activity and stability, their regeneration is also crucial for the reforming processes and catalyst lifespan. Therefore, catalyst regeneration after heavy coke deposition and after exposure to 100 ppm of NH₃ or 5 ppm of H₂S was studied using different treatments.

3.3.3.1 Oxidation of coke deposits

The regeneration of the catalyst NiLaGa/WI.800 was studied in 2 consecutive cycles. Firstly, it was reduced using 50 mL/min of H₂ at 800 °C for 1.5 h and flushed for 15 min with 100 mL/min of Ar. Afterwards, the gas mixture CH₄/CO₂/N₂ = 60:30:10 vol.% was fed at p = 1 bar and GHSV = 170 L/(g_{cat}·h) at 750 °C for 16 h. Afterwards, a mixture CH₄/N₂ = 90:10 vol.% was fed for 2 h to accelerate coke deposition (GHSV = 170 L/(g_{cat}·h)), followed by repeating the initial conditions for 1 h to identify catalyst deactivation. Then, the catalyst was flushed for 15 min using 100 mL/min of Ar at 800 °C. The second cycle consisted of exposing the catalyst to 50 mL/min of synthetic air for 2 h at 800 °C (coke oxidation was monitored using GC by tracking CO₂ formation), flushing for 15 min using 100 mL/min of Ar and reducing the catalyst using 50 mL/min of H₂ at 800 °C for 1.5 h and flushing for 15 min using 100 mL/min of Ar at the same temperature. Then, the reaction mixture was fed again for another 16 h at

750 °C ($\text{CH}_4/\text{CO}_2/\text{N}_2 = 60:30:10$ vol.%, $p = 1$ bar, $\text{GHSV} = 170 \text{ L}/(\text{g}_{\text{cat}} \cdot \text{h})$), 2 h of $\text{CH}_4/\text{N}_2 = 90:10$ vol.% at 800 °C and 1 h of initial reaction conditions. This cycle contemplating oxidation-reduction + reaction under the initial conditions was repeated a second time (reaction monitored for another 16 h).

3.3.3.2 Dry reforming of model biogas – effect of NH_3 and catalyst regeneration

NiLaGa/WI.800 was reduced using 50 mL/min of H_2 at 800 °C for 1.5 h and then flushed for 15 min with 100 mL/min of Ar. Afterwards, the gas mixture $\text{CH}_4/\text{CO}_2/\text{N}_2 = 60:30:10$ vol.% was fed at $p = 1$ bar and $\text{GHSV} = 170 \text{ L}/(\text{g}_{\text{cat}} \cdot \text{h})$ at 750 °C for 16 h. Then, 100 ppm of NH_3 were included in the reaction mixture (resembling the previous conditions) for 18 h at 750 °C. Afterwards, the flow of NH_3 was interrupted and the reaction monitored for 4 h at 750 °C (using first conditions). The catalyst was then regenerated using oxidation and reduction treatment as described in section 3.3.3.1, and finally, exposed again to the initial reaction conditions for 2 h at 750 °C.

3.3.3.3 Dry reforming of model biogas – effect of H_2S and catalyst regeneration

Several reactivation treatments were investigated to regenerate the catalysts after deactivation using 5 ppm of H_2S in $\text{CH}_4/\text{CO}_2 = 2:1$. For that purpose, thermal, reductive, and oxidative-reductive treatments were studied. All these experiments started similarly, i.e., with catalyst reduction using 50 mL/min of H_2 at 800 °C for 1.5 h, followed by reaction under the following conditions: $\text{CH}_4/\text{CO}_2/\text{N}_2 = 60:30:10$ vol.%, $p = 1$ bar and $\text{GHSV} = 170 \text{ L}/(\text{g}_{\text{cat}} \cdot \text{h})$ at 750 °C for 2 h. Afterwards, 5 ppm of H_2S were included in the previous feed and the experiment was monitored until complete catalyst deactivation. These poisoned catalysts were then used for the succeeding regeneration.

Two strategies were used for thermal regeneration. In the first one, the flow of the deactivating reaction mixture (with 5 ppm of H_2S) was uninterrupted, while the temperature was increased from 750 °C to 850 and 900 °C (at 2 K/min) for 2 h each step, followed by isothermal hold at 900 °C for 2 h without gas flow. Afterwards, the temperature was decreased to 750 °C and the gas mixture (without H_2S) was fed again for 2 h. In the second one, the reaction mixture (without H_2S) was continuously fed, while the temperature was increased to 900 °C (at 2 K/min) and held for 2 h, followed by decreasing it to 750 °C (at 2 K/min) hold for 2 h.

Regarding regeneration using reductive treatment, the poisoned catalysts were firstly flushed with 100 mL/min of Ar for 15 min, followed by reduction with 50 mL/min of H_2 at 800 °C overnight (ON, for 16 h). Afterwards, the catalysts were flushed with 100 mL/min of Ar for 15 min and then, the reaction mixture (without H_2S) was fed at 750 °C for 4 h. Finally, the oxidative-reductive treatments were performed by firstly flushing the sample with 100 mL/min of Ar for 15 min, followed by oxidation with 50 mL/min of synthetic air at 800 °C for 2 h or 16 h, and reduction with 50 mL/min of H_2 at the same temperature for 1.5 h. Afterwards, the catalysts were flushed with 100 mL/min of Ar for 15 min and the reaction mixture (without H_2S) was fed again for 6 h.

4. Results and Discussion

4.1 Development of low-loading Ni catalysts for DRM

This chapter explores the impacts of specific preparation parameters on DRM catalysts using commercial (calcined) Mg-Al mixed oxides as supports. The catalysts obtained were categorized in four groups:

- Group I: focuses on the effect of the Mg content in the support's structure.
- Group II: studies the impacts of changing the pH during catalyst preparation using citric acid (CA).
- Group III: investigates the effect of using different organic acids as chelating agents.
- Group IV: rationalizes the influence of incorporating additional metals into the catalyst formulation.

The prepared materials (calcined, *ex situ* reduced and spent catalysts) were thoroughly characterized using solid-state characterization techniques and screened in stoichiometric DRM. Finally, outstanding catalysts from each group were tested in long-term runs under deactivating reaction regimes.

As discussed in chapter 2, the reforming activity, stability, selectivity, and tendency to deposit coke strongly depend on different physicochemical parameters of the catalysts in intricate ways, including the interaction between Ni species and the support (MSI), the catalysts' surface chemical and electronic properties, the Ni particle size, among others. As can be anticipated, the modifications done in each group of samples (Group I-IV) altered the physicochemical properties of the catalysts in different ways. Thus, making a systematic comparison between the catalysts of different groups to establish universal structure-activity relationships is challenging. Thus, each group of catalysts was individually analyzed, and the comparison between groups of catalysts was excluded from the discussion.

4.1.1 Effect of the support's Mg content (Group I)

4.1.1.1 Characterization of calcined catalysts

Initially, the effect of modifying the support's Mg content (Group I) was studied using four commercial HTC-derived Mg-Al powdered materials: Pural MG30, 50, 63 and 70 (Sasol, GmbH), which have MgO loads of 30, 50, 63 and 70 wt.% (rest Al_2O_3), respectively. These fresh solids were calcined at 550 °C for 6 h under static air to obtain the supports used for catalyst preparation (S1, S2, S3 and S4, respectively). The calcination of Mg-Al HTC structures at high temperatures under static air leads to structural collapse of the HTC parental structure and produces thermally stable $\text{MgO-Al}_2\text{O}_3$ mixed oxides, which have attractive textural properties [168], as discussed in section 1.4. To be able to make statements about these calcined supports, the same as the resulting catalysts, these samples were characterized with ICP, BET and XRD, and the corresponding results are summarized in Table 4-1, while their diffractograms are displayed in Figure 4-1 a-b, respectively.

Table 4-1. Chemical composition (ICP), textural properties (BET) and H₂ consumption (H₂-TPR) of the studied support materials and selected catalysts.

Sample name	ICP				BET			H ₂ -TPR	
	Ni content (wt.%)	Mg content (wt.%)	Al content (wt.%)	Mg/Al ^a	S _{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	T. H ₂ (μmol/g) ^b	E. H ₂ (μmol/g) ^c
S1	-	16.5	35.0	0.5	245	7.1	0.5	-	-
S2	-	25.3	22.4	1.3	139	4.8	0.2	-	-
S3	-	34.3	17.9	2.1	197	3.1	0.2	-	-
S4	-	38.0	15.5	2.8	199	5.5	0.3	-	-
S2.800	-	-	-	-	123	4.7	0.2	-	-
Ni/S2	2.5	27.5	25.0	1.2	96	3-10	0.3	426	400
Ni(CA)/S1	2.4	15.8	33.9	0.5	120	2-15	0.3	409	382
Ni(CA)/S2	2.6	28.2	25.7	1.2	124	3-10	0.3	443	427
Ni(CA)/S3	2.4	34.0	18.3	2.1	77	3-12	0.2	409	375
Ni(CA)/S4	2.4	35.5	15.2	2.7	32	3-12	0.1	409	386

^a: molar ratio. ^b: theoretical H₂ consumption related to the measured ICP Ni content. ^c: measured H₂ consumption during the H₂-TPR experiments.

Regarding the chemical composition (see Table 4-1), the measured Mg contents of the calcined supports increased following the order: S1 (calcined Pural MG30) < S2 (calcined Pural MG50) < S3 (calcined Pural MG63) < S4 (calcined Pural Mg70), as expected. Additionally, these calcined materials displayed high surface area (S_{BET}) ranging between 139 – 245 m²/g, pore sizes ranging between 3.1 – 7.1 nm and pore volumes ranging between 0.2 – 0.5 cm³/g.

From a structural point of view, the phases present in the materials calcined at 550 °C strongly depended on the support's Mg content. For example, the samples richest in Mg (S3 and S4) only showed reflections associated to periclase MgO (cubic, ICDD: 00-045-0946, main reflections centered at 2θ = 36.9, 42.9, 62.3, 74.7 and 78.6°), which were slightly shifted towards lower angles at increasing MgO content. Such shift indicated less degree of incorporation of Al³⁺ into the periclase structure at increasing MgO loading [168]. Contrarily, the supports with lower Mg content (S1 and S2) showed broad reflections of MgO and MgAl₂O₄ (cubic, ICDD: 01-075-6826, main reflections centered at 2θ = 18.9, 36.8, 44.8, 59.3 and 65.2°). The previous indicated that decreasing the Mg loading (i.e., increasing the Al content accordingly) promoted the formation of MgAl₂O₄. Furthermore, the sample with intermediate Mg loading was calcined at 800 °C for 6 h (S2.800) to identify possible structural modifications provoked during the calcination procedure used for the Ni-containing catalysts. Increasing the calcination temperature led to sharp and well resolved reflections of MgO and MgAl₂O₄ (Figure 4-1 a), indicating that, on the one hand, the solid increased its degree of crystallinity, and on the other hand, the MgAl₂O₄ phase was formed at 800 °C. In connection to this, the formation of crystalline MgAl₂O₄ phase needs T > 700 °C under static air, which is notoriously higher than the temperature used during support preparation [169]. Thus, the calcination of the catalysts at 800 °C for 6 h would be sufficient to produce powder materials with defined solid phases, which ultimately depend on their Mg composition.

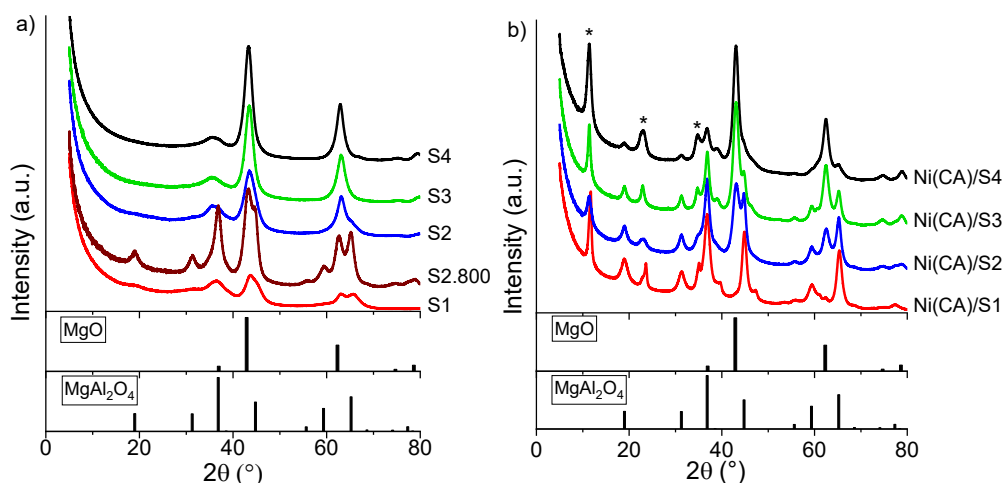


Figure 4-1. Diffractograms of: a) calcined supports S1, S2, S3, S4 and S2.800 and b) calcined catalysts Ni(CA)/S1, Ni(CA)/S2, Ni(CA)/S3 and Ni(CA)/S4. Legend: “*”: $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3)(\text{H}_2\text{O})_3$ monoclinic (ICDD: 01-080-4930).

After characterization of the support materials, these were used for the preparation of Group I of catalysts, i.e., 4 low Ni loading (2.5 wt.% Ni) samples assisted with CA, namely Ni(CA)/S1, Ni(CA)/S2, Ni(CA)/S3 and Ni(CA)/S4. In this sense, CA was used to improve the distribution of Ni precursors during preparation, and based on previous results of our group [1], the latter leads to stabilized Ni nanoparticles on the support via strong MSI after calcination and activation. Thus, and by following the discussion provided in chapter 2, CA-assisted catalysts would display improved catalytic performance at lower carbon deposition rates during reforming reaction.

Regarding the chemical composition (Table 4-1), the prepared catalysts showed Ni contents close to the expected 2.5 wt.% Ni loading, while the Mg/Al molar ratios agreed well with those of their corresponding calcined support materials. The previous evidenced that the Ni uptake was successful and no remarkable Mg and/or Al loss was provoked during preparation. Besides, the impregnated catalysts displayed surface areas (S_{BET}) ranging between 32 and 124 m^2/g , being lower compared to those of the calcined supports. The previous suggested that Ni impregnation and calcination caused partial blockage of the support's pores and/or the support's porous structure was modified by the high calcination temperatures used (for example, by clogging of mesopores, deformation and/or collapse of the porous network [170]). Moreover, the catalysts prepared using supports with $\text{MgO} > 50$ wt.% (Ni(CA)/S3 and Ni(CA)/S4) displayed the lowest S_{BET} among the series. Particularly, the S_{BET} decreased from 77 m^2/g for Ni(CA)/S3 to 32 m^2/g for Ni(CA)/S4, suggesting that the supports with very high Mg contents formed porous structures susceptible to collapse at the high calcination temperature used, which was clearly detrimental for the catalyst's textural properties. Thus, the least decrease in S_{BET} identified for Ni(CA)/S2 highlighted its robust porous structure among other supports and catalysts of the series, which also led to the best material for the reaction (see below, section 4.1.1.2). This discussion is deepened with XRD analysis (see below).

Interestingly, the diffractograms of the supports and corresponding catalysts differed. Firstly, independently of the Mg load, the Ni-based catalysts displayed sharper reflections (compared to the respective supports calcined at 550 °C), which suggested that the solids were more crystalline after calcination at 800 °C for 6 h. For example, the latter can be clearly observed in the reflection centered at $2\theta = 66^\circ$ for the pair S1 support – Ni(CA)/S1 catalyst, similar to what was previously discussed for S2 and S2.800. Apart from that, new reflections were observed in the calcined catalysts. For example, the Mg-rich sample Ni(CA)/S4 showed reflections ascribed to MgAl_2O_4 (for example at $2\theta \sim 36$ and 66°), which were barely detectable in the bare S4. In connection to this, the reflections of MgAl_2O_4 decreased in intensity, while these were simultaneously shifted towards lower angles at increasing the

MgO content of the support. Thus, less Al was available to form MgAl_2O_4 (i.e., reflections of lower intensity), while the shift towards lower angles can be ascribed to less Al incorporation within the crystalline phases. Thus, the predominance of MgO vs. MgAl_2O_4 as crystalline phase, less Al incorporation, and/or potential structural rearrangements provoked during calcination at 800 °C for 6 h could explain the lowest S_{BET} measured for Ni(CA)/S4.

Interestingly, no reflections associated to Ni phases were identified in any of the catalysts. The latter was most likely due to the low loading of Ni (2.5 wt.% Ni) [171]. Other points that might explain the absence of Ni reflections in the catalysts' diffractograms are: i) the overlapping of the signals of MgO and NiO oxides and/or MgAl_2O_4 and NiAl_2O_4 aluminates (due to similar ionic radius and crystallographic lattices between both oxides and aluminates [172, 173]) and/or ii) fine Ni distribution throughout the support (i.e., formation of small and particles undetectable by XRD) provoked by CA complexation during preparation.

Finally, the calcined catalysts displayed reflections of HTC: magnesium aluminum hydroxide carbonate hydrate phase ($\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3)(\text{H}_2\text{O})_3$, denoted as '*' in Figure 4-1 b (monoclinic, ICDD: 01-080-4930, main reflections centered at $2\theta = 11.6, 23.5, 40.2^\circ$) most likely formed by the reversible hydration of the calcined catalysts stored in closed vials at ambient conditions. The rehydration of calcined Mg-Al mixed oxides to form HTC and the collapse of HTC into Mg-Al mixed oxides via calcination are reversible processes, which mostly depend on the temperature [174]. Generally, $T > 350^\circ\text{C}$ collapse the Mg-Al HTC parental structure [175]. Thus, reduction at 700 °C before catalyst application converts the HTC into MgO- Al_2O_3 mixed oxides, eliminating the HTC phase during catalytic testing. No HTC reflections were observed in the *ex situ* reduced catalysts of Group II and III (see below, sections 4.1.2.1 and 4.1.3.1, respectively).

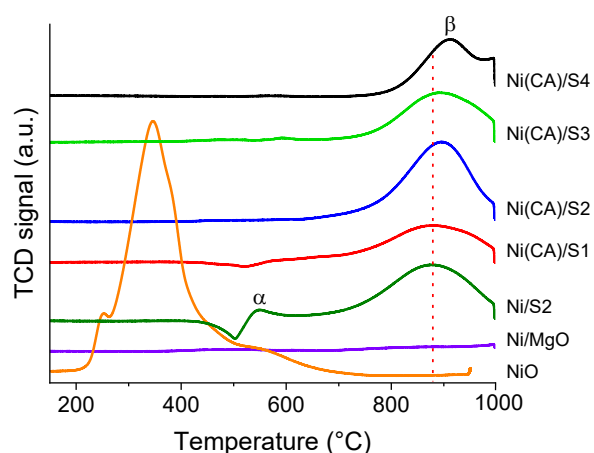


Figure 4-2. H_2 -TPR profiles of calcined NiO, Ni/MgO, Ni/S2, Ni(CA)/S1, Ni(CA)/S2, Ni(CA)/S3 and Ni(CA)/S4.

To get further insights regarding the samples' reducibility and MSI, H_2 -TPR was used for characterization (profiles displayed in Figure 4-2). The samples NiO, Ni/S2 and Ni/MgO were included as references. Firstly, the NiO H_2 -TPR profile displayed three reduction peaks: a shoulder centered at 250 °C, the main peak centered at 350 °C and another shoulder centered at 550 °C. These peaks were ascribed to the reduction of surface NiO reduced at $T_{\text{red}} < 300^\circ\text{C}$, bulk NiO at $T_{\text{red}} = 350^\circ\text{C}$, and large defective NiO- Ni^0 particles formed during the reduction process at $T_{\text{red}} > 500^\circ\text{C}$ [176].

Supporting NiO on Mg-containing supports impacted on the reduction of Ni species, as these are dispersed throughout a porous matrix which stabilizes them. Such stabilization was reflected on the higher temperatures needed to reduce oxidic Ni species in the supported catalysts ($T_{\text{red}} > 550^\circ\text{C}$) compared to the reference NiO. Particularly, at least two types of reducible Ni^{2+} (i.e., α - and β -Ni species) were identified in some of the H_2 -TPR profiles of Figure 4-2 (see Ni/S2 and Ni(CA)/S1). On the one

hand, easily reducible Ni^{2+} (α -Ni species) are generally deposited on the catalysts' surface and/or they are not deeply embedded/stabilized within the support's structure [177]. Consequently, these α -Ni display moderate MSI and require mild $T_{\text{red}} \approx 550$ °C to be reduced. Contrarily, the high temperature peak ($T_{\text{red}} > 800$ °C) is associated to the reduction of β -Ni species, i.e., those which are finely distributed on the catalysts' surface and/or embedded in the Mg-rich phases of the MgO-Al₂O₃ mixed oxide supports and expose very strong MSI [177].

Going one step forward, including CA in the preparation turned most of the α -Ni into strongly stabilized β -Ni species vs. the bare Ni/S2 (see Figure 4-2). Thus, using CA led to reducible Ni species exposing stronger MSI compared to Ni/S2, which was ascribed to a finer distribution of these on the support favored by initial precursor Ni-CA complexation (this discussion is deepened in the section 4.1.2) [129]. Moreover, it seems that not only the CA addition, but also the support's Mg content influenced the catalysts' MSI (see the H₂-TPR profiles of the different CA-assisted catalysts). For example, the low-Mg loading Ni(CA)/S1 was the only one (among the CA-assisted catalysts) which showed a broad reduction profile, ranging between $T_{\text{red}} = 550 - 1000$ °C, suggesting the reduction of both α -Ni ($T_{\text{red}} \approx 550 - 700$ °C) and β -Ni species ($T_{\text{red}} > 800$ °C). Contrarily, Ni(CA)/S2, Ni(CA)/S3 and Ni(CA)/S4 displayed only β -Ni species in their H₂-TPR profiles, evidencing that CA and a support with > 30 wt.% MgO were needed to form solely β -Ni species displaying strong MSI. Additionally, the maximum reduction temperature required to reduce these β -Ni species was shifted towards higher values as the MgO load of the support increased, following the order: Ni(CA)/S2 ($T_{\text{red}} = 895$ °C; 50 wt.% MgO) < Ni(CA)/S3 ($T_{\text{red}} = 905$ °C; 63 wt.% MgO) < Ni(CA)/S4 ($T_{\text{red}} > 920$ °C; 70 wt.% MgO). Thus, Ni(CA)/S4 showed the highest T_{red} among the series, disclosing how strongly Mg stabilizes the Ni species in these catalysts.

The previous observation was confirmed by increasing the Mg load even further, i.e., supporting Ni on MgO (Ni/MgO). This sample displayed Ni species with remarkably strong MSI, which was evidenced by the absence of reduction peaks in its H₂-TPR profile, even up to 1000 °C. Thus, the formation of hardly reducible NiO-MgO solid solution explains such high reduction temperature, and it seemed to prevail at increasing Mg loads in the CA-assisted catalysts.

Likewise, the authors in [178] reported very high T_{red} of 850 °C and very low Ni reducibility (< 15%) for 8 wt.% Ni/MgO calcined at $T \geq 800$ °C due to the very strong interaction between NiO-MgO forming solid solutions. Please, note that the presence of very low intensity peaks in the H₂-TPR discussed in [178] relates to the 3 times higher Ni load used vs. the Ni amount used in this work (2.5 wt.%). Thus, and as already discussed in section 2.4.1, higher Ni loads generally produce Ni species easier to reduce.

Finally, the catalysts' H₂ consumptions were tracked, and the values are reported in Table 4-1. Thus, all catalysts displayed lower experimental H₂ consumption to the theoretical possible value. Therefore, the formation of an unreducible Ni fraction strongly stabilized within the Mg-containing supports and/or formation of NiO_{1-x} species can be suggested, which have already been reported for Ni DRM catalysts supported on Mg-containing oxides [179].

4.1.1.2 Effects of the support's Mg content on catalyst performance

The characterized materials were screened in DRM to study the effect of the support's Mg content on the catalysts' activity, stability and coke deposition. Firstly, the calcined supports (at 550 °C) were tested using the developed screening protocol and no conversions were observed at any reaction temperature, thus, the bare supports were inactive towards DRM (not shown).

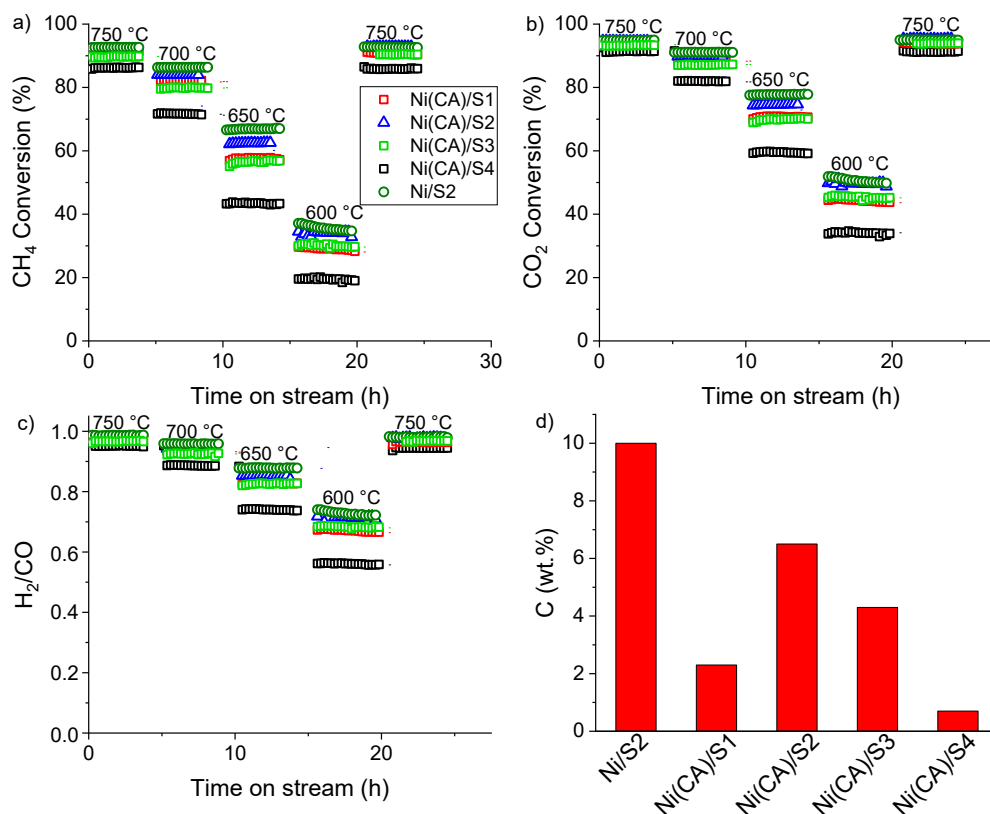


Figure 4-3. a) CH₄ and b) CO₂ conversions, c) H₂/CO ratio with TOS, and d) measured carbon using CHN analysis of spent catalysts of Group I and bare Ni/S2 after 25 h TOS. Reaction conditions: $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h, CH₄/CO₂/N₂ = 45:45:10 vol.%, $p = 1\text{ bar}$, $m_{\text{cat}} = 50\text{ mg}$, GHSV = 170 L/(g_{cat}·h). The numbers on top of each data cluster indicate the temperature (in the middle of the catalyst bed) at which the data was collected.

Lower reduction temperatures were used for activating the catalysts before testing compared to the those measured using H₂-TPR. This was done for the following reasons: i) to prevent particle sintering by using excessively high reduction temperatures (i.e., $T_{\text{red}} > 800\text{ }^{\circ}\text{C}$) before reaction, which decreases the number of active sites and fosters coke deposition [180] (see sections 2.3.2 and 2.4.4 for more details), and ii) as the catalysts displayed competitive performance anyways without using their corresponding maximum T_{red} (H₂-TPR). The impacts of using different activation conditions on the resulting reforming activity are displayed in Figure A 1 c-d, and further discussed in section 4.1.2.2.

Afterwards, the different Ni-based catalysts were screened. Generally, the conversions obtained for the catalysts depended on the reaction temperature set, and higher conversions were recorded at increasing temperatures (maximum recorded at $T = 750\text{ }^{\circ}\text{C}$, see Figure 4-3). The previous observations agreed with the endothermicity of the DRM reaction, as discussed in section 2.1. The screening campaigns covered a wide range of temperatures, which can be differentiated in two reaction regimes: the low temperature ($T = 600 - 650\text{ }^{\circ}\text{C}$) and the high temperature ($T = 700 - 750\text{ }^{\circ}\text{C}$) ones. The former are more severe for the catalysts, as these promote coke formation simultaneously via the exothermic Boudouard reaction (Eq. 8) and the endothermic CH₄ cracking (Eq. 9) to certain extent, while the reaction is kinetically controlled. On the contrary, high temperature regimes ($T > 700\text{ }^{\circ}\text{C}$) generally lead to high (but similar) performances between the catalysts, as the reaction is thermodynamically controlled. Moreover, the Boudouard reaction is discouraged at $T > 700\text{ }^{\circ}\text{C}$, therefore, deactivation due to coke formation is not as severe as in the low temperature regimes. Consequently, lower T are better conditions to differentiate the catalysts' activity, stability, and coke resistance, thus, these were used to evaluate the long-term stability of the prepared catalysts. Besides, the reaction temperature impacted on the selectivity towards H₂ (i.e., H₂/CO ratio). Particularly, $\text{H}_2/\text{CO} < 1$ was observed for all the samples at all temperatures, which indicated the occurrence of the RWGS (Eq. 7). The latter led to higher CO₂ conversion (compared to that of CH₄) and lower H₂ yield.

Particularly, bare Ni/S2 showed averaged CH_4 and CO_2 conversions $X_{\text{CH}_4} = 92.6\%$, $X_{\text{CO}_2} = 94.9\%$ and molar ratio $\text{H}_2/\text{CO} = 0.99$ at 750°C and $X_{\text{CH}_4} = 35.7\%$, $X_{\text{CO}_2} = 50.7\%$ and $\text{H}_2/\text{CO} = 0.73$ at 600°C . Thus, it displayed high activity compared to most of the CA-assisted catalysts. The latter was ascribed to its lowest reduction temperature (Figure 4-2), thus, many Ni^{2+} species were reduced to form the Ni^0 active sites to catalyze the DRM reaction. Despite its good activity, only this catalyst deactivated (averaged) by 5% after 5 h TOS at 600°C . Such activity loss might be related to agglomeration of weakly bound Ni particles to the support, Ni^0 re-oxidation with CO_2 and/or partial blockage of Ni active sites with coke, as this sample formed the highest amount of C after 25 h TOS (10.0 wt.% C, Figure 4-3 d). Additionally, the activity of the bare Ni/S2 was restored after increasing the temperature back to 750°C (comparison between the first and last steps at 750°C). The previous observation might be related to partial coke removal during the reaction by the inverse Boudouard reaction (Eq. 8), and/or *in situ* reduction of re-oxidized (deactivated) Ni^{2+} sites during operation by the H_2 formed in the DRM reaction. Thus, H_2 production was the highest at $T = 750^\circ\text{C}$ ($\text{H}_2/\text{CO} = 0.99$), and based on its H_2 -TPR profile (Figure 4-2), these temperatures would be sufficient to reduce Ni^{2+} species, at least, partially. On the other hand, including CA in the preparation led to stable catalysts compared to the bare Ni/S2 as all CA-assisted catalysts did not deactivate during screening, while the activity of these depended on the Mg content of the support. The order in activity was as follows: $\text{Ni}(\text{CA})/\text{S4} < \text{Ni}(\text{CA})/\text{S1} \approx \text{Ni}(\text{CA})/\text{S3} < \text{Ni}(\text{CA})/\text{S2} \approx \text{Ni}/\text{S2}$. Thus, the catalyst Ni(CA)/S2 outstood among the CA-assisted catalysts.

Additionally, the amount of coke formed after tests was measured using CHNS analysis. As previously discussed in chapter 2, the catalysts' physicochemical properties (mostly their basicity, concentration of oxygen vacancies and particle size of active sites) and the reaction conditions used determine how efficiently these gasify the C^* species formed during reaction. The bare Ni/S2 formed 10.0 wt.% C after cycling (25 h TOS), which was 35% higher than that formed by Ni(CA)/S2 (6.4 wt.% C) at comparable activity levels. Therefore, adding CA to the preparation aided in discouraging coke deposition, most likely due to improved distribution of Ni species, which remained active over TOS due to the strong MSI (see H_2 -TPR profiles in Figure 4-2). Furthermore, the other CA-assisted catalysts formed lower amounts of coke after 25 h TOS than Ni(CA)/S2 (0.2 wt.%, 2.2 wt.% and 4.3 wt.% C, for Ni(CA)/S4, Ni(CA)/S1 and Ni(CA)/S3, respectively), but these were also the least active among the series.

The activity order identified for the catalysts of Group I most likely depended on the distribution of the active Ni species on the support with different Mg content and the catalysts' MSI, the same as their propensity to deposit/gasify coke during DRM operation. However, this section aimed to identify the support's best Mg content focusing on catalytic performance results. A deeper understanding of the support with 50 wt.% $\text{MgO-Al}_2\text{O}_3$ and its impacts on the activity and stability of selected catalysts are discussed in the following chapter.

Therefore, the support chosen for succeeding catalyst development was S2. Despite the good performance displayed by Ni(CA)/S2, this sample also formed a large amount of coke after cycling (25 h TOS). As previously discussed in chapter 2, coke deposition is one of the main reasons of catalyst deactivation in DRM. Therefore, decreasing coke deposition by tuning the catalyst composition (but still focusing on S2) motivated the development of the other groups of catalysts (II, III and IV).

4.1.2 Optimization of the preparation pH value of Ni(CA)/S2 (Group II)

As previously observed, including CA during the preparation led to Ni-based catalysts with strengthened MSI, improved catalyst stability and decreased coke formation after screening tests. Evidently, catalyst improvement was observed by adding CA during catalyst preparation, which rose the question if further improvements can be achieved by adding CA at different preparation pH.

Before exploring the previous question further, it is worthy to discuss first how sole CA addition improves the catalysts' physicochemical properties, activity, and stability. Once the previous was identified, the impacts of changing the pH on Ni-CA precursor formation and their interactions with the support material in solution can be discussed.

The benefits of adding complexing agents during preparation were firstly discussed in section 2.4.1. Particularly, initial complexation of the Ni^{2+} ions with dissolved CA species occurs in solution during preparation, which separates these Ni-CA complexes from each other. Then, the coordination sphere of the Ni-CA complexes undergoes exchange reactions with the surface OH^- groups of the $\text{MgO-Al}_2\text{O}_3$ support, which anchors the dissolved complexes on the support's surface. Upon calcination at high temperatures under oxidative atmospheres, the organic moieties of the Ni-CA complexes are oxidized, leading to small and finely distributed Ni particles over the support. Thus, the resulting Ni particles generally display strong MSI and are more stable under the DRM operation conditions [133].

Then, to understand the effect of changing the pH on the complexation efficiency between the CA and Ni^{2+} , the molecular structure of CA and its ionization at different pH should be considered. In this sense, CA is an organic acid which has 3 carboxylic and one hydroxyl groups in its structure, which can protonate/deprotonate depending on the pH of the media [134]. Each ionization step is described with an ionization equilibrium, however, only the ionization of the COOH groups was considered due to the pH range ($\text{pH} < 9$) used during preparation, and their superior acidity compared to the hydroxyl (OH) group. The molecular structure of CA and the different ionization equilibria are displayed in Figure 4-4 a and c, respectively. Changing the pH would shift the previous equilibria, thus, different CA-derived species predominate at different pH ranges, and these can also complex Ni^{2+} with different efficiency [181]. Therefore, the Ni^{2+} -CA complexes formed depend on the chosen pH. Summed to CA, complexation of Ni^{2+} with H_2O and/or added NH_3 (as NH_3OH to adjust the pH) should also occur depending on the preparation conditions, thus, these should also be considered. The fraction of the Ni-complexes formed at the different preparation conditions are summarized in the so-called Ni distribution functions. Thus, the latter were calculated at the conditions used during catalyst preparation using Medusa software [182] (displayed in Figure 4-4 b) to determine the different Ni complexes formed at different pH. The main objective was to rationally design catalysts under preparation conditions (pH) which improve the catalysts' physicochemical properties and performance. Based on the previous, the chosen preparation pH values were $\text{pH} < 1$, $\text{pH} = 2$ (without pH modification), 4, 5.5 and 9. The precursor solutions were characterized using liquid UV-visible spectroscopy to study the complexes formed in solution at the different preparation conditions (see Figure A 2 and discussion therewith).

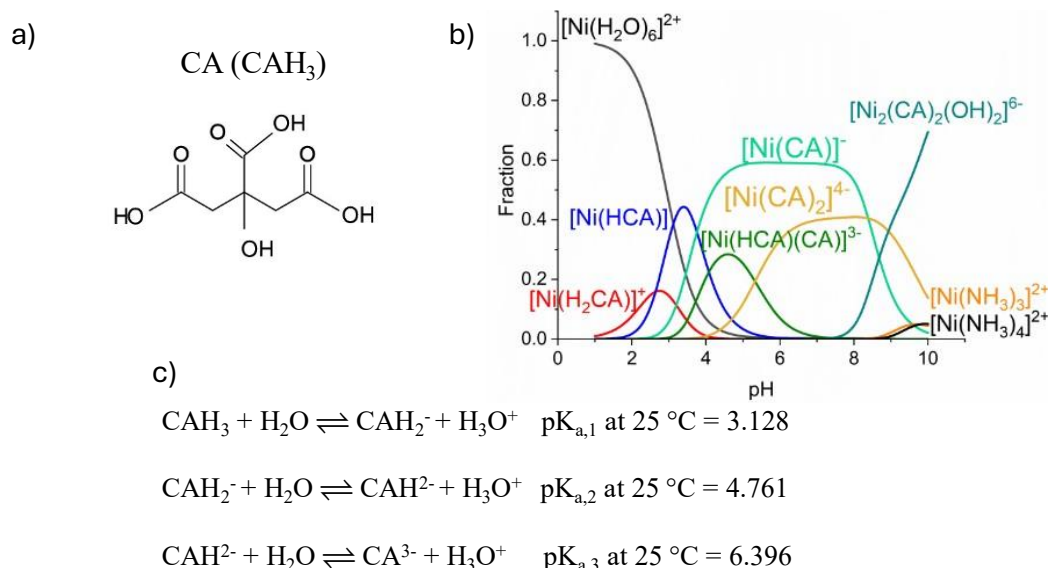


Figure 4-4. a) molecular structure, b) calculated distribution functions of Ni-complexes under simulated preparation conditions using Medusa software [182] and c) ionization equilibria of CA [183]. Note: Ni- NH_3 complexes were also considered for the calculations as NH_3OH (NH_3 is an efficient Ni ligand) was used to adjust the preparation pH.

Summed to the chemistry occurring in the liquid, the pH also impacts on the support's surface, as the surficial OH^- groups are also pH sensitive (discussed in section 2.4.3). Thus, the interaction between the

dissolved Ni-CA complexes and the support's surface also depends on the chosen pH. To get better insights regarding the influence of the preparation pH on the support's charge, the salt addition method and zeta potentiometry were used (see section 7.1.3 for further details). On the one hand, the salt addition method disclosed a PZC = 10.5, while on the other hand, zeta potentiometry evidenced an IEP = 10.2, thus, a fair match was observed between both characterization techniques. Therefore, considering that the highest pH chosen during catalyst preparation was pH = 9, the support's surface would possess an overall positive charge during all preparations. Then, choosing preparation pH values which promote the formation of negatively charged Ni-CA complexes would foster the interaction between the precursors and the support via strong electrostatic adsorption (SEA) and consequently, strengthen the MSI [184]. The concept of SEA was already discussed in section 2.4.3.

Modifying the preparation pH not only altered the support's surface charge, but also provoked partial dissolution of Mg or Al from the support, especially at extreme pH conditions. The dissolution of corresponding ions was quantified in the mother liquors by ICP after filtration. It was observed that the catalyst prepared at pH < 1 suffered the highest Mg leaching (180.2 mg/L Mg, no Al), the catalysts prepared at pH = 4 – 5.5 suffered low Mg-Al leaching (6.9 mg/L Mg, 10.7 mg/L Al), while Al leaching predominated for the catalyst prepared at pH = 9 (0.3 mg/L Mg, 26.4 mg/L Al). Even though the quantified Mg/Al amounts seem to be low, it should be noted that Mg-Al quantification was performed after filtration of the preparation solutions, and the obtained mother liquors did not go through stepwise evaporation of the solvent. Thus, the leached Mg-Al fractions during catalyst preparation might be higher during evaporation in rotavapor compared to what was measured after filtration due to the concentration of the remaining acidic/basic solution (water removal), which might impart a stronger effect. Apart from the leaching, all preparation solutions experienced pH increase over the 16 h of the impregnation towards pH = 9, possibly due to MgO hydrolysis to form Mg(OH)₂ [185], which was independent of the initial pH chosen. Considering the dissolution of Mg²⁺ or Al³⁺ ions from the support, these might be deposited back on the catalyst surface during solvent evaporation. Consequently, the latter modifies the solids' surface chemistry and how these stabilize the Ni species and promote the adsorption of the reactants during DRM.

The previous discussion described the chemistry occurring in the preparation solutions and how these modifications shape the initial interaction between precursors and support. However, sample calcination and pre-reduction determine the catalysts' physicochemical properties and activity. Therefore, the characterization of the catalysts is discussed below.

4.1.2.1 Characterization of calcined and *ex situ* reduced catalysts

The calcined catalysts of Group II were characterized using ICP, BET, XRD and H₂-TPR, while the *ex situ* reduced catalysts at T_{red} = 700 °C were characterized using XRD, XPS and TEM. Before discussing sample characterization, the catalyst Ni(CA)/S2 is referred from now on as Ni(CA-2)/S2, as the preparation solution of Ni + CA without pH adjustment had a pH = 2. Relevant characterization results are summarized in Table 4-2. Briefly, independently of the pH chosen, all catalysts displayed Ni contents close to 2.5 wt.% Ni, as expected. Besides, the catalysts exposed S_{BET} ranging between 96 and 124 m²/g (Table 4-2), being slightly lower to that of the calcined S2 support material (139 m²/g; see Table 4-1). Thus, partial blockage of the pores with Ni can be suggested, as discussed for the catalysts of Group I. Apart from the latter, no remarkable differences were provoked in the catalysts' pore size and volume after adding CA at any pH.

Table 4-2. Chemical composition (ICP), textural properties (BET), reducibility (H₂-TPR) of fresh, and surface chemical composition (XPS) and observed particle size (TEM) of *ex situ* reduced catalysts of Group II.

Sample name	ICP	BET			H ₂ -TPR			XPS	TEM
	Ni content (wt.%)	S _{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	T. H ₂ (μmol/g) ^a	E. H ₂ (μmol/g) ^b	T _{max} (°C)	Ni/(Mg + Al)	Particle size (nm)
Ni/S2	2.5	96	3-10	0.3	426	400	870	-	1-14
Ni(CA<1)/S2	2.5	99	3-8	0.2	426	406	841	0.02	2-13
Ni(CA-2)/S2	2.6	124	3-10	0.3	443	427	895	0.08	2-12
Ni(CA-4)/S2	2.6	97	3-10	0.3	443	416	920	0.12	-
Ni(CA-5.5)/S2	2.6	91	3-10	0.3	443	423	937	0.11	2-10
Ni(CA-9)/S2	2.6	100	3-8	0.2	443	403	944	0.08	2.5-20

^a: theoretical H₂ consumption related to the measured ICP Ni content. ^b: measured H₂ consumption during the H₂-TPR experiments.

Regarding the crystalline structure of the catalysts of Group II, the calcined samples (diffractograms displayed in Figure 4-5 a) showed analogous crystalline structure to Ni(CA)/S2, thus, the discussion in section 4.1.1.1 can be extended to this group of calcined samples. However, it is noteworthy to mention that using CA at all preparation pH did not provoke major structural transformations detectable by XRD, despite the partial dissolution of Mg and/or Al from the support's structure previously discussed. Apart from that, the diffractograms of the samples reduced *ex situ* at 700 °C for 1.5 h (Figure 4-5 b) were also collected. These resembled to those of the calcined catalysts to a great extent, suggesting that the samples' crystalline structure remained mostly unchanged after reduction, and no Ni⁰ was detected by XRD. However, and as anticipated before, no reflections of rehydrated Mg-Al HTC structure were observed upon reduction of Ni(CA-2)/S2, thus, it can be argued that this phase is absent during reaction.

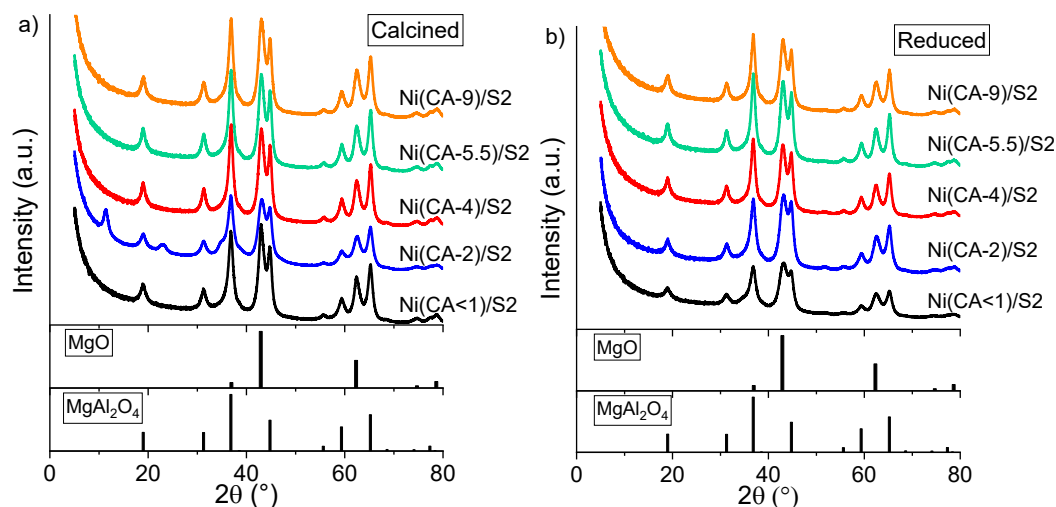


Figure 4-5. a) diffractograms of calcined and b) *ex situ* reduced (at T_{red} = 700 °C for 1.5 h) catalysts of Group II.

Before discussing the reducibility of these samples, a brief statement must be given. As previously mentioned, independently of the initial preparation pH set, the pH of these dispersions increased to the same pH = 9 after 16 h of impregnation. MgO hydrolysis (into Mg(OH)₂) from the Mg-rich support ruled the pH increase. Recalling the impacts of changing the pH of the media on precursor formation (see distribution functions in Figure 4-4 b), similar Ni-CA complexes might have formed at one point of the impregnation in all preparations. Additionally, the composition of the support's surface evolved over the course of the impregnation due to Mg²⁺ and/or Al³⁺ dissolution (discussed in section 4.1.2), which most likely impacted on the interaction between the support's surface and the Ni²⁺ precursors in the liquid. A further remark is that CA can also complex Mg²⁺ during preparation [186], but to a less extent compared to Ni²⁺. However, competitive complexation between CA and Ni²⁺/Mg²⁺ can still occur, which could modify the distribution of the Ni precursors throughout the support during preparation, and

their resulting MSI upon calcination. Despite the previous discussion, the different initial pH values set were sufficient to modify specific physicochemical properties of this group of catalysts, such as the reducibility, the MSI, the Ni surface content, the Ni particle size and how this evolved during reaction (see below).

Thus, the catalysts prepared under acidic conditions ($\text{pH} \leq 2$) displayed the weakest MSI among the series (required lowest T_{red}), however, these two samples showed remarkable differences between their H_2 -TPR profiles (see Figure 4-6 a). On the one hand, only the catalyst prepared at $\text{pH} < 1$ showed a broad reduction profile in the temperature range 600 – 1000 °C (maximum $T_{\text{red}} = 839$ °C), suggesting the formation of Ni species exposing different degrees of interaction with the support. Considering that $\text{Ni}(\text{CA}<1)/\text{S2}$ and $\text{Ni}(\text{CA-2})/\text{S2}$ formed the same $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ precursor in solution at the initial preparation stage (see Figure 4-4 b), the different fractions of Mg^{2+} leached out from both samples during preparation most likely defined the catalysts' MSI (see section 4.1.2). For example, the sample prepared at $\text{pH} < 1$ leached more Mg^{2+} ions to the solution, which were most likely complexed by the CA-species. Thus, competitive complexation between Ni^{2+} and Mg^{2+} for the finite number of molecules of CA most likely prevented a fine distribution of Ni precursors throughout the support, which evolved into Ni species exposing overall the weakest MSI upon calcination in $\text{Ni}(\text{CA}<1)/\text{S2}$.

On the other hand, all catalysts prepared at $\text{pH} \geq 2$ displayed only one reduction peak centered at very high temperatures (maximum at $T_{\text{red}} \geq 895$ °C), which was also shifted towards even higher temperatures when the preparation $\text{pH} \geq 4$ (Figure 4-6 b). Such peak in the H_2 -TPR profiles was ascribed to the reduction of finely distributed and strongly interacting β -Ni species with the support (strong MSI), as discussed in section 4.1.1.1. Thus, the catalysts $\text{Ni}(\text{CA-5.5})/\text{S2}$ and $\text{Ni}(\text{CA-9})/\text{S2}$ displayed the highest $T_{\text{red}} = 937$ and 944 °C, respectively, thus, the strongest MSI among the series. The previous can be explained by advantageous precursor formation (negatively charged Ni-CA complexes, see Figure 4-4 b) during initial impregnation stages, which strengthen the MSI due to SEA.

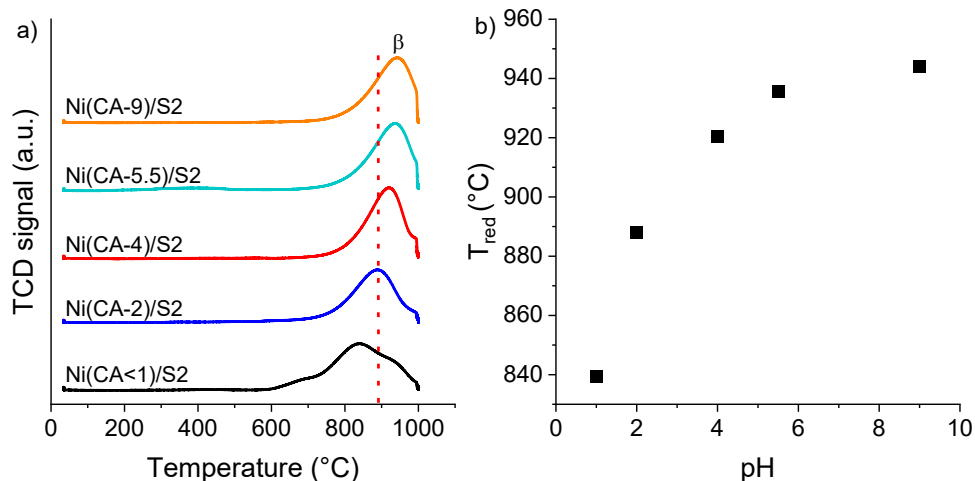


Figure 4-6. a) H_2 -TPR profiles and b) maximum reduction temperature (T_{red}) as a function of the pH of the impregnating solution for catalysts of Group II.

Furthermore, the Ni oxidation state and the surface chemistry of the catalysts *ex situ* reduced at $T_{\text{red}} = 700$ °C for 1.5 h was studied using XPS, and their spectra in the Ni 2p region (binding energy BE = 850 – 890 eV) are displayed in Figure 4-7 a. The main peaks and their corresponding satellite features recorded for all *ex situ* reduced catalysts can be ascribed to Ni^0 ($\text{Ni}^0 2p_{3/2} = 852$ eV and $\text{Ni}^0 2p_{1/2} = 867$ eV, satellite at 882 eV [187]) and Ni^{2+} ($\text{Ni}^{2+} 2p_{3/2} = 856$ eV and $\text{Ni}^{2+} 2p_{1/2} = 874$ eV, satellites at 862 and 879 eV [188]), suggesting incomplete Ni reduction and/or partial Ni^0 re-oxidation during sample insertion inside the XPS apparatus. Interestingly, all samples showed similar BE for both peaks of Ni^{2+} , however, the main 2p Ni^0 peaks were slightly shifted towards higher BE. For example, $\text{Ni}(\text{CA}<1)/\text{S2}$ displayed its $\text{Ni}^0 2p_{3/2}$ signal at 852.1 eV, while $\text{Ni}(\text{CA-4})/\text{S2}$ and $\text{Ni}(\text{CA-5.5})/\text{S2}$ showed it at 852.3 eV, and 852.4 eV for $\text{Ni}(\text{CA-9})/\text{S2}$. In this sense, it is reported that a shift in BE towards higher values

correlate with strengthened MSI effect [189]. Therefore, the observations derived from XPS correlated with those made through H₂-TPR characterization techniques, indicating that the catalysts prepared at higher pH displayed the strongest MSI.

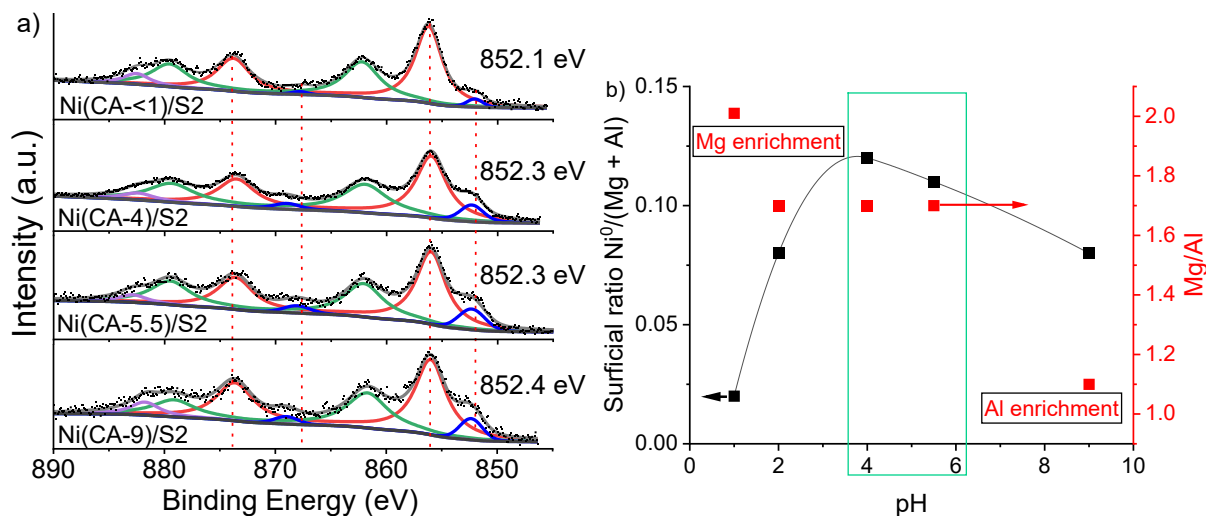


Figure 4-7. a) Ni 2p XP spectra of *ex situ* reduced (at $T_{\text{red}} = 700$ °C for 1.5 h) Ni(CA<1)/S2, Ni(CA-4)/S2, Ni(CA-5.5)/S2 and Ni(CA-9)/S2 and b) surface Ni⁰/(Mg+Al) and Mg/Al surface content as a function of the pH of the impregnating solution for catalysts of Group II.

Apart from the identification of different Ni oxidation states and the nature of their interaction with the support, surface quantification was also performed (see Table 4-2). On the one hand, the normalized Ni⁰ surface amount (reported as total Ni⁰/(Mg + Al)) as a function of the impregnation pH displayed a volcanic shaped curve (Figure 4-7 b), which maximum Ni⁰ content was recorded for the catalysts Ni(CA-4)/S2 and Ni(CA-5.5)/S2, being their Ni⁰/(Mg + Al) = 0.12 and 0.11, respectively. Analogously, the samples that displayed the lowest normalized Ni⁰ surface content were those which displayed the highest Mg or Al leaching, i.e., those prepared under acidic and basic conditions. However, the different complexes formed during the preparations at different initial pH most likely impacted on the surficial distribution of Ni active sites as well. Thus, the catalysts Ni(CA<1)/S2 showed Ni⁰/(Mg + Al) = 0.02, while Ni(CA-9)/S2 displayed Ni⁰/(Mg + Al) = 0.08. Additionally, the Mg/Al atomic surface ratio was also plotted against the preparation pH (Figure 4-7 b). Thus, Ni(CA<1)/S2 showed the most remarkable surficial Mg enrichment (Mg/Al = 2.0), followed by Ni(CA-2)/S2, Ni(CA-4)/S2 and Ni(CA-5.5)/S2 with Mg/Al = 1.7, while Ni(CA-9)/S2 exposed comparatively Al surface enrichment (Mg/Al ~ 1.1). Therefore, the trend identified for the quantified surficial Mg or Al by XPS agreed with the quantification of Mg and Al in the leaching experiments. Thus, the hypothesis which considered Mg-Al leaching, followed by redeposition and coverage of Ni sites during solvent evaporation was supported by different characterization methods.

Sample characterization was deepened using TEM to study the morphology, size, and distribution of the Ni particles of selected catalysts reduced *ex situ* at 700 °C for 1.5 h. The particle sizes reported in Table 4-2 are given as an approximate size range obtained after evaluation of many Ni containing particles from several representative TEM micrographs, as different Ni species, including Ni⁰ and oxidic Ni-containing particles were present throughout the catalysts (Ni speciation is discussed below). Thus, inhomogeneous Ni speciation led to various particle sizes and therefore, the calculation of the Ni particle size distribution as histograms would not provide realistic information. Generally, all catalysts displayed bright dots in the TEM-HAADF images (Figure 4-8), which were identified as Ni particles using EELS (see Figure 4-9). The latter had irregular shapes and were non-uniformly distributed throughout the catalysts, which was also independent of the initial pH chosen. However, the particle size was modified by the pH in the initial preparation stage. In this sense, the catalysts prepared at pH ≤ 5.5 displayed most of their Ni containing particles sized between 2 and 14 nm (see Figure 4-8 a and b), while the catalyst prepared at pH= 9 showed larger particles ranged in a wider interval between 2.5 and 20 nm (Figure 4-8

c). Thus, using CA at pH = 5.5 led to the best conditions for the distribution of Ni precursors over the support during preparation, which evolved after calcination and reduction into the smallest (2 – 10 nm) and most abundant Ni particles among the series (high surface ratio $\text{Ni}^0/(\text{Mg}+\text{Al})$, see XPS) and which also displayed very strong MSI (H_2 -TPR and XPS). Finally, the larger particles observed for Ni(CA-9)/S2 might be explained by exchange and condensation reactions between Ni- NH_3 derived precursors (formed by NH_4OH addition to adjust the pH = 9 during preparation) and H_2O during grafting to the support, which possibly led to larger Ni agglomerates [21].

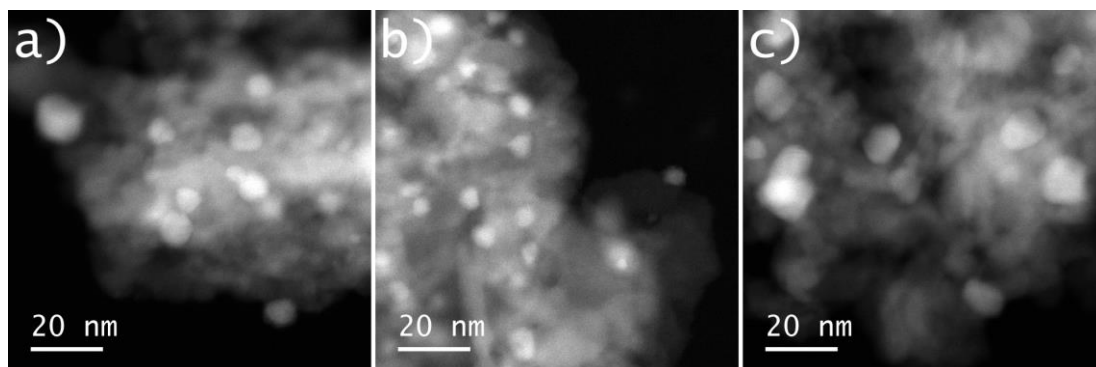


Figure 4-8. TEM-HAADF micrographs of *ex situ* reduced (at $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h) a) Ni(CA<1)/S2, b) Ni(CA-5.5)/S2 and c) Ni(CA-9)/S2.

Moreover, the catalysts' Ni oxidation state was further studied using EELS. For example, Figure 4-9 a displays a representative TEM micrograph of the *ex situ* reduced Ni(CA-5.5)/S2, and Figure 4-9 b, the corresponding EEL spectra collected at two regions of a Ni-containing particle (Area 1: core; Area 2: outer layer). Only the latter sample is discussed, as all other samples of this series displayed similar features. In this case, it was observed that Ni particles were generally constituted by a Ni^0 core (spectrum of Area 1 in Figure 4-9 b, evidenced by high intensity ratio of L2/L3; L2 centered at 855 eV, L3 centered at 872 eV) and a Ni^{2+} shell (spectrum of Area 2 in Figure 4-9 b, evidenced by low intensity ratio of L2/L3 [190, 191]). Thus, both XPS and EELS evidenced the co-existence of $\text{Ni}^0/\text{Ni}^{2+}$, especially on the catalysts' surface. Therefore, sample pre-reduction at $700\text{ }^{\circ}\text{C}$ for 1.5 h produced Ni active sites with different degree of oxidation. As discussed in section 2.2, co-existence of Ni^0 and Ni^{2+} in the active sites might facilitate C-H bond activation via partial electron withdrawal of CH_4 , which enhances the conversion of CH_4 . Further investigations in this direction were outside the scope of this work.

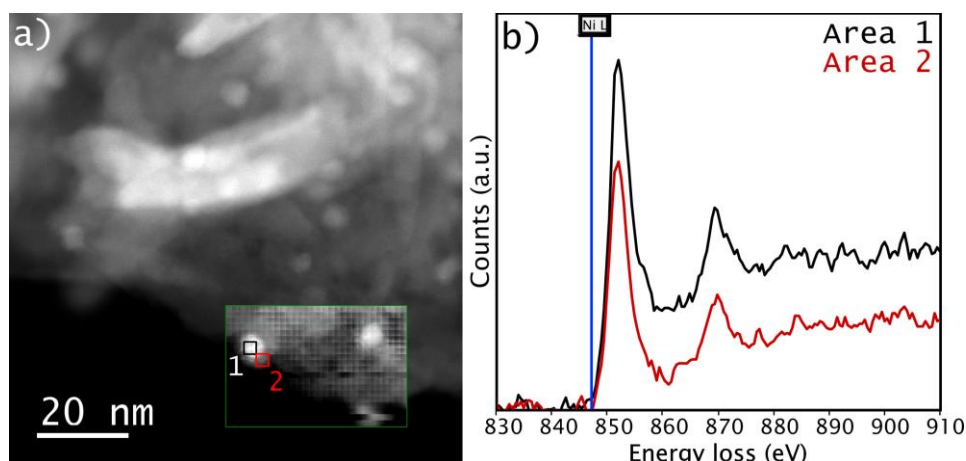


Figure 4-9. a) TEM-HAADF micrograph of *ex situ* reduced (at $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h) Ni(CA-5.5)/S2. Inset boxes 1 and 2 indicate the regions in which the EEL spectra were collected. b) Corresponding EEL spectra taken from areas 1 (black box) and 2 (red box), respectively.

4.1.2.2 Effects of adding CA at specific pH values on catalyst activity and stability

After extensive catalyst characterization, the samples of Group II were screened in DRM, while the stability of selected samples was evaluated in long-term tests at $T = 600\text{ }^{\circ}\text{C}$. Thus, the X_{CH_4} , X_{CO_2} and H_2/CO over TOS and coke measured after 25 h TOS are displayed in Figure 4-10 a-d, respectively. Analogous to what was observed for the catalysts of Group I, the samples of Group II showed increased activity at increasing temperatures, and higher X_{CO_2} than X_{CH_4} and $\text{H}_2/\text{CO} < 1$ at all temperatures due to the occurrence of the RWGS (Eq. 7). Another remark was that all catalysts prepared with CA displayed stable activity over TOS, independently of the pH used during impregnation. However, notable differences were observed among the catalysts of Group II. Firstly, the sample Ni(CA-2)/S2 was considered as the comparison point for Group II to identify catalyst improvement. In this sense, the lowest activity was recorded for Ni(CA<1)/S2 at all temperatures. For example, the former catalyst displayed averaged $X_{\text{CH}_4} = 25.8\%$, $X_{\text{CO}_2} = 40.9\%$ and $\text{H}_2/\text{CO} = 0.64$ at $T = 600\text{ }^{\circ}\text{C}$, which was $\sim 20\%$ lower than that of Ni(CA-2)/S2 (averaged $X_{\text{CH}_4} = 33.9\%$, $X_{\text{CO}_2} = 49.8\%$ and $\text{H}_2/\text{CO} = 0.74$ at $T = 600\text{ }^{\circ}\text{C}$). Moreover, the least active catalyst also formed the lowest amount of coke after 25 h TOS (0.3 wt.% C). It could be argued that, on the one hand, the observed low catalytic performance was related to its low fraction of surficial Ni^0 active sites (as identified with XPS), which suffered agglomeration/oxidation during operation due to its weakest MSI (further discussed in section 4.1.2.3). On the other hand, the observed lowest coke deposition might correlate with its richest Mg surface fraction (XPS), which promoted CO_2 adsorption and C^* gasification via the inverse of the Boudouard reaction (Eq. 8).

Furthermore, by increasing the preparation pH to mildly acidic conditions, the resulting catalysts Ni(CA-4)/S2 and Ni(CA-5.5)/S2 displayed the highest activity among the series, with averaged $X_{\text{CH}_4} = 40.6\%$, $X_{\text{CO}_2} = 55.4\%$ and $\text{H}_2/\text{CO} = 0.75$ at $T = 600\text{ }^{\circ}\text{C}$, while both formed 5.8 wt.% C after 25 h TOS. Thus, these outstanding catalysts displayed $\sim 20\%$ higher activity at $600\text{ }^{\circ}\text{C}$, while forming $\sim 10\%$ less coke compared to Ni(CA-2)/S2 (6.4 wt.% C). The latter was ascribed to their highest surface Ni^0 fraction, smallest particle size, Mg surface enrichment and strong MSI, which seemed to be the best features for preparing active DRM catalysts (identified using XPS, TEM and H_2 -TPR, respectively). Additionally, increasing the pH further (Ni(CA-9)/S2) led to an average of $X_{\text{CH}_4} = 36.4\%$, $X_{\text{CO}_2} = 51.3\%$ and $\text{H}_2/\text{CO} = 0.73$ at $T = 600\text{ }^{\circ}\text{C}$, i.e., $\sim 8\%$ less active than those catalysts prepared at pH = 4 and 5.5. The latter was most likely due to a lower Ni^0 surficial fraction (XPS) and formation of larger particles (TEM), which might have promoted less CH_4 and CO_2 adsorption for catalysis.

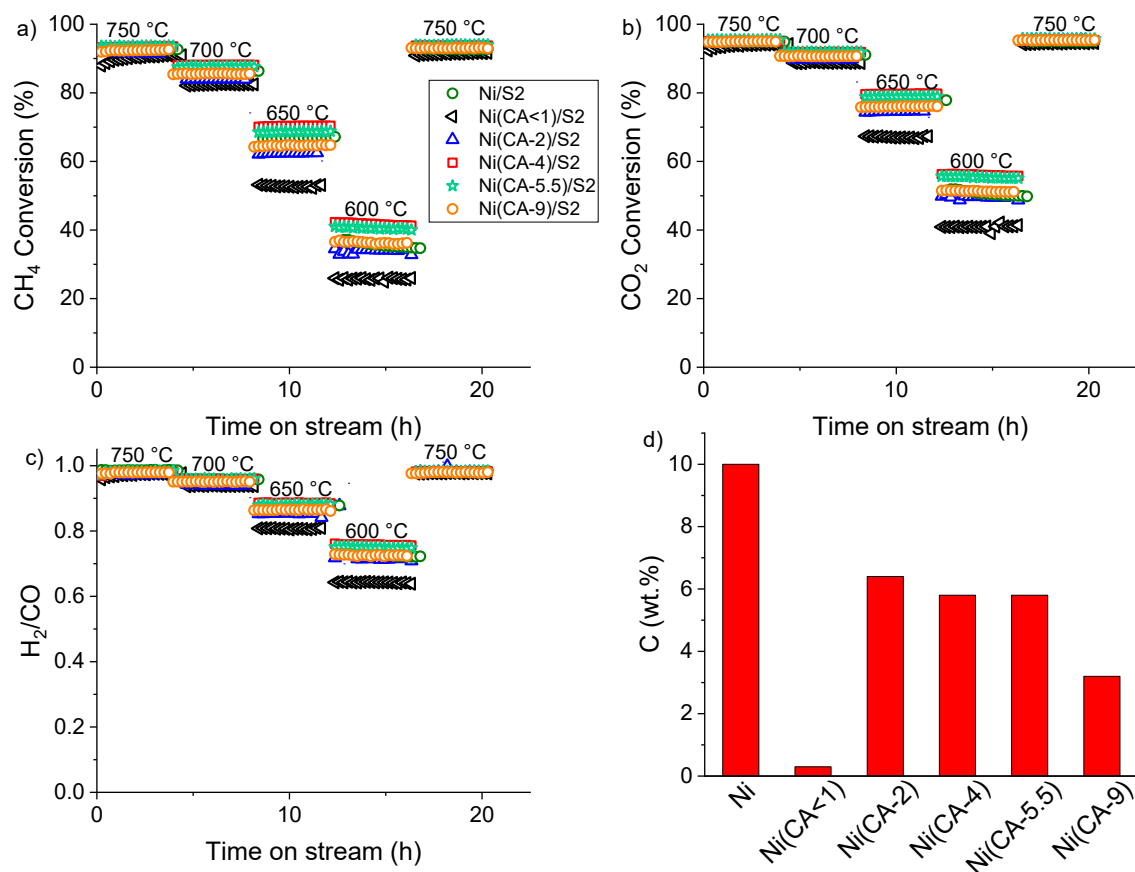


Figure 4-10. a) CH₄ conversion, b) CO₂ conversion, c) H₂/CO ratio with TOS, and d) measured carbon using CHN analysis of spent catalysts of Group II and bare Ni/S2 after 25 h TOS. Reaction conditions: $T_{\text{red}} = 700$ °C for 1.5 h, CH₄/CO₂/N₂ = 45:45:10 vol.%, $p = 1$ bar, $m_{\text{cat}} = 50$ mg, GHSV = 170 L/(g_{cat}·h). The numbers on top of each data cluster indicate the temperature (in the middle of the catalyst bed) at which the data was collected.

Before discussing the long-term stability tests, the influence of the pre-reduction temperature is examined, i.e., from $T_{\text{red}} = 700$ °C before the screening tests, to $T_{\text{red}} = 750$ °C before the long-term runs (both for 1.5 h). As previously discussed in section 4.1.1.2, 600 °C is a good temperature to differentiate between catalysts due to the severity of these DRM reaction regimes. Therefore, the long-term tests were performed at this temperature. Lack of DRM activity was recorded at $T = 600$ °C after reducing the catalysts at 700 °C for 1.5 h (not shown). The previous was firstly identified during the design of the screening experiments (see Figure A 1 c-d and discussion therewith). The original idea was to screen the catalysts from low (600 °C) to high (750 °C) temperatures, but obviously, all catalysts were inactive using this protocol. Alternatively, and by keeping the $T_{\text{red}} = 700$ °C for 1.5 h, the order of the reaction temperatures was inverted, i.e., the screening started from high (750 °C) to low (600 °C) temperatures instead. In this case, high activity was recorded at all consecutive temperatures. Thus, it was hypothesized that insufficient number of Ni⁰ active sites were produced at $T_{\text{red}} = 700$ °C for 1.5 h for reaction at $T = 600$ °C. In order to prove this assumption, the Ni reducibility degree was calculated using TPR measurements. The samples were then reduced at $T_{\text{red}} = 700$ °C using the same experimental conditions as those used before the screening tests. Independently on the initial pH chosen, the catalysts showed ca. 44% of Ni²⁺ reduced, which might increase during DRM operation at $T = 750$ °C, as the presence of CH₄ fed and/or H₂ generated might reduce an additional proportion of Ni²⁺ species [180]. Furthermore, by increasing the reduction temperature to $T_{\text{red}} = 750$ °C, the reducibility degree increased to 55% (corroborated for Ni(CA-5.5)/S2, i.e., one of the samples with the strongest MSI). After reduction at $T_{\text{red}} = 750$ °C for 1.5 h, the catalysts displayed high and stable activity at $T = 600$ °C, which revealed that a higher Ni⁰ fraction was indeed needed for proper catalyst activation.

In connection to the previous discussion, the relationship between reducibility degree and activity has also been reported in the literature. For example, almost doubled X_{CH_4} was reported in DRM at $T = 600$ °C using 12 wt.% Ni/Mg(Al)O catalyst [180] by increasing the reduction temperature from $T_{red} = 650$ to 700 °C, which was associated to improved Ni reducibility, while keeping a small particle size < 6 nm. By contrast, reducing the same catalyst at higher temperatures ($T_{red} = 750 - 800$ °C) increased Ni particle size to > 6 nm, which increased the coke formation and decreased catalysts' stability over TOS simultaneously. The differences between their optimum reduction temperature ($T_{red} = 700$ °C) and the temperature used in this work before long runs ($T_{red} = 750$ °C) is related to the almost 5-times higher Ni loading in their catalyst, thus, lower reduction temperatures are needed for their samples to get sufficient reducibility degree. The connection between the catalyst's Ni loading and the temperature needed for its activation was previously discussed in sections 2.4.1 and 4.1.1.1.

Therefore, long-term stability tests were performed at $T = 600$ °C after pre-reduction at $T_{red} = 750$ °C for 1.5 h with the catalysts Ni(CA-2)/S2, Ni(CA-4)/S2, Ni(CA-5.5)/S2 and Ni(CA-9)/S2 (X_{CH_4} , X_{CO_2} and H_2/CO over TOS displayed in Figure 4-11). Developing active and stable catalysts is important to ensure consistent and efficient conversion of feedstocks into desired products, to avoid frequent catalyst replacements in large reactors, which reduce the process environmental footprint (less disposal of catalysts) and the process costs (the unit is not stopped), among others [118]. Thus, a slight increase in initial activity was observed for all catalysts, possibly due to a higher Ni^0 fraction formed at higher T_{red} . All catalysts displayed similar initial activity, however, the stability of these samples depended on the pH used during preparation. In this sense, the least stable catalysts were Ni(CA-2)/S2 and Ni(CA-9)/S2, which lost $\sim 10\%$ of activity in ca. 30 h TOS and formed 4.8 and 4.0 wt.% coke after tests, respectively. Contrarily, the outperforming catalysts Ni(CA-4)/S2 and Ni(CA-5.5)/S2 displayed comparable conversion over TOS, with ca. 10% of activity loss in approximately 80 h TOS (initial $X_{CH_4} \approx 41.5\%$, $X_{CO_2} \approx 56.5\%$ and $H_2/CO \approx 0.76$ and final $X_{CH_4} \approx 37.5\%$, $X_{CO_2} \approx 52.4\%$ and $H_2/CO \approx 0.72$), revealing remarkable enhancement of stability compared to the other catalysts of this series, while these formed 3.2 wt.% C after tests. The highest and stable activity over 80 h TOS of Ni(CA-4)/S2 and Ni(CA-5.5)/S2 highlighted the beneficial impacts of adding CA and setting the preparation pH within an optimum window ranged between pH = 4 – 5.5. To better understand the previous trends, selected spent samples were further characterized to disclose the changes provoked in the catalysts over TOS, the same as the origin of catalyst deactivation. The results are discussed in the following section.

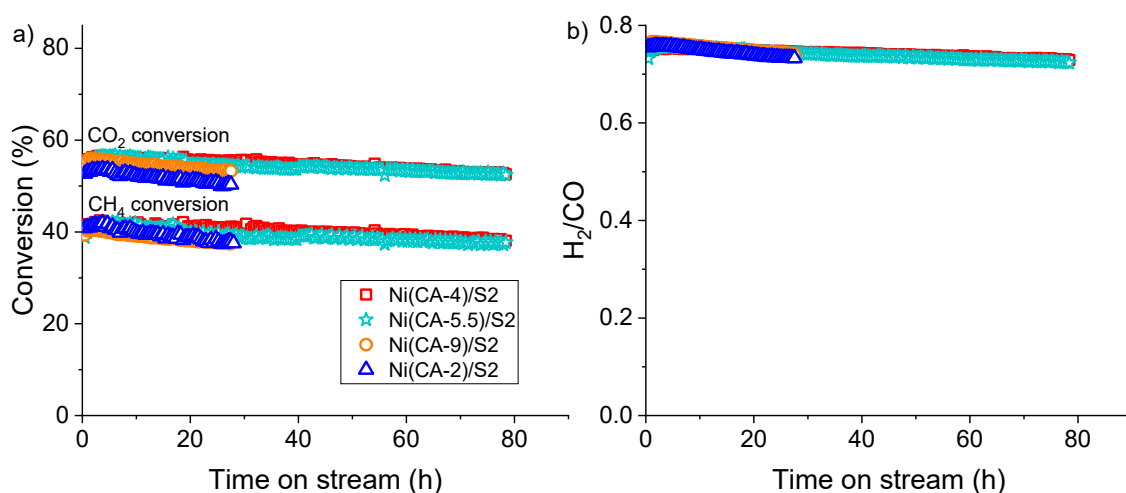


Figure 4-11. a) X_{CH_4} and X_{CO_2} , and b) H_2/CO ratios over TOS with Ni(CA-2)/S2, Ni(CA-4)/S2, Ni(CA-5.5)/S2 and Ni(CA-9)/S2. Reaction conditions: $T_{red} = 750$ °C for 1.5 h, $CH_4/CO_2/N_2 = 45:45:10$ vol.%, $T = 600$ °C, $p = 1$ bar, $m_{cat} = 50$ mg, GHSV = 170 L/(g_{cat}·h).

4.1.2.3 Characterization of spent catalysts

Selected spent samples recovered after screening (25 h TOS) and long-term stability tests (80 h TOS) were characterized using TEM, and representative micrographs are displayed in Figure 4-12 and Figure 4-13, respectively. Different types of Ni-containing particles were identified in the spent samples (Figure 4-12). These species were pure Ni^0 , $\text{Ni}^0/\text{Ni}^{2+}$ core-shell particles, and Ni-based hollow structures constituted by a Ni^0 core, a shell of Ni^{2+} and a void between both parts (see the lack of contrast within the core and shell of the particles in Figure 4-12), possibly formed by the Kirkendall Effect [117, 192]. Here, the formation of Kirkendall structures deserves an explanation. It is reported to occur when at least two chemical species in a solid (in this case, Ni^0 and Ni^{2+}) are in close contact with each other, and their diffusion coefficients differ significantly. The diffusion of both species occurs in different directions at high temperatures, creating different local concentration profiles. The diffusion of atoms within the crystalline structure at different speed creates atomic vacancies, which migrate and combine into voids to decrease their surface energy.

Moreover, the Kirkendall particles are reported to evolve over time, and these oxidic structures might fragmentate and eventually collapse, and redisperse Ni^{2+} on the catalyst surface [192]. The latter oxidized species can be reduced by the H_2 produced during the reforming reactions [180], leading to more Ni^0 active sites and contribute to the catalyst performance. However, the oxidation of Ni^0 cores can proceed until completion, leading to inactive Ni^{2+} particles and consequently, decrease catalyst activity. Although not completely understood yet, it could be argued that the fed CO_2 or H_2O formed *in situ* (and/or reaction intermediates formed under the reaction conditions, like OH^* , COOH^* , as discussed in section 2.2) oxidizes the Ni^0 sites [193], which leads to the hierarchical Kirkendall particles. All the previous structural transformations imply incorporation of oxygen within the Ni lattice, and consequently, particle size increase is difficult to be avoided.

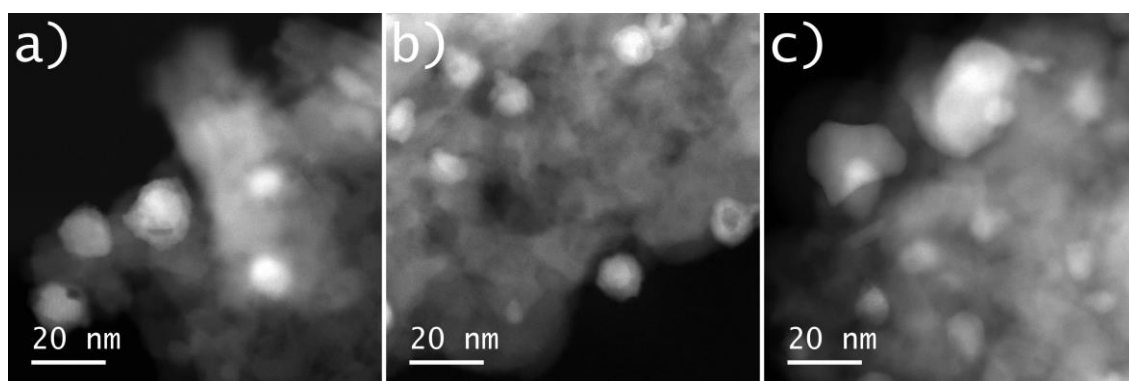


Figure 4-12. TEM-HAADF micrographs of spent a) Ni(CA<1)/S2, b) Ni(CA-5.5)/S2 and c) Ni(CA-9)/S2 after cycling (25 h TOS). Reaction conditions: $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h, $\text{CH}_4/\text{CO}_2/\text{N}_2 = 45:45:10$ vol.%, $T = 600 - 750\text{ }^{\circ}\text{C}$, $p = 1$ bar, $m_{\text{cat}} = 50$ mg, GHSV = $170\text{ L}/(\text{g}_{\text{cat}}\cdot\text{h})$.

In addition to Ni re-oxidation, particle agglomeration is also possible, as the temperatures used during the experiments are higher than the Ni Tammann temperature of $691\text{ }^{\circ}\text{C}$ [85], thus, Ni migrates throughout the catalyst, which leads to crystal growth. Consequently, particle agglomeration induced at high temperatures also contributes to the observed particle size increase as well. In this sense, the Ni particles grew after tests, and the observed order was as follows: Ni(CA-5.5)/S2 (from 2 – 10 nm to 4 – 20 nm) < Ni(CA<1)/S2 (from 2 – 13 nm to 5 – 20 nm) < Ni(CA-9)/S2 (from 2.5 – 20 nm to 3 – 30 nm). As a matter of fact, larger and oxidized particles correlate with fewer active sites for the reforming reactions, which impacts on the catalytic activity and stability [180, 194]. Thus, the catalyst Ni(CA-5.5)/S2 was the most efficient in preventing particle agglomeration, most likely due to the formation of the smallest particles during reductive pretreatment among the series, which were also strongly attached to the support via strong MSI (as identified by H_2 -TPR and XPS, see section 4.1.2.1). Therefore, Ni(CA-5.5)/S2 exposed finely distributed Ni active sites over TOS to catalyze the DRM reaction, explaining its outstanding activity and low coke deposition.

Moreover, carbonaceous structures were rarely observed after 25 h TOS (not shown). For example, some of these were free CNTs or containing Ni particles placed at their tips, but without encapsulating Ni sites within their structures. Considering the discussion provided in section 2.3.1, the observed CNTs belong to the non-deactivating type, as Ni is still available to convert the reactants. Besides, only few Ni particles covered with graphitic coke were observed, thus, the observations derived from TEM suggested that carbon deposition played a minor role in catalyst deactivation. However, it should be considered that this characterization technique only provides local information of a small portion of the sample and not a global average. Thus, the rare carbon deposition observed by TEM did not correlate well with the measured C contents using CHN analysis (Figure 4-10 d), being the latter a more realistic value concerning the problems of the DRM.

Regarding the spent catalyst Ni(CA-5.5)/S2 after the long-term run (80 h TOS) (see Figure 4-13), it displayed Ni particles ranging between 2 – 20 nm. Analogously to its spent counterpart after screening (25 h TOS), the spent catalyst after 80 h TOS displayed the same types of Ni containing particles (see Figure 4-13 b), which suggested that oxidation and agglomeration of the active sites took place even at lower reaction temperatures. Thus, it seems that $T = 600\text{ }^{\circ}\text{C}$ (for 80 h) was enough to promote both deactivating phenomena, as similar features were observed in the spent catalysts after screening and long-term runs.

Moreover, CNTs were somehow more frequently observed throughout the spent Ni(CA-5.5)/S2 after the stability tests vs. after 25 h TOS. However, most of these CNTs were of the non-deactivating type (representative image displayed in Figure 4-13 c). Interestingly, no graphitic coke was observed after 80 h TOS. Thus, it seemed that $T = 600\text{ }^{\circ}\text{C}$ was not enough to promote the deposition of graphitic coke, evidencing how the reaction conditions influence the carbonaceous structures formed over TOS. By contrast, much fewer Ni^0 active sites were observed in the spent catalyst after 80 h TOS, which suggested a more profound re-oxidation effect. Therefore, catalyst deactivation seems to be more related to oxidation of the Ni^0 active sites than to carbon deposition on the long run under the chosen reaction conditions.

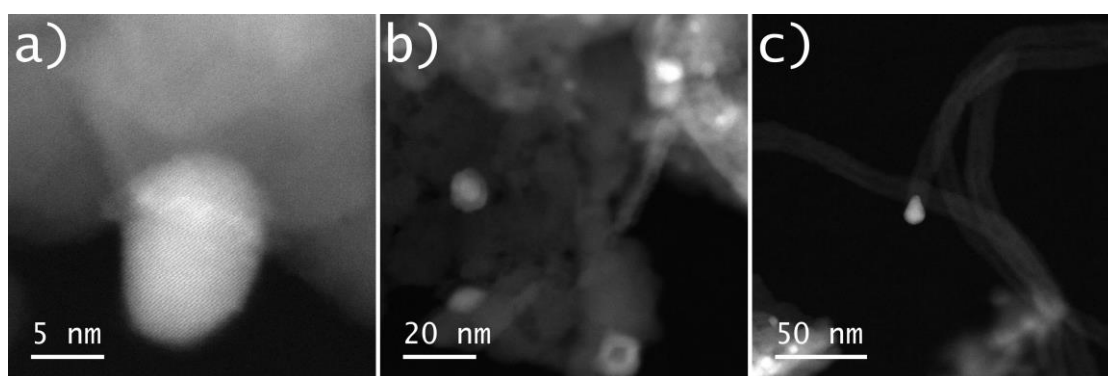


Figure 4-13. a – c) TEM-HAADF micrographs of recovered (spent) Ni(CA-5.5)/S2 after 80 h TOS. Reaction conditions: $T_{\text{red}} = 750\text{ }^{\circ}\text{C}$ for 1.5 h, $\text{CH}_4/\text{CO}_2/\text{N}_2 = 45:45:10$ vol.%, $T = 600\text{ }^{\circ}\text{C}$, $p = 1$ bar, $m_{\text{cat}} = 50$ mg, GHSV = $170\text{ L}/(\text{g}_{\text{cat}}\cdot\text{h})$.

4.1.3 Impacts of different chelating agents (Group III)

The discussion provided in the previous sections demonstrated that CA-assisted catalysts can be further improved by adjusting the preparation pH within the range $\text{pH} = 4 - 5.5$. However, Groups I and II of catalysts only focused on CA for catalyst improvement, thus, the impacts of adding other chelating agents for Ni complexation were not investigated. In this sense, alternative organic ligands to CA have already been reported to improve Ni-based catalysts for DRM, including acetic acid (HAc), ethylenediamine (ED), ethylenediaminetetraacetic acid (EDTA), among others [21, 182]. As a general trend, these organic molecules promote a fine Ni distribution throughout the support, decrease the catalysts' Ni particle size and strengthen the MSI, which was already discussed in section 2.4.1. Apart from these, there is a huge variety of chelating agents which complex Ni^{2+} efficiently, however, this

section only focuses on the use of organic acids with increasing number of carboxyl groups in their structures. Therefore, glycine (Gly), tartaric acid (TA), and diethylenetriaminepentaacetic acid (DTPA) were chosen as alternatives to CA, which have 1, 2, and 5 carboxylic groups in their structures, respectively, while CA has 3 carboxylic groups. Their corresponding molecular structures are displayed in Figure 4-14.

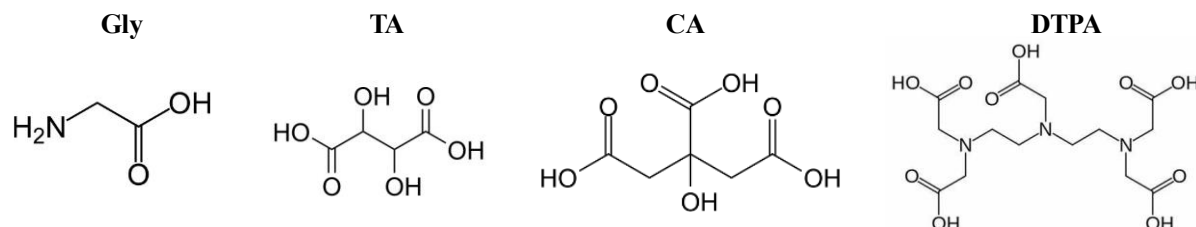


Figure 4-14. Molecular structures of Gly, TA, CA and DTPA.

The fundamentals exposed for Ni-CA complexation can be extended for these other chelating agents, i.e., the formation of precursors via Ni^{2+} complexation is affected by the pH of the media and the dissolution of Mg^{2+} ions from the support. Analogously to CA, sole addition of Gly, TA or DTPA led to partial dissolution of Mg^{2+} from the support, as these three molecules have acidic character and can also complex the Mg^{2+} ions with certain efficiency [195-197]. The measured Mg^{2+} contents in the mother liquors were 0.11, 0.15 and 0.41 g/L, for Gly, TA (and CA) and DTPA, respectively. In these cases, the fractions of the different Ni^{2+} and Mg^{2+} complexes formed were calculated for two conditions using Visual MINTEQ 3.1 software [198]: i) at the initial pH of the impregnating solution (which depended on the acidity of the ligand chosen), and ii) at pH = 9, i.e., the pH measured after impregnation of the support for 16 h due to hydrolysis of MgO. These results can be found in the Table A 1-4, for CA, Gly, TA and DTPA complexes, respectively.

Finally, and analogously to CA, each complexing agent chosen would complex Ni^{2+} differently as a function of the preparation pH (different Ni-c.a. distribution functions), and consequently, different Ni^{2+} complexes might form at varying conditions. The optimization of the impregnation pH for each complexing agent was not performed, as it was outside the scope of this work.

4.1.3.1 Characterization of catalysts of Group III

The fresh, *ex situ* reduced and spent catalysts of Group III were characterized using techniques like those used for the catalysts of Groups I and II. As expected, using other chelating agent than CA led to catalysts which possessed comparable chemical composition (all catalysts had ~ 2.5 wt.% Ni). Additionally, all these catalysts displayed resembling textural properties: $S_{\text{BET}} \sim 100 \text{ m}^2/\text{g}$, pore size ranging between 3 and 12 nm and pore volumes of 0.2 – 0.3 cm^3/g (see Table 4-3). Moreover, the catalysts only displayed MgO and MgAl_2O_4 as crystalline phases (see diffractograms of *ex situ* reduced catalysts of Group III in Figure A 3). No hints regarding Ni-containing phases were detected using XRD. All the previous evidenced that similar impacts were imparted (compared to using CA at any pH value) by changing the chelating agent during the preparation considering: the catalysts' chemical composition, and textural and crystallographic features.

Table 4-3. Chemical composition (ICP), textural properties (BET), reducibility (H₂-TPR) of fresh, and surface chemical composition (XPS) and observed particle size (TEM) of *ex situ* reduced catalysts of Group III.

Sample name	ICP	BET			H ₂ -TPR			XPS	TEM
	Ni content (wt.%)	S _{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	T. H ₂ (μmol/g) ^a	E. H ₂ (μmol/g) ^b	T _{max} (°C)	Ni/(Mg + Al)	Particle size (nm)
Ni/S2	2.5	96	3-10	0.3	426	400	870	-	1-14
Ni(CA)/S2	2.6	124	3-10	0.3	443	427	895	0.08	2-12
Ni(DTPA)/S2	2.5	113	3-10	0.3	426	430	904	0.17	1-17
Ni(TA)/S2	2.6	107	3-12	0.3	443	426	922	0.08	1-18
Ni(Gly)/S2	2.6	103	3-12	0.2	443	418	924	0.11	1.5-15

^a: theoretical H₂ consumption related to the measured ICP Ni content. ^b: measured H₂ consumption during the H₂-TPR experiments.

On the contrary, the different chelating agents modified the catalysts' reducibility, MSI, surface Ni⁰ amount and Ni particle size. Firstly, the H₂-TPR profiles of all chelate-assisted catalysts (Figure 4-15) displayed only one reduction peak centered at very high temperatures ($T_{red} > 850$ °C) ascribed to the reduction of strongly stabilized β -Ni species, suggesting that all studied ligands led to Ni particles displaying very strong MSI. Additionally, the maxima of reduction temperature depended on the chelating agent chosen during preparation, which suggested that the different Ni-complexes formed and the degree of Mg²⁺ dissolution altered the MSI. In this sense, Ni(TA)/S2 displayed the highest reduction temperature among the series, therefore, its Ni species displayed the strongest MSI, possibly due to a finer Ni distribution originating from efficient Ni²⁺ complexation and low Mg²⁺ dissolution from the support's matrix.

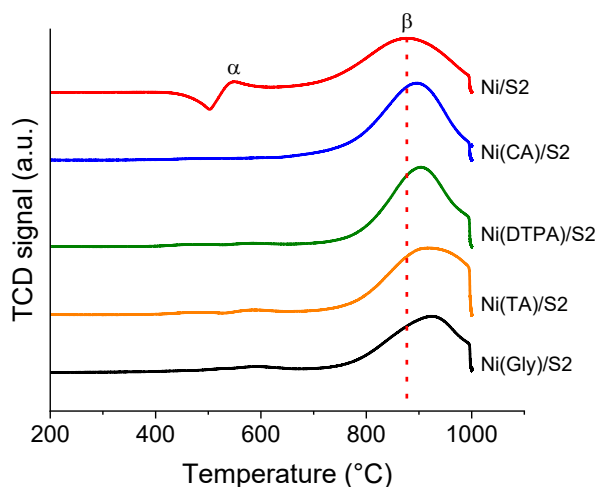


Figure 4-15. H₂-TPR profiles of Ni(CA)/S2, Ni(TA)/S2, Ni(Gly)/S2 and Ni(DTPA)/S2. Republished with permission from [199]. Copyright 2024 Elsevier.

Moreover, *ex situ* reduced catalysts of Group III were characterized using XPS, and surface quantification was also performed (see Table 4-3). Similar to what was discussed in section 4.1.2.1 for the catalysts of Group II, the Ni 2p spectra (see Figure A 4) of the catalysts of Group III showed features ascribable to Ni²⁺ and Ni⁰ upon reductive pre-treatment, evidencing incomplete reduction of surface Ni species and/or partial surface oxidation during handling of the sample before measurement. Apart from that, the three catalysts modified with other chelating agents than CA displayed shifts towards higher BE of the Ni⁰ 2p_{3/2} peak: from 852.1 eV for Ni(CA)/S2, to 852.5 eV for Ni(DTPA)/S2 and Ni(Gly)/S2, and to 852.6 eV for Ni(TA)/S2. As already mentioned for Group II of catalysts, such shifting towards higher BE can be related to strengthened MSI. Thus, Ni(TA)/S2 displayed both the maximum T_{red} and highest BE of Ni⁰ 2p_{3/2} among the series, confirming the formation of Ni species with the strongest MSI.

Apart from the XP spectra, surface quantification revealed that the normalized Ni⁰ content (as Ni⁰/(Mg+Al)) depended on the chelating agent used. In this sense, the order of normalized surface Ni⁰

content was as follows: Ni(TA)/S2 (0.08) ~ Ni(CA)/S2 (0.08) < Ni(Gly)/S2 (0.11) < Ni(DTPA)/S2 (0.17). One possible explanation for the observed trend considers the precursor species formed during preparation. On the one hand, both Ni(TA) and Ni(DTPA) preferentially form complexes L/Ni = 1:1 at pH = 9 (see Table A 3-4, respectively), and it could be argued that the most voluminous precursor species (DTPA-based) experienced resistance to diffuse within the support's pores, and consequently, the Ni precursors were deposited preferably on the catalysts' outer surface. On the other hand, the concentration of precursor species with L/Ni = 2:1 were the highest for Ni(CA) and Ni(Gly) at pH = 9 (see Table A 1-2, respectively), thus, the amount of complexing agent provided (L/Ni = 1.5) might have not been sufficient to complex all Ni²⁺, which also contributed to surface deposition. Additionally, competitive complexation between Ni²⁺ and Mg²⁺ might have also decreased the available molecules of ligands further. Thus, precursor formation seemed to affect the location of the Ni species and how these were stabilized by the support, at least, at the preparative stage. However, and as previously discussed in section 4.1.2, the chemistry occurring in the preparation liquid differs to the solid state one, as solvent evaporation and calcination at T = 800 °C for 6 h form the catalysts' Ni particles. Surface rearrangements might also occur during pre-reduction, complicating the description of the system even more.

Particle size and their distribution throughout the *ex situ* reduced materials were studied with TEM. The catalysts of this group displayed finely distributed Ni-containing nanoparticles displaying different degrees of oxidation (representative micrographs are displayed in Figure A 5 a-d). It should be noted that the particle size was somehow modified by the chelating agent used, as Ni-containing particles of similar sizes (ranging between 4 and 10 nm) were present in all *ex situ* reduced catalysts of this group. However, isolated larger particles were also observed, with sizes of 50, 30, and 28 nm, for Ni(CA)/S2, Ni(DTPA)/S2, and both Ni(Gly)/S2 and Ni(TA)/S2, respectively.

4.1.3.2 Effects of chelating agents on catalyst activity and stability

All catalysts of Group III were screened using the same protocol used for Group I and II of catalysts, and the catalytic results, the same as the amount of coke formed after cycling (25 h TOS) are displayed in Figure 4-16 a-d, respectively. Evidently, the type of chelating agent used during the preparation determined the catalyst activity and coke deposition after cycling (25 h TOS). In this sense, the catalyst Ni(TA)/S2 and Ni(Gly)/S2 outperformed the series with averaged X_{CH₄} = 42.2%, X_{CO₂} = 57.5% and H₂/CO = 0.76 (at 600 °C), and X_{CH₄} = 42.7%, X_{CO₂} = 57.8% and H₂/CO = 0.76 (at 600 °C), and 4.4 wt.% and 4.6 wt.% of formed coke after 25 h TOS, respectively. Thus, using TA or Gly as chelating agents enhanced the X_{CH₄} by ~30% (based on the averaged CH₄ conversion at 600 °C), while the formation of coke was ca. 20% lower compared to Ni(CA)/S2. Therefore, it could be suggested that the smallest particles observed for Ni(TA)/S2 and Ni(Gly)/S2 have the strongest MSI among the series (identified using TEM, H₂-TPR and XPS), which provided a better combination for reaching higher activity levels and lower coke deposition. Furthermore, it seems that the slightly different Ni⁰ surface contents measured for Ni(TA)/S2 and Ni(Gly)/S2 (XPS) were not decisive in shaping the catalytic performance, but the MSI seemed to play a more significative role instead. This statement was further investigated in the spent catalysts recovered after the long-term runs (discussed below).

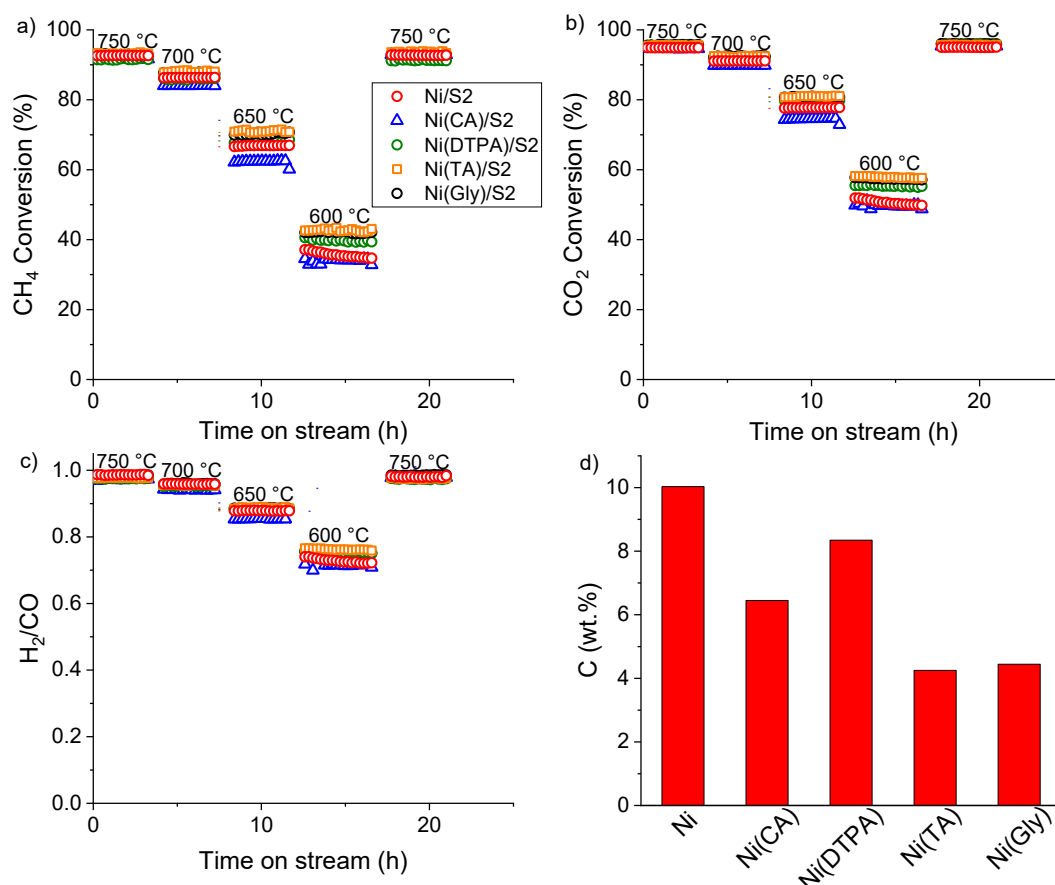


Figure 4-16. a) CH₄ conversion, b) CO₂ conversion, c) H₂/CO ratio with TOS, and d) measured carbon using CHN analysis of spent catalysts of Group III and bare Ni/S2 after 25 h TOS. Reaction conditions: $T_{\text{red}} = 700\text{ °C}$ for 1.5 h, CH₄/CO₂/N₂ = 45:45:10 vol.%, $p = 1\text{ bar}$, $m_{\text{cat}} = 50\text{ mg}$, GHSV = 170 L/(g_{cat}·h). The numbers on top of each data cluster indicate the temperature (in the middle of the catalyst bed) at which the data was collected.

Selected catalysts of Group III were pre-reduced at $T_{\text{red}} = 750\text{ °C}$ and their activity was recorded at $T = 600\text{ °C}$ (see Figure 4-17). The activity was slightly higher compared to the results obtained during the screening at $T = 600\text{ °C}$, possibly due to higher degree of Ni²⁺ reduction by reducing the samples at higher temperature (as discussed before). Particularly, the catalyst Ni(CA)/S2 was the least active and most instable, as it displayed initial $X_{\text{CH}_4} \approx 41.5\%$, $X_{\text{CO}_2} \approx 53.5\%$ and $\text{H}_2/\text{CO} \approx 0.76$ and final $X_{\text{CH}_4} \approx 37.1\%$, $X_{\text{CO}_2} \approx 49.8\%$ and $\text{H}_2/\text{CO} \approx 0.73$, while it formed 4.8 wt.% C over ca. 30 h TOS. Contrarily, Ni(TA)/S2 outstood among the series, with initial $X_{\text{CH}_4} = 45.6\%$, $X_{\text{CO}_2} \approx 58.0\%$ and $\text{H}_2/\text{CO} \approx 0.77$ and final $X_{\text{CH}_4} \approx 42.1\%$, $X_{\text{CO}_2} \approx 56.4\%$ and $\text{H}_2/\text{CO} \approx 0.76$, and formed 5.0 wt.% C over 50 h TOS. Interestingly, the catalyst Ni(Gly)/S2 also showed comparable activity to the TA-modified one, possibly due to their similar physicochemical properties. As discussed via H₂-TPR, XPS and TEM characterization techniques, Ni(TA)/S2 and Ni(Gly)/S2 displayed the highest maximum T_{red} and BE of Ni⁰ 2p_{3/2}, the same as the smallest particles among the series. Thus, these parameters defined the catalytic activity and stability. What is to highlight from this section is that both TA and Gly acted as more efficient chelating agents compared to CA, as the resulting Ni species displayed the strongest MSI, and consequently, prevented the agglomeration of the Ni⁰ active sites over TOS. To evaluate the previous observations better, selected spent samples after screening and long-term experiments were characterized, and the results are discussed in the following section.

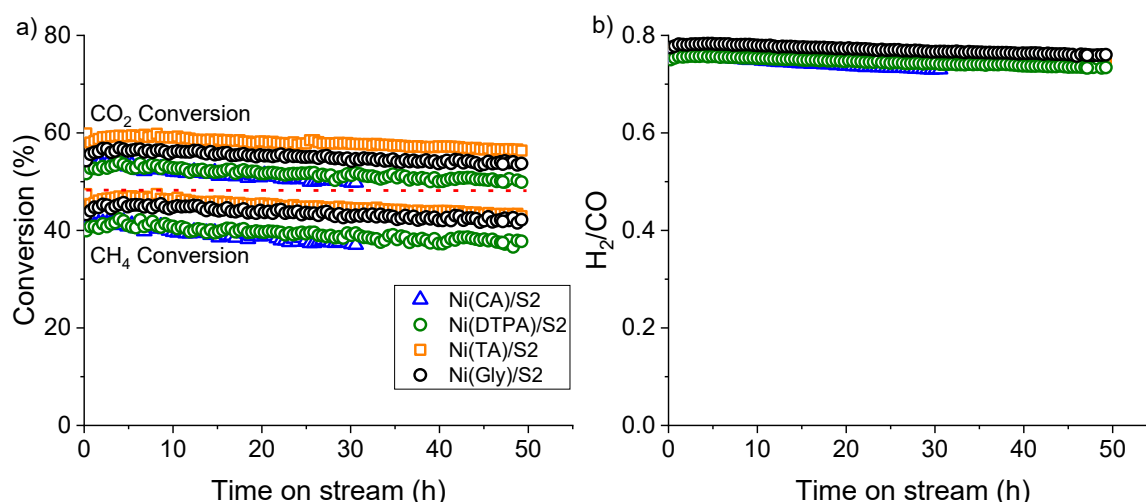


Figure 4-17. a) X_{CH_4} and X_{CO_2} , and b) H_2/CO ratios over TOS with Ni(CA)/S2, Ni(DTPA)/S2, Ni(TA)/S2 and Ni(Gly)/S2. Reaction conditions: $T_{\text{red}} = 750^\circ\text{C}$ for 1.5 h, $\text{CH}_4/\text{CO}_2/\text{N}_2 = 45:45:10$ vol.%, $T = 600^\circ\text{C}$, $p = 1$ bar, $m_{\text{cat}} = 50$ mg, GHSV = $170 \text{ L}/(\text{g}_{\text{cat}} \cdot \text{h})$.

4.1.3.3 Characterization of spent catalysts

TEM was firstly used to evaluate the morphological evolution of Ni particles and coke formation after different reaction regimes. Thus, the spent catalysts of Group III after 25 h TOS (see Figure 4-18 a-b) displayed larger Ni-containing particles of different nature, including Ni^0 , $\text{Ni}^0/\text{Ni}^{2+}$ core-shell and hierarchical Kirkendall particles. A more profound discussion regarding the nature of the Ni particles and their evolution during reaction was already provided in section 4.1.2.1. Firstly, the following order was observed regarding particle size after cycling (25 h TOS): Ni(TA)/S2 (3 – 20 nm) < Ni(Gly)/S2 (1.5 – 28 nm) < Ni(CA)/S2 (3 – 38 nm) < Ni(DTPA)/S2 (3 – 60 nm). Thus, the least particle size increase of Ni(TA)/S2 was linked to its strongest MSI (as evidenced by H_2 -TPR and XPS). It could also be argued that its lower fraction of surface Ni^0 (XPS) might have also played a role in keeping a small particle size over TOS, as the active sites might have been ‘confined’ within the support’s pores and prevented Ni migration and crystal growth. On the contrary, Ni(DTPA)/S2 suffered the most remarkable particle size increase after cycling (25 h TOS). The previous might be due to its intermediate MSI (compared to TA or Gly-assisted catalysts) and the highest Ni^0 fraction on its surface, which might be weakly bound to the support and might have agglomerated during the reaction at high temperatures. The previous suggested that strong MSI aided in keeping the Ni species closely attached to the support, while Ni incorporation within the support’s matrix seemed to prevent further particle agglomeration. In addition to the size increase, oxidation of the Ni^0 sites was observed, possibly due to the fed CO_2 and/or in situ formed water by the RWGS (Eq. 7) at high temperatures.

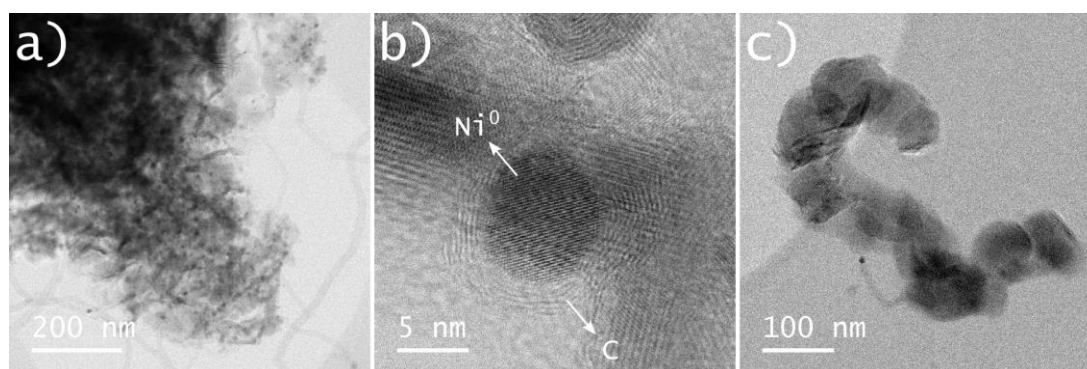


Figure 4-18. TEM-BF micrographs of: a) and b) spent Ni(TA)/S2 after 25 h TOS and c) after 50 h TOS. Specific reaction conditions for a) and b): $T_{\text{red}} = 700^\circ\text{C}$ for 1.5 h, $T = 600 - 750^\circ\text{C}$, while for c) $T_{\text{red}} = 750^\circ\text{C}$ for 1.5 h, $T = 600^\circ\text{C}$. All tests were performed using $\text{CH}_4/\text{CO}_2/\text{N}_2 = 45:45:10$ vol.%, $p = 1$ bar, $m_{\text{cat}} = 50$ mg, GHSV = $170 \text{ L}/(\text{g}_{\text{cat}} \cdot \text{h})$. Republished with permission from [199]. Copyright 2024 Elsevier.

Not only changes in the nature of the Ni-containing particles were observed after tests, but also different carbonaceous structures. In this sense, CNTs and graphitic coke were observed after 25 h TOS (Figure 4-18 a-b, respectively), while only CNTs were formed after the long runs (Figure 4-18 c). Thus, the type of coke formed strongly depended on the reaction conditions used, i.e., CNTs were readily formed at $T \geq 600$ °C, while graphitic coke required higher temperatures ($T > 600$ °C). Independently of the reaction temperature used during reaction, most of the observed CNTs detached Ni particles from the support (i.e., active Ni^0 placed at the CNT's tip), while some of them also encapsulated active sites within their structure. The latter decreased the accessibility of some of the Ni^0 sites to the reactants and impacted on the catalyst performance, in a similar way to the effect imparted by graphitic coke (as discussed in section 2.3.1). As previously mentioned, by increasing the reaction temperature to $T > 600$ °C, highly ordered graphitic layers formed surrounding some Ni^0 particles only after the screening tests (Figure 4-18 b). Despite the presence of different types of coke after 25 h TOS, the encapsulation of the Ni^0 sites was not sufficient to cause deactivation during the screening tests, as no activity loss was recorded.

The catalyst Ni(TA)/S2 was investigated after 50 h TOS using TEM (Bright Field (BF)-micrograph in Figure 4-18 c and HAADF-micrograph in Figure 4-19 a). In this case, Ni^0 was rarely observed, while most of the Ni particles showed almost exclusively oxidic character (see EEL spectra Figure 4-19 b). Moreover, the Ni-containing particles displayed sizes between 1.5 and 13 nm, thus, slight particle increase was evidenced. The latter can be ascribed to the lower reaction temperature used during the stability tests (vs. screening), which most likely prevented particle sintering. As the oxidation proceeded almost until completion, few Kirkendall particles were observed, although some were still present and might have aided in re-dispersing Ni. This characterization revealed that profound Ni oxidation took place, thus, it must have played a key role in catalyst deactivation. The same was also evidenced for Group II of catalysts.

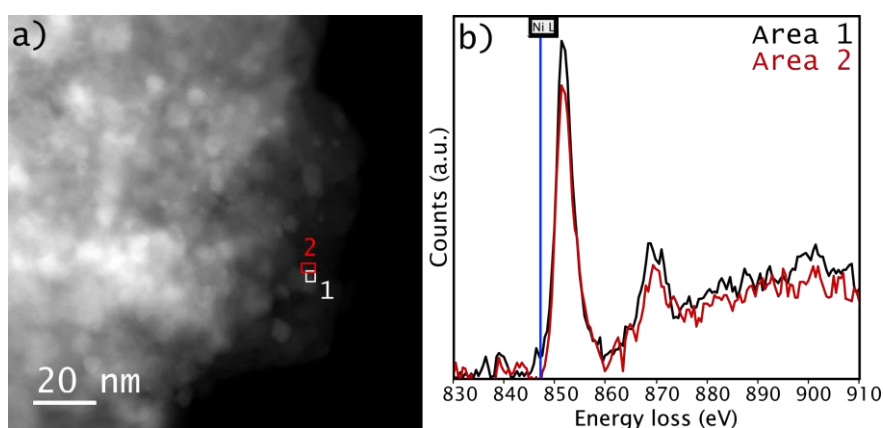


Figure 4-19. a) TEM-HAADF micrograph of spent Ni(TA)/S2 after 50 h TOS. Inset boxes 1 and 2 indicate the regions in which the EEL spectra were collected. b) Corresponding EEL spectra taken from areas 1 and 2, respectively. Reaction conditions: $T_{\text{red}} = 750$ °C for 1.5 h, $\text{CH}_4/\text{CO}_2/\text{N}_2 = 45:45:10$ vol.%, $p = 1$ bar, $T = 600$ °C, $m_{\text{cat}} = 50$ mg, GHSV = 170 L/(g_{cat}·h).

Finally, the nature of the coke deposits and the temperature needed to gasify them under oxidative atmosphere was studied using O_2 -TPO. The obtained profiles of the spent samples after 25 h TOS are displayed in Figure 4-20. The studied catalysts showed two peaks in their O_2 -TPO profiles, centered at $T_{\text{ox}} \sim 340$ °C and $T_{\text{ox}} \sim 670$ °C, ascribed to the oxidation of at least two types of carbonaceous structures with different stability against oxidation. In this sense, it is reported that higher temperatures are needed to combust carbon species with higher structural order, thus, amorphous ($T_{\text{ox}} \sim 340$ °C) and graphitic ($T_{\text{ox}} \sim 670$ °C) [153] coke formed after 25 h TOS, which agreed well with the TEM observations. Unfortunately, the oxidation profiles of the studied spent samples did not show remarkable differences, however, these helped to corroborate graphitic coke as the predominant carbonaceous structure after 25 h TOS.

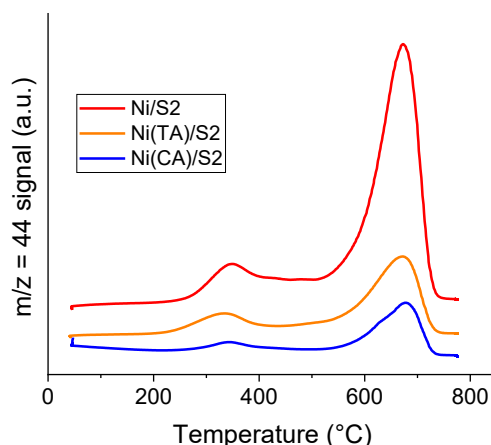


Figure 4-20. O₂-TPO profiles (signal $m/z = 44$) of spent Ni/S2, Ni(CA)/S2 and Ni(TA)/S2 after cycling (25 h TOS). Reaction conditions: $T_{\text{red}} = 700$ °C for 1.5 h, CH₄/CO₂/N₂ = 45:45:10 vol.%, $p = 1$ bar, $T = 600 - 750$ °C, $m_{\text{cat}} = 50$ mg, GHSV = 170 L/(g_{cat}·h). Republished with permission from [199]. Copyright 2024 Elsevier.

4.1.4 Effects of adding different metals to Ni/S2 (Group IV)

Despite the improvements reached so far, coke deposition and especially Ni⁰ re-oxidation have been recurrently identified as the main causes of catalyst deactivation. Thus, it seems that more impactful modifications are needed to control these deactivating processes, thus, different metals were added into the formulation of Ni/S2, considering both single element (Ce or Ga) and dual element (La+Ga or Gd+Sc) approaches. Following the discussion provided in section 2.4.2, the metals chosen for this group of catalysts (Group IV) are reported to impact differently on the catalysts' physicochemical properties. For example, Ce can alter the redox properties, Ga alloys with Ni and leads to active sites with modified electronic and reactivity properties, while the rare-earth metals La, Gd and Sc enhance the basicity of the catalysts and induce defects/oxygen vacancies in the catalysts' structure. Generally, the adsorption of O-containing reactants (such as CO₂, H₂O or O₂) is promoted upon incorporation of these elements, which enhances the activity and promotes the gasification of coke simultaneously. The impacts of adding these metals in the catalysts' formulations were identified and correlated with their resulting physicochemical features and the catalytic activity (both in screening and long-term experiments). These discussions are found below.

4.1.4.1 Characterization of catalysts of Group IV

This group of catalysts was characterized with ICP, BET, XRD and H₂-TPR, while selected catalysts reduced *ex situ* at $T_{\text{red}} = 700$ °C for 1.5 h were analyzed with XPS and TEM. Firstly, the chemical composition of the promoted catalysts evidenced that the Ni contents of most of these samples were lower than the target 2.5 wt.% Ni. Apart from the chemical composition, textural characterization revealed that the S_{BET} and pore volume were further reduced in 38 – 55% and 33 – 66% after incorporation of additional elements compared to Ni/S2, which also suggested blockage of the porous structure with the impregnating material (see Table 4-4).

Table 4-4. Chemical composition (ICP), textural properties (BET) and reducibility (H₂-TPR) of catalysts of Group IV.

Sample name	ICP Content (wt.%)	BET			H ₂ -TPR		
		S _{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	T. H ₂ (μmol/g) ^a	E. H ₂ (μmol/g) ^b	T _{max} (°C)
Ni/S2	2.5 Ni	96	3-10	0.3	426	400	870
NiGa/S2	2.3 Ni, 2.1 Ga	43	2-10	0.1	842 ^c	567	897
NiCe/S2	2.1 Ni, 4.0 Ce	43	3-13	0.1	501 ^d	657	893
NiLaGa/S2	2.1 Ni, 2.0 La, 0.6 Ga	45	2-8	0.1	487 ^d	556	863
NiGdSc/S2	1.9 Ni, 2.2 Gd, 0.5 Sc	59	3-12	0.2	324	390	874

^a: theoretical H₂ consumption related to the measured ICP Ni content. ^b: measured H₂ consumption during the H₂-TPR experiments. ^c: the calculation also contemplated the reduction of Ce⁴⁺ to Ce³⁺. ^d: the calculation also contemplated the reduction of Ga³⁺ to Ga⁰.

The investigation of the crystalline structure of the *ex situ* reduced catalysts revealed that the predominant phases were MgO and MgAl₂O₄ for all samples, while the Ce-promoted catalyst also displayed reflections associated to CeO₂ (denoted as ‘▲’ in Figure 4-21 a, cubic, ICDD = 00-064-0737, main reflections centered at 2θ = 28.5, 33.0, 47.4°). Additionally, a reflection of low intensity centered at 2θ ~ 50.5 – 52° was observed for the bi-/trimetallic catalysts, which suggested the presence of Ni⁰ (denoted as ‘◆’ in Figure 4-21 a, ICDD: 00-004-0850 cubic, main reflections centered at 2θ = 44.5 and 51.9°). Particularly, the reflection of the Ni⁰ (200) crystalline plane of the catalysts Ni/S2, NiCe/S2 and NiGdSc/S2 was centered exactly at 2θ = 51.9°, which agreed with the reference card of Ni⁰. On the contrary, the catalysts NiGa/S2 and NiLaGa/S2 showed the previous reflection centered at 2θ = 50.5° and 51.4°, respectively. The latter suggested that the Ni⁰ lattice was expanded, possibly by incorporation of a bigger atom, which provoked a shift of the Ni⁰ (200) reflection towards lower angles [200]. In this sense, and as already discussed in section 2.4.2, NiGa alloys and/or intermetallic compounds might form during calcination/reduction under the conditions used in this work [201], and the observed shift towards lower angles would match with the insertion of bigger Ga ions into the Ni lattice. Although no unequivocal hints regarding the formation of NiGa alloy/intermetallics were found using XRD due to the low concentration of these metals, acceptable correlation existed with the reflection centered at 2θ = 50.5° of NiGa/S2 with that of a HTC-derived reduced NiMgGa catalyst [200], in which the formation of intermetallic Ni₃Ga was unambiguously disclosed (reflection centered at 2θ = 50.9°, which increased its intensity at increasing Ga/Ni ratios). The differences might arise from the low Ni and Ga contents used in this work, compared to those used in [200], which of course made the detection of NiGa challenging. Therefore, the formation of NiGa species was further investigated using TEM (see below). Apart from that, no additional crystalline phases were formed after reduction, which was a common feature among all the other *ex situ* reduced catalysts of this series.

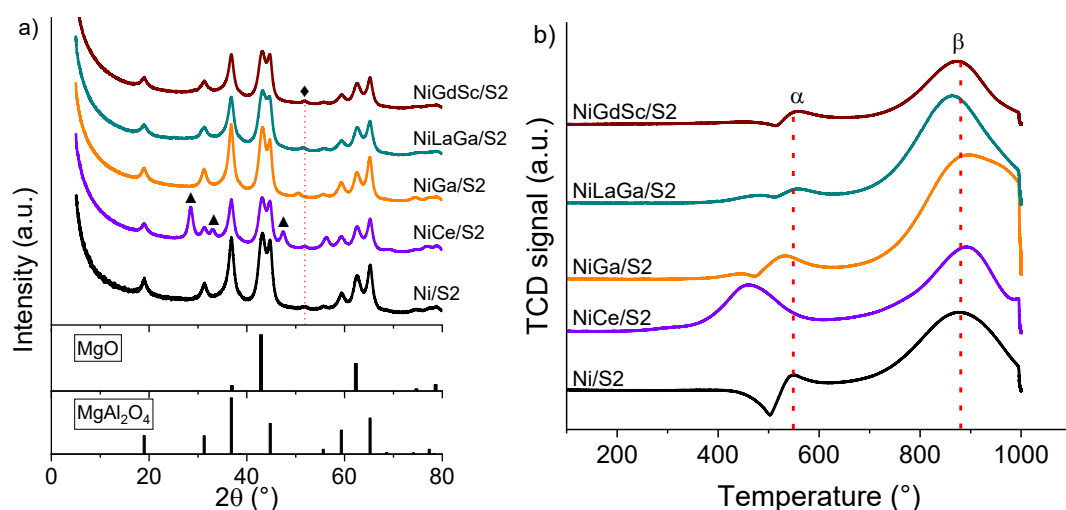


Figure 4-21. a) diffractograms of *ex situ* reduced (at $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h) and b) H_2 -TPR profiles of catalysts of Group IV. Legend: '▲': CeO_2 cubic (ICDD: 00-064-0737) and '◆': Ni^0 cubic (ICDD: 00-004-0850).

Additionally, catalyst reducibility depended on the metal(s) used (see Figure 4-21 b). First, NiCe/S2 displayed two broad reduction peaks centered at $T_{\text{red}} = 460\text{ }^{\circ}\text{C}$ and $893\text{ }^{\circ}\text{C}$, ascribed to the reduction of Ce^{4+} to Ce^{3+} and strongly interacting β -Ni species, respectively. According to literature [151], reduction of surface Ce^{4+} to Ce^{3+} occurred at $T_{\text{red}} \sim 350 - 450\text{ }^{\circ}\text{C}$ in Ni/CeO₂-La₂O₃, which agreed with the temperatures found for NiCe/S2 in Figure 4-21 b. Besides, the high-temperature peak was shifted towards higher temperatures (compared to bare Ni/S2), indicating that the β -Ni species interacted strongly with the support, most likely due to improved distribution of Ni mediated by Ce and/or due to strong interaction between Ni and Ce species [202, 203].

Moreover, NiGa/S2 displayed three reduction peaks (Figure 4-21 b): at $T_{\text{red}} = 445\text{ }^{\circ}\text{C}$, $530\text{ }^{\circ}\text{C}$, and the main peak centered at $897\text{ }^{\circ}\text{C}$, evidencing the presence of at least three types of reducible species. Thus, α - and β -Ni species were reduced at $T_{\text{red}} = 530\text{ }^{\circ}\text{C}$ and $T_{\text{red}} = 897\text{ }^{\circ}\text{C}$, respectively. Compared to Ni/S2, the α -Ni species were reduced at lower T_{red} (i.e., weakened MSI) possibly due to a poor distribution of surface Ni. Contrarily, β -Ni species were reduced at higher T_{red} , evidencing stronger MSI, most likely due to the formation of NiGa intermetallic compounds/alloys [204]. Additionally, Ga was also reduced during H_2 -TPR in two steps: at mild temperatures $T_{\text{red}} = 445\text{ }^{\circ}\text{C}$ (Ga^{3+} to Ga^{2+}) and high temperatures $T_{\text{red}} > 900\text{ }^{\circ}\text{C}$ (Ga^{2+} to Ga^0) [200, 205]. Based on literature, formation of NiGa sites strengthened the MSI in NiMgGa HTC-derived [51] and NiGa/MCM-41 [204] catalysts for DRM, which agreed with the high temperature needed to reduce NiGa/S2 in this work.

Furthermore, NiLaGa/S2 also showed three reduction peaks, which suggested the reduction of Ni and Ga species similarly to NiGa/S2. However, the reduction profiles of these catalysts also displayed differences due to their composition (discussed below). On the one hand, the α -Ni species in NiLaGa/S2 required higher temperatures to be reduced ($T_{\text{red}} = 560\text{ }^{\circ}\text{C}$) compared to NiGa/S2, possibly due to stronger interaction of these with surficial La₂O₃ centers. In this sense, surface La deposition predominates in MgAlO_x supports using impregnation and calcination due to the large ionic size of La^{3+} ions [206]. The previous was further investigated with TEM characterization (see below). Contrarily, the reduction of β -Ni species in NiLaGa/S2 required lower temperature ($T_{\text{red}} = 863\text{ }^{\circ}\text{C}$) than NiGa/S2, revealing improved Ni reducibility by adding La. Then, the strong stabilization mediated by Ga was weakened by adding La simultaneously, possibly due to modification of the electronic environment of these NiGa sites, and/or to the formation of defective Ni oxidic structures easier to reduce [78]. Finally, NiGdSc/S2 displayed two reduction peaks centered at $T_{\text{red}} = 560\text{ }^{\circ}\text{C}$ and $874\text{ }^{\circ}\text{C}$, ascribed to the reduction of α - and β -Ni species, respectively. No reduction of Sc and/or Gd were evidenced. This sample required higher T_{red} to reduce the α -Ni species compared to Ni/S2, possibly due to improved distribution of surface Ni sites, which were then better stabilized by the Mg-rich support. In this sense, it was reported that using Sc or Gd promoters individually enhances Ni dispersion in Ni/Mg_{1.3}AlO_x, which strengthens

MSI [78]. Moreover, the high reduction temperature peak was centered at comparable T_{red} to that of Ni/S2, suggesting similar MSI between β -Ni species and the support.

Additionally, the bi-/trimetallic catalysts displayed higher H_2 consumption compared to the theoretical possible values according to their ICP Ni loads (Table 4-4). The latter revealed the simultaneous reduction of other metals and/or the formation of Ni^{n+} species ($n > 2$), for example, within perovskite-like phase, which required more H_2 to be reduced [207, 208].

Regarding the Ni oxidation state and surficial composition of the bi-/trimetallic *ex situ* reduced catalysts (displayed in Figure A 6, spectra collected in the Ni 2p region between 850 – 890 eV), only the spectrum of the sample NiLaGa/S2 is not displayed due to the overlapping between the Ni 2p and La 3d electrons in the region of interest. On the contrary, the spectra of the other catalysts of the series displayed features ascribable to Ni^0 and Ni^{2+} , thus, the discussion provided for the catalysts of Group II-III can be extended here (see, for example, section 4.1.2.1).

The most remarkable difference in Figure A 6 are the Ce 3d peaks of NiCe/S2 in the region between 870 – 890 eV, ascribed to the redox pair Ce^{3+} (peaks centered at 881.2 eV and 885.1 eV) and Ce^{4+} (peaks centered at 882.7 eV and 886.9 eV) [209]. Thus, both Ce^{4+}/Ce^{3+} species co-existed at the surface of NiCe/S2 after reduction. Moreover, the Ce peaks partially overlapped with one of the satellite features of Ni^0 (at ca. 880 eV) but did not affect the quality of Ni spectra and/or quantification of surface Ni species. Moreover, the position of all peaks depended on the catalysts' composition. Focusing on the Ni^0 2p_{3/2} peak, the order in BE was as follows: NiGa (851.7 eV) < NiGdSc (852.2 eV) < NiCe/S2 (852.7 eV), revealing that the electronic properties of the surface Ni species were affected by the metals used. In this case, NiCe/S2 required the highest BE to eject Ni^0 2p_{3/2} electrons, suggesting strong MSI, which agreed well with the high temperature needed to reduce this sample in its H_2 -TPR profile (Figure 4-21 b). Similar observations were done for Ni/Al₂O₃ and Ce-modified Ni/Al₂O₃ catalysts, where the shift towards higher BE of the peak of Ni^0 2p_{3/2} electrons upon Ce incorporation was associated to strengthened MSI effect mediated by surface Ce-species [210].

On the contrary, NiGa/S2 displayed the lowest BE, which deserves a deeper discussion. Based on previous literature [211], Ni_xGa_y species displayed a Ni^0 2p_{3/2} peak centered at 851.4 eV (considering same reference C 1s at 284.8 eV as the value used in this work), which the authors unequivocally correlated to alloyed NiGa species. Even though the measured Ni^0 2p_{3/2} peak for NiGa/S2 showed 0.3 eV of difference with the one of literature, it was the lowest value measured so far for any other sample. Thus, XPS evidenced formation of surface NiGa species, which agreed with the observations derived from XRD. The lower BE might originate from a richer electron density surrounding the Ni species due to electron transfer from Ga (richer in electrons: [Ar]3d¹⁰4s²4p¹) to Ni (poorer in electrons: [Ar]3d⁸4s²), which could also correlate well with their same electronegativity [212]. An analogous argument was provided for NiPr/Al₂O₃ catalysts [213]. The authors argued that electron-rich Pr donated electrons to the empty 3d orbitals of Ni, which caused a shift of the BE of Ni^0 2p_{3/2} towards lower values.

Additionally, surface quantification was performed, and all the metals of all samples were detected by XPS, evidencing the presence of them on the catalysts' surface to certain extent. Besides, the order of normalized $Ni^0/(Mg+Al)$ was as follows: NiCe (0.05) < NiGa (0.07) < NiGdSc/S2 (0.1). Therefore, it could be argued that the latter catalyst displayed the highest surface Ni^0 amount, possibly due to improved surface Ni deposition mediated by Gd and Sc metals. A similar effect was identified for 2.5 wt.% Ni catalyst/Mg_{1.3}AlO_x modified with Gd or Sc (individually) in previous work in our group [78].

Finally, the *ex situ* reduced (at $T_{\text{red}} = 700$ °C for 1.5 h) NiLaGa/S2 catalyst was characterized by TEM. The previous was done due to the impossibility to measure a reliable XP spectrum (as discussed before). In this case, the reduced catalyst displayed finely distributed Ni-containing particles (see Figure 4-22 a and c), which were present both as nanoparticles on the support (mostly sized between 5 and 7 nm), and highly dispersed on/incorporated within the support's matrix (with sizes below 2 nm; see small intensity of Ni in the EDX spectrum 2 in Figure 4-22 b). These results indicated that the simultaneous addition

of La and Ga improved the distribution of Ni and produced very small Ni particles, which were predominantly of metallic character (Ni^0) with only slight surficial oxidation (see Figure 4-22 c).

Besides, no isolated Ga particles were detected, but this element was incorporated within the finely distributed Ni-containing particles (see the EDX spectrum 1 in Figure 4-22 b), suggesting the formation of NiGa intermetallic compounds/alloys, as previously argued based on XRD and H_2 -TPR results. Besides, finely distributed La particles were observed throughout the support, and eventually, scattered as La single atoms (see very small bright dots in Figure 4-22 c). Moreover, these lanthanoid species even decorated the surface of the NiGa nanoparticles, which could modify their electronic properties and improve CO_2 activation and coke gasification via formation of $\text{La}_2\text{O}_2\text{CO}_3$ species and the inverse of the Boudouard reaction (Eq. 8), as discussed in sections 2.2 and 2.3.1, respectively.

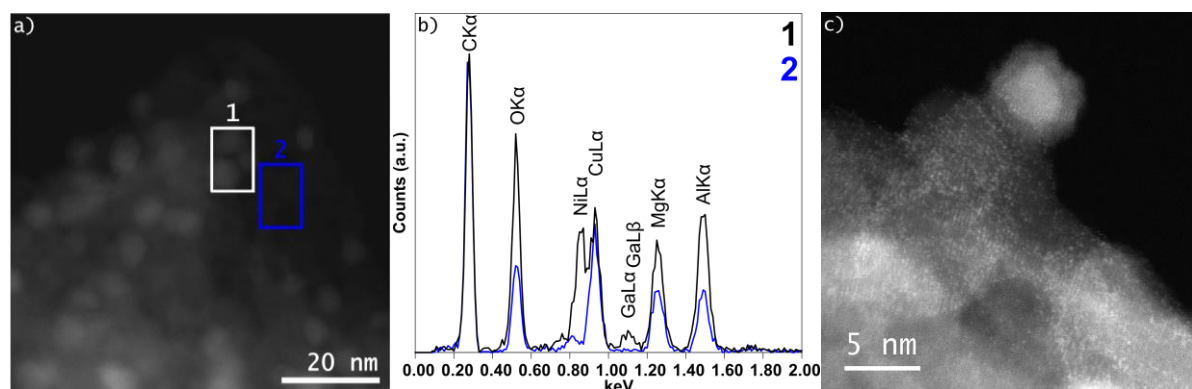


Figure 4-22. a) TEM-HAADF micrograph and b) corresponding EDX spectra of highlighted areas of a), and c) STEM-HAADF micrograph of *ex situ* reduced (at $T_{\text{red}} = 700^\circ\text{C}$ for 1.5 h) NiLaGa/S2. The small bright dots scattered overall in c) are La single atoms (EDX).

4.1.4.2 Impacts of bi-/trimetallic catalysts' composition on their activity and stability

The catalysts of Group IV were screened, and selected samples were further evaluated in long-term runs at 600°C . The conversion of CH_4 , CO_2 and H_2/CO ratio over TOS, as well as the carbon formed after 25 h TOS are displayed in Figure 4-23 a-d, respectively.

The conversion of CO_2 was slightly higher than that of CH_4 , while the ratio $\text{H}_2/\text{CO} < 1$ for all samples and at all temperatures evidenced the occurrence of the RWGS (Eq. 7). Thus, none of the catalysts of this group prevented this side reaction. On the one hand, the bimetallic catalysts were more active than Ni/S2 at all conditions and did not deactivate (especially at $T = 600^\circ\text{C}$), indicating a positive impact on both the activity and the stability upon Ce or Ga addition. Particularly, NiCe/S2 was approximately 5% more active than NiGa/S2, which revealed only a slight activity improvement by using Ce. However, the most interesting remark was their different tendency to deposit coke, which clearly depended on the promoter used. In this sense, NiGa/S2 formed 11.4 wt.% C, while NiCe/S2 formed 3.2 wt.% over 25 h TOS. The reasons regarding the previous improvements vs. Ni/S2 are discussed below.

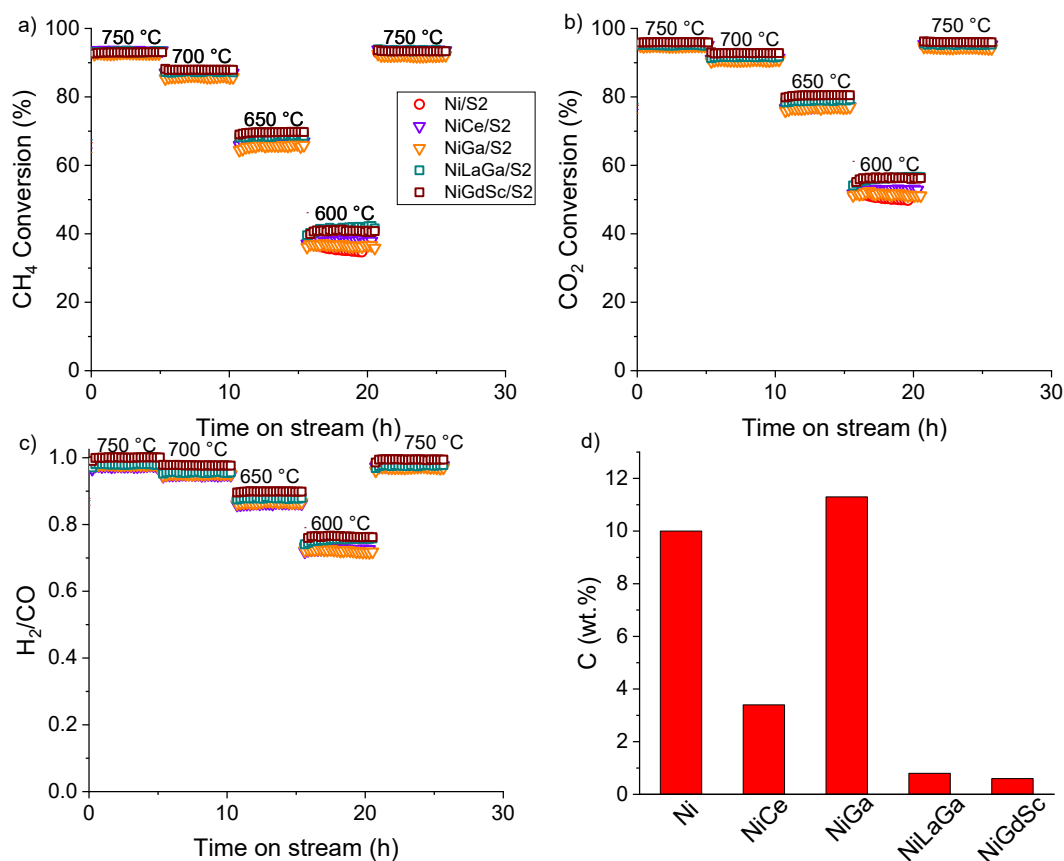


Figure 4-23. a) CH₄ conversion, b) CO₂ conversion, c) H₂/CO ratio with TOS, and d) measured carbon using CHN analysis of spent catalysts of Group IV and bare Ni/S2 after 25 h TOS. Reaction conditions: $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h, CH₄/CO₂/N₂ = 45:45:10 vol.%, $p = 1\text{ bar}$, $m_{\text{cat}} = 50\text{ mg}$, GHSV = 170 L/(g_{cat}·h). The numbers on top of each data cluster indicate the temperature (in the middle of the catalyst bed) at which the data was collected.

Thus, the better performance of NiCe/S2 over NiGa/S2 might relate to the formation of more Ni⁰ active sites during pre-reduction at $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ in the former, as its maximum T_{red} was lower than NiGa/S2 (see Figure 4-21 b). Another possible origin relates to the inherent basicity and redox properties of Ce and how these impact on the adsorption of CO₂ during reaction. Thus, partial reduction of basic CeO₂ during operation (from Ce⁴⁺ to Ce³⁺, as identified through H₂-TPR and XPS surface analysis, see section 4.1.4.1) creates oxygen vacancies throughout the catalyst's structure, which act as adsorption sites for acidic CO₂ [203]. The latter is beneficial for both the activity (more reactant molecules available on the surface) and coke gasification (via the inverse of the Boudouard reaction Eq. 8) [214]. Contrarily, Ga promotion is reported to enhance the acidity of the catalysts [204], which most likely promoted coke deposition via CH₄ decomposition (Eq. 9) (already discussed in section 2.3.1). Besides, more acidic sites also imply hindered adsorption of CO₂ for the reaction, which decreases the catalysts' activity and hinders coke gasification via the inverse of the Boudouard reaction (Eq. 8). Finally, it also seems reasonable that some Ni active sites were covered by coke (11.4 wt.% C after screening test), which most likely affected the performance of NiGa/S2 further.

Going one step forward, the trimetallic catalysts NiLaGa/S2 and NiGdSc/S2 outstood among the series, with comparable (averaged) $X_{\text{CH}_4} \approx 41.0\%$, $X_{\text{CO}_2} \approx 56.0\%$ and $\text{H}_2/\text{CO} \approx 0.75$ at $T = 600\text{ }^{\circ}\text{C}$. Interestingly, NiGdSc/S2 and NiLaGa/S2 formed 0.4 and 0.6 wt.% C over 25 h TOS, respectively, i.e., by far the least amount of coke after 25 h TOS. Compared to Ni/S2, the trimetallic catalysts were ~ 10% more active at $T = 600\text{ }^{\circ}\text{C}$ and formed ~ 20-times less coke. The reasons for these improvements are discussed below.

Finally, the stability of NiLaGa/S2 and NiGdSc/S2 was tested at $T = 600\text{ }^{\circ}\text{C}$ after reducing them at $T_{\text{red}} = 750\text{ }^{\circ}\text{C}$ for 1.5 h (Figure 4-24). Thus, the trimetallic catalysts displayed exceptional performance with no activity loss after ca. 48 h TOS, while both formed approximately 1.2 wt.% C over TOS.

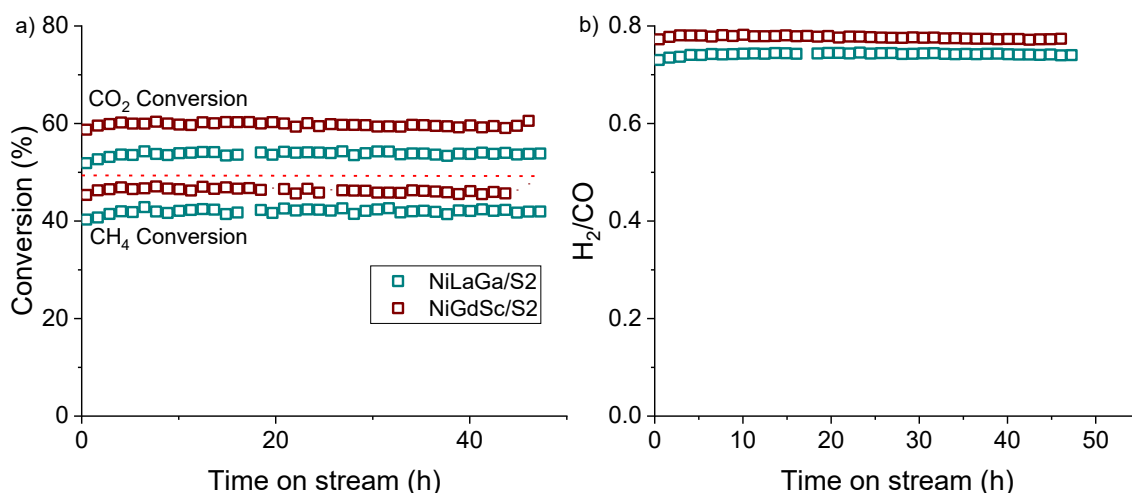


Figure 4-24. Long-term stability tests of NiLaGa/S2 and NiGdSc/S2. Reaction conditions: $T_{\text{red}} = 750\text{ }^{\circ}\text{C}$ for 1.5 h, $\text{CH}_4/\text{CO}_2/\text{N}_2 = 45:45:10$ vol.%, $T = 600\text{ }^{\circ}\text{C}$, $p = 1\text{ bar}$, $m_{\text{cat}} = 50\text{ mg}$, $\text{GHSV} = 170\text{ L}/(\text{g}_{\text{cat}}\cdot\text{h})$.

On the one hand, NiLaGa/S2 displayed improved reducibility (H₂-TPR), thus, more active Ni⁰ sites might have formed upon pre-reduction. Besides, this sample exposed highly dispersed surface (basic) La species surrounding the small NiGa active sites (TEM), which most likely enhanced the CO₂ adsorption and gasified carbonaceous intermediates through La₂O₂CO₃ formation. Additionally, Ga incorporation most likely prevented the re-oxidation of the Ni⁰ sites by tuning their electronic properties. The latter statement was identified for sole Ga-promotion in NiGa/S2 (see XPS), but it seems reasonable to also occur in the trimetallic NiLaGa/S2 catalyst. On the other hand, NiGdSc/S2 showed the highest amount of surface Ni⁰ species (XPS), which were finely distributed throughout the support and strongly attached to it (as evidenced by H₂-TPR and XPS). The latter enhanced the activity and prevented coke deposition. Additionally, Gd is reported to prevent the formation of Ni-aluminate phases, which facilitates the formation of Ni⁰ sites during pre-reduction [209]. Finally, both Gd and La are reported to induce defects in the catalysts' structure due to their mismatching size (compared to the host catalysts' structure), which are adsorption sites for CO₂ [209, 215]. Thus, the latter most likely contributed to the increased catalytic activity and decreased coke deposition in both catalysts, too.

4.1.4.3 Characterization of spent catalysts

Upon screening, the spent NiLaGa/S2 after cycling (25 h TOS) displayed larger Ni particles overall (between 2 and 20 nm, see Figure 4-25), however, these displayed predominantly metallic state, while few oxidic Ni layers were observed surrounding some larger Ni⁰ sites (see Figure 4-25 c). Regarding the promoters, Ga still co-existed within the Ni particles after 25 h TOS, which implied that no Ga segregation/exsolution occurred, probably due to its close interaction with Ni (see EDX spectra in Figure 4-25 b). Moreover, La was still present throughout the sample, but in this case, both as single atoms and separate large La agglomerates (see small bright dots in Figure 4-25 c, and large agglomerates in Figure A 7, respectively). The latter evidenced migration and growth of some La species at high temperatures. However, La remained finely distributed throughout the catalysts over TOS to a great extent. Thus, the presence of small NiGa sites (< 10 nm), and single atoms of La (involved in the activation of CO₂ and formation of La₂O₂CO₃; see section 2.3.1) enhanced the activity and discouraged coke deposition. The latter explained the absence of deactivating coke structures in the TEM micrographs and the low amount of coke measured after test using CHN analysis.

Therefore, re-oxidation of Ni⁰ during reaction was somehow prevented upon simultaneous incorporation of La and Ga, which might relate to the improved reducibility provoked by La and the close interaction between Ni and Ga species. Thus, adding promoters in the formulation was the best strategy to prevent catalyst deactivation so far, which largely outstood among all the catalysts presented throughout this chapter.

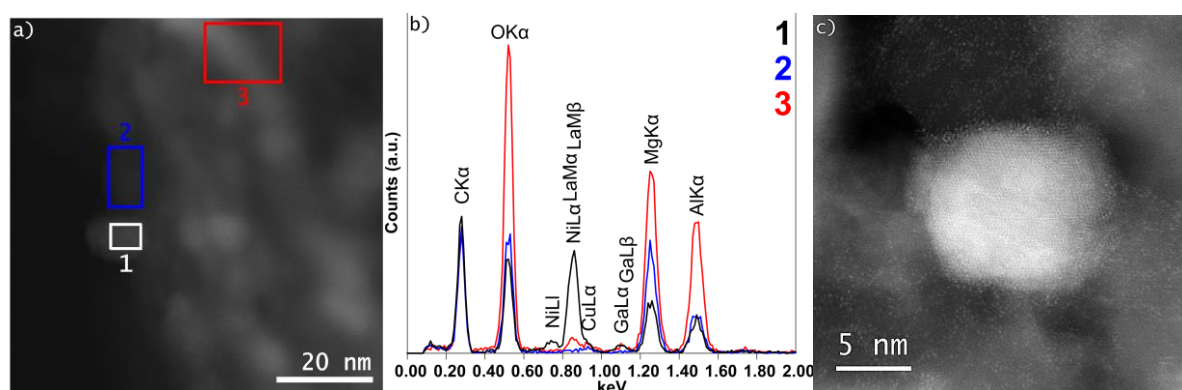


Figure 4-25. a) TEM-HAADF micrograph and b) corresponding EDX spectra of highlighted areas of a), and c) STEM-HAADF micrograph of spent NiLaGa/S2 after 25 h TOS, respectively. Reaction conditions: CH₄/CO₂/N₂ = 45:45:10 vol.%, p = 1 bar, m_{cat} = 50 mg, GHSV = 170 L/(g_{cat}·h).

4.1.5 Intermediate conclusions

The effect of the MgO content in MgO-Al₂O₃ mixed oxide supports was investigated for low-loading 2.5 wt.% Ni catalysts (Group I). Particularly, Ni(CA)/S2 (supported on 50:50 wt.% MgO:Al₂O₃) outstood among the series due to the formation of Ni species displaying moderate (but still strong) MSI, which was beneficial for the formation of the Ni⁰ active sites upon activation. Increasing the MgO content > 50 wt.% strengthened the MSI further, but it obstructed the Ni²⁺ reduction, which decreased the catalytic performance significantly. Finally, assisting the preparation with CA improved Ni dispersion and strengthened the catalysts' MSI, which prevented catalyst deactivation and remarkably decreased the amount of coke deposited compared to CA-free Ni/S2.

Group II revealed that using CA at varying pH altered the precursors formed at the preparative stage. Thus, CA at pH = 4 – 5.5 formed negatively charged precursor species, which were strongly attracted by the positively charged support via strong electrostatic absorption. Moreover, the preparation pH contributed to the partial dissolution of the support's metallic ions to different extent, which altered the surface composition upon stepwise evaporation of the solvent. Calcination of these precursors led to finely distributed Ni species exposing strong MSI, the highest Ni surface fraction, Mg surface enrichment, and the smallest particle size among the series. These parameters correlated with their high and stable catalytic performance. By this approach, catalyst activity was improved by 20% during screening, while coke formation was decreased by 10% (these catalysts formed 5.8 wt.% C), compared to the CA-assisted catalyst without pH adjustment (6.4 wt.% C). The outstanding catalysts only lost 10% activity in 80 h TOS at T = 600 °C, while only forming 3.2 wt.% C.

Moreover, the outstanding chelating agents of Group III were TA and Gly, as they led to the finest Ni distribution, smallest particles and strongest MSI among the series after calcination and H₂-activation. The Gly- and TA-assisted catalysts showed ~ 20% improved catalytic activity and ~ 30% decreased coke formation compared to Ni/S2. Despite the improvements identified for the chelate-assisted catalysts (vs. bare Ni/S2), these inevitably deposited coke and displayed high degree of oxidation after catalytic testing, thus, these effects seemed to play a crucial role in catalyst deactivation over TOS.

Finally, the trimetallic catalysts NiLaGa/S2 and NiGdSc/S2 (Group IV) displayed ~ 20% improved performance compared to Ni/S2, while they were highly stable against deactivation during the long-term experiments and formed a very low amount of coke (i.e., 0.5 wt.% C over 25 h TOS, and 1.2 wt.% C over ~ 48 h TOS for NiLaGa and NiGdSc/S2). Thus, strong MSI, fine Ni distribution, and structural defects/oxygen vacancies were crucial for assisting CO₂ adsorption and promoting coke gasification. Further investigations revealed that NiLaGa/S2 formed intermetallic NiGa compounds, which seemed to protect the Ni⁰ sites against agglomeration and re-oxidation during operation, while promoting CO₂ activation via highly dispersed La sites and formation of La₂O₂CO₃. This approach was clearly the most efficient in improving DRM catalyst under the severe reaction conditions used.

Finally, the main characterization results of the outstanding catalysts of Groups II-IV are tabulated in Table 4-5, while their averaged CH_4 conversion at 600 °C, the amount of coke formed during tests and their approximated deactivation rate (calculated after each individual induction period) are summarized in Figure 4-26. Overall, it seems that high surface Mg content and high fraction of (small) Ni^0 sites strongly attached to the support via MSI were needed to achieve outstanding catalytic performance. However, such structure-activity relationships were not applicable to all outstanding catalysts of the different groups, which disclosed the complexity of the DRM, and the complicated dependences between specific physicochemical parameters and catalytic performance.

Table 4-5. Summary of main characterization results of selected catalysts of different groups supported on S2.

Sample name	BET ^a	H ₂ -TPR ^a		XPS ^b		Mg/Al ^c	TEM ^b
	S _{BET} (m ² /g)	Max. T _{red} (°C)	% unreduced Ni	BE Ni ⁰ 2p _{3/2} (eV)	Ni/(Mg+Al)		
Ni(CA-4)/S2	97	920	6.1	852.3	0.12	1.7	2 – 10
Ni(CA-5.5)/S2	91	940	4.5	852.3	0.11	1.7	2 – 10
Ni(TA)/S2	107	922	3.8	852.6	0.08	1.3	1 – 18
Ni(Gly)/S2	103	924	5.6	852.5	0.11	1.4	1.5 – 15
Ni(DTPA)/S2	113	904	0	852.5	0.17	1.4	1 – 17
NiLaGa/S2	45	863	- ^e	- ^d	- ^d	- ^d	5 – 7
NiGdSc/S2	59	874	- ^e	852.2	0.1	1.5	- ^d

^a: results correspond to the fresh catalysts. ^b: results correspond to the *ex situ* reduced catalysts at 700 °C for 1.5 h. ^c: atomic ratio. ^d: not measured. ^e: not given due to simultaneous reduction of Ga species (NiLaGa/S2) and/or formation of Ni^{n+} ($n > 2$).

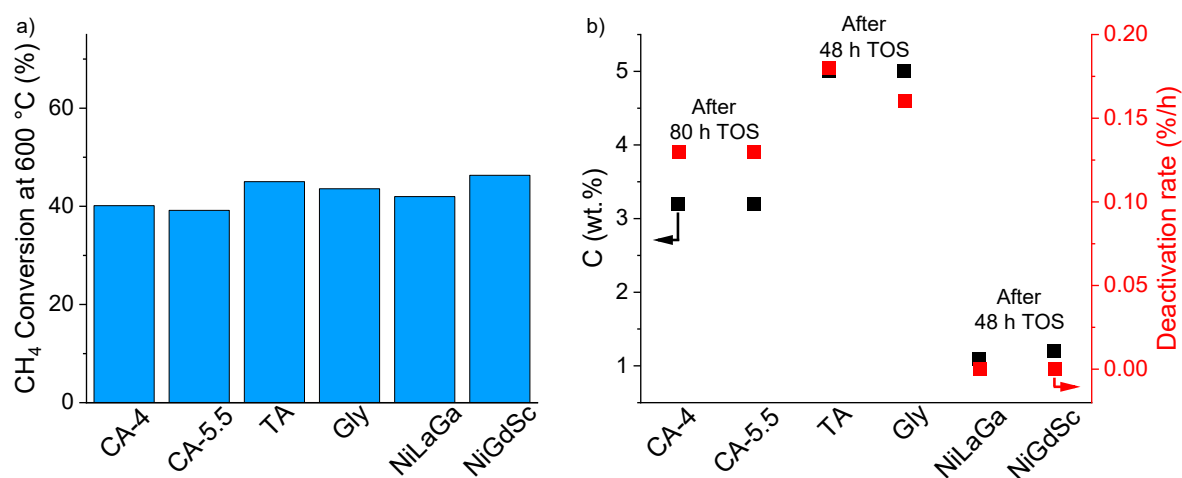


Figure 4-26. a) averaged X_{CH_4} at $T = 600$ °C and b) coke deposited after long-term tests and deactivation rate (calculated after each induction period) of outstanding catalysts of Group II-IV. Reaction conditions: $T_{\text{red}} = 750$ °C for 1.5 h, $\text{CH}_4/\text{CO}_2/\text{N}_2 = 45:45:10$ vol.%, $T = 600$ °C, $p = 1$ bar, $m_{\text{cat}} = 50$ mg, $\text{GHSV} = 170$ L/(g_{cat}·h). Note: the run time of each long-term experiments is indicated in b), and coke quantification was performed after tests.

4.2 Influence of the MgO-Al₂O₃ support on the catalysts' reforming activity and stability

4.2.1 Introduction

As discussed in the previous chapter, Pural MG50 (S2; Mg/Al = 1.3) was identified as a suitable support for preparing low-loading 2.5 wt.% Ni DRM catalysts. The developed samples displayed overall high activity and stability over TOS under severe DRM reaction conditions, mostly due to strong MSI, fine distribution of active Ni species and high concentration of surface Ni⁰ sites. However, catalyst deactivation due to coke accumulation, particle sintering, and re-oxidation of the active sites affected most of the prepared catalysts during the stability tests. Therefore, the main objective of this chapter was to improve the support material used during the formulation of the catalysts, aiming to increase their reforming activity, while improving their resistance against deactivation simultaneously.

For the previous purpose, different preparation methods were used to prepare MgO-Al₂O₃ mixed oxides with the same composition as S2 (i.e., molar ratio Mg/Al = 1.3). Thus, a newly engineered support prepared by wet impregnation of commercial Pural MG63 (S3; molar ratio Mg/Al = 2.2) with Al(NO₃)₃·9H₂O and calcined at 800 °C for 6 h (nomenclated as WI.800) outstood among the series, as the catalysts supported on this new carrier material displayed tendentially higher activity and much lower coke deposition. Thorough characterization of the catalysts on WI.800 was performed to identify structure-activity relationships. The outperforming samples of this chapter were then used in the following chapter for the reforming of model biogas (CH₄/CO₂ = 2:1) in different reaction regimes (DRM, BRM, TRM), while the recovered catalysts after tests were characterized to identify the origin of catalyst deactivation.

4.2.2 Impacts of the developed MgO-Al₂O₃ supports on the catalytic performance

The supports developed in this section were prepared using several chemical methods, while targeting the same chemical composition than S2, as previously mentioned. The following methods were used: i) co-precipitation of Mg-Al nitrates at pH = 8.5 – 9.0 (CP), ii) the hydrothermal dissolution-precipitation (HT), iii) the hydrothermal dissolution-precipitation using urea for hydrolysis (UH) and iv) the wet impregnation of commercial Pural MG63 (S3) with Al(NO₃)₃·9H₂O calcined at 800 °C for 6 h under static air (WI.800). In connection to the latter, 800 °C for 6 h under static air was used for WI.800 to repeat the calcination protocol used after impregnating Ni species in previously developed catalysts throughout this work.

First, these different home-made supports were used for preparing CA-assisted catalysts at pH = 5.5 (following the preparation method discussed in section 3.1.2 for the benchmark supported on commercial S2) and screened using the standard DRM protocol used in the previous chapter. Please note that only the different supports are denoted in the x-axis in Figure 4-27 a-c, but the results displayed refer to the activity of the catalysts prepared using them and CA at pH = 5.5.

Thus, the averaged X_{CH₄}, X_{CO₂} and H₂/CO ratio at 600 °C and coke amount measured after screening experiments (25 h TOS) are displayed in Figure 4-27 a-b, respectively. As previously mentioned in section 2.1, the low temperature regime (600 °C) was used to compare the catalysts better, as this temperature promotes the simultaneous occurrence of the main coke forming reactions: exothermic Boudouard reaction (Eq. 8) and endothermic CH₄ decomposition (Eq. 9). See sections 2.1 and 2.3.1 for more details. Moreover, none of the supports developed could prevent the incidence of the RWGS reaction (Eq. 7), as the X_{CH₄} was lower than X_{CO₂}, the same as the molar ratio between H₂ and CO lower than unity (H₂/CO < 1) for all catalysts displayed in Figure 4-27.

Particularly, Ni(CA-5.5)/WI.800 displayed comparable catalytic activity to the benchmark Ni(CA-5.5)/S2, with averaged X_{CH₄} = 39.1% vs. 40.5%, X_{CO₂} = 54.8% vs. 55.4% and H₂/CO = 0.75 vs. 0.75 at T = 600 °C, respectively. However, the most interesting remark was the 3.5 times less coke formed after 25 h TOS for Ni(CA-5.5)/WI.800: 1.6 wt.% vs. 5.8 wt.% C for Ni(CA-5.5)/S2, respectively. The latter

was a great improvement considering that coke deposition is one of the biggest problems of DRM. Please note that the coke amount formed for the catalysts Ni(CA-5.5)/HT was not measured due to its lowest performance.

Furthermore, catalyst reproducibility was also evaluated by repeating the preparation and testing of Ni(CA-5.5)/WI.800 four consecutive and independent times (Figure 4-27 c). Thus, averaged $X_{CH_4} = 41.0\%$ and $X_{CO_2} = 55.1\%$ were obtained, which evidenced that this preparation method was highly reproducible.

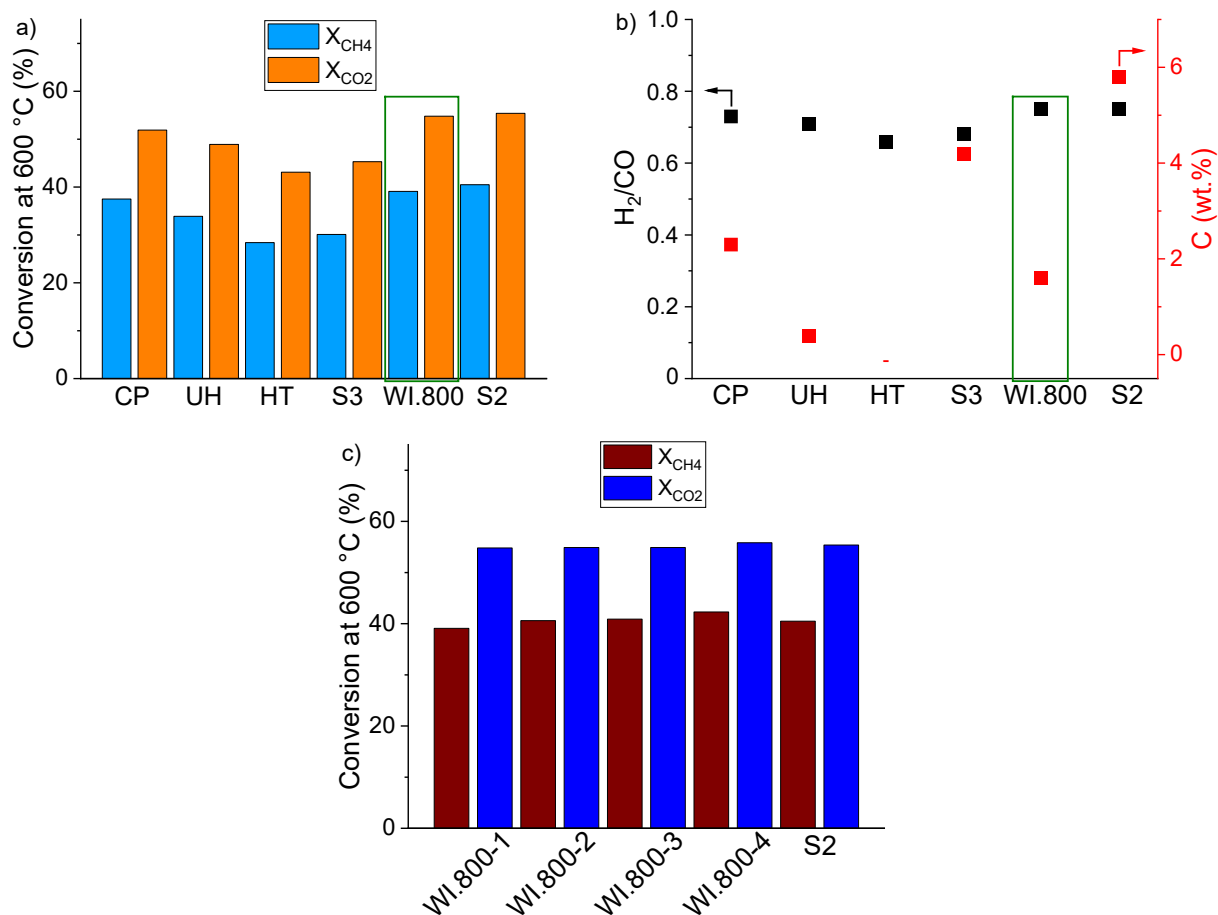


Figure 4-27. a) X_{CH_4} (blue bars) and X_{CO_2} (orange bars) and b) H_2/CO ratio at 600 °C and carbon deposited over screening tests (25 h TOS) with different CA-assisted Ni catalysts prepared at pH = 5.5 supported on commercial S2 and S3, and home-made materials. c) X_{CH_4} (brown bars) and X_{CO_2} (dark blue bars) at 600 °C during screening tests with the four independent batches of Ni(CA) prepared at pH = 5.5 on WI.800 and compared to its counterpart supported on S2. Reaction conditions: $T_{red} = 700$ °C for 1.5 h, $CH_4/CO_2/N_2 = 45:45:10$ vol.%, $p = 1$ bar, $T = 600 - 750$ °C, $m_{cat} = 50$ mg, GHSV = 170 L/(g_{cat}·h).

Afterwards, selected catalysts of Group II-IV (chapter 4.1) were prepared again, but using WI.800 as support material, to further investigate the impacts of the newly developed support. Thus, these catalysts were screened, and their averaged X_{CH_4} and X_{CO_2} at 600 °C are displayed in Figure 4-28. Evidently, the samples supported on WI.800 were tendentially more active than their counterparts on S2 (except for NiLaGa/WI.800), which revealed that not only the support's Mg composition played a role in the catalytic performance, but also the method of preparation chosen for the support.

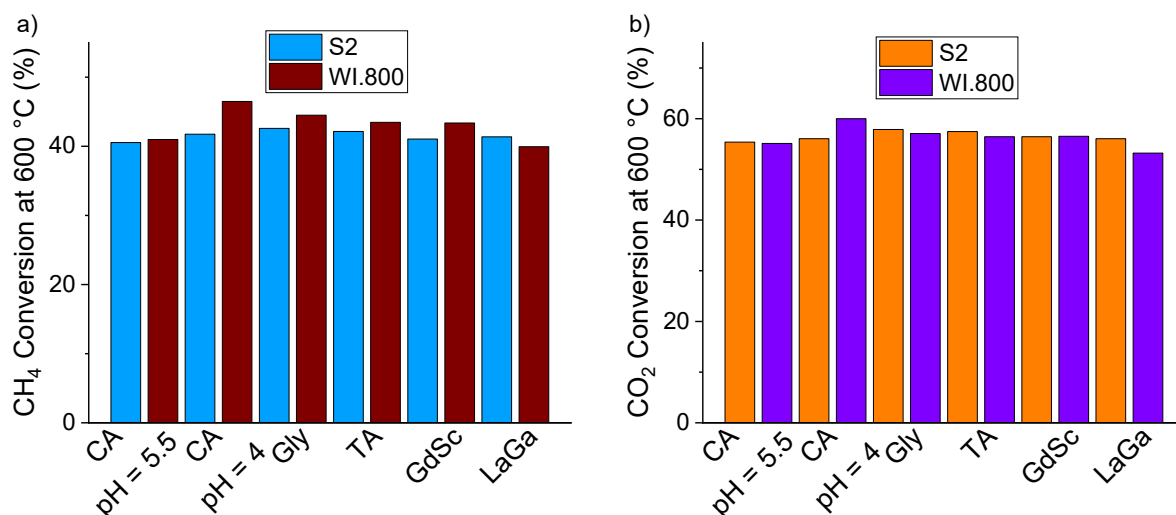


Figure 4-28. a) X_{CH_4} and b) X_{CO_2} measured at 600 °C during screening tests with selected catalysts supported on commercial S2 and home-made WI.800. Reaction conditions: $T_{red} = 700$ °C for 1.5 h, $CH_4/CO_2/N_2 = 45:45:10$ vol.%, $p = 1$ bar, $T = 600$ °C, $m_{cat} = 50$ mg, GHSV = 170 L/(g_{cat}·h).

As previously discussed in section 2.4.1, the physicochemical properties of the support depend on the chosen method of preparation to a great extent. For example, the elemental distribution (i.e., overall vs. surface chemical composition), surface area, structural phases and their crystallinity, the number of defects within its structure, among others, are mostly defined during the preparation [118]. It is then logic that supporting Ni species on solid matrices with unique properties leads to catalysts with different reforming performance and stability.

Therefore, and considering that the catalysts supported on WI.800 displayed improved activity and decreased coke formation, some specific features of the catalysts were benefited by using this new method of preparation. To make precise statements regarding the origin of these improvements, the developed catalysts were thoroughly characterized, and the results are discussed below.

4.2.3 Origin of the catalytic performance and decreased coke deposition

Intensive characterization of selected catalysts was performed to identify the reasons behind the improved catalytic performance and remarkably low coke deposition of the samples supported on WI.800 vs. their counterparts on S2. First, the CA-assisted catalysts prepared at pH = 5.5 were investigated, as it was used as the benchmark system. Then, the trimetallic NiGdSc/WI.800 and NiLaGa/WI.800 catalysts were investigated.

As a side note, the catalysts' nomenclature was slightly modified (from this chapter until the end of this work) to specify the temperature at which the sample was pre-reduced. For example, Ni(CA-5.5)/WI.800-R700 is the calcined catalyst prepared using CA at fixed pH = 5.5 over home-made support WI.800, followed by reduction at $T_{red} = 700$ °C for 1.5 h with pure H₂.

4.2.3.1 Composition, texture, and crystallinity of catalysts prepared with CA at pH = 5.5

First, the chemical composition of Ni(CA-5.5)/WI.800 matched the expected values for Ni (2.3 wt.% Ni) and Mg/Al (Mg/Al = 1.2), indicating that the chosen preparation method was successful (see Table 4-6). Regarding the textural properties (also see Table 4-6), the support material S2.800 displayed $\approx 25\%$ larger S_{BET} compared to WI.800, while their pore sizes and volumes were similar. Additionally, the porous structure of S2.800 was partially blocked upon impregnating Ni, as its S_{BET} decreased from 123 m²/g to 91 m²/g for Ni(CA-5.5)/S2. By contrast, the calcination of Ni-CA precursors led to improved distribution of Ni species and/or created new pores in Ni(CA-5.5)/WI.800, as its S_{BET} increased from 90 m²/g (WI.800) to 110 m²/g. However, as only slight differences in the catalysts' S_{BET} were found, while

these displayed comparable pore size and volume, the textural properties of these samples were arguably similar.

Table 4-6. Overall and surface chemical composition (ICP and XPS), textural properties (BET) and reducibility (H_2 -TPR) of selected CA-assisted Ni catalysts prepared at pH = 5.5 on commercial S2 and home-made WI.800.

Sample name	ICP		BET			H ₂ -TPR		XPS
	Ni content (wt.%)	Mg/Al ^a	S _{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	T. H ₂ (μmol/g) ^b	E. H ₂ (μmol/g) ^c	Mg/Al
S2	-	1.3	139	4.8	0.2	-	-	-
S2.800	-	1.3	123	4.7	0.2	-	-	-
WI.800	-	1.2	90	4.8	0.1	-	-	-
Ni(CA-5.5)/S2	2.6	1.3	91	3-10	0.3	443	423	1.7
Ni(CA-5.5)/WI.800	2.3	1.2	110	3-12	0.3	392	387	1.0

^a: molar ratio. ^b: theoretical H₂ consumption related to the measured ICP Ni content. ^c: measured H₂ consumption during the H₂-TPR experiments.

In terms of structure, both support materials S2.800 and WI.800 displayed reflexes ascribed to MgO and MgAl₂O₄ (Figure 4-29), which evidenced that the supports had comparable crystalline structure. However, WI.800 showed sharper reflexes, thus, this preparation method produced a more crystalline support material. However, no remarkable differences were observed upon supporting Ni species, as both catalysts Ni(CA-5.5)/WI.800 and Ni(CA-5.5)/S2 displayed similar diffractograms, being only the supports' phases found, with reflexes of comparable shape and intensity (Figure 4-29). The latter meant that the crystalline structure was comparable between these catalysts as well, and that no Ni-containing phases were observed. The reasons regarding the absence of Ni reflexes were already discussed in section 4.1.1.1.

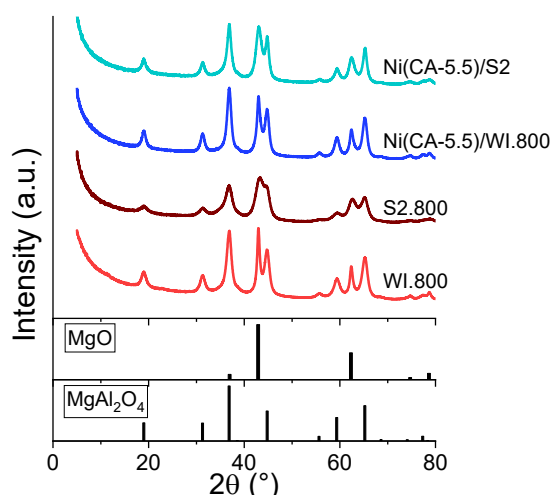


Figure 4-29. Diffractograms of calcined supports S2.800 and WI.800, and catalysts Ni(CA-5.5)/S2 and Ni(CA-5.5)/WI.800.

To this point, both catalysts displayed comparable chemical composition, textural and crystalline properties, which could help to explain their comparable catalytic activity to certain extent. However, the characterization techniques performed so far did not provide valuable information regarding the decreased coke deposition of Ni(CA-5.5)/WI.800 vs. the benchmark Ni(CA-5.5)/S2, thus, catalysts' characterization was deepened using additional techniques. These results are discussed below.

4.2.3.2 Reducibility and surface properties of catalysts prepared with CA at pH = 5.5

The interaction between the Ni species and the support, the same as the surface chemistry and electronic properties were investigated with H₂-TPR and XPS. First, the H₂-TPR profiles of the benchmark Ni(CA-5.5)/S2 and Ni(CA-5.5)/WI.800 clearly differed, which revealed that the support used modified the type of reducible Ni species formed (see Figure 4-30). Particularly, Ni(CA-5.5)/WI.800 displayed its main reduction peak at $T_{\text{red}} = 864$ °C, and a shoulder of appreciable intensity at higher temperature ($T_{\text{red}} \sim 960$ °C). Therefore, at least two types of reducible Ni²⁺ species displaying various MSI were present in this sample. By contrast, the benchmark Ni(CA-5.5)/S2 displayed a single broad reduction peak centered at $T_{\text{red}} = 940$ °C, suggesting that this sample only exposed one type of reducible Ni²⁺ species displaying stronger MSI compared to Ni(CA-5.5)/WI.800.

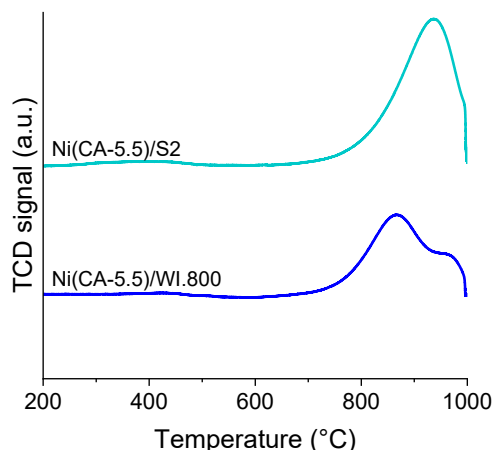


Figure 4-30. H₂-TPR profiles of the benchmark Ni(CA-5.5)/S2 and Ni(CA-5.5)/WI.800.

Regarding the hydrogen consumption, only 1.3% of the Ni species in Ni(CA-5.5)/WI.800 remained unreduced throughout the H₂-TPR experiments, which contrasted to 4.6% of unreducible Ni in Ni(CA-5.5)/S2 (see H₂ consumptions in Table 4-6). Therefore, H₂-TPR revealed that Ni(CA-5.5)/WI.800 was easier to reduce compared to the benchmark Ni(CA-5.5)/S2, which would be beneficial for the catalytic performance of Ni(CA-5.5)/WI.800 by forming more Ni⁰ active sites after reduction.

By next, the surface composition and electronic properties of the *ex situ* reduced Ni(CA-5.5)/S2-R700 and Ni(CA-5.5)/WI.800-R700 were investigated using XPS, and the recorded Ni 2p and Al 2p XP spectra are shown in Figure 4-31 a-b, respectively. Thus, both catalysts displayed peaks associated to Ni²⁺ and Ni⁰ 2p photoelectrons, suggesting the co-existence of oxidic and metallic Ni on their surfaces. For more details regarding the assignments of these Ni peaks, the reader is referred to section 4.1.2.1. Interestingly, the Ni 2p peaks of Ni(CA-5.5)/WI.800-R700 were recorded at lower BE compared to Ni(CA-5.5)/S2-R700, which revealed that surface Ni species of Ni(CA-5.5)/WI.800-R700 were easier to ionize. For example, Ni(CA-5.5)/WI.800-R700 displayed its Ni⁰ 2p_{3/2} peak centered at 851.4 eV, while Ni(CA-5.5)/S2-R700 displayed the same signal at 852.3 eV.

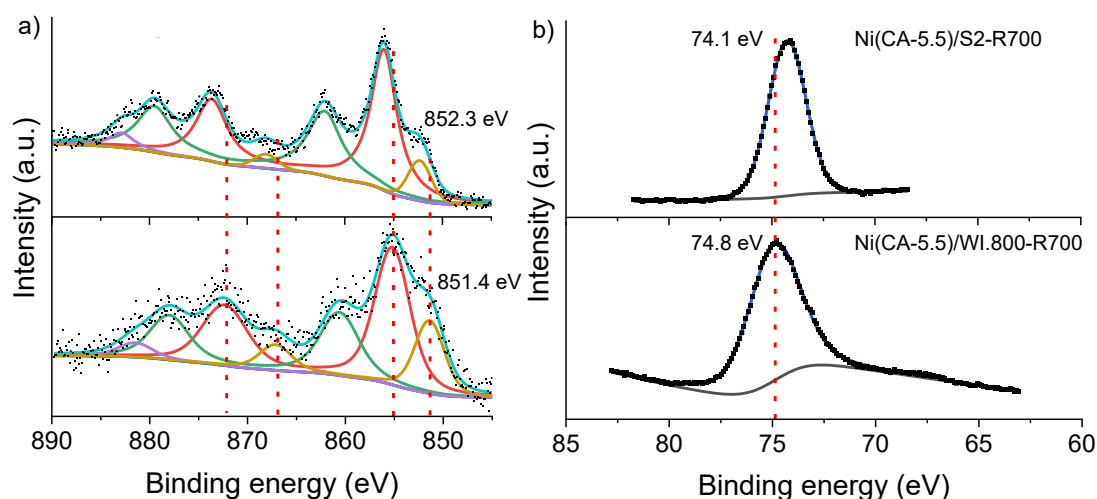


Figure 4-31. a) Ni 2p and b) Al 2p XPS spectra of the *ex situ* reduced Ni(CA-5.5)/S2-R700 (upper row) and Ni(CA-5.5)/WL800-R700 (lower row).

By contrast, the position of the Al 2p photoelectrons (Figure 4-31 b) followed the opposite trend compared to Ni 2p, as Ni(CA-5.5)/WL800-R700 displayed the Al 2p peak at higher BE (74.8 eV) compared to Ni(CA-5.5)/S2-R700 (74.1 eV). Thus, XPS analysis revealed that the Ni and Al species displayed different electronic properties at the surface of both samples, suggesting that the support material chosen also altered the stabilization of surface species, which correlated well with the observations derived from H₂-TPR characterization (see Figure 4-30). This discussion is deepened below.

It is argued that the energy required to ionize surface atoms (BE) relates to their electron density, and generally, changes in the atoms' electron density are reflected in the recorded BE [216]. For example, surface atoms rich in electrons are easier to ionize by X-rays, thus, the ionization of electron-rich species corresponds to lower BE. Contrarily, surface species deficient in electrons are harder to ionize by X-rays, therefore, higher energy is needed to ionize them [216]. Thus, the XPS spectra of Ni(CA-5.5)/WL800-R700 revealed that its surface Ni species displayed higher electron density (i.e., Ni signals recorded at lower BE), while the surface Al species were poorer in electrons (i.e., Al signals recorded at higher BE) compared to those in Ni(CA-5.5)/S2-R700. Therefore, surficial Al species most likely transferred electrons to the Ni sites in Ni(CA-5.5)/WL800-R700, which contributed to its improved reducibility (H₂-TPR profile displayed in Figure 4-30). Similar observations were done for a mixed oxide CaNiO_x + AlO_x catalyst, being both CaNiO_x and AlO_x prepared by sol-gel method, and then mechanically mixed [217]. The authors reported that the Ni⁰ 2p_{3/2} peak of CaNiO_x + AlO_x appeared at the lowest BE (centered at 851.5 eV), while the Al 2p peak was simultaneously shifted towards higher BE. The authors concluded that surface Al species transferred electrons to the Ni sites.

Additionally, the analysis of the surface chemical composition disclosed that both catalysts reduced at T_{red} = 700 °C for 1.5 h, Ni(CA-5.5)/S2-R700 and Ni(CA-5.5)/WL800-R700, displayed comparable normalized Ni⁰ content: Ni⁰/(Mg+Al) = 0.11. However, Ni(CA-5.5)/WL800-R700 displayed more Al at its surface compared to Ni(CA-5.5)/S2-R700: Mg/Al = 1.0 and Mg/Al = 1.7, respectively (see Table 4-6). Therefore, XPS revealed that the Ni⁰ active sites of Ni(CA-5.5)/S2-R700 and Ni(CA-5.5)/WL800-R700 displayed different chemical and electronic properties, which most likely impacted on the adsorption of the DRM reactants and the catalytic performance.

By considering the results of H₂-TPR and XPS, the two peaks identified in the H₂-TPR profile of Ni(CA-5.5)/WL800 (see Figure 4-30) were ascribed to the reduction of: i) surface Ni species interacting moderately with Al-rich surface domains of WL800 via electron transfer (at T_{red} = 864 °C), and ii) Ni species strongly stabilized by the Mg-rich regions of the WL800 support in NiO-MgO (at T_{red} = 960 °C). By contrast, the Ni species in Ni(CA-5.5)/S2 were stabilized throughout the Mg-rich support (overall Mg/Al = 1.3, surface Mg/Al = 1.7) in NiO-MgO solid solution in a 'more homogeneous way' as S2 was

not chemically modified before use, which led to a symmetrical H₂-TPR profile at very high reduction temperatures (maximum at $T_{\text{red}} = 940$ °C). This discussion also implied that the Al-rich surface of Ni(CA-5.5)/WI.800 weakened the interaction between Ni species and the support compared to Ni(CA-5.5)/S2, most likely by modifying the electron density of Ni and/or impeding the formation of strongly interacting NiO-MgO domains. The reader is referred to section 4.1.1.1 for more details regarding the nature of the strong NiO-MgO interaction.

Interestingly, the different MSI and surface properties of Ni(CA-5.5)/S2 and Ni(CA-5.5)/WI.800 did not play a crucial role in their catalytic activity under the conditions (and time) used during catalyst screening, as these samples performed similarly. However, Ni(CA-5.5)/S2 and Ni(CA-5.5)/WI.800 displayed different tendency to deposit coke, which could be (in part) ascribed to their different surface electronic/chemical properties and how these modify the adsorption of the DRM reactants. More work is needed to completely rule out this effect.

Based on literature, surface electron-rich Ni⁰ sites are reported to activate the antibonding orbital of C-H ($\sigma_{\text{C-H}}^*$) of CH₄ via electron transfer, and this step is considered as the rate-determining step of the DRM reaction [218]. This would explain, on the one hand, the high activity of Ni(CA-5.5)/WI.800, but not its anti-coking properties. On the other hand, the electron-poor surface Al domains (which donate electrons to Ni, as evidenced by XPS) close to electron rich Ni⁰ sites are reported to increase the adsorption strength of electron-rich oxygenated compounds on the surface, such as O, CO, CO₂, etc. [219]. Thus, these adsorbed oxygen-containing species contribute to the gasification of coke deposits. Consequently, high activity would be obtained at low coking rates.

4.2.3.3 Morphology and structure of catalysts prepared with CA at pH = 5.5

The morphology of the catalysts and distribution of the Ni particles were investigated using TEM-EDX. Thus, the *ex situ* reduced Ni(CA-5.5)/WI.800-R700 displayed some similar features to those of Ni(CA-5.5)/S2-R700, for example, the presence of Ni-containing particles of irregular shape throughout the support, exposing some degree of oxidation (see Figure 4-32). However, some differences between both catalysts were also identified. For example, the catalyst Ni(CA-5.5)/WI.800-R700 displayed larger Ni particles sized between 2 and 15 nm vs. 2 and 10 nm for Ni(CA-5.5)/S2-R700. The latter evidenced that Ni was poorly distributed throughout WI.800 and/or the high reduction/calcination temperature used provoked the agglomeration of weakly bound surface Ni sites (see H₂-TPR profile in Figure 4-30). Interestingly, these larger Ni particles in Ni(CA-5.5)/WI.800-R700 did not enhance coke formation.

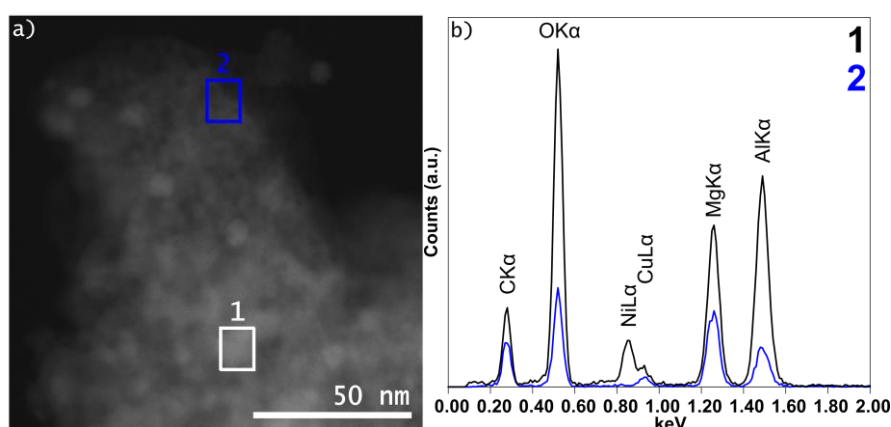


Figure 4-32. a) TEM micrograph and b) corresponding EDX spectra collected in the specified regions of a) (white square: spectrum 1; blue square: spectrum 2) of *ex situ* reduced Ni(CA-5.5)/WI.800-R700.

Besides, the Ni particles in Ni(CA-5.5)/WI.800-R700 were tendentiously supported on Al-rich regions of the support (see representative TEM micrograph and corresponding EDX spectra Figure 4-32 a-b, respectively), which differed to a more Mg-oriented distribution in Ni(CA-5.5)/S2-R700 (see Figure A

8). These observations suggested that some Al-rich domains on the surface of the WI.800 support acted as anchoring points for Ni^{2+} species during the preparation of Ni(CA-5.5)/WI.800-R700.

Additionally, the *ex situ* reduced catalyst Ni(CA-5.5)/WI.800-R700 displayed comparatively more metallic Ni^0 sites than Ni(CA-5.5)/S2-R700, suggesting that the former catalyst was easier to reduce. Thus, it seems that not only the moderate interaction between Ni and Al improved the reducibility of Ni(CA-5.5)/WI.800, but also the presence of larger Ni particles (> 10 nm), which most likely required lower temperature for reduction.

Finally, Ni(CA-5.5)/S2 and Ni(CA-5.5)/WI.800 were studied using EPR to get insights regarding the catalysts' structure and chemical species formed after different sample pre-treatments. As a side note, the EPR spectra of the *ex situ* reduced catalysts at 700 °C for 1.5 h, Ni(CA-5.5)/S2-R700 and Ni(CA-5.5)/WI.800-R700, were also measured, but they did not provide useful information, as the co-existence of many Ni^+-Ni^0 species provoked intense ferromagnetic interaction with the sample's unpaired electrons, and consequently, the EPR spectra in the region of interest was strongly distorted.

First, and independently on the pretreatment used, the EPR spectra of the studied catalysts displayed a signal at $g_1 = 2.002$ (see Figure 4-33), which was ascribed to oxygen vacancies [220, 221]. Interestingly, Ni(CA-5.5)/WI.800 displayed a more intense signal of oxygen vacancies even before reduction vs. Ni(CA-5.5)/S2 (see inset in Figure 4-33), which evidenced that using WI.800 as support led to a catalyst structure with more defects. The origin of the higher concentration of oxygen vacancies in Ni(CA-5.5)/WI.800 was most likely related to some or combination of the following factors: i) a higher calcination temperature used to prepare the support compared to Ni(CA-5.5)/S2 (i.e., WI.800 was calcined at 800 °C for 6 h vs. 550 °C for 6 h for S2), ii) the interaction between Ni and Al species and/or iii) to the mismatching atom radius between Ni and Al [219, 221-223].

Moreover, after *in situ* reduction at 300 °C, the intensity of the EPR signal at $g_1 = 2.002$ increased for both catalysts, indicating that more oxygen vacancies were formed after reduction (see spectrum B and D in Figure 4-33, respectively; see also the inset in Figure 4-33 for better comparison). However, this increase was more pronounced for Ni(CA-5.5)/WI.800, thus, it exposed more defects throughout its structure after heating and reductive treatment, too. The further increase in the intensity of the signal of oxygen vacancies after reduction is explained by oxygen loss and structural rearrangements provoked by partial reduction of oxidic Ni^{2+} species, which formed more defects and ionic vacancies in the catalysts' structure [224]. Thus, as the catalyst Ni(CA-5.5)/WI.800 displayed improved reducibility compared to Ni(CA-5.5)/S2 (previously identified by H_2 -TPR and XPS, see section 4.2.3.2), more oxygen loss and/or structural rearrangements occurred in the former upon reduction. Thus, one of the reasons for the superior coke resistance of Ni(CA-5.5)/WI.800 compared to Ni(CA-5.5)/S2 was related to an improved adsorption of oxygenated compounds during DRM due to the presence of more defects in its structure (see Figure 4-27). This discussion is deepened below.

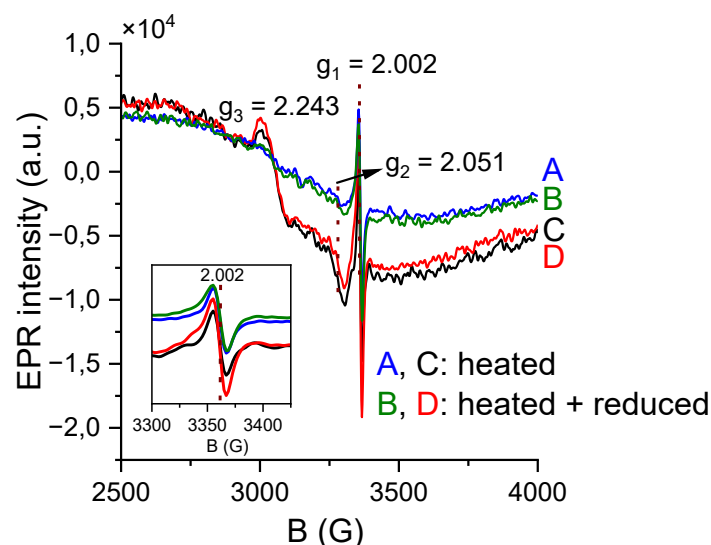


Figure 4-33. EPR spectra collected at $-173\text{ }^{\circ}\text{C}$ of Ni(CA-5.5)/S2 (spectra A and B) and Ni(CA-5.5)/WI.800 (spectra C and D) after different treatments. Spectra A and C: pre-heating the samples from RT in Ar to $300\text{ }^{\circ}\text{C}$ for 30 min, followed by cooling down to $-173\text{ }^{\circ}\text{C}$ under Ar. Spectra B and D: after pre-heating the samples in Ar to $300\text{ }^{\circ}\text{C}$, these were reduced with H_2 at same temperature for 30 min, followed by cooling down to $-173\text{ }^{\circ}\text{C}$ under H_2 . Inset magnifies the region between $3300\text{ G} < B < 3450\text{ G}$ for better comparison.

Besides, the catalyst Ni(CA-5.5)/WI.800 displayed signals of Ni^+ ($g_2 = 2.051$ and $g_3 = 2.243$ [225]) even before reduction, the intensity of which increased after reductive treatment (spectra C and D in Figure 4-33, respectively). By contrast, only a low intensity signal at $g_2 = 2.051$ was observed for Ni(CA-5.5)/S2 after *in situ* reduction (spectrum B in Figure 4-33), indicating that this sample was difficult to reduce. Thus, much more Ni^+ species were present in Ni(CA-5.5)/WI.800, especially after reduction, which indicated that this catalyst was easier to reduce compared to Ni(CA-5.5)/S2. Thus, the EPR results correlated well with the improved reducibility (H_2 -TPR and XPS, see section 4.2.3.2) and more reduced Ni^0 sites observed through and TEM-EDX (see Figure 4-32).

Thus, after intensive catalyst characterization, two main effects were identified depending on the support preparation method used for Ni(CA-5.5)/S2 and Ni(CA-5.5)/WI.800, which are most likely interrelated: i) modification of the catalysts' chemical and electronic surface properties, and ii) the formation of defects (oxygen vacancies) in the catalysts' structure. Thus, it seems that these parameters improved the coke gasification properties of Ni(CA-5.5)/WI.800 over Ni(CA-5.5)/S2, most likely by fostering the adsorption of oxygenated compounds during DRM. However, more work is needed to completely rule out to which extent each of these effects impacts on the catalysts' activity, stability, and coke deposition.

Based on literature [220, 226, 227], catalytic systems with defects in their structures are generally desired in DRM to accelerate the activation of CO_2 and remove coke deposits via the inverse of the Boudouard reaction (Eq. 8). For example, incomplete reduction of low Ni loading NiAl_2O_4 ($< 5\text{ wt.}\%$) was reported to form surface Ni^0 sites supported on defective $\text{Ni}_x\text{Al}_1\text{O}_{2-\delta}$ structures [220]. Thus, removing Ni^{2+} from the aluminate phase by reduction led to defective $\text{Ni}_x\text{Al}_1\text{O}_{2-\delta}$ species displaying oxygen vacancies, which promoted the adsorption of oxygenated compounds (CO_2 and/or H_2O) and improved coke gasification. Besides, the number of oxygen vacancies and unsaturated surface Al species increased upon appropriate pretreatment of the support Al_2O_3 , for example, by changing the pH of the media [221]. The latter species were found to anchor the Ni precursors during catalysts' preparation, forming defective NiAlO_x , while avoiding the formation of hardly reducible NiAl_2O_4 . On the other hand, the oxygen vacancies enhanced the adsorption of CO_2 , which increased the activity and accelerated carbon elimination simultaneously. Consequently, a highly active and stable catalyst for 100 h TOS for stoichiometric DRM was developed, which also formed low amount of coke. Obviously, the later discussion correlated well with the findings done for the Ni(CA-5.5)/WI.800 system.

4.2.3.4 Composition, texture, structure, and morphology of promoted catalysts

As already displayed in Figure 4-28, other catalysts supported on WI.800 were screened, and these were subsequently characterized. Particularly, the *ex situ* reduced NiLaGa/WI.800-R700 and -R800 were thoroughly studied, as they outperformed other catalysts in different reaction regimes ($\text{CH}_4/\text{CO}_2 = 2:1$, addition of H_2O and/or O_2 for BRM and TRM, respectively, etc.), especially after $T_{\text{red}} = 800^\circ\text{C}$. The results obtained in different reaction regimes are discussed in the following chapter. However, the following sections address aspects regarding catalyst characterization, while the catalytic activity and stability, the same as the characterization of spent NiLaGa/WI.800-R800 after use in different reaction regimes are discussed in the following chapter.

Regarding ICP, the trimetallic catalysts (NiLaGa/WI.800 or NiGdSc/WI.800) displayed chemical compositions ranging between 1.8 and 2.1 wt.% Ni (vs. 2.5 wt.% target Ni content) and molar ratios $\text{Mg}/\text{Al} = 1.1$ (target $\text{Mg}/\text{Al} = 1.3$) (Table 4-7). These contents were lower than expected but agreed well with those measured for their counterparts on S2 (see also Table 4-7).

The trimetallic catalysts NiLaGa/WI.800 and NiGdSc/WI.800 displayed S_{BET} around 3 and 18% lower than their support WI.800, possibly due to the blockage of the porous structure with impregnating metals. However, these were remarkably larger than the S_{BET} measured for NiLaGa/S2 and NiGdSc/S2, suggesting that different structural transformations occurred during preparation [228], which ultimately depended on the method of preparation used for the support. Furthermore, the pore size and volume of NiLaGa/WI.800 and NiGdSc/WI.800 were the largest compared to WI.800 and to the catalysts supported on S2.

Table 4-7. Chemical composition (ICP), textural properties (BET) and reducibility (H_2 -TPR) of the trimetallic catalysts supported on commercial S2 and home-made WI.800.

Sample name	ICP			BET			H ₂ -TPR	
	Content (wt.%)	Mg/Al	Metal ratio ^a	S_{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	T. H ₂ (μmol/g) ^b	E. H ₂ (μmol/g) ^c
WI.800	-	1.2	-	90	4.8	0.1	-	-
NiLaGa/S2	2.1 Ni, 2.0 La, 0.6 Ga	1.3	1.7	45	2-8	0.1	360	556
NiLaGa/WI.800	2.0 Ni, 1.9 La, 0.6 Ga	1.1	1.6	87	5-30	0.3	343	552
NiGdSc/S2	1.7 Ni, 2.0 Gd, 0.5 Sc	1.2	1.1	59	3-12	0.2	291	390
NiGdSc/WI.800	1.8 Ni, 2.0 Gd, 0.5 Sc	1.1	1.1	73	2-30	0.2	309	409

^a: ICP molar ratio of La/Ga or Gd/Sc. ^b: theoretical H₂ consumption related to the measured ICP Ni content. ^c: measured H₂ consumption during the H₂-TPR experiments.

The crystalline structures of the *ex situ* reduced NiLaGa/WI.800-R700 and -R800 were studied using XRD and compared to that of the *ex situ* reduced NiLaGa/S2-R700 (see Figure 4-34). At first, and independently of the support material and reduction temperature used, both catalytic systems displayed MgO and MgAl₂O₄ as the main crystallographic phases. Increasing the reduction temperature neither modified the crystallinity of the previously mentioned phases, nor formed new ones. Besides, a reflection of low intensity was observed at $2\theta \sim 51.4^\circ$ (denoted as ‘♦’ in Figure 4-34. Reference Ni⁰ (200) diffraction plane centered at $2\theta = 51.9^\circ$) for all reduced catalysts, which was ascribed to Ni⁰ with some degree of Ga incorporation, most likely forming NiGa intermetallic compounds/alloys. The previous observation was already done for NiLaGa/S2-R700 (see Figure 4-21 a), which was a common feature between these samples. Moreover, increasing the reduction temperature to 800°C (NiLaGa/WI.800-R800) increased the intensity of such reflection and shifted it slightly to $2\theta = 51.3^\circ$. The latter suggested that, on the one hand, more Ni⁰ sites were formed and/or the Ni⁰ lattice was more crystalline, and on the other hand, the Ni⁰ lattice was slightly expanded, possibly by more Ga

incorporation. Another difference of the catalysts on WI.800 were the subtle reflections of La_2O_3 (denoted as '▼' in Figure 4-34, ICDD: 01-083-1344 hexagonal, main reflections centered at $2\theta = 26.1$, 29.1 and 46.1°), which were absent in NiLaGa/S2-R700. Thus, a comparatively poorer dispersion of the La species in NiLaGa/WI.800 catalysts can be suggested based on XRD data. The distribution of La species was further analyzed using TEM-EDX (see below).

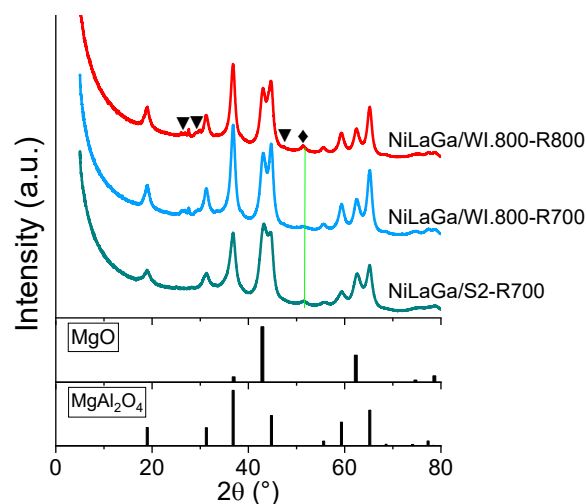


Figure 4-34. Diffractograms of *ex situ* reduced NiLaGa/S2-R700 and NiLaGa/WI.800-R700 and -R800. Legend: '◆': metallic Ni^0 (cubic, ICDD: 00-004-0850) and '▼': La_2O_3 (hexagonal, ICDD: 01-083-1344).

Further insights regarding the morphology and distribution of the active species of NiLaGa/WI.800-R700 and -R800 were collected through TEM-EDX. First, the *ex situ* reduced NiLaGa/S2-R700 (Figure 4-22) and NiLaGa/WI.800-R700 are compared. These two catalysts displayed some similar features, i.e., most of their Ni containing particles sized between 5 and 8 nm, which were mostly metallic with minimal surface oxidation. Besides, no Ga or La agglomeration was found in NiLaGa/WI.800-R700, being the Ga species mostly incorporated within the Ni particles (see micrograph and EDX spectra in Figure 4-35 a-b, respectively), while La was highly dispersed as single atoms both on the support and over the NiGa particles (see the small scattered brighter dots in Figure 4-35 c). However, some differences between the previous catalysts were also observed. Analogously to what was described for Ni(CA-5.5)/WI.800-R700 in section 4.2.3.3, some NiGa particles in NiLaGa/WI.800-R700 were deposited on surface Al-rich regions of the support or incorporate Al within them. The latter also pointed out to interaction of Ni and/or Ga species and surface Al of the WI.800 support (see spectra 1 and 2 in Figure 4-35 b). Contrarily, NiLaGa/S2-R700 displayed a more random NiGa distribution throughout its structure (see Figure 4-22 and Figure 4-25), which revealed that the composition of the NiGa sites and/or their chemical environment differed, which most likely impacted on the adsorption of the reactants during reaction.

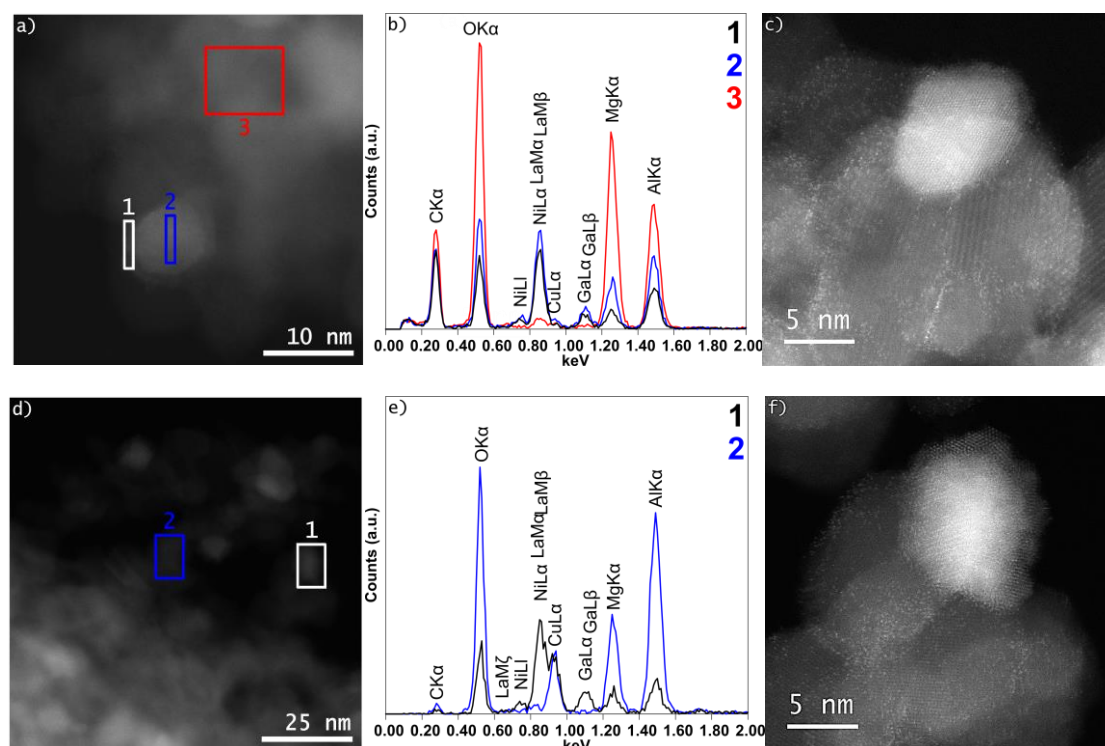


Figure 4-35. a) HAADF-TEM micrograph, b) corresponding EDX spectra collected in the denoted regions of a) and c) HAADF-STEM micrograph of *ex situ* reduced NiLaGa/WI.800-R700. d) HAADF-TEM micrograph, e) corresponding EDX spectra collected in the denoted regions of d) and f) HAADF-STEM micrograph of *ex situ* reduced NiLaGa/WI.800-R800.

Moreover, NiLaGa/WI.800-R800 displayed more Ni-containing particles of slightly larger size (7 – 10 nm) compared to NiLaGa/WI.800-R700, but these were mostly metallic and still constituted by Ni and Ga (see micrograph and EDX spectra in Figure 4-35 d-e, respectively). The slight particle size increase could be ascribed to thermal agglomeration at higher reduction temperatures. However, as the latter barely happened, it seemed that the NiGa particles were strongly attached to the support, which prevented agglomeration at higher reduction temperatures. Moreover, NiLaGa/WI.800-R800 also displayed some NiGa particles incorporating Al within them and/or interacting with the Al-rich domains of the WI.800 support (EDX spectra: see Figure 4-35 e). Thus, the different surface composition of WI.800 (vs. S2) most likely intervened in the stabilization of the NiGa particles, which was further investigated using H₂-TPR (discussed in the following section).

Besides, La was still observed as highly dispersed particles over the whole sample, which means that no La agglomeration occurred at higher reduction temperatures (see small bright dots scattered overall in Figure 4-35 f). Thus, La was accessible for the reactants after reduction at both temperatures, thus, improved CO₂ adsorption via La₂O₂CO₃ formation and coke gasification most likely occurred during reaction [38].

Thus, and although the trimetallic catalysts displayed comparable chemical composition on both supports, their textural and crystalline properties differed, which contributed to their different performance. Besides, the chemical environment of supported NiGa particles strongly depended on the support used. Deeper investigations regarding the interaction between the Ni active species and the support are discussed below.

4.2.3.5 Stabilization of Ni species: the role of the support on the MSI

The reducibility and MSI of selected catalysts was investigated using H₂-TPR, and the obtained profiles are displayed in Figure 4-36, while the H₂ consumptions are tabulated in Table 4-7. The H₂-TPR profile of Ni(CA-5.5)/S2, NiLaGa/S2 and NiGdSc/S2 were also included in Figure 4-36 for comparison.

Regarding the chelate-assisted catalysts (both supported on S2 and WI.800), these displayed reduction peaks only at very high temperatures $T_{\text{red}} > 750$ °C, thus, all reducible Ni species exposed very strong MSI (see Figure 4-36) [229]. Analogously to what was discussed for Ni(CA-5.5)/WI.800 in section 4.2.3.2, Ni(TA)/WI.800 also displayed a broad H₂-TPR profile constituted of two unresolved maxima centered at $T_{\text{red}} \sim 860$ and $T_{\text{red}} \sim 960$ °C. The latter was already attributed in Ni(CA-5.5)/WI.800 to the reduction of Ni species interacting moderately with Al surface domains (easier to reduce, $T_{\text{red}} \sim 860$ °C) and strongly interacting NiO-MgO (difficult to reduce, $T_{\text{red}} \sim 960$ °C). Thus, the H₂-TPR profile of Ni(TA)/WI.800 provided extra hints regarding the formation of at least two types of reducible Ni species on the developed WI.800 support.

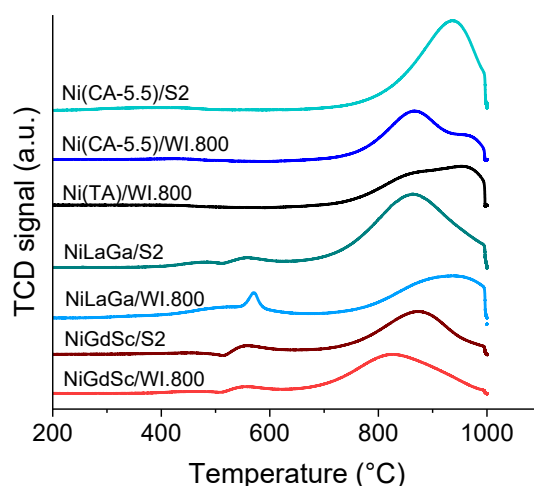


Figure 4-36. H₂-TPR profiles of selected catalysts supported on commercial S2 and home-made WI.800.

The MSI of the trimetallic catalysts supported on WI.800 was investigated and compared to their counterparts supported on S2. On the one hand, the catalyst NiGdSc/WI.800 displayed reduction peaks at $T_{\text{red}} = 550$ °C and 825 °C, while NiGdSc/S2 displayed these centered at $T_{\text{red}} = 555$ °C and 874 °C, respectively. Clearly, NiGdSc/WI.800 was reduced at lower temperature, thus, it was endowed with improved reducibility. Therefore, it seems that the Ni-support interaction was weakened by the co-impregnation of Gd and Sc on the WI.800 support (of different composition compared to S2), and/or by a poorer Ni distribution throughout the support (i.e., larger Ni particles), leading to more weakly bound Ni species easier to reduce.

On the other hand, NiLaGa/WI.800 displayed two unresolved reduction peaks between $400 < T_{\text{red}} < 600$ °C and a third one centered at high $T_{\text{red}} = 935$ °C (see section 4.1.4.1 for more details regarding specific reduction events). Thus, the combination NiLaGa required much higher temperature for reduction when using WI.800 as support (compared to NiLaGa/S2; maximum $T_{\text{red}} = 863$ °C), which clearly contrasted to what was previously discussed for NiGdSc/WI.800 and NiGdSc/S2. Thus, the co-impregnation of Ni + La + Ga on WI.800 led to very strong MSI, which was most likely due to the deposition of NiGa species on Al-rich domains of support and/or including Al within them (as discussed through TEM-EDX, see Figure 4-35). Another possible origin of the strong MSI could be the formation of thermally stable ternary systems of NiAlGa of different stoichiometry [230], which could occur under the conditions used during this work. Despite these NiAlGa species were not unequivocally identified with the characterization techniques used, they should not be completely disregarded.

Besides, both NiLaGa/WI.800 and NiGdSc/WI.800 catalysts also displayed higher H₂ consumptions than the highest possible theoretical value (see table Table 4-7), possibly due to the simultaneous reduction of Ni and Ga species in NiLaGa/WI.800, and/or formation of Niⁿ⁺ ($n > 2$) in both catalysts, which resembled the reduction behavior discussed for their counterparts supported on S2 (see section 4.1.4.1).

Therefore, the different chemical and electronic properties of the supports used (S2 vs. WI.800) determined the strength of the Ni-support interactions for the trimetallic catalysts (NiLaGa and NiGdSc) as well, which supported the discussion provided in section 4.2.3.3 for the Ni(CA-5.5) systems. Moreover, the stabilization of the Ni sites not only depended on the composition of the support's surface *per se*, but was influenced by the co-impregnated promoters, too. It could then be argued that the interaction between the promoters and the support played a role in the Ni-support interaction as well, but the exact mechanism of this phenomenon is still unclear. More work is needed in this regard.

Finally, the physicochemical properties of the promoted catalysts were correlated to their catalytic performance. Thus, the improved reducibility of NiGdSc/WI.800 (compared to NiGdSc/S2) most likely explained its superior catalytic activity (see Figure 4-28), as more active surface Ni⁰ sites formed after activation at T_{red} = 700 °C. Contrarily, NiLaGa/WI.800-R700 was less active than its counterpart NiLaGa/S2-R700 (see Figure 4-28), probably due to the formation of less active Ni⁰ sites after activation at T_{red} = 700 °C, which agreed well with the much stronger MSI of NiLaGa/WI.800 compared to NiLaGa/S2 (H₂-TPR). The impacts of the reduction temperature on the reforming catalytic performance using CH₄-rich feeds are further investigated in the following chapter.

The findings done for the trimetallic catalysts were compared to literature. The type of support used in the catalysts' formulation intervenes in the modifications imparted by the promoters chosen, including the MSI, the dispersion of Ni active sites and adsorption of reforming reactants, among others [139, 201, 230-234]. For example, adding 3 wt.% Gd in 10 wt.% Ni/Gd-Al₂O₃ [231] improved Ni reducibility (compared to Ni/Al₂O₃) due to the interaction between the Gd promoter and Al₂O₃, which prevented the formation of NiAl₂O₄. Consequently, the Gd-promoted catalyst displayed ~ 20% improved activity in DRM and ca. 3-times less coke after tests compared to the unpromoted Ni/Al₂O₃. On the contrary, adding Gd to a 2.5 wt.% Ni/Mg_{1.3}AlO_x DRM catalyst [78] strengthened the catalyst's MSI (compared to bare Ni/Mg_{1.3}AlO_x), which was ascribed to a finer Ni dispersion mediated by Gd. Then, agglomeration of the active Ni sites was prevented due to Gd promotion, which explained the exceptional activity and low coke deposition rates of Gd.Ni/Mg_{1.3}AlO_x over time on stream in the reforming of CH₄-rich model biogas.

On the other hand, a La-promoted 25 wt.% Ni/Al₂O₃ catalyst prepared by co-precipitation displayed strengthened MSI effect (vs. unpromoted 25 wt.% Ni/Al₂O₃) due to an improved dispersion of Ni species and a better stabilization of these Ni particles mediated by La promoter [233]. It was found that La promotion did not improve the activity compared to Ni/Al₂O₃, but the recovered catalyst after test displayed almost no Ni agglomeration and very low coke deposits. However, the previous report contrasted somehow to the findings discussed in [78], as La addition to 2.5 wt.% Ni/Mg_{1.3}AlO_x facilitated the reduction of Ni, probably due to improved oxygen mobility mediated by La promoter and/or to the formation of defective Ni oxidic species easier to reduce. Thus, La.Ni/Mg_{1.3}AlO_x displayed almost doubled catalytic activity compared to the unpromoted Ni/Mg_{1.3}AlO_x.

4.2.4 Intermediate conclusions

A newly engineered support material was developed, which outperformed the commercial support S2 (Mg-rich Pural MG50) identified as a promising candidate in chapter 4.1 of this work. Among different methods of preparation, the best option was Al-impregnated Pural MG63 (S3) calcined at 800 °C for 6 h (WI.800). Systematic catalyst preparation using the WI.800 as support and DRM testing evidenced that the catalysts supported on WI.800 were tendentiously more active than those supported on S2, while the amount of coke deposited was remarkably decreased. Based on the results of solid-state characterization, the MSI, the catalysts' surficial composition, and presence of oxygen vacancies were crucial to obtain high DRM catalytic activities under severe reaction conditions at very low coking rates.

Besides, the role of the Al-rich surface of WI.800 was discussed, and depending on the catalyst formulation, the support's high surface Al content determined the catalysts' MSI. For example, the

deposition of active NiGa particles on Al-rich surface domains and/or the incorporation of Al within the NiGa sites strengthened the MSI in NiLaGa/WI.800. Thus, it can be concluded that not only the bulk composition, structural defects and MSI are critical for improving the activity and minimizing the tendency for depositing coke in DRM catalysts, but also their chemical and electronic properties at their surface.

To sum up, the main characterization and catalytic results of Ni(CA-5.5)/S2, Ni(CA-5.5)/WI.800, NiLaGa/S2 and NiLaGa/WI.800 are summarized in Table 4-8 and Table 4-9, respectively, to identify correlations between structure and activity in DRM. Unfortunately, no clear structure-activity relationships were identified, which might relate to the significative influence of the support in the resulting physicochemical properties and DRM performance of the prepared catalysts. Another possible origin of this might relate to the multiple reaction steps involved in the formation of syngas through DRM and the dependence of the individual steps on the catalysts' physicochemical properties.

Table 4-8. Summary of main characterization results of the catalysts prepared with CA at pH = 5.5 and NiLaGa supported on S2 and WI.800.

Sample name	ICP	BET		H ₂ -TPR		XPS ^a		TEM ^a	
	Ni content (wt.%)	S _{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Max. T _{red} (°C)	% Ni unreduced	Ni/(Mg+Al)	Mg/Al	Part. Size (nm)
Ni(CA-5.5)/S2	2.6	91	3-10	0.3	940	4.6	0.11	1.7	2-10
Ni(CA-5.5)/WI.800	2.3	110	3-12	0.3	860	1.3	0.11	1.0	2-15
NiLaGa/S2	2.1	45	2-8	0.1	863	b	c	c	5-7
NiLaGa/WI.800	2.0	87	5-30	0.3	935	b	c	c	5-8

^a: measured after *ex situ* reduction at 700 °C for 1.5 h. ^b: not given due to co-reduction of Ni and Ga, and formation of Niⁿ⁺ (n > 2) species. ^c: not given due to overlapping of Ni 2p and La 3d signals in the region of interest.

Table 4-9. Averaged conversions of CH₄ and CO₂, and H₂/CO ratio collected at 600 °C during catalyst screening, and carbon quantified in the recovered spent catalysts (CHN) after screening.

Sample name	X _{CH4} (%)	X _{CO2} (%)	H ₂ /CO	C (wt.%) ^a
Ni(CA-5.5)/S2	40.6	55.4	0.75	5.8
Ni(CA-5.5)/WI.800	39.1	54.8	0.75	1.6
NiLaGa/S2	41.0	56.0	0.75	0.6
NiLaGa/WI.800	40.0	53.2	0.74	0.7

^a: measured after catalyst screening (25 h TOS). Reaction conditions: T_{red} = 700 °C for 1.5 h, CH₄/CO₂/N₂ = 45:45:10 vol.%, p = 1 bar, T = 600 – 750 °C, m_{cat} = 50 mg, GHSV = 170 L/(g_{cat}·h).

4.3 Process variants for reforming model biogas and development of regeneration strategies

4.3.1 Overview

The previous two chapters demonstrated that highly active and coke resistant DRM catalysts were developed by modifying 2.5 wt.% Ni catalysts supported on Mg-rich (molar ratio Mg/Al = 1.3) MgO-Al₂O₃ with chelating agents (CA at pH = 4 – 5.5, Gly or TA) or bimetallic addition (NiGdSc or NiLaGa). However, only stoichiometric (CH₄/CO₂ = 1:1) feeds were tested in DRM, and as already discussed in the introduction of this work, these DRM conditions might not be meaningful for reforming real biogas. Therefore, this chapter dives into the impacts of changing the reactions conditions, aiming to work under regimes closer to practical applications. Particularly, the effects of changing the GHSV in the catalytic performance were evaluated first using stoichiometric DRM feeds, followed by reforming CH₄-rich feeds (CH₄/CO₂ = 2:1) to mimic the composition of real biogas or landfill gas sources [235]. Then, CH₄-rich feeds were also valorized in BRM and TRM to produce syngas with H₂/CO > 1 ratio, in views of utilizing the obtained syngas in downstream processes (for example, methanol synthesis). Finally, reaction conditions even closer to real biogas were investigated, to test the resistance of selected catalysts against deactivation in CH₄-rich feeds with poisonous compounds (CH₄/CO₂ = 2:1 and NH₃ or H₂S at relevant levels), followed by developing feasible processes to regenerate deactivated samples and to prolong their lifespan. Finally, systematic characterization of selected spent samples was performed to disclose the origin of catalyst deactivation.

4.3.2 Impacts of the reaction conditions on the DRM catalyst activity and stability

4.3.2.1 Influence of GHSV variation in CH₄/CO₂ = 1:1

The impacts of changing the GHSV on the catalysts' conversion, stability and H₂ productivity were studied with selected catalysts. The different GHSV were adjusted by changing all volumetric gas flows, while the feed composition and catalyst load remained constant across the experiments. The catalyst Ni(CA-5.5)/WI.800 is discussed throughout this chapter to identify process improvements. The other chelate-assisted catalysts were not further investigated, as the trimetallic catalysts outperformed them in stoichiometric DRM, thus, NiLaGa/WI.800 and NiGdSc/WI.800 are intensively evaluated throughout this chapter.

Please note that the reduction temperature used in this section for studying the effects of the GHSV on the catalytic performance was higher compared to that used during catalyst screening, as the tests were performed at low temperature (600 °C). As previously discussed in section 4.1.2.2, a higher reduction degree of Ni is needed to perform the DRM reaction at low temperatures.

Thus, the catalysts Ni(CA-5.5)/WI.800-R750 and NiLaGa/WI.800-R750 were firstly tested in stoichiometric DRM (CH₄/CO₂ = 1:1) at 600 °C using various GHSV ranging between 42.5 and 190 L/(g_{cat}·h). Figure 4-37 a-c evidence that the catalysts displayed high and comparable activity at all GHSV evaluated. For example, the highest conversions and H₂/CO ratios were achieved at GHSV = 42.5 L/(g_{cat}·h), i.e., X_{CH₄} = 54.9%, X_{CO₂} = 68.4% and H₂/CO = 0.86 at 600 °C, which remarkably decreased to X_{CH₄} = 38.3%, X_{CO₂} = 51.0% and H₂/CO = 0.75 at GHSV = 190 L/(g_{cat}·h). The decrease in conversions was related to a shorter contact time between the Ni⁰ active sites and the reactant gases [236]. Besides, the X_{CO₂} was higher than X_{CH₄} at all GHSV tested, suggesting that the RWGS reaction (Eq. 7) took place and impacted on the selectivity of the reaction. Moreover, the H₂/CO ratio (or selectivity towards H₂) dropped at increasing GHSV (Figure 4-37 c), which evidenced that the rate of CO production was faster compared to that of H₂ [237]. Thus, it can be suggested that mass transfer limitations promoted undesired

side reactions at increasing flow rates, which favored CO production over H₂ at shorter contact times [238]. In addition to that, increasing the GHSV increased the reactor throughput, which might have impacted on local heat consumption throughout the catalyst bed during the reaction. Consequently, even slight temperature deviations at different points of the catalyst bed might have affected the reaction rates of product formation differently. However, no catalyst deactivation was recorded in these experiments, as the conversions of the reactants and H₂/CO were successfully restored by repeating the first set point at GHSV = 42.5 L/(g_{cat}·h). A precise kinetic analysis of the developed catalytic systems was outside the scope of this work.

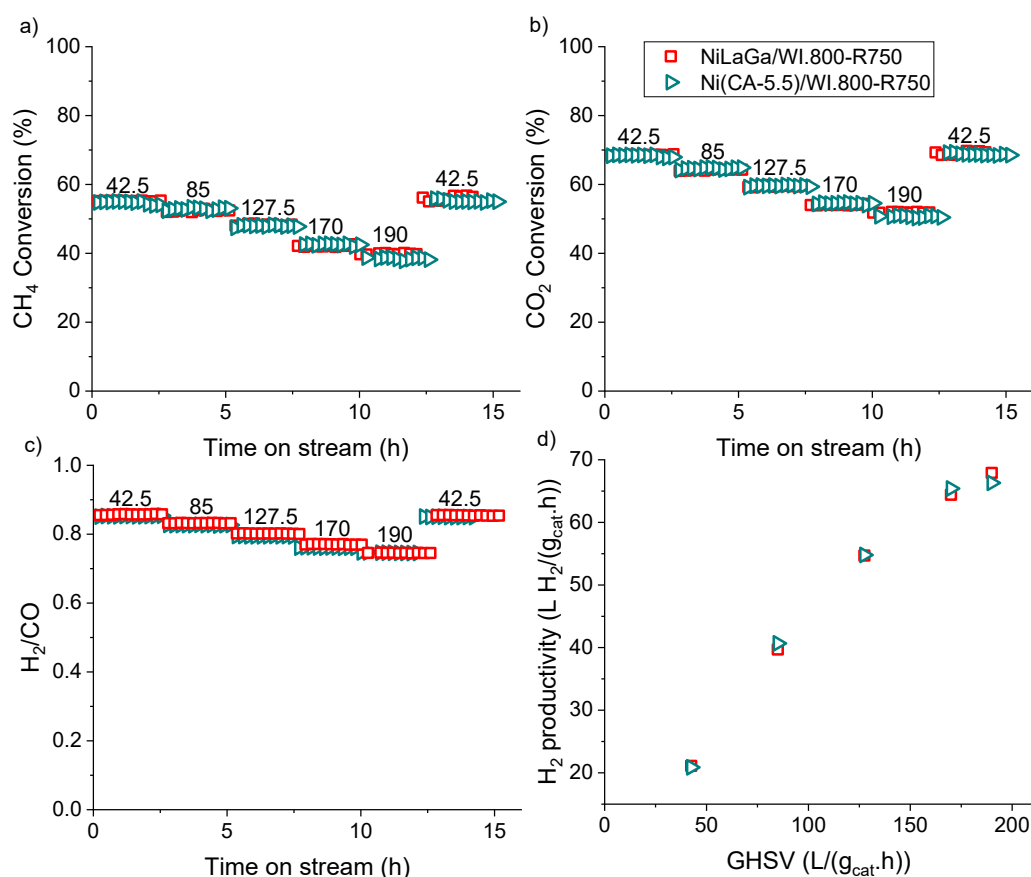


Figure 4-37. a) X_{CH_4} , b) X_{CO_2} and c) H_2/CO ratio with Ni(CA-5.5)/WI.800-R750 and NiLaGa/WI.800-R750 at different GHSV over TOS. The numbers on top of each data cluster indicate the GHSV applied. d) H_2 productivity calculated at different GHSV (based on averaged X_{CH_4}). Reaction conditions: $T_{red} = 750$ °C for 1.5 h, $CH_4/CO_2/N_2 = 45:45:10$ vol.%, $p = 1$ bar, $T = 600$ °C, $m_{cat} = 50$ mg.

Moreover, the H₂ productivity of NiLaGa/WI.800-R750 was calculated for each GHSV (see Figure 4-37 d). Thus, the latter parameter increased quite linearly with the GHSV up to 170 L/(g_{cat}·h), while increasing it further to GHSV = 190 L/(g_{cat}·h) did not lead to remarkable improvements due to mass transfer limitations respective availability of active sites. Consequently, GHSV = 170 L/(g_{cat}·h) was selected for continuing the catalytic testing under various reaction regimes, as it led to very high H₂ productivity at very short contact times.

Finally, the performance of NiLaGa/WI.800-R750 was compared with other catalysts from literature at comparable reaction conditions (see Table 4-10), demonstrating its competitive activity and very high H₂ productivity under heavy coke reaction regimes ($T = 600$ °C), only 10% feed dilution, low metal load (2.5 wt.% Ni) and very short contact times.

Table 4-10. Comparison of the activity of NiLaGa/WI.800-R750 with other state-of-the-art catalysts reported in literature under comparable reaction conditions (stoichiometric DRM: CH₄/CO₂ = 1:1).

Catalyst	Ni (wt.%)	m _{cat} (mg)	GHSV (L/(g _{cat} ·h))	T (°C)	X _{CH4} (%)	X _{CO2} (%)	H ₂ p. ^a (L H ₂ /(g _{cat} ·h))	TOS (h)	Ref
NiLaGa/WI.800-R750	2.1	50	42.5	600	55	70	21.0	3	*
			85		52	65	39.8	3	
			127.5		48	60	55.1	3	
			170		41	55	62.7	3	
			190		38	50	65.0	3	
Ni(CA)/S2	2.5	50	85	650	65	73	49.7	8	[1]
Ni_{0.05}Al₁O_{2-d}	4.5	50	36	650	65	75	7.0	100	[220]
Ni_{0.025}Al₁O_{2-d}	2.3	50	36	650	70	83	7.6	100	[220]
Ni/CeO₂-BN	0.5	120	25	600	25	n.a.	6.3	2	[239]
Ni/Ce_{0.95}Nd_{0.05}O₂	5.0	100	60	600	31	37	14.9	n.a.	[240]
				650	45	50	21.6		
1.5Ce-Ni5/MgAl₂O₄	5.0	200	60	600	57	70	13.7	24	[179]
5ZrO₂-Ni/γ-Al₂O₃	5.0	50	72	600	13	n.a.	9.4	100	[241]
Ni-Co/γ-Al₂O₃	6.0	300	12	650	68	70	8.2	72	[242]
Ni/Ce_{0.9}Eu_{0.1}O_{1.95}	3.0	40	60	600	21	34	12.8	12	[243]
NiMgGa-LDH	13.6	50	54	600	48	52	17.3	72	[51]
Ni@C/MC -750	5.4	200	18	600	55	58	5.0	25	[244]
Ni/SiO₂-0.7G	5.0	10	600	600	36	48	64.8	20	[245]

^a H₂ p.: H₂ productivity = (2 × X_{CH4} × F_{CH4})/g_{cat}; being: X_{CH4}: methane conversion, and F_{CH4}: volumetric methane flow rate. n.a.: not provided.

4.3.2.2 Dry reforming of model biogas: effect of CH₄/CO₂ = 2:1

As previously discussed in chapter 1 and 2, waste-derived biogases are attractive CH₄-sources for DRM. However, these are rich in CH₄ (CH₄/CO₂ = 2:1), which makes their valorization challenging using DRM, as catalyst deactivation due to coke deposition is accelerated in CH₄-rich conditions and hinders the proper implementation of this reaction.

Therefore, dry reforming of such CH₄-rich feeds was performed to investigate the applicability and robustness of the developed catalysts using constant GHSV = 170 L/(g_{cat}·h) during screening (at various temperatures T = 600 – 750 °C) and long-term experiments (at T = 750 °C).

First, Ni(CA-5.5)/WI.800-R700, NiGdSc/WI.800-R700 and NiLaGa/WI.800-R700 displayed similar catalytic performance during screening (see Figure 4-38). The X_{CH4}, X_{CO2} and H₂/CO decreased as the reaction temperature decreased due to the endothermicity of the DRM reaction, which was analogous to DRM using CH₄/CO₂ = 1:1. Besides, the X_{CH4} was much lower than that recorded during stoichiometric DRM at all temperatures (chapter 4.2), as the concentration in volume of CH₄ in the feed doubled that of CO₂. Consequently, the X_{CO2} was much higher than X_{CH4} across the experiment. Besides, the RWGS reaction (Eq. 7) also occurred during tests, which contributed to the high X_{CO2}. The latter was evidenced by the H₂/CO ratio < 1 across the experiment.

Despite the similar activity, the amount of coke deposited slightly differed between these samples following the order: NiLaGa/WI.800-R700 ~ NiGdSc/WI.800-R700 (0.8 wt.% C) < Ni(CA-5.5)/WI.800-R700 (1.2 wt.% C). Thus, low amounts of coke were quantified after 25 h TOS in CH₄/CO₂ = 2:1, which are to be highlighted, as CH₄-rich feeds (CH₄/CO₂ = 2:1 with only 10% of dilution) and very high GHSV = 170 L/(g_{cat}·h) were used. Thus, it was demonstrated that selected outperforming

catalysts for stoichiometric DRM condition were also efficient for reforming synthetic biogas ($\text{CH}_4/\text{CO}_2 = 2:1$) at very low coking rates and apparently no deactivation.

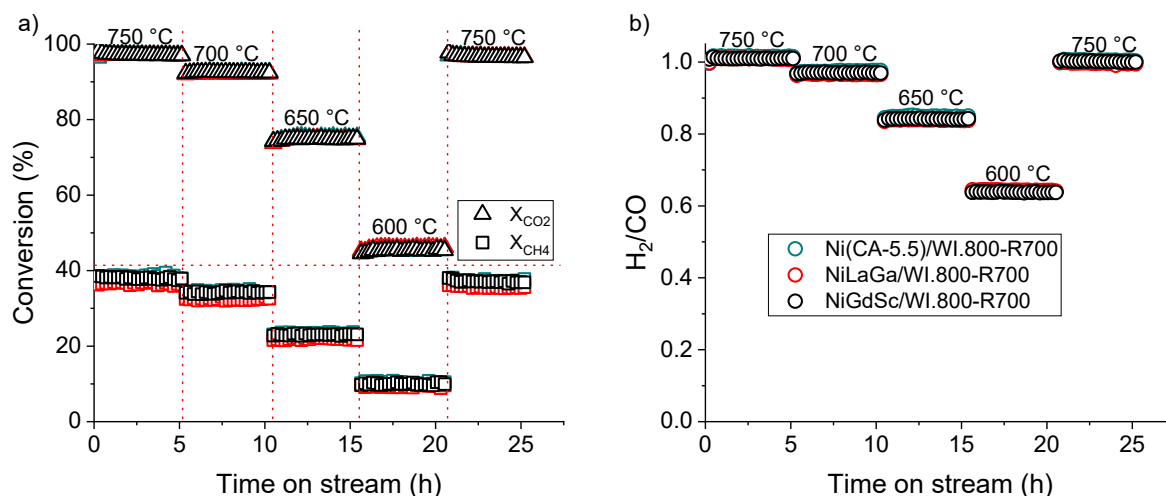


Figure 4-38. a) X_{CH_4} and X_{CO_2} , and b) H_2/CO ratio with selected catalysts over TOS. Reaction conditions: $T_{\text{red}} = 700$ °C for 1.5 h, $\text{CH}_4/\text{CO}_2/\text{N}_2 = 60:30:10$ vol.%, $p = 1$ bar, $T = 600$ °C, $m_{\text{cat}} = 50$ mg, GHSV = $170 \text{ L}/(\text{g}_{\text{cat}} \cdot \text{h})$. The numbers on top of each data cluster indicate the temperature at which the data was collected.

Besides, the long-term stability of the previous samples was evaluated at $T = 750$ °C and GHSV = $170 \text{ L}/(\text{g}_{\text{cat}} \cdot \text{h})$. These experiments also aimed to study the impacts of the reduction temperature ($T_{\text{red}} = 700$, 750 and 800 °C, respectively) on the catalysts' performance and long-term stability. Please note that the color code was changed in Figure 4-39 to facilitate the comparison between the different samples reduced at the same temperature (black: $T_{\text{red}} = 700$ °C; red: $T_{\text{red}} = 750$ °C; blue: $T_{\text{red}} = 800$ °C).

Thus, it was found that the catalytic activity and long-term stability of the previous samples differed (see Figure 4-39). Interestingly, the activity and stability of NiGdSc/WI.800 and Ni(CA-5.5)/WI.800 were basically independent of the reduction temperature used, while only the catalyst NiLaGa/WI.800 showed improved performance by increasing the reduction temperature up to $T_{\text{red}} = 800$ °C. Recalling the characterization of these samples discussed in chapter 4.2, it seemed logic that the catalysts which showed improved reducibility (NiGdSc/WI.800 and Ni(CA-5.5)/WI.800) also displayed high activity even upon reducing them at the lowest temperature. By contrast, the sample which displayed the strongest MSI (NiLaGa/WI.800) required higher reduction temperatures for proper activation. However, no further characterization of the former two samples was performed due to their worse stability over TOS at all reduction temperatures (vs. NiLaGa/WI.800, see Figure 4-39 below), and the impacts of the T_{red} were assessed on a catalytic basis.

Therefore, the comparison of these samples was done using the data for $T_{\text{red}} = 800$ °C. Thus, NiGdSc/WI.800-R800 and Ni(CA-5.5)/WI.800-R800 displayed initial $X_{\text{CH}_4} = 36.3\%$ and final $X_{\text{CH}_4} \approx 32.0\%$ (after 48 h TOS), and initial $X_{\text{CH}_4} = 35.2\%$ and final $X_{\text{CH}_4} = 33.0\%$ (after 55 h TOS), respectively. The latter evidenced that both catalysts displayed comparable performance, however, these deactivated quite fast under the severe CH_4 -rich reaction conditions, which contrasted with their robust performance in stoichiometric DRM, especially for the NiGdSc/S2 system (see chapter 4.1). By contrast, NiLaGa/WI.800-R800 displayed initial $X_{\text{CH}_4} = 36.5\%$ and final $X_{\text{CH}_4} = 33.0\%$ after 116 h TOS, which only represents 10% activity loss, but over more than double TOS vs. the former catalysts. The approximated deactivation rates of the previous samples were: $0.086 \text{ \%}/\text{h}$ (NiLaGa/WI.800-R800) $< 0.114 \text{ \%}/\text{h}$ (Ni(CA-5.5)/WI.800-R800) $< 0.200 \text{ \%}/\text{h}$ (NiGdSc/WI.800-R800). Remarkably, the NiLaGa system outperformed the series.

Besides, coke deposition after tests increased as the reduction temperature increased (see Table 4-11), which might be due to particle sintering at increasing T_{red} [180]. As previously discussed in section 2.3.1, larger Ni particles at higher temperatures tend to form weak MSI, and consequently, these deposit more coke. Focusing on the outperforming sample of this series, NiLaGa/WI.800-R800 only formed 3.2 wt.% C after 116 h TOS, evidencing its superior coke gasifying properties under severe reaction conditions.

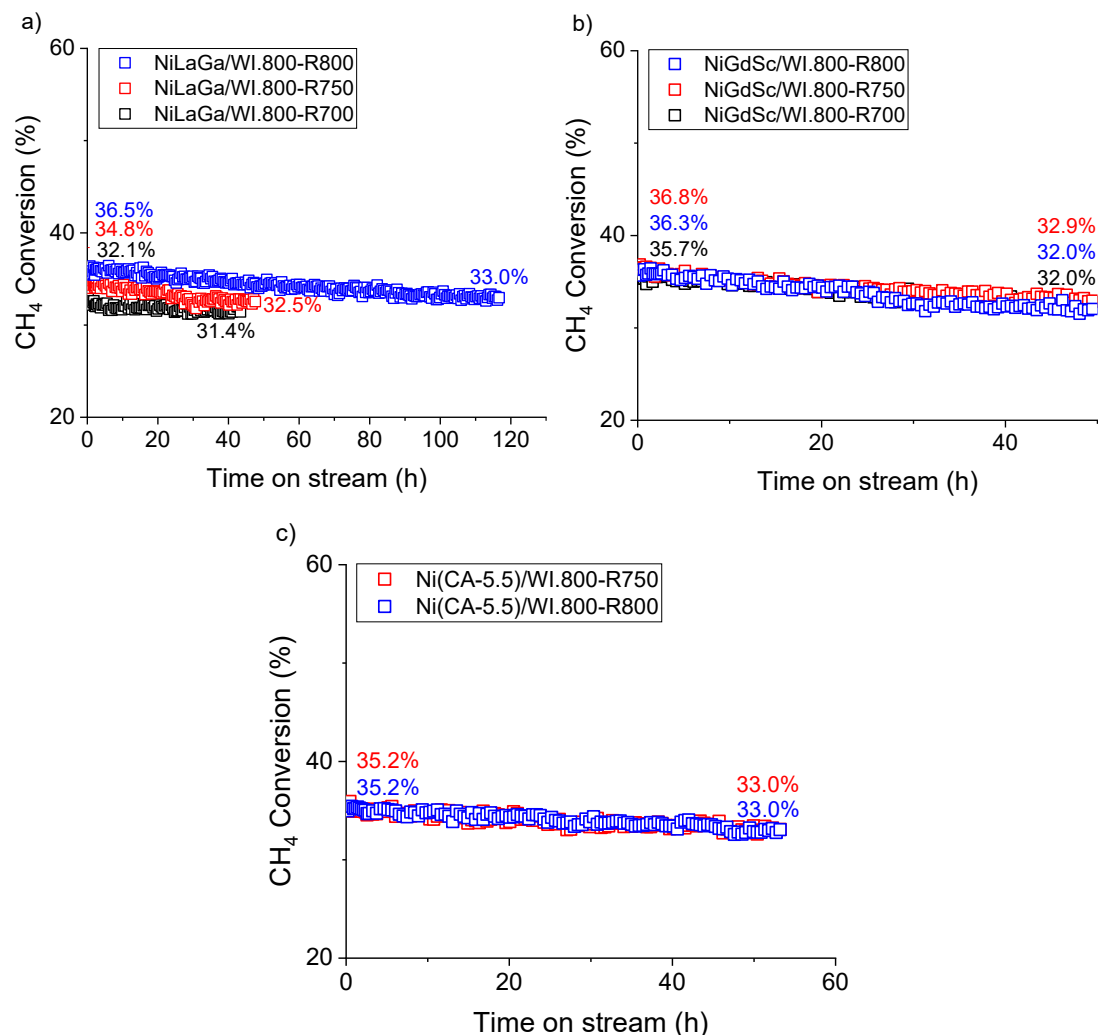


Figure 4-39. X_{CH_4} over TOS of selected samples reduced at different temperatures. a) NiLaGa/WI.800, b) NiGdSc/WI.800 and c) Ni(CA-5.5)/WI.800. Reaction conditions: $CH_4/CO_2/N_2 = 60:30:10$ vol.%, $p = 1$ bar, $T = 750$ °C, $m_{cat} = 50$ mg, GHSV = 170 L/(g_{cat}·h).

Table 4-11. Quantified carbon content in the recovered spent catalysts after long-term tests using different reduction temperatures ($T_{red} = 700$, 750 and 800 °C for 1.5 h, respectively). The numbers in brackets indicate the TOS.

Catalyst	$T_{red} = 700$ °C	$T_{red} = 750$ °C	$T_{red} = 800$ °C
Ni(CA-5.5)/WI.800	-	1.3 (55 h)	1.7 (55 h)
NiLaGa/WI.800	0.7 (42 h)	1.9 (48 h)	3.2 (116 h)
NiGdSc/WI.800	2.3 (48 h)	3.1 (48 h)	4.1 (48 h)

Therefore, the catalytic activity and stability of NiLaGa/WI.800-R800 were compared with the very few available reports which used reaction feeds equal or close to $CH_4/CO_2 = 2:1$ (see Table 4-12). Please note that the only report found (last entry) which evaluated the stability for longer times than those reported in this work used an extremely diluted reaction feed, which does not represent the composition of real biogas and is therefore meaningless. Thus, by comparison to other state-of-the-art catalysts, it

was demonstrated that NiLaGa/WI.800-R800 displayed highly competitive catalytic performance at very low coke deposition rates for the dry reforming of CH₄-rich model biogas.

Table 4-12. Comparison of the catalytic performance of NiLaGa/WI.800-R800 with other state-of-the-art catalysts previously reported in literature for dry reforming of synthetic biogas (CH₄/CO₂ = 2:1).

Catalyst	Ni (wt.%)	GHSV (L/(g _{cat} ·h))	Feed CH ₄ /CO ₂ / D ^a (vol.%)	t (h)	T (°C)	X _{CH₄} (%)	X _{CO₂} (%)	C ^b (wt.%)	Ds. ^c	R ^d
NiLaGa/ WI.800-R800	2.1	170	60:30:10 N ₂	116	750	35	86	3.2	10	*
NiLaZr pyrochlore	10	30	65:35:0	24	700	40	80	17	25	[246]
e _{0.5} Ni _{0.5} Al ₂ O ₃	5	36	10.7:5.9:8 3.3 Ar	13	700	45	90	4	0	[247]
NaNi/ZrO ₂	3	120	68:31:1 Ar	24	675	28	72	23	30	[248]
Ni7Ce/MgO	10	12	66.6:33.4	20	700	40	n.a.	n.a.	0	[58]
NiSrZrO ₃	4 mol.%	60	5:2.5:92.5 He	240	850	50	n.a.	10	0	[249]

^a: D: dilutant. Specified in the different reaction feeds used in the cited reports. ^b: C: amount of coke measured after the stability tests. ^c: Ds: percentage of deactivation calculated comparing initial steady state operation and final activity point measured. ^d: R: reference. *: information collected in this work. n.a.: not specified.

4.3.2.2.1 Origin of catalyst deactivation in CH₄/CO₂ = 2:1

The origin of catalyst deactivation was investigated through characterization of the spent NiLaGa/WI.800-R800 after 116 h TOS in CH₄/CO₂ = 2:1. Compared to the *ex situ* reduced NiLaGa/WI.800-R800, the spent catalyst displayed slightly larger NiGa particles mostly sized between 5 and 15 nm (vs. 7 – 10 nm for freshly reduced at same T_{red}), with very few of ca. 30 nm (see large bright dots in Figure 4-40). The only slight increase in particle size was related to the catalyst's strong MSI which prevented particle agglomeration, as discussed in chapter 4.2. Interestingly, most of the particles displayed metallic character after tests, which contrasted with the higher degree of oxidation in spent samples after long-term tests in CH₄/CO₂ = 1:1 at T = 600 °C (see chapter 4.1). Reasonably, a less-oxidizing reaction atmosphere in CH₄-rich conditions promoted less oxidation of the reduced active sites.

Coke formation was somehow difficult to avoid, which demonstrated the severity of reforming model biogas (CH₄/CO₂ = 2:1). Thus, the scattered larger Ni particles contributed to coke deposition, especially through CH₄ cracking (Eq. 9) in CH₄-rich conditions. Interestingly, La retained its high dispersion over the long-term run (see small bright dots scattered throughout Figure 4-40 b), which assisted in coke gasification by formation of La₂O₃CO₃, as discussed in section 2.2. Thus, gasification of carbonaceous structures mediated by La species competed with coke accumulation on larger Ni sites in CH₄-rich feeds. As a result, coke accumulated over TOS, but only 3.2 wt.% C were measured after reforming model biogas for ca. 120 h TOS, which is to be highlighted. In this sense, the observed carbonaceous structures were mostly CNTs, both with NiGa at their tips (non-deactivating type) and encapsulating NiGa particles within their structure (highlighted with black arrows in Figure 4-40 c). Consequently, the latter type blocked the NiGa sites for DRM, and consequently, the catalyst deactivated over time. Thus, catalyst deactivation in CH₄/CO₂ = 2:1 was more related to coke accumulation and particle sintering over TOS, rather than to re-oxidation of the active sites, which contrasted to stoichiometric DRM.

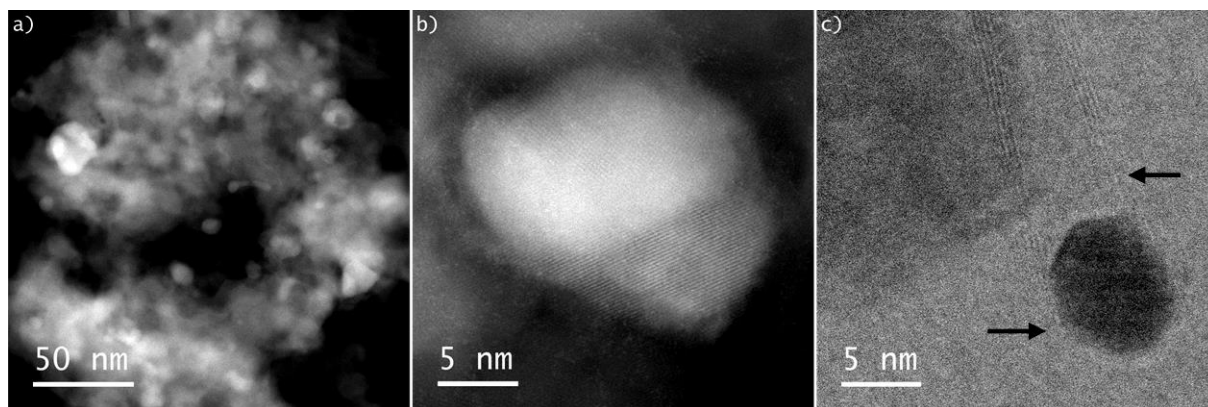


Figure 4-40. a) TEM-HAADF, b) STEM-HAADF and c) TEM-BF micrographs of spent NiLaGa/WI.800-R800 after 116 h TOS. Reaction conditions: $\text{CH}_4/\text{CO}_2/\text{N}_2 = 60:30:10$ vol.%, $p = 1$ bar, $T = 750$ °C, $m_{\text{cat}} = 50$ mg, GHSV = $170 \text{ L}/(\text{g}_{\text{cat}} \cdot \text{h})$. The black arrows in c) highlight a CNT detaching from the WI.800 support and encapsulating a NiGa particle.

4.3.3 Production of H_2 -rich ($\text{H}_2/\text{CO} > 1$) syngas using BRM and TRM

As previously discussed in chapter 1 and 2, the reforming reactions could be coupled with other downstream processes of industrial relevance depending on the resulting H_2/CO composition. To this point, only $\text{H}_2/\text{CO} < 1$ was achieved using DRM (both in $\text{CH}_4/\text{CO}_2 = 1:1$ and $2:1$), which would limit the applications of the obtained syngas. If the objective is to use the DRM-derived syngas in other downstream processes which require $\text{H}_2/\text{CO} > 1$, external H_2 should be added to increase the ratio accordingly. An alternative approach to increase the H_2/CO ratio without feeding external H_2 is to include O_2 and/or H_2O in appropriate concentrations in the feed for BRM and TRM, respectively, to tune the product syngas composition by means of process variants.

4.3.3.1 Bi-reforming of methane (BRM)

Firstly, benchmark Ni(CA-5.5)/WI.800-R700 and -R800 and NiLaGa/WI.800-R800 catalysts were investigated in BRM using the following feed composition: $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}/\text{N}_2 = 45:15:30:10$ vol.%. This gas feed was used to continue the study of the reforming of CH_4 -rich gas mixtures to mimic real biogas, and to increase the H_2/CO ratio by using less H_2O in the feed compared to SRM (i.e., generally > 40 vol% H_2O) [250]. Thus, Ni(CA-5.5)/WI.800-R700-1 (-1: first catalytic run) displayed high BRM activity at 750 °C ($X_{\text{CH}_4} = 83\%$, $X_{\text{CO}_2} = 86\%$, $X_{\text{H}_2\text{O}} = 83\%$ and $\text{H}_2/\text{CO} = 2.0$), but surprisingly, it completely deactivated in just 4 h TOS (Figure 4-41). The latter experiment was repeated to corroborate the previous catalytic behavior, and reproducible results were obtained a second time (indicated as Ni(CA-5.5)/WI.800-R700-2 in Figure 4-41). Due to the latter, it was firstly hypothesized that the fast deactivation was due to complete re-oxidation of the Ni^0 active sites by the high temperatures and the more oxidative reaction feed (i.e., $T = 750$ °C and 30 vol% $\text{H}_2\text{O} + 15$ vol% CO_2). By next, a higher reduction temperature ($T_{\text{red}} = 800$ °C) was set, aiming to stabilize better these Ni^0 sites to the support. Surprisingly, the catalytic activity of Ni(CA-5.5)/WI.800-R800 was similar to its counterpart reduced at $T_{\text{red}} = 700$ °C, but it dropped to zero even faster in just 30 min TOS. The latter indicated that, on the one hand, the activity was not enhanced by reducing this sample at higher temperatures, which correlated well with what was observed in the long-term stability test using $\text{CH}_4/\text{CO}_2 = 2:1$ (see Figure 4-39 c). On the other hand, including 30 vol% H_2O in the feed increased the severity of the reaction conditions remarkably, as this very fast deactivation over short TOS was unprecedented in DRM.

By contrast, the catalyst NiLaGa/WI.800-R800 displayed higher activity than the benchmark catalyst (for example, $X_{\text{CH}_4} = 86\%$, $X_{\text{CO}_2} = 87\%$, $X_{\text{H}_2\text{O}} = 82\%$ and $\text{H}_2/\text{CO} = 2.0$ at 750 °C) and stable performance over ca. 80 h TOS at $T = 750 - 850$ °C. Moreover, the X_{CH_4} , X_{CO_2} and $X_{\text{H}_2\text{O}}$ increased with the reaction temperature, which agreed well with the endothermicity of the BRM reaction [26], while the $\text{H}_2/\text{CO} \sim$

2 was constant at all studied temperatures. The latter evidenced that side reactions played a minor role during BRM under the conditions set, possibly due to the low amount of CO₂ in the feed (compared to CH₄) and the large volumes of H₂O, which could inhibit the RWGS reaction (Eq. 7) by shifting its equilibrium towards the reactants [251]. Regarding coke deposition, only 0.5 wt.% C was measured after ca. 80 h TOS under the previous reaction regime, highlighting the role of the catalyst's properties and feed composition (specially H₂O) in preventing coke deposition.

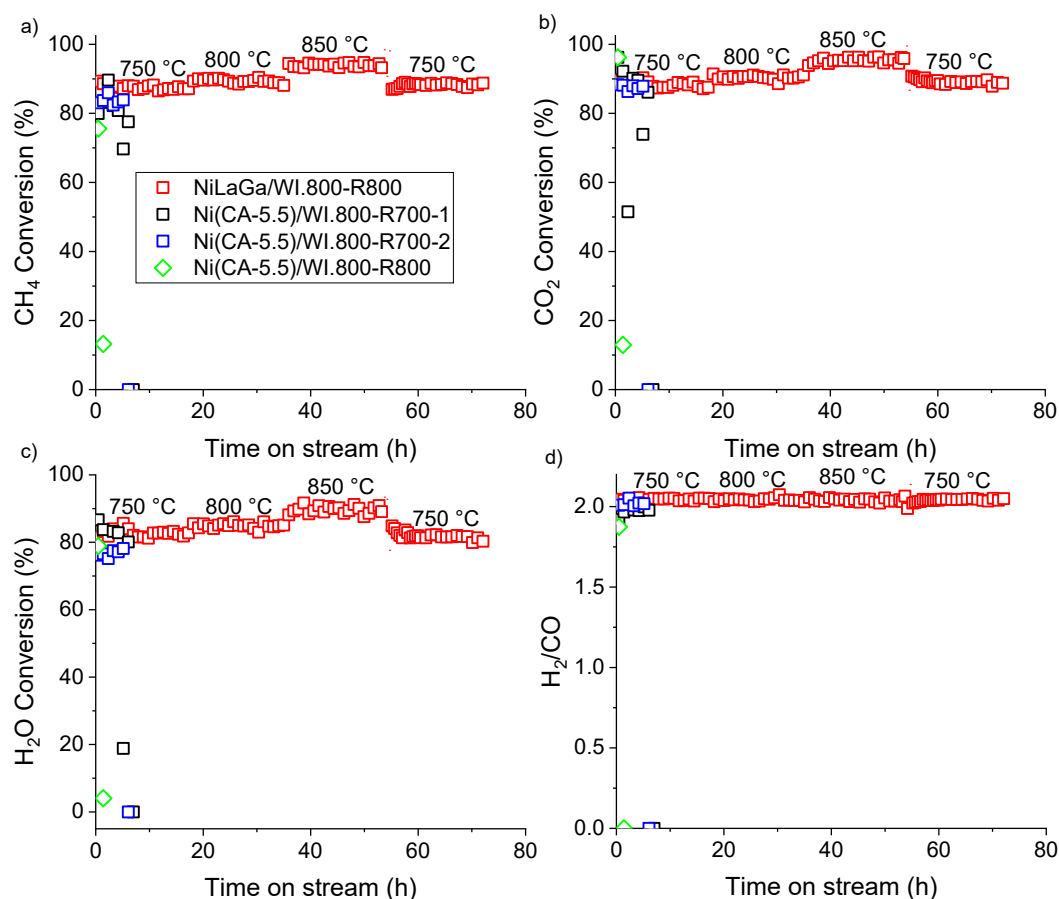


Figure 4-41. a) X_{CH_4} , b) X_{CO_2} c) X_{H_2O} and d) H_2/CO ratio of selected catalysts over TOS in BRM. Reaction conditions: CH₄/CO₂/H₂O/N₂ = 45:15:30:10 vol.%, p = 1 bar, T = 750 – 850 °C, m_{cat} = 50 mg, GHSV = 170 L/(g_{cat}·h). The numbers on top of each data cluster indicate the temperature (in the middle of the catalyst bed) at which the data was collected.

Therefore, and analogously to what was done for DRM of CH₄-rich mixtures, the BRM activity of NiLaGa/WI.800-R800 was compared with various catalytic systems developed in the past five years (see Table 4-13). Thus, NiLaGa/WI.800-R800 displayed high activity and stability for the bi-reforming of CH₄-rich feeds, especially considering its comparatively lower Ni loading, high GHSV and very low coke deposition rates (only 0.5 wt.% C). Besides, high-grade syngas ($H_2/CO = 2$) was obtained at various reaction temperatures, evidencing the application potential of the developed catalyst. Finally, X_{H_2O} was not included in the table, as water conversions by means of GC analysis have not been reported in BRM so far (to the best of my knowledge).

Table 4-13. Comparison of the catalytic performance of NiLaGa/WI.800-R800 with other state-of-the-art catalysts reported in literature in the past 5 years for BRM of CH₄-rich feeds.

Catalyst	Ni (wt.%)	GHSV (L/(g _{cat} ·h))	Feed CH ₄ /CO ₂ /H ₂ O/ D ^a (vol.%)	t (h)	T (°C)	X _{CH₄} (%)	X _{CO₂} (%)	H ₂ /CO	C (wt.%) ^b	R ^c
NiLaGa/ WI.800-R800	2.1	170	45:15:30:10 N ₂	80 ^d	750	86 ^e	87 ^e	2 ^e	0.5	*
LaNiO₃/ Ce_{0.75}Zr_{0.25}O₂	8.0	257	50:16.7:33.3	24	800	40	30	3	< 2.0	[252]
NiLa₂Zr₂O₇	10.0	30	25:25:25:25 N ₂	24	700	54	39	1.5	0	[251]
60CeO_x- Ni/Al₂O₃	n.a. ^e	72	50:16.7:33.3	72	850	87	-	2.05	0.8	[253]
Ni/CeO₂-SrO	12.0	n.a.	30.3:15.2:24.2:3 0.3 N ₂	250	850	< 95	75	2	0	[254]
Ce_{0.6}La_{0.4}NiO₃/ SiO₂	23.0	30	45.5:18.2:36.4	100	700	86	97	1.5	2.4	[255]
3%B-Ni/ SBA-15	10.0	36	45.5:18.2:36.4	24	800	75	71	2.7	0	[256]
Ni-6%Sr/ ZrO₂-MgO	10.0	n.a.	45.5:18.2:36.4	36	800	95	85	1.8	n.a.	[257]
NiCeSnRh/ Al₂O₃	n.a.	3200 h ⁻¹	45.5:18.2:36.4	20	700	55	45	2	48	[258]
Ni-0.3V/CeO₂	10.0	30	45.5:18.2:36.4	30	700	97	77	2.1	0	[259]
Ni/15%ZrO₂- MgO	10.0	36	45.5:18.2:36.4	20	800	81.5	82.5	1.7	n.a.	[260]

^a: D: dilutant. Specified in the different reaction feeds used in the cited reports. When 3 gases are specified, no dilutant was used as internal standard. ^b: C: amount of coke measured after the stability tests. ^c: R: reference. ^d: corresponds to the total screening time. ^e: averaged X_{CH₄}, X_{CO₂} and H₂/CO ratios obtained at 750 °C. *: information collected in this work. ^e: n.a.: not specified.

4.3.3.1.1 Origin of the catalytic activity and deactivation in BRM

Selected spent catalysts after BRM experiments were analyzed using TEM-EDX to investigate the origin of catalyst deactivation. On the one hand, the EDX elemental mapping of the deactivated Ni(CA-5.5)/WI.800-R700 displayed only very weak signals of Ni overall (Figure 4-42 b), indicating that partial Ni leaching took place over TOS. The latter observation was corroborated with ICP measurements. Thus, the Ni content was higher in the fresh Ni(CA-5.5)/WI.800-R700 catalyst (2.4 wt.% Ni) compared to the deactivated Ni(CA-5.5)/WI.800-R700 after 4 h TOS in BRM (1.7 wt.% Ni). Besides, as no carbon was measured with CHN analysis in the deactivated Ni(CA-5.5)/WI.800-R700, it seemed that the lower value of Ni measured was more related to leaching during reaction than to ‘dilution’ with deposited C. It can then be argued that those weakly bound Ni species to the support were leached during the BRM reaction, and recalling the characterization results of H₂-TPR, XPS and TEM (discussed in sections 4.2.3.2 and 4.2.3.3), these species could be those interacting with the Al-rich domains.

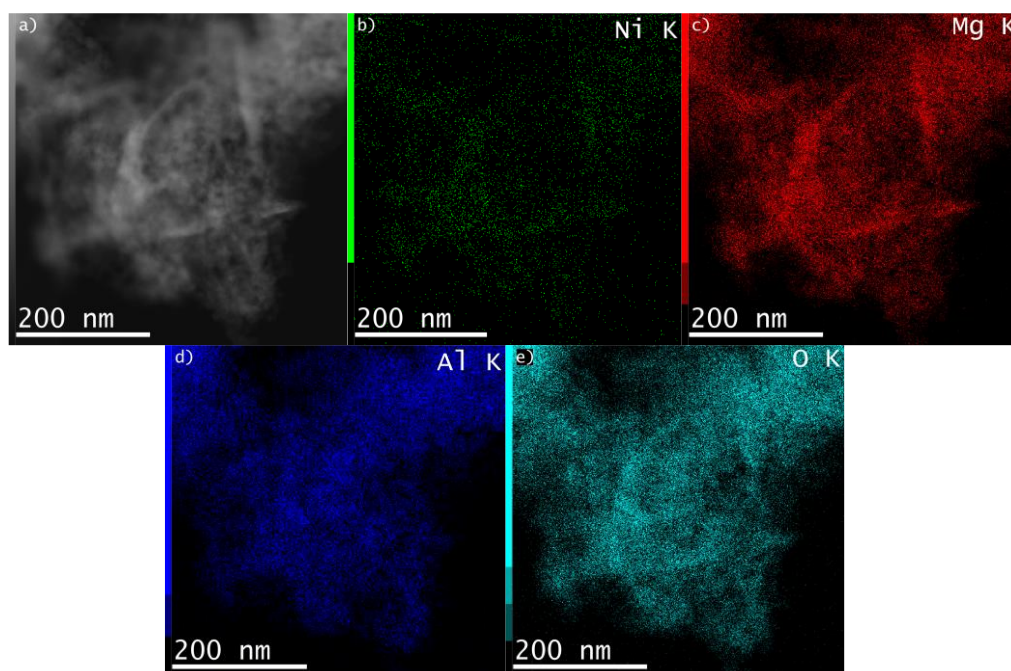


Figure 4-42. a) TEM-HAADF micrograph, and b) Ni-K, c) Mg-K, d) Al-K and e) O-K edge EDX elemental mappings (of the micrograph displayed in a)) of spent Ni(CA-5.5)/WI.800-R700 after 4 h TOS in BRM. Reaction conditions: $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}/\text{N}_2 = 45:15:30:10$ vol.%, $p = 1$ bar, $T = 750$ °C, $m_{\text{cat}} = 50$ mg, GHSV = $170 \text{ L}/(\text{g}_{\text{cat}} \cdot \text{h})$.

Additionally, it seemed that the BRM reaction conditions formed needle-like Mg-rich structures on the catalyst (see Figure 4-42 a and c), pointing out to structural changes over TOS. Moreover, these needles also contained Ni and high oxygen content, as evidenced by the intense O-K signals displayed in the sample's elemental mapping (see Figure 4-42 e). Thus, intensive re-oxidation of Ni^0 species most likely occurred, which contributed to the massive activity loss. Unfortunately, the determination of the oxidation state of Ni species using EELS was not possible due to the very low intensity signals recorded for Ni. Therefore, complete catalyst deactivation over short TOS in BRM was mostly due to leaching of weakly bound surface Ni and re-oxidation of the active sites provoked by using 30 vol.% H_2O and high reaction temperatures.

The previous findings were compared to literature. First, it is reported that steam pre-treatment at 850 °C provokes leaching of mildly attached metal ions in Ni/ Al_2O_3 catalysts, which most likely occurred during the BRM at high temperatures [261]. Moreover, Ni leaching from solid fuel cells anodes is also reported as one of the reasons of catalyst deactivation during the steam + oxygen reforming (ATR) of methane at $T = 800$ °C, which is also potentiated at increasing water contents [262, 263].

On the other hand, the spent NiLaGa/WI.800-R800 after ca. 80 h TOS in BRM retained its morphology to a great extent (see Figure 4-43 a), which explained its stable BRM catalytic performance. However, Ni particle agglomeration took place (3 – 40 nm), the same as partial Ni^0 re-oxidation. For example, Ni^0 cores covered with Ni^{2+} shells (for example, Figure 4-43 c) were observed, which co-existed with fully oxidized Ni^{2+} species. The latter evidenced that including 30 vol.% water and higher reaction temperatures also promoted particle agglomeration. Additionally, some big La agglomerates were identified (highlighted with red arrows in Figure 4-43 b), further suggesting the ‘sintering atmosphere’ provided by the BRM reaction conditions used. However, neither the presence of large Ni particles (up to 40 nm) nor big La agglomerates (i.e., less CO_2 adsorption sites) promoted heavy coke deposition in BRM (as CHN: 0.5 wt.% C), which highlighted the efficiency of H_2O to gasify coke. In this sense, particle sintering can be promoted depending on the reaction atmosphere used, and H_2O is known to accelerate particle growth and oxidation at high temperatures [250]. Therefore, it seems reasonable that Ni and La experienced remarkable agglomeration and oxidation in BRM due to the large volumes of water used in BRM, which was not observed even after 116 h TOS in DRM using $\text{CH}_4/\text{CO}_2 = 2:1$.

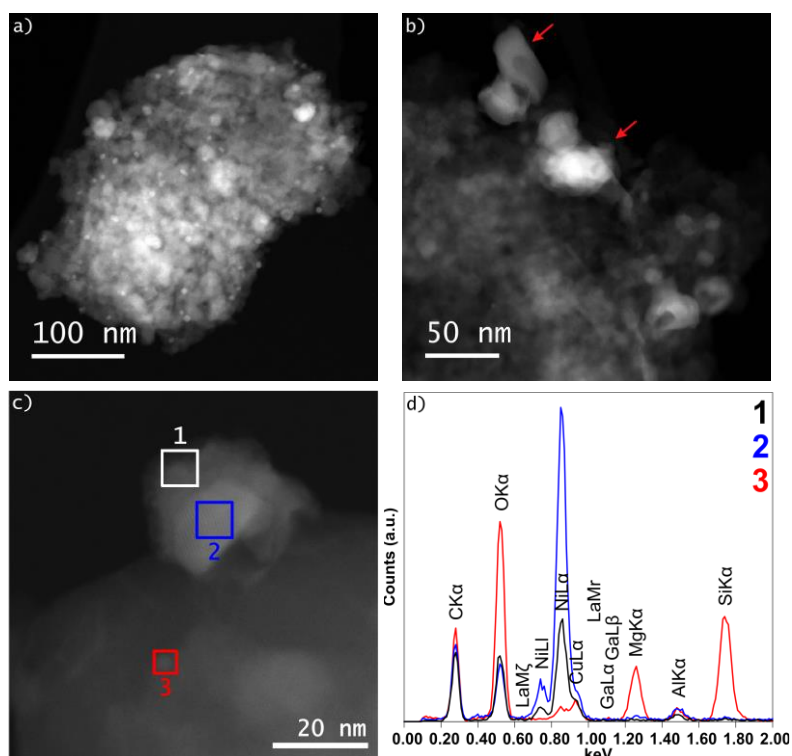


Figure 4-43. a), b) and c) TEM-HAADF micrographs and d) EDX spectra collected in the specified regions of c) (white square: spectrum 1; blue square: spectrum 2; red square: spectrum 3) of spent NiLaGa/WI.800-R800 after ca. 80 h TOS in BRM. Reaction conditions: $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}/\text{N}_2 = 45:15:30:10$ vol.%, $p = 1$ bar, $T = 750 - 850$ °C, $m_{\text{cat}} = 50$ mg, $\text{GHSV} = 170$ L/(g_{cat}·h). Red arrows in b) highlight agglomerated La particles.

Furthermore, intensive TEM imaging and EDX spectral analysis throughout different areas of this sample evidenced that Ga was scarcely found within the Ni particles (i.e., no Ga signals in the EDX spectra: Figure 4-43 c). The latter demonstrated that Ga was leached out from the active sites during the BRM experiment. Thus, ICP measurements were used to corroborate the previous statement: 0.6 wt.% Ga, 2.1 wt.% Ni and 1.9 wt.% La (NiLaGa/WI.800-R800) vs. 0.3 wt.% Ga, 2.0 wt.% Ni and 1.8 wt.% La (NiLaGa/WI.800-R800 spent after 80 h TOS BRM). Half of the Ga species were lost over 80 h TOS in BRM, while Ni and La leaching barely took place during reaction. Regarding Ga loss, physical evaporation of Ga^0 during DRM or BRM reaction at $T < 850$ °C from the NiGa sites seems unlikely, as these NiGa sites displayed very strong MSI. Contrarily, Ga loss over TOS in BRM was related to Ga's oxophilicity and its tendency to form volatile Ga_2O and/or soluble GaOOH in the presence of steam [264], which were leached out from the active sites, but interestingly, did not provoke catalyst deactivation over the time tested.

Therefore, prevented Ni loss after 80 h TOS in BRM explained the stable activity of NiLaGa/WI.800-R800. The latter was ascribed to the very strong interaction of Ni species with the Al-impregnated support material (see its H_2 -TPR profile, Figure 4-34 b). Despite that appreciable Ga leaching took place during reaction, not all Ga species were leached out after test, thus, the strengthening effect discussed in chapter 4.2 (i.e., formation of NiGa incorporating Al or supported on Al-rich regions) could also justify the catalyst's stable activity, even upon significative Ga loss.

To corroborate that metal leaching was promoted under the BRM reaction conditions, the spent NiLaGa/WI.800-R800 after 116 h TOS in DRM using $\text{CH}_4/\text{CO}_2 = 2:1$ (without steam) was analyzed with ICP and compared to the spent NiLaGa/WI.800-R800 after 80 h TOS in BRM. Due to the higher amount of coke in this spent sample (3.2 wt.%) and potentially, due to SiO_2 stems difficult to remove by sieving and/or a higher oxygen content due to oxidation, its metal composition (in wt.%) was lower for all the elements (1.5 wt.% Ni, 1.5 wt.% La, 0.3 wt.% Ga) vs. the *ex situ* reduced NiLaGa/WI.800-R800 (2.1 wt.% Ni, 1.9 wt.% La, 0.6 wt.% Ga). Therefore, the molar ratios $\text{Ni}/(\text{Ga} + \text{La})$ were compared

before (*ex situ* reduced NiLaGa/WI.800-R800) and after long-term reaction (116 h TOS). Thus, the *ex situ* reduced and spent NiLaGa/WI.800-R800 samples displayed the same molar ratio $\text{Ni}/(\text{Ga} + \text{La}) = 1.6$, which indicated that no metal leaching occurred under dry reforming conditions over 116 h. By contrast, the spent NiLaGa/WI.800-R800 after 80 h TOS in BRM displayed a molar ratio $\text{Ni}/(\text{Ga} + \text{La}) = 2.0$, which confirmed that Ga was leached out from the active sites during 80 h TOS in BRM.

4.3.3.2 Tri-reforming of methane (TRM)

This study was deepened by testing the outperforming NiLaGa/WI.800-R800 in TRM using a feed composition of $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}/\text{O}_2/\text{N}_2 = 55:20:5:10:10$ vol.% at $T = 750 - 850$ °C and GHSV = 170 L/(g_{cat}·h). The previous gas mixture was used to continue exploring the applicability of the NiLaGa/WI.800-R800 in reforming CH_4 -rich feeds, but in this case, with lower water content than BRM. The objective was to decrease the water amount fed further vs. BRM and SRM, while keeping a $\text{H}_2/\text{CO} > 1$ [265].

Thus, the TRM activity increased upon increasing the reaction temperature, however, only a slight activity increase was recorded by increasing the reaction temperature to $T = 800 - 850$ °C (see Figure 4-44). The latter might be due to the very low amount of unreacted CO_2 or O_2 in the feed at high temperatures, i.e., the X_{CO_2} and X_{O_2} were almost 100% (X_{O_2} not shown). Considering the comparatively low water content in the feed (5 vol.%) vs. BRM (30 vol.%) and lower $X_{\text{H}_2\text{O}}$ (vs. X_{CO_2} and X_{O_2}), it can be argued that the DRM and POM prevailed vs. the SRM reaction at high temperatures. Besides, high $X_{\text{CH}_4} > 70$ % was achieved across the studied temperature range, however, repeating the first set point at 750 °C evidenced that 7.5 % deactivation took place (averaged initial $X_{\text{CH}_4} = 80\%$ and final $X_{\text{CH}_4} = 74\%$, respectively). It could be argued that partial Ni^0 re-oxidation and/or particle sintering provoked this activity loss, as the measured amount of coke after 25 h TOS was only 0.9 wt.% C. Finally, constant $\text{H}_2/\text{CO} \sim 1.5$ was recorded at all studied temperatures, which demonstrated that H_2 -rich syngas was also obtained with NiLaGa/WI.800-R800 in the TRM of CH_4 -rich mixtures using lower H_2O contents in the feed (vs. BRM).

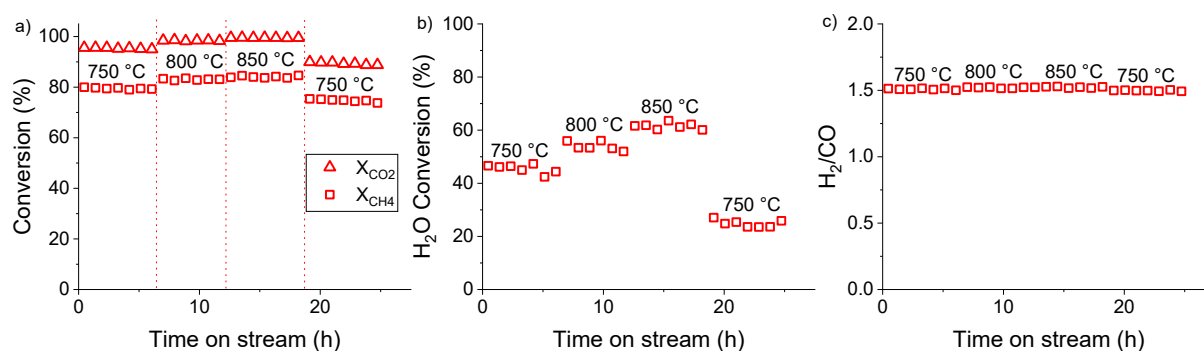


Figure 4-44. a) X_{CH_4} and X_{CO_2} , b) $X_{\text{H}_2\text{O}}$ and c) H_2/CO ratio with NiLaGa/WI.800-R800 over TOS in TRM. Reaction conditions: $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}/\text{O}_2/\text{N}_2 = 55:20:5:10:10$ vol.%, $p = 1$ bar, $T = 750 - 850$ °C, $m_{\text{cat}} = 50$ mg, GHSV = 170 L/(g_{cat}·h). The numbers close to each data cluster indicate the temperature (in the middle of the catalyst bed) at which the data was collected.

4.3.4 Reforming of model biogas: effects of trace compounds and catalyst regeneration

By next, NiLaGa/WI.800-R800 was studied in the reforming of dry CH_4 -rich feeds including poisonous compounds (i.e., $\text{CH}_4/\text{CO}_2 = 2:1$ with 100 ppm NH_3 or 5 ppm H_2S) to work under conditions even closer to real application. Subsequently, feasible regeneration strategies were studied to reactivate the deactivated catalyst and to prolong its lifespan.

4.3.4.1 Effects of heavy coke deposition and catalyst regeneration

It was demonstrated in section 4.3.2.2 that coke formation was accelerated by using CH_4 -rich feeds and only CO_2 as oxidant, which affected the catalysts' long-term stability. Moreover, it was also demonstrated in sections 4.3.3.1 and 4.3.3.2 that H_2O is an efficient coke gasifying agent, but it promotes

the oxidation and agglomeration of the active sites. Besides, H₂O is barely found in biogas sources [235]. Therefore, this section focuses on reactivating heavily coked catalysts after dry reforming of CH₄-rich feeds through oxidative removal of C(s) as CO₂ using undiluted synthetic air at 800 °C followed by H₂ reactivation. High temperatures were selected to remove carbon, as hard coke deposits are oxidized at T > 650 °C with oxygen [153].

Thus, the catalyst was firstly exposed to 16 h TOS in CH₄/CO₂ = 2:1, followed by 2 h of CH₄/N₂ = 90:10 vol.% to accelerate coke deposition at T = 750 °C (indicated as ‘1’ and ‘2’ in Figure 4-45, respectively). Afterwards, the activity was evaluated using the initial reaction conditions for 1 h (‘1’ in Figure 4-45 at 20 h running time), and it was evidenced that ca. 37.5% of activity was lost due to heavy coke deposition. Obviously, missing CO₂ in the feed to gasify coke and excessive CH₄ decomposition (Eq. 9) maximized coke formation. Consequently, the coked catalyst was *in situ* oxidized with synthetic air at T_{ox} = 800 °C for 2 h, while the effluents were monitored using GC sampling every 15 min. Thus, O₂, N₂ and CO₂ were observed in the chromatograms during the oxidation treatment, being the peak areas of the first two gases comparatively constant over time, while the peak area of CO₂ decreased until disappearance as the oxidation progressed (coke completely removed as CO₂ in 2 h, see Figure A 9). Afterwards, the oxidized catalyst was reduced *in situ* for 1.5 h at T_{red} = 800 °C (oxidation + reduction indicated as ‘3’ in Figure 4-45). The activity was then restored to the initial level (‘1’ in Figure 4-45 at approximately 24 h running time), which decayed ca. 40 % by promoting heavy coke deposition in a comparable way to what was previously described. Finally, the catalyst was reactivated a second time (‘1’ in Figure 4-45 at 55 h running time) using oxidation-reduction treatment. Therefore, it was demonstrated that CH₄-rich feeds maximized coke formation at 750 °C, while the developed oxidation-reduction treatment successfully restored the activity by coke removal from NiLaGa/WI.800-R800 in two consecutive catalytic cycles using CH₄/CO₂ = 2:1.

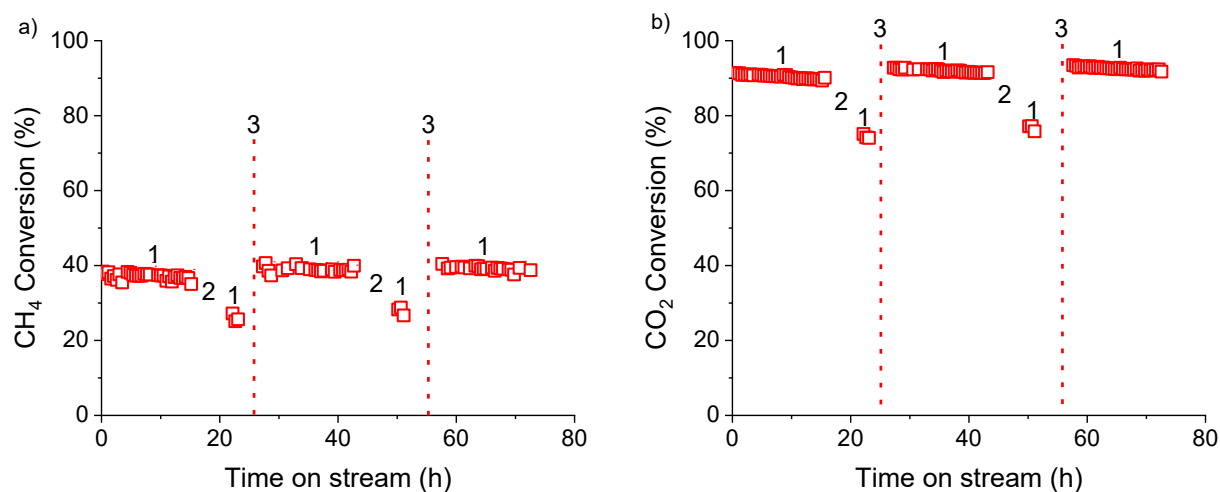


Figure 4-45. a) X_{CH_4} and b) X_{CO_2} of NiLaGa/WI.800-R800 over TOS in CH₄-rich DRM. Reaction conditions of 1: CH₄/CO₂/N₂ = 60:30:10 vol.%, p = 1 bar, T = 750 °C, m_{cat} = 50 mg, GHSV = 170 L/(g_{cat}·h). Reaction conditions of 2: CH₄/N₂ = 90:10 vol.% at GHSV = 170 L/(g_{cat}·h) for 2 h. Reaction conditions of 3: oxidation using 50 mL/min synthetic air for 2 h at 800 °C, followed by reduction using 50 mL/min H₂ for 1.5 h at 800 °C.

4.3.4.2 Reforming of model biogas: effects of NH₃ and catalyst regeneration

Firstly, the catalyst NiLaGa/WI.800-R800 was exposed for 16 h TOS to CH₄/CO₂ = 2:1 at 750 °C (‘1’ in Figure 4-46), followed by co-feeding 100 ppm NH₃ to the previous conditions for 20 h TOS (‘2’ in Figure 4-46). The catalytic activity dropped by ca. 10% immediately after NH₃ addition, while slow deactivation took place over the course of the poisoning stage. Besides, the H₂/CO ratio (Figure 4-46 b) followed the same deactivation trend, indicating that the reaction’s selectivity was also affected by feeding NH₃. After these 20 h TOS with NH₃, the latter was removed from the feed but keeping CH₄/CO₂

= 2:1 ('1' in Figure 4-46 at ca. 37 h running time), however, the catalytic activity did not increase to the initial level. The latter indicated that NH₃ might be strongly adsorbed on the Ni active sites, and/or that coke accumulation blocked them.

Thus, to release the Ni⁰ sites, the catalyst was oxidized at T_{ox} = 800 °C for 2 h with synthetic air, aiming to remove NH₃ as NO_x or N₂ and C(s) as CO₂, as previously mentioned. The oxidation was monitored using GC. The chromatograms displayed peaks of O₂ and N₂ (synthetic air) of constant peak area over time, while no peaks of NH₃ (or any NO_x) were recorded. Moreover, the characteristic CO₂ peak was clearly identified, the area of which decreased to zero in 2 h (displayed in Figure A 9). The latter suggested that, if these oxidized N-containing molecules were formed, their concentrations were too low to be detected by the BID detectors. Additionally, coke accumulation occurred, which might play a role in catalyst deactivation using CH₄-rich feeds containing 100 ppm NH₃. Moreover, after oxidation, the catalyst was reduced at T_{red} = 800 °C for 1.5 h with H₂ (oxidation + reduction indicated as '3' in Figure 4-46), which completely restored the activity in CH₄/CO₂ = 2:1 to the initial levels ('1' in Figure 4-46 at 44 h run time). Thus, it was demonstrated that, on the first place, 100 ppm NH₃ was a mild poison for NiLaGa/WI.800-R800 under biogas-like reaction conditions, as the activity slowly dropped over TOS. Secondly, coke deposition also provoked catalyst deactivation when using more realistic CH₄-rich feed with NH₃, suggesting that NH₃ promoted its formation. However, regeneration with oxidation and reduction was successful to restore initial activity levels after 40 h TOS.

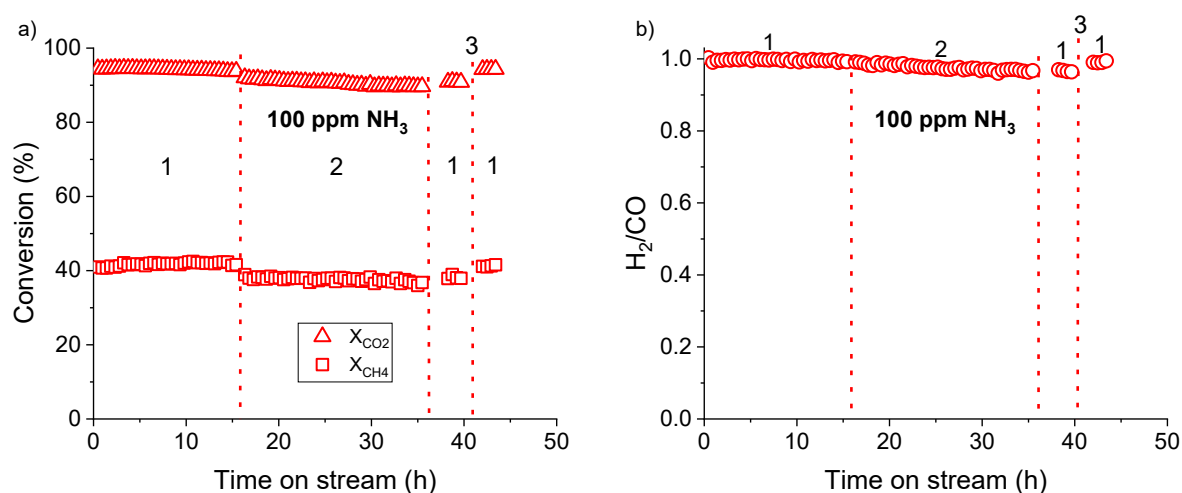


Figure 4-46. a) X_{CH4} and X_{CO2} and b) H₂/CO ratio with NiLaGa/WI.800-R800 over TOS in CH₄-rich DRM with 100 ppm NH₃. Reaction conditions of 1: CH₄/CO₂/N₂ = 60:30:10 vol.%, p = 1 bar, T = 750 °C, m_{cat} = 50 mg, GHSV = 170 L/(g_{cat}·h). Reaction conditions of 2: same conditions than in 1, but with 100 ppm NH₃ in the reaction feed. Reaction conditions of 3: oxidation using 50 mL/min synthetic air for 2 h at 800 °C, followed by reduction using 50 mL/min H₂ for 1.5 h at 800 °C.

The observed deactivation trend of the NiLaGa/WI.800-R800 caused by 100 ppm NH₃ agreed with literature. The authors in [72] also reported fast initial deactivation, followed by slow activity loss on the long-run at similar reaction conditions to those used in this work. The latter was ascribed to progressive coverage of Ni⁰ with NH₃ (or dissociative species: NH_{3-x}, 1 < x < 3) through a two-stage adsorption process on Ni⁰ sites: incomplete (but fast) initial adsorption, followed by slow coverage of the remaining Ni⁰ active sites with nitrogenated compounds over time. Besides, coke deposition was promoted simultaneously, which was related to the CH₄-rich conditions and less CO₂ adsorbed to gasify coke over the surface of the poisoned catalyst [73].

4.3.4.3 Reforming of model biogas: effects of H₂S poisoning and catalyst regeneration

Afterwards, the effects of H₂S on the catalytic activity using CH₄/CO₂ = 2:1 were investigated. As can be anticipated, 5 ppm H₂S provoked rapid catalyst deactivation of the 2.5 wt.% Ni catalysts in approximately 2 h on stream (see Figure 4-47). Consequently, several regeneration strategies were evaluated to tackle this problem. All of these were applied after S-poisoning of NiLaGa/WI.800-R800 in the following sequence: DRM of CH₄/CO₂ = 2:1 for 2 h ('1' in Figure 4-47), followed by co-feeding 5 ppm of H₂S until complete catalyst deactivation ('2' in Figure 4-47). The strong deactivation potential of 5 ppm H₂S was evidenced by the rapid drop of activity and H₂/CO ratios after only 2 h TOS. Consequently, the completely deactivated catalyst was characterized to get insights regarding the origin of the observed drastic deactivation.

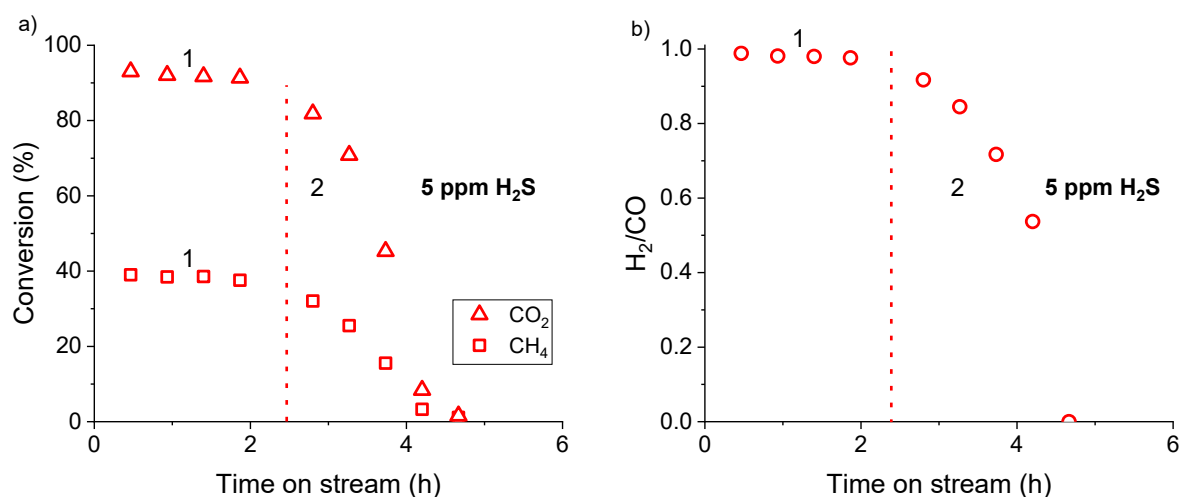


Figure 4-47. a) X_{CH_4} and X_{CO_2} and b) H_2/CO ratio with NiLaGa/WI.800-R800 over TOS in CH₄-rich DRM with 5 ppm H₂S. Reaction conditions of 1: CH₄/CO₂/N₂ = 60:30:10 vol.%, p = 1 bar, T = 750 °C, m_{cat} = 50 mg, GHSV = 170 L/(g_{cat}·h). Reaction conditions of 2: co-feeding 5 ppm H₂S to conditions of 1.

4.3.4.3.1 Origin of catalyst deactivation by co-feeding H₂S in CH₄/CO₂ = 2:1

First, this spent sample was analyzed using CHNS analysis, being 10.0 wt.% C (corroborated with DTA-TGA; thermogram displayed in Figure A 10) and 0.2 wt.% S measured. The latter evidenced that coke was heavily deposited in only 5 h TOS (compared to 3.2 wt.% C after 116 h TOS in S-free CH₄/CO₂ = 2:1; see Figure 4-39 c) by co-feeding 5 ppm H₂S, while a very low amount of S was measured. Thus, the low amount of S, and the massive activity drop over TOS suggested that only the surficial Ni⁰ were poisoned with S. Consequently, surface analysis of the S-poisoned catalyst was performed using XPS, but unfortunately, no S peaks in the S 2s or 2p region or S surface quantification could be recorded (spectra shown in Figure A 11), possibly due to the very low amount of S deposited in this sample and the XPS detection limit. Likewise, other researchers found that no surface S could be measured in a 10 wt.% Ni/MgO DRM catalyst even upon exposing it to 10 ppm H₂S for 12 h at 750 °C in CH₄/CO₂ = 1:1 [72]. The authors detected S signals (S 2p) in the XP spectra only when the concentration of H₂S was increased to ≥ 20 ppm for 12 h. Thus, by comparing the conditions used in this work and in [72], it was reasonable that no S was measured on the surface of the S-deactivated NiLaGa/WI.800.

Moreover, the H₂S-poisoned NiLaGa/WI.800-R800 was further analyzed using TEM. Particle agglomeration was evidenced after only ca. 5 h TOS in the presence of H₂S (H₂S-poisoned NiLaGa/WI.800-R800 after ca. 5 h TOS: 5 – 15 nm vs. *ex situ* reduced NiLaGa/WI.800-R800: particles mostly sized between 7 and 10 nm; see Figure 4-48). Regarding their composition, these Ni-containing particles also contained Ga, and displayed different degree of oxidation, including Kirkendall structures (Figure 4-48 a) and fully oxidized Ni²⁺ particles (darker particle with low contrast with respect to the

support of Figure 4-48 b, respectively). No hints of Ga leaching were found, which resembled the TEM characterization of this spent catalyst after 116 h TOS in S-free $\text{CH}_4/\text{CO}_2 = 2:1$ condition (see section 4.3.2.2.1). Besides, La was finely distributed throughout the sample as single atoms (see small bright dots scattered in Figure 4-48 b) and also as big separate particles (pointed with red arrows in Figure 4-48 c), indicating that both Ni and La agglomerated over short TOS. Thus, less sites were available to form $\text{La}_2\text{O}_2\text{CO}_3$ and gasify coke due to agglomeration, which consequently promoted coke accumulation. In connection to the latter, highly ordered, encapsulating carbonaceous structures were observed surrounding the Ni particles (ordered structures surrounding dark Ni-containing particles in Figure 4-48 d), blocking them and contributing to the activity loss. Again, no S could be identified using EELs or EDX spectra (thus, not shown), possibly due to the low amount of S measured.

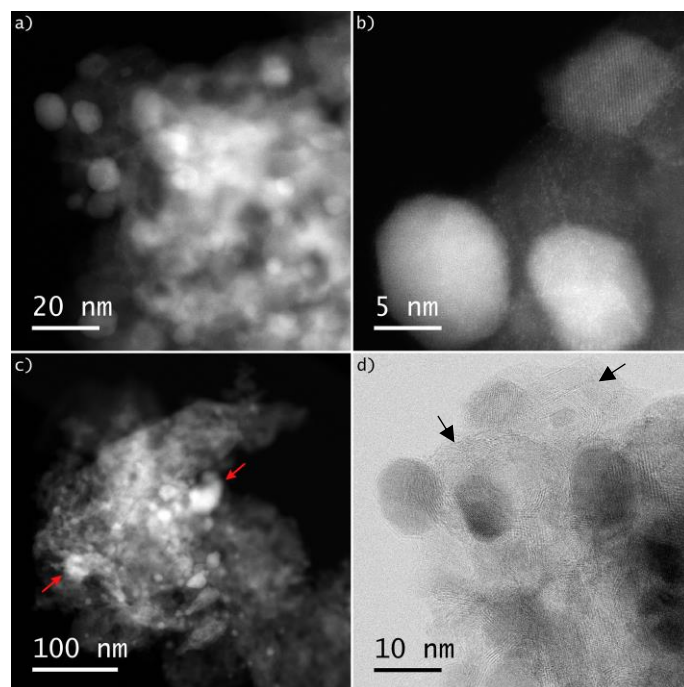


Figure 4-48. a - c) TEM-HAADF and d) TEM-BF micrographs of H_2S poisoned NiLaGa/WI.800-R800. The red arrows in c) highlight La agglomerated particles. The black arrows in d) highlight encapsulating coke on Ni sites. Reaction conditions: 3 h using $\text{CH}_4/\text{CO}_2/\text{N}_2 = 60:30:10$ vol.%, $p = 1$ bar, $T = 750$ °C, $m_{\text{cat}} = 50$ mg, GHSV = 170 $\text{L}/(\text{g}_{\text{cat}} \cdot \text{h})$, followed by co-feeding 5 ppm H_2S (to the previous conditions) for 2 h.

The characterization results obtained so far revealed that Ni agglomeration and heavy coke deposition were promoted by co-feeding 5 ppm H_2S in $\text{CH}_4/\text{CO}_2 = 2:1$ at 750 °C in very short TOS. Unfortunately, no surface S-containing species were measured with the used techniques, but the massive deactivation in very short TOS and the very low amount of S measured in the spent sample pointed to surface poisoning of Ni^0 sites with S.

In this sense, most available research suggests that, under the regular DRM conditions, H_2S is dissociatively adsorbed on surface Ni^0 sites forming inactive NiS_x of different stoichiometry [75, 112, 266]. Obviously, poisoning of the surface-active sites is critical for surface sensitive reactions, as it is the case for DRM [74, 112]. Additionally, and by focusing on the selected NiLaGa catalytic system, La has been reported to also form thermally stable sulfides (for example, LaS_x or $\text{La}_2\text{O}_2\text{S}$ [76]) under reforming conditions. Thus, the highly dispersed surficial La sites could also act as H_2S adsorption centers. Logically, enhanced H_2S adsorption (by Ni and/or La species) on a continuously evolving catalyst's surface seems reasonable, which might accelerate catalyst S-poisoning and deactivation. Besides, the formation of La sulfides also imply that less basic sites were available to adsorb CO_2 and gasify coke, which consequently led to coke accumulation. Furthermore, H_2S promotes Ni

agglomeration at DRM reaction conditions, as it requires several adjacent Ni atoms for adsorption, which consequently weakens the Ni-Ni bonds [112]. The latter would facilitate coke deposition under DRM of CH₄-rich feeds. Moreover, adsorption of H₂S can impact on the electronic properties of the Ni⁰ sites as the H₂S poisoning takes place [74]. Consequently, the adsorption of the DRM reactants is further affected, which impacts on the activity in intricate ways. For example, decreased CO₂ uptake hinders coke gasification, thus, coke accumulates over TOS.

4.3.4.3.2 Regeneration of S-poisoned catalysts

Different strategies were investigated to reactivate the S-poisoned catalyst. Firstly, the effect of increasing the reaction temperature was studied with and without co-feeding H₂S in CH₄-rich conditions, respectively. This strategy focused on using high temperatures to decompose surface NiS_x as H₂S, and to recover the active Ni⁰ sites [267].

Thus, the first regeneration strategy (with H₂S) started after complete deactivation (Figure 4-47): the temperature was subsequently increased to 850 °C for 2 h using 5 ppm H₂S + CH₄/CO₂ = 2:1, and then to 900 °C for another 2 h using the previous reaction conditions. No conversions were measured at any temperature (not shown). After the thermal treatment, the S-free CH₄/CO₂ = 2:1 mixture was fed for 3.5 h at 750 °C. Unfortunately, no activity was recorded even after removing H₂S from the feed. Thus, the catalyst was irreversibly deactivated by H₂S, and this strategy was unsuccessful.

The second regeneration procedure (without H₂S) was performed after complete deactivation with H₂S ('2' in Figure 4-49), which started by increasing the temperature to 900 °C under the S-free CH₄-rich feed ('3' in Figure 4-49). Interestingly, an induction period of ca. 30 min was observed, after which the catalyst displayed high (and stable) activity over 2 h TOS. The latter observation might relate to the stepwise elimination of surface S species by oxidizing compounds (for example CO₂ or *in situ* produced H₂O to form SO_x) at sufficiently high temperatures [267]. By next, the reaction temperature was decreased to 750 °C under the same reaction conditions ('4' in Figure 4-49), but the catalytic activity was lower compared to the initial set point at 750 °C ('1' in Figure 4-49), while it rapidly dropped to zero in only 1 h TOS. The activity drop could be explained by large Ni agglomerates formed at 900 °C (i.e., less active sites) covered by coke, as C was not completely gasified during reaction (C: 7.0 wt.% vs. 10 wt.% directly after H₂S poisoning). No further characterization was performed due to the massive activity loss, even upon regeneration.

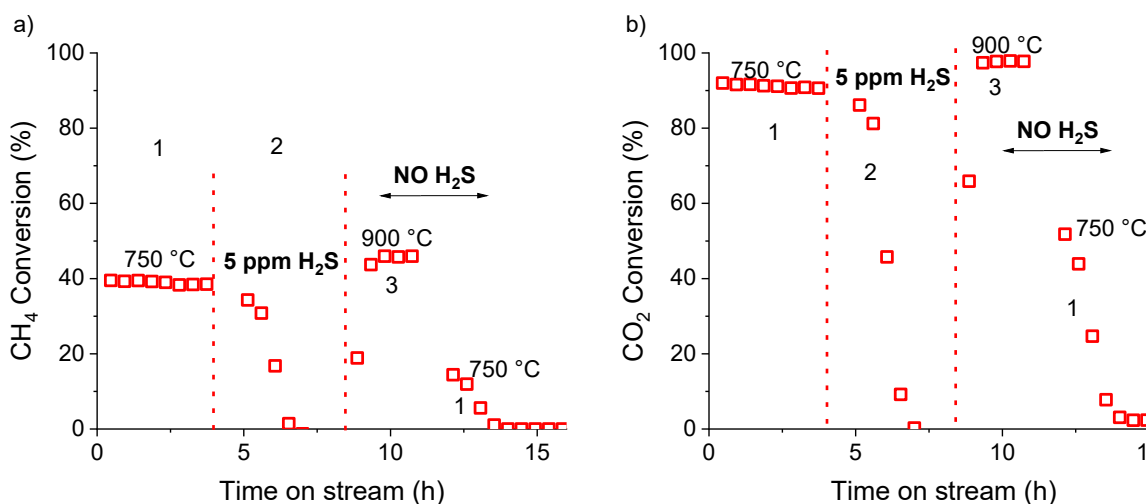


Figure 4-49. a) X_{CH_4} and b) X_{CO_2} with NiLaGa/WI.800-R800 over TOS in CH₄-rich DRM with 5 ppm H₂S. Reaction conditions of 1: CH₄/CO₂/N₂ = 60:30:10 vol.%, p = 1 bar, T = 750 °C, m_{cat} = 50 mg, GHSV = 170 L/(g_{cat}·h). Reaction conditions of 2: 5 ppm H₂S were co-fed to conditions used in 1. Reaction conditions of 3: same conditions than in 1, but T = 900 °C. The numbers over each data cluster indicate the temperature (in the middle of the catalyst bed) at which the data was collected.

By next, catalyst regeneration using reduction or oxidation + reduction treatments were investigated. On the one hand, using H₂ as regeneration agent is based on the following equation: $\text{Ni} + \text{H}_2\text{S} (\text{g}) \rightleftharpoons \text{NiS} (\text{s}) + \text{H}_2 (\text{g})$ [267]. Thus, feeding H₂ at sufficiently high temperatures would shift the equilibrium of the previous reaction from the products to the reactants, which means that NiS (s) could be transformed into H₂S (g) and metallic Ni. However, the driving force of the previous reaction is reported to be extremely small, thus, long H₂ exposure times at high temperatures might be required [267], which could also promote Ni agglomeration. On the other hand, the oxidation treatment with synthetic air at $T > 750$ °C of sulfided Ni catalysts would produce SO_x [73, 266], but unfortunately, re-oxidation of Ni⁰ sites is difficult to avoid. Thus, subsequent reduction at appropriate temperatures is needed to restore the Ni⁰ active sites. However, high temperature treatments using different atmospheres could promote particle agglomeration and/or affect the catalysts' performance and physicochemical properties, which has been previously discussed throughout this work and literature.

Thus, the completely deactivated NiLaGa/WI.800, R800 ('2' in Figure 4-50) was reduced for 16 h using H₂ at 800 °C ('3' in Figure 4-50). Afterwards, the CH₄/CO₂ = 2:1 mixture was fed ('1' in Figure 4-50 at ca. 20 h running time), and despite that the activity increased to certain extent, it dropped rapidly in only 1 h TOS. As previously discussed, coke deposition and particle sintering took place during the H₂S poisoning step, while 16 h under H₂ most likely enlarged the Ni sites further and consequently enhanced coke deposition in very short TOS. Besides, coke gasification hardly occurs under reductive H₂ treatment at 800 °C, which also pointed out to deactivation due to coke accumulation over the Ni active sites [268, 269].

Afterwards, regeneration using oxidation and reduction was investigated. Firstly, the catalyst was *in situ* oxidized for 2 h at T_{ox} = 800 °C with synthetic air, which produced CO₂ in the chromatograms, the peak area of which decreased to zero in 2 h (see Figure A 9). The latter was analogous to what was previously discussed in coke and NH₃ removal (see sections 4.3.4.1 and 4.3.4.2, respectively), indicating that either H₂ treatment for 16 h was not efficient for removing coke deposits or coke formation was remarkably encouraged in only 1 h TOS under CH₄-rich DRM conditions after S-poisoning. Afterwards, the catalyst was reduced for 1.5 h using H₂ (oxidation + reduction nomenclated as '4' in Figure 4-50), followed by feeding the S-free mixture CH₄/CO₂ = 2:1 again ('1' in Figure 4-50 at ca. 27 h running time). Thus, the activity recorded was comparable to the initial levels, but unfortunately, it rapidly decreased ca. 15% in only 4 h TOS (from X_{CH_4} = 37.2 % to X_{CH_4} = 29.9% and from X_{CO_2} = 88.9% to X_{CO_2} = 76.4%). Clearly,

oxidation + reduction was a better regenerative strategy than H₂ reduction for 16 h at 800 °C. However, the stability of NiLaGa/WI.800-R800 was seriously affected, which suggested any or combination of the following: i) S was not completely eliminated from the catalyst's structure, ii) severe coke deposition occurred in only 4 h TOS, or iii) exposing the catalyst for 2 h to 5 ppm H₂S provoked irreversible effects in the catalyst's physicochemical features, for example, massive particle agglomeration.

Finally, the oxidative treatment was repeated, but for 16 h at T_{ox} = 800 °C this time, to investigate if S elimination required longer oxidation times. Again, coke was removed as CO₂ in 2 h, revealing that only 4 h TOS under S-free CH₄/CO₂ = 2:1 produced coke, which most likely contributed to catalyst deactivation. Subsequently, the catalyst was reactivated with H₂ at T_{red} = 800 °C for 1.5 h ('5' in Figure 4-50), which restored the DRM activity in CH₄/CO₂ = 2:1 ('1' in Figure 4-50 at 48 h running time) to acceptable levels a second time compared to the initial values. Additionally, this regeneration treatment enhanced the stability of NiLaGa/WI.800-R800, as the same deactivation levels were reached after 10 h TOS (comparison between '1' at ca. 27 h TOS vs. '1' at ca. 48 h TOS in Figure 4-50). Thus, it could be argued that the elimination of S in NiLaGa/WI.800-R800 is a slow process which requires long exposure times of synthetic air and high temperatures.

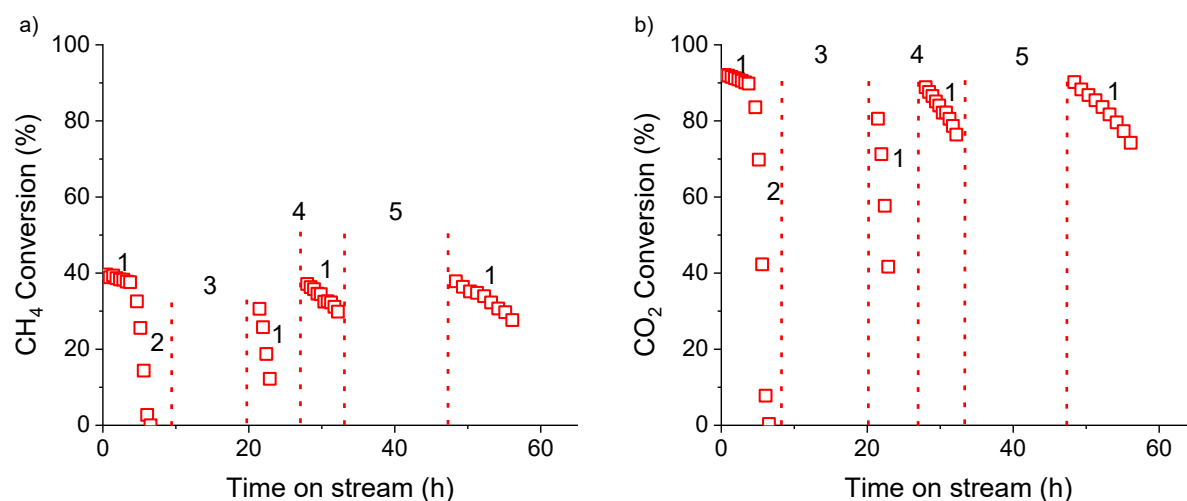


Figure 4-50. a) X_{CH₄} and b) X_{CO₂} with NiLaGa/WI.800-R800 over TOS in CH₄-rich DRM with 5 ppm H₂S. Reaction conditions of 1: CH₄/CO₂/N₂ = 60:30:10 vol.%, p = 1 bar, T = 750 °C, m_{cat} = 50 mg, GHSV = 170 L/(g_{cat}·h); Reaction conditions of 2: 5 ppm H₂S were co-fed with the conditions used in 1; Reaction conditions of '3': reduction with 50 mL/min H₂ at T_{red} = 800 °C for 16 h; Reaction conditions of '4': oxidation with 50 mL/min synthetic air at T_{ox} = 800 °C for 2 h, followed by reduction with 50 mL/min H₂ at T_{red} = 800 °C for 1.5 h; Reaction conditions of '5': same conditions as in '4', but the oxidation time was prolonged to 16 h.

No further characterization was performed, as it was clear that only 5 ppm H₂S imparted a massive deactivation effect on NiLaGa/WI.800-R800, and no complete reactivation (vs. the initial level) could be done after S-poisoning, even upon long oxidative + reductive treatments. However, it was demonstrated that coke deposition and particle agglomeration were promoted using CH₄-rich feeds containing trace amounts of H₂S. Thus, complete upstream H₂S elimination is mandatory to successfully reform real biogas mixtures with the developed catalytic system.

4.3.5 Intermediate conclusions

From several developed catalysts, the trimetallic NiLaGa/WI.800-R750 displayed exceptional performance using alternative reaction regimes vs. many literature reports available in stoichiometric DRM. For example, it led to high H₂ productivity even at very high GHSV and under coke prone regimes (T = 600 °C and GHSV = 170 L/(g_{cat}·h)). Moreover, upon reducing it at T_{red} = 800 °C, this catalyst displayed highly competitive activity and long-term stability using model biogas (CH₄/CO₂ = 2:1). In this sense, coke formation, which is one of the main problems of DRM catalysts, was controlled to a great extent even upon using CH₄-rich reaction conditions with only 10% dilution (3.2 wt.% C after ca. 120 h TOS). Additionally, the NiLaGa system was highly versatile, as it produced high grade syngas

($H_2/CO > 1$) when using CH_4 -rich gas mixtures in oxidative BRM (with H_2O) and TRM (with $H_2O + O_2$). In connection to the latter, it was demonstrated that more oxidative reaction regimes (vs. DRM) eliminated coke deposition problems, but enabled other (less discussed) deactivating mechanisms, i.e., the re-oxidation of the active sites, leaching of metallic components and particle agglomeration.

Furthermore, the robustness of NiLaGa/WI.800-R800 was further evaluated by reforming model biogases with poisonous compounds NH_3 and H_2S at relevant levels. Thus, the deactivation provoked by NH_3 or coke was completely reverted using intermediate oxidation + reduction: in two consecutive cycles after heavy coke deposition, and in one cycle after 100 ppm NH_3 in $CH_4/CO_2 = 2:1$. However, H_2S is by far the strongest poison for Ni catalysts, as it triggered massive deactivation in very short TOS. Thus, for the successful reforming of CH_4 -rich biogas-alike gases, complete upstream removal of H_2S is necessary. Characterization of spent samples revealed that coke deposition and particle agglomeration were potentiated by co-feeding H_2S at the studied levels, which disclosed its severity.

5. Thesis Conclusions and Outlook

5.1 Conclusions

Several low-loading Ni-based catalysts supported on Mg-rich MgAl hydrotalcite-derived mixed oxides were presented throughout this PhD work, aiming to control current environmental concerns through the valorization of CH₄-rich waste-derived feedstocks using oxidative reforming reactions (DRM, BRM and TRM). For this purpose, several 2.5 wt.% Ni catalysts were developed using the facile wet impregnation technique and knowledge-based formulations, to valorize CH₄-rich synthetic gas mixtures resembling available waste-derived biogas or landfill gas sources (DRM).

After a thorough analysis in stoichiometric DRM of outstanding samples supported on commercial MgO-Al₂O₃ (50:50 wt.%, Mg/Al = 1.3), an acceptable correlation was established between high surface fraction of small-sized Ni⁰ sites strongly stabilized by the Mg-rich support and high catalytic activity. However, this trend did not apply to all outperforming catalysts, which revealed that the DRM is a complex reaction, and that the different physicochemical features of the catalysts shape their activity, selectivity, and stability in complicated ways. Consequently, it was challenging to determine universal structure-activity relationships applicable to catalytic systems modified through different approaches.

Specifically, highly active catalysts (averaged X_{CH₄} = 40%, X_{CO₂} = 56%, H₂/CO = 0.75 at 600 °C and GHSV = 170 L/(g_{cat}·h)) were developed by following two alternative pathways: Ni complexation with organic ligands under selected conditions (CA at pH = 4 – 5.5 or TA and Gly) or using trimetallic NiLaGa or NiGdSc and MgO-Al₂O₃ (50:50 wt.%; S2) mixed oxides. However, and despite the similar activity among these catalysts, only the trimetallic NiLaGa/S2 and NiGdSc/S2 displayed no deactivation over 48 h TOS and formed < 1.5 wt.% C under highly deactivating reaction conditions. Thus, it was demonstrated that basic rare-earth metals improved the performance of DRM catalysts significantly, most likely by improving the CO₂ adsorption, while preventing the re-oxidation of the active sites simultaneously.

Additionally, a new support material was developed using the conventional wet impregnation method, to enhance the activity of developed catalysts and to prevent the deactivation observed over TOS of outperforming catalysts supported on commercial S2. Intensive catalytic testing under severe DRM reaction conditions demonstrated that the samples supported on the Al-impregnated Pural MG63 calcined at 800 °C (WI.800, Mg/Al = 1.2) performed slightly better than those previously prepared on commercial MgO-Al₂O₃ supports. Moreover, these catalysts supported on WI.800 displayed remarkable coke suppression ability, which brings value to this work, especially considering that coke deposition is one of the big concerns which hinder the mature implementation of the DRM of CH₄-rich biogas. The improved coke resistance was linked to the resulting catalysts' surface composition and electronic properties, and to the high concentration of structural defects (oxygen vacancies), which are believed to be interrelated and shaped by the Al-rich surface of WI.800. Thus, it was demonstrated that the support played a crucial role in the DRM activity and stability of the developed catalysts.

Despite the previous improvements discussed for DRM, the application of these materials in BRM using large volumes of H₂O (30 vol.%) was challenging. Thus, BRM was only successful with NiLaGa/WI.800-R800, as it was the only sample which displayed high activity (averaged X_{CH₄} = 86%, X_{CO₂} = 87%, X_{H₂O} = 82% and H₂/CO = 2.0 at 750 °C) over 80 h TOS with almost negligible coke formation (0.5 wt.% C), potentially due to retaining its structure and avoiding Ni and La leaching after reaction. The latter was ascribed to the finely distributed intermetallic/alloyed NiGa sites strongly attached to Al-rich surface of WI.800 (or potentially including Al within them). However, 50% of Ga species were leached from these NiGa sites during reaction, but interestingly, it did not affect the activity

during the time tested. Therefore, the role of H₂O in BRM as an efficient coke gasifying agent was clearly identified, however, it also provided a more oxidative reaction atmosphere, which accelerated catalyst deactivation by leaching, re-oxidation, and sintering of the active sites. Thus, this work provided a better understanding of the origin of catalyst deactivation in highly oxidative reforming regimes, which are not frequently discussed in literature. Finally, including O₂ in the reaction feed for TRM led to $X_{CH_4} = 80\%$, $X_{CO_2} \approx 100\%$, $X_{H_2O} = 45\%$, $X_{O_2} \approx 100\%$ and $H_2/CO = 1.5$ at 750 °C, but it deactivated NiLaGa/WI.800-R800 even in shorter TOS (< 30 h), possibly due to fast re-oxidation of metallic sites using this highly oxidizing reaction atmosphere. However, these aspects should be better investigated.

Working under even more realistic conditions, i.e., $CH_4/CO_2 = 2:1$ with NH₃ or H₂S at resembling levels to those present in real biogas, unveiled the difficulties of using it for the reforming reactions. Despite its attractiveness, catalyst deactivation over TOS was a main concern, especially using CH₄-rich gas mixtures containing traces of H₂S. Thus, subsequent catalyst reactivation was needed to bring the activity back to acceptable levels. It was demonstrated that co-feeding H₂S or NH₃ to $CH_4/CO_2 = 2:1$ accelerated coke deposition and particle sintering. Thus, and among different studied strategies, regenerative oxidation-reduction treatment at 800 °C was the best method for catalyst regeneration. By these means, the outperforming NiLaGa/WI.800-R800 was successfully reactivated after heavy coke deposition (in 2 consecutive catalytic cycles) and NH₃ poisoning, and despite deactivation caused by H₂S was difficultly reversed, acceptable activity levels were achieved anyways. Although this work did not unequivocally identify the poisoning mechanisms, these seemed to stem up from a complex dissociative adsorption of H₂S or NH₃ on the surface Ni sites (which block the adsorption of the reforming reactants), Ni particle agglomeration and massive deposition of coke.

Therefore, one non-noble catalyst 2.5 wt.% NiLaGa/WI.800-R800 prepared using facile methods was developed in this work which could be used for the valorization of real biogas upon efficient upstream H₂S removal below deactivating levels. Additionally, NiLaGa/WI.800-R800 could be utilized in consecutive catalytic cycles in $CH_4/CO_2 = 2:1$ after deactivation using oxidation-reduction regeneration treatments, or to produce H₂-rich $H_2/CO > 1$ syngas in BRM or TRM, enabling downstream couplings and disclosing its application potential.

5.2 Outlook

Thus, the combined approach contemplating intensive catalytic evaluation and characterization followed throughout this work provided a better understanding of the different reforming reactions and the origin of catalyst deactivation by using low-loading Ni catalysts on MgAl mixed oxides, based on which future developments can be built on. However, several gaps were identified during this work, which should be further researched to understand the developed catalysts more profoundly. First, only powdered catalysts were tested in lab-scale fix-bed reactors, thus, upscaling the outperforming catalyst into tablets/monoliths/pellets could be an attractive approach to evaluate their real applicability. In this sense, the upscaled catalysts could be used for BRM or TRM to enhance syngas production (of adequate purity) and to couple it with the downstream synthesis, e.g., of methanol. Second, a detailed understanding of the mechanisms of catalyst deactivation using real biogas could provide fundamental knowledge for the preparation of active and resistant catalysts for its direct valorization without upstream purification processes. In relation to the previous point, alternative catalysts formulations including S-resistant elements could be also evaluated, to increase their resistance against deactivation during biogas valorization. For example, by recalling knowledge of hydrodesulfurization catalysts, elements like Mo, P, Pd, Pt, W [270-273] could be added to the Ni-based formulations, the same as the optimization of their preparation/pre-treatment conditions (calcination or reduction temperature and atmospheres), etc. Third, the role of Al-impregnated surface on the catalytic performance deserves deeper investigations, especially to understand if electron poor Al species can enhance the adsorption of oxygenated compounds and contribute to its superior coke gasification properties. Thus, more sophisticated

characterization techniques, the same as refined DFT calculations should be performed for the previous purposes. For example, EXAFS, XANES, *in situ/operando* spectroscopic techniques (FTIR, Raman, etc.) under relevant DRM reaction conditions, etc., could disclose the strengths of this new generation of materials. Fourth, similar to citric acid, the optimization of the impregnation pH should be also studied with tartaric acid or glycine, as these efficiently enhanced the catalytic performance without pH modification. Fifth, the previous successful modifications could also be combined, i.e., using TA or Gly (at optimized pH) with La+Ga or Gd+Sc, to unveil potential catalytic improvements/synergies. Finally, TRM displayed huge optimization potential, the reaction conditions of which should be carefully optimized to maximize the syngas productivity of $H_2/CO = 2$ at lower H_2O contents, compared to SRM or BRM.

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7. Appendix

7.1 Fundamentals and description of the characterization methods used (section 3.2)

7.1.1 Inductively coupled plasma - optical emission spectroscopy (ICP-OES)

The inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used for the chemical analysis of the catalysts. Basically, the ICP-OES technique correlates the intensity of light emitted by the metals (when excited by a high energy plasma) with their concentration [118]. It can be used to identify and quantify metals in the catalysts, but these need to be firstly removed from their matrix (for example, via chemical digestion). The plasma excites the metals, and the excess of energy can be released as photons of specific wavelength (corresponding to the energy difference between two electronic states: considering $\Delta E = hc/\lambda$, being h the Planck constant, c is the speed of light in vacuum and λ the emitted wavelength). As each element has its characteristic electronic levels, the spectra obtained using ICP-OES can be used to identify the metals present in the material. Apart from qualitative analysis, quantification is also possible, as the intensity of the emitted light is generally function of the concentration of the emitting metals (as observed in Eq. S1). However, the validity of this equation (linearity) must be previously corroborated within an appropriate concentration range.

$$I = kc \quad (\text{Eq. S1})$$

Being I : the intensity of the light emitted by the measured solution containing the target metal, k a proportionality constant related to the emission properties of the metal at a specific wavelength and the measuring device, and c the metal concentration.

Experimentally, ~ 10 mg of sample were chemically digested with 8 mL aqua regia in a 'Multiwave PRO' (Anton Paar) microwave-assisted heating furnace (220 °C and 50 bar), then the digested sample was diluted with water in a 100 mL calibration flask. Afterwards, the solution was introduced to the apparatus (Varian 715-ES ICP-OES) by a capillary and brought to a high energy plasma. The emitted light was collected using special optical devices and measured at a specific wavelength in the detection system. Finally, the emitted intensity was correlated to the specimen's concentration.

Additionally, leaching tests were performed to analyze the dissolution of Mg from the support during preparation. The preparation procedure of selected catalysts reported in section 3.1.2 was repeated, but instead of removing the solvent with rotavapor, the solids were filtered using vacuum pump, washed with deionized water at room temperature, and the as-obtained mother liquor was analyzed by ICP (the procedure for the ICP analysis was repeated, without pre-treatment of the sample with aqua regia).

7.1.2 Catalytic combustion of deposited coke and sulfur (CHNS)

As already mentioned, the reforming reactions generally promote the formation of coke. These deposits are sensitive to catalytic oxidation at high temperatures under oxidative atmospheres (synthetic air, oxygen, among others), thus, the production of CO_2 (or $\text{CO} + \text{CO}_2$) can be correlated to the total amount of coke formed during the reaction. Additionally, the S present in a S-poisoned catalyst can also be quantified by its oxidative removal (by formation of SO_2 and/or SO_3) at adequate temperatures [274].

Experimentally, the CHNS elemental analysis of the spent catalysts was performed on a microanalyser (TruSpec Micro CHNS, Leco) equipped with a calibrated infrared detector. Around 10 mg of the spent sample were oxidized using a V_2O_5 catalyst and 5 vol.% O_2/He at 1000 °C. Subsequently, the coke or S present were evaluated via CO_2 or SO_2 quantification.

7.1.3 Determination of the support's surface charge at different preparation pH

The surface charge of the solids was measured using two methods: zeta potentiometry and the salt addition method [158]. The first method measures the mobility (which is proportional to the zeta potential) of charged particles dispersed in a conducting liquid at known conditions when an external electric field is applied. The latter forces the charged particles to move to the electrode of the measuring cell with opposite sign. Changing the pH of the media affects the surface charge by the acid-base equilibrium of the surface OH groups (as explained in section 2.4.3), therefore, measuring the zeta potential at different pH identifies the pH at which there is no mobility of these particles (being this pH the isoelectric point, IP). The second method tracks the changes in the pH over time (before and after equilibration for 24 h) of several dispersions made of a known amount of solid sample and same volume of conducting liquid (at same temperature and ionic strength) but at different initial pH. Based on this method, the dispersing liquid causes ionization of the surface OH groups when its pH is higher or lower than the solid's point of zero charge (PZC, as discussed in section 2.4.3). If the pH of the dispersing liquid is the same as the solid's PZC, there would be no changes in the pH over time.

For the zeta potentiometry measurements, 50 mg of the support (sized between 25 – 50 μm) were dispersed in 40 mL of solution 50:50 vol.% ethanol/water. The zeta potential was measured in a Zetasizer Ultra (Malvern Panalytical) using auto mode and an automatic titrator. The measurements were carried out between pH = 6 - 12 (the pH was adjusted using solutions of known concentration of HCl and NaOH) with continuous stirring using a disposable cuvette with two gold electrodes. Before each measurement, the cuvettes were flushed with compressed air to remove dust particles. The mobility was measured three times at each pH to get an average value.

Salt addition method: experimentally, seven portions of the solid (0.125 g each) were suspended in individual flasks containing 25 mL of 0.1 M KNO_3 solution. The initial pH of the suspensions was adjusted using 0.1 M HNO_3 or 0.1 M NH_4OH when needed. The chosen initial pH values were 5, 6, 7, 8, 9, 10, 11. The suspensions were shaken for 24 h at room temperature at 450 rpm on an IKA LABORTECHNIK KS125 Basic apparatus. The final pH was measured after 24 h, and the differences between the final and initial pHs (ΔpH) were plotted against the initial pH. The initial pH value at which the ΔpH is zero was considered as the point of zero charge (PZC)

7.1.4 Isothermal adsorption of N_2 at low temperatures (BET)

This technique is used to determine the sample's surface area, and its pore size and volume, i.e., the sample's textural properties, via the adsorption of an inert gas at low and constant temperature. In this sense, the capacity of a solid material to adsorb a probe gas molecule like N_2 or Ar is related to its textural properties by applying suitable mathematical models, as described below [118].

To understand the previous, the surface of a solid material needs to be considered. Generally, the atoms on a solid's surface have higher energy compared to those in the bulk, as these species are not fully coordinated with neighbor atoms. Thus, when a probe molecule contacts a solid, it interacts with surface sites to decrease the surficial energy. These solid – gas interphase interactions are generally non-specific (London dispersion and intermolecular repulsion) and are benefitted at lower temperatures, therefore, the experiments require very low temperatures to saturate the solid's surface [118]. N_2 is generally used as probe molecule because of its low price, non-toxicity, inertness and small size (beneficial to access throughout the solid's porous structure).

The isothermal adsorption at low temperature of N_2 has been explained using different mathematical models, being the one proposed by Brunauer-Emmet-Teller (BET) a fairly accurate approach to explain the gas adsorption (see Eq. S2) [118]. The applicability of the model must be corroborated for each experiment/solid individually.

$$\frac{\left(\frac{p}{p_0}\right)}{\left[\ln\left(\frac{1}{1-p}\right)\right]} = \left(\frac{1}{n_m C}\right) + \left[\frac{(C-1)}{n_m C}\right] \frac{p}{p_0} \quad (\text{Eq. S2})$$

Being: p : the pressure of the inlet N_2 gas, p_0 : the saturation pressure of the solid with that gas at a fixed temperature, n : the amount of gas adsorbed, n_m : monolayer capacity, C : BET empiric factor which gives some hints regarding the efficiency of the solid-gas interaction.

Generally, there is a finite range of pressures (mostly $p/p_0 = 0.05 - 0.3$) in the Eq. S2 can be applied to get a successful fit between the collected data with a linear graph ($\frac{p}{p_0}$ vs $\frac{(\frac{p}{p_0})}{[n(\frac{1-p}{p_0})]}$). From the slope and the intercept of the previous graph, n_m is obtained, and then the surface area can be calculated using Eq. S3 [118]:

$$S_{BET} = n_m N_{av} \sigma_i \quad (\text{Eq. S3})$$

Being: N_{av} Avogadro's number and σ_i the averaged area occupied by N_2 when the monolayer is fully formed. Generally, this value is $\sigma_{N_2} = 0.162 \text{ nm}^2$.

Obviously, each solid material interacts differently with N_2 depending on its physicochemical features. The IUPAC classified the adsorption behavior of the solids within the BET model in 6 different types of adsorption isotherms (types I to VI). More details can be found in [275].

Finally, the Barrett-Joyner-Halenda (BJH) method is used to study the porosity of the solid based on the recorded experimental BET isotherms (especially the desorption branch). This approach is based on the Kelvin equation (Eq. S4) and is valid only under specific conditions: it assumes that the pores are rigid and of regular shape (generally cylindrical) and that there is condensation of N_2 within the pores. Generally, the validity of this method must be corroborated.

$$r_k = \frac{-2\sigma^l g v^l}{RT \ln(\frac{p_0}{p})} \quad (\text{Eq. S4})$$

Being: r_k : Kelvin radius, σ^l : surface tension of the liquid condensate, v^l : N_2 molar volume.

Once the r_k is obtained, the pore radius can be calculated using the Eq. S5:

$$r_p = r_k + t \quad (\text{Eq. S5})$$

Being r_p : pore radius and t : the thickness of the adsorbed film on the pores.

Experimentally, ~ 250 mg of powdered sample were placed in a quartz reactor in a Micromeritics ASAP 2020 apparatus and degassed at 200°C in vacuum for 3 h. Then, the reactor was cooled to -196°C with liquid N_2 , followed by feeding gaseous N_2 at increasing partial pressures and allowing the system to equilibrate each time (for the adsorption branch of the isotherm). Then, the desorption branch was obtained by removing stepwise the adsorbed N_2 . Finally, the surface area of the materials was calculated using Eq. S3 and the pore size was calculated from the desorption branch of the isotherm using the BJH model (Eq. S5).

7.1.5 X-Ray diffraction (XRD)

This is a non-destructive characterization technique used to study the crystallographic structure of the solid materials [118, 276]. This determination is based on the physical phenomena known as diffraction X-rays. When an electromagnetic wave interacts with matter, it can only be diffracted when its wavelength is comparable to the size scale of the body with which it interacts. Considering the X-rays, these can only be diffracted when they interact with the atoms present in the different crystallographic planes of the solids under analysis. The Bragg's Law (Eq. S6) is used to describe each individual diffraction phenomenon.

$$n\lambda = 2d \sin\theta \quad (\text{Eq. S6})$$

Being: n the diffraction order of light, λ the wavelength, d the distance between the different crystallographic planes producing the diffraction and θ is the incidence angle of the X-rays with respect to the normal.

By using monochromatic X-rays, it is possible to calculate the distance d between the different crystallographic planes. Then, the distance d can be linked with the cell parameter (a) of a particular solid phase: for example, Eq. S7 relates the previous for a perfect solid cubic system (such as NiO single crystal). This information is useful to determine changes in the cell structure when including additional elements in a solid.

$$d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}} \quad (\text{Eq. S7})$$

Being h , k and l the different Miller indexes. Combining equations Eq. S6 and Eq. S7:

$$\sin^2\theta = \frac{\lambda^2 (h^2 + k^2 + l^2)}{4a^2} \quad (\text{Eq. S8})$$

Thus, the different crystallographic planes responsible for the diffractions can be identified using Eq. S8. The resolution of the previous equation will be more complex when increasing the complexity of the crystal cell structure (for example, comparing a simple cubic with an orthorhombic crystal structure) and/or analyzing amorphous solids with many defects in their structures [276]. Apart from that, due to the constructive or destructive interaction between the diffracted X-rays, some crystallographic planes are displayed more intense than others (and some are even not observed) in the diffractograms. However, this technique is powerful enough to get valuable insights regarding the crystallographic nature of the sample under study.

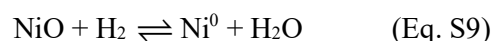
Experimentally, a small amount (5 – 10 mg) of powder sample is placed over a sample holder inside a Panalytical X'Pert $\theta/2\theta$ -diffractometer. The measurements were done using automatic divergence slits and radiation of Cu $K\alpha_1/\alpha_2$ transitions (40 kV, 40 mA, $\lambda = 0.15406$ nm or 0.154443 nm, respectively). Cu beta-radiation was excluded using a nickel filter foil. The incidence angle was swiped with a scanning speed of 0.005 °/s and the diffracted X-rays were collected with an Xcelerator detector. Signal positions and profiles (diffractograms) were fitted with Pseudo-Voigt function using the HighScore Plus software package (Panalytical). Phase identification was done by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

7.1.6 Temperature-programmed Methods

These methods are used to determine different physicochemical properties of the catalysts (for example, the reducibility, the basicity and the type of coke formed on spent catalysts, for H_2 -TPR, CO_2 -TPD and O_2 -TPO, respectively) at increasing temperatures and under controlled reaction atmospheres. Each of them is described below.

7.1.6.1 Temperature-programmed Reduction using H_2 (H_2 -TPR)

This method determines the amount of reducible species present in a solid material, and the temperature needed for their reduction (i.e., its reducibility). The measurements are done by feeding a diluted reducing gas on the sample, while the temperature is increased (at constant rate) and the signal is continuously recorded using a calibrated thermal conductivity detector (TCD) [118, 277]. The moles of H_2 fed to the reactor are monitored before and after interacting with the sample. For example, the reduction process of NiO to metallic Ni using H_2 can be modelled with Eq. S9. Thus, it is possible to track the number of reducible precursor species present in the sample by correlating them with the number of moles of H_2 consumed during the reduction experiment.



The reducibility of the samples depends on the type of metal, on its particle size, shape and spatial position (i.e., bulk, surface, among others) and on the capacity of the precursor particles to interact with the H₂ molecules and be reduced.

Experimentally, the measurements were done using a 3-Flex apparatus. Around 300 mg of sieved sample (sized between 315 – 500 μm) were loaded in a U-shaped quartz reactor and pretreated at 400 °C (20 K/min) under Ar flow for 30 min to remove any adsorbed species. The sample was then cooled down to room temperature under Ar flow. Finally, 50 mL/min of 5% H₂/Ar were fed at constant heating rate (10 K/min) to 1000 °C, followed by 30 min of isothermal hold under such conditions. The H₂-TPR profiles were obtained, and the H₂ consumptions were calculated based on the obtained peak areas and the calibrated TCD detector.

7.1.6.2 Temperature-programmed Desorption of CO₂ (CO₂-TPD)

This technique is used to determine the basicity of a solid sample, i.e., the amount of acidic CO₂ adsorbed, and temperature needed for its desorption. During the CO₂-TPD experiments, the sample's surface is firstly saturated with a controlled amount of CO₂, and then, the temperature is linearly increased with time. When the thermal energy provided to the sample overcomes the interaction energy between the surface and the adsorbed CO₂, the latter begins to desorb from the surface, and this desorption is monitored using a calibrated detector, for example, a mass spectrometer. In this case, the signal at $m/z = 44$ is tracked during the experiment (which corresponds to the molecular ion peak of CO₂) to quantify the total amount of CO₂ adsorbed/desorbed. Generally, basic samples adsorb more CO₂ than acidic samples, thus, the amount of CO₂ adsorbed during the CO₂-TPD experiment correlates with the basicity of the measured sample and the temperature, to the strength of this adsorption.

Experimentally, approximately 150 mg of the sample were loaded into a U-shaped quartz reactor, hanged in a Micromeritics Autochem 2910 instrument, and reduced under 5%H₂/Ar (50 mL/min) at 700 °C (20 K/min) for 60 min. The sample was cooled to 100 °C under He flow (50 mL/min) and exposed to controlled flow of 1.2% CO₂ in He 50 mL/min for 90 min at 100 °C. The fraction of physisorbed CO₂ was removed by flushing it with He (50 mL/min) for 30 min at 100 °C. Afterwards, the temperature was decreased to 70 °C for 10 min and then ramped to 900 °C using a heating rate of 10 K/min under He flow (50 mL/min) and held for 60 min. The analysis of the effluent gases was performed with a calibrated quadrupole mass spectrometer (Balzers Omnistar).

7.1.6.3 Temperature-programmed Oxidation using O₂ (O₂-TPO)

Generally, during DRM reaction, coke deposition is one of the main reasons for catalyst deactivation. As discussed in section 2.3.1, different types of carbonaceous structures with various degrees of structural order can be formed during reaction, therefore, the oxidation of these carbon species requires different temperatures. In this sense, O₂-TPD technique is used to study the type of the coke deposits formed, and the temperature needed to oxidize them under controlled conditions. This information is valuable for catalyst regeneration, as the temperature needed to oxidize these coke deposits is obtained. Generally, carbon structures with high order (mostly associated to catalyst deactivation) require higher temperatures to be oxidized under an O₂ flow. During the measurements, the amount of O₂ is controlled before and after interacting with the sample, and the evolution of the oxidation of coke is followed using a mass spectrometer. In that case, the signals of $m/z = 28$ and 44 are monitored (related to the CO and CO₂ molecular ion peaks, respectively).

Experimentally, approximately 10 mg of the spent catalysts were loaded into a U-shaped quartz reactor, hanged in a Micromeritics Autochem 2910 instrument and pretreated at 200 °C with He (50 mL/min) for 60 min to remove adsorbed water. Then, the sample was cooled to room temperature and subsequently ramped to 800 °C under a flow of 5%O₂/He (50 mL/min) with 10 K/min and held for 60 min. The reaction was monitored using a calibrated quadrupole mass spectrometer detector (Balzers Omnistar).

7.1.7 (Scanning) transmission electronic microscopy ((S)TEM)

The transmission electronic microscopy (TEM) is used to evaluate the metal particle size, the morphology and the distribution of the nanoparticles throughout a support material [118, 276]. For this purpose, a flux of electrons at adjustable acceleration voltage (for example, 200 kV) is passed through a sufficiently thin sample. The electrons interact with the analyzed material, i.e., these can be absorbed, scattered (deflection from its original path), etc., and these interactions create different signals. For the TEM, the electrons after interacting with the sample are collected and focused to a special detecting system, which turns the current of electrons into an image. The scanning mode of TEM (STEM) is used to identify the different sections of the sample 'pixelwise', which means that tiny sections of the sample are analyzed at a time (typical spot size of 0.05 – 0.2 nm), which provides a better resolution to the resulting image (atomic scale).

It is possible to differentiate between the parts (and composition) of a solid sample due to how they interact with the charged particles coming from the beam. In this sense, different properties such as the atomic number of the measured element (Z), its electronic environment and oxidation state, different crystallographic features (ordered molecular arrangements), etc., contribute to this differentiation (or contrast) during the imaging process [276]. Generally, heavy elements (with high Z) display a brighter intensity in the images (they can scatter the incident electrons better), and therefore, these can be better identified, especially when the support has light atoms (lower Z). In terms of detection systems, two modes of STEM are generally used, which correspond to analysis of the unscattered (Bright Field, BF) or scattered (High-Angle Annular Dark Field, HAADF) electrons. In the first one, the background is observed brighter and the sections which cause a stronger modification of the incident beam are displayed darker, while in dark field, the background is observed darker, while the different sections of the solid are generally displayed brighter.

The interaction between the incident electron beam and the materials can be used for the identification of the samples' chemical composition/elemental mapping (qualitative) and/or the oxidation states of the constitutive elements via coupled spectroscopic techniques. Firstly, the Energy-Dispersive X-ray spectroscopy (EDX) is used to analyze the X-rays emitted by the different elements present in the samples. These elements emit X-rays as a radiative energy-loss mechanism after the interaction with the incident high energy electron beam. As the wavelength/energy of the emitted X-rays depend on each element (i.e., the energy difference between specific electronic states), EDX could be used as a fingerprint for the identification of the elements in the sample. On the other hand, the oxidation state can be determined using the Electron Energy Loss Spectroscopy (EELS). In this case, some electrons of the beam might lose energy after inelastic scattering with the electrons of the sample. After interaction, the remanent energy of the scattered electrons is measured, and if there was any loss of their energy, it is, in the end, related to the different constitutive elements and their oxidation states. Thus, the composition and electronic properties of the elements can be elucidated.

Experimentally, a small portion (~ 5 mg) of selected *ex situ* reduced and spent samples were firstly dry deposited on a holey carbon supported Cu-grid (mesh 300) and inserted within the JEM-ARM200F (JEOL, Corrector: CEOS) apparatus. The measurement requires vacuum conditions to avoid the absorption/scattering of electrons by air molecules before and after interacting with the sample. The solids were firstly irradiated with an electron beam at 200 kV, and the transmitted electrons and the emitted X-rays were collected with different detection systems (for general imaging: High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF) detectors, for EDX: a silicon drift detector dry SD60GV, and for EELS: an Enfinium ER (GATAB) electron energy-loss spectrometer with dual EELS), and the signals were transformed into images and different spectra. The Annular Dark Field detector was used for position control for EELS acquisition. Then, the particle size is obtained after rational evaluation of many representative images, the same as the morphology and particle distribution. The catalysts' elemental mapping/distribution was obtained using EDX. Finally, the EEL spectrum is compared to reference spectra to identify the different elements and their oxidation states.

7.1.8 X-Ray photoelectron spectroscopy (XPS)

This characterization method is used to study the composition and oxidation state of the species present on the catalysts' surface. Basically, this technique is based on the photoelectric effect, in which a solid material ejects electrons from its surface whenever is irradiated with a light source of appropriate energy (in this case, a source of X-rays). These electrons have consequently discrete values of kinetic energy, which is measured with a XPS spectrometer, and it is then used to calculate their binding energy. The process can be modelled with Eq. S10 [276, 278]. Obviously, only those photoelectrons which escaped the sample's surface can be detected, which are generally within a < 10 nm depth range (the technique's detection limit). Therefore, by going deeper than 10 nm from the surface, the emitted photoelectrons are more likely to undergo inelastic collisions, be re-absorbed and excite other atoms in the sample, etc., and thus, these are more difficult to be detected.

$$E_b = h\nu - E_k - \phi \quad (\text{Eq. S10})$$

Being: E_b : binding energy, h : Planck's constant, ν : frequency of the light source used, E_k : kinetic energy of the ejected electron, ϕ is a constant related to how the analyzed element can be ionized, i.e., related to the ejected electrons.

Each element emits photoelectrons at specific binding energies, and therefore, this technique can be used to identify the elements present on a solid material's surface. Moreover, the energy provided by the X-ray source is sufficient to eject photoelectrons from different electronic shells, thus, the XP spectrum is a compendium of several signals related to the ionization of different elements and also to different electronic shells of them. The elemental identification is generally carried out by the analysis of the photoemission of the inner electrons (for example, 1s shell), while the photoemission of the outer shells (for example, 2p shell) allows the identification of the oxidation states of the components. Moreover, XPS can be used to quantify the elements on the surface, as the number of the ejected photoelectrons depends (at least theoretically) on the number of atoms ionized (thus, their concentration) present on the surface of the analyzed material.

Sometimes, the spectra show additional signals known as the shake-up satellites arising from the interaction between the ejected photoelectron and other valence electrons. Thus, the ejected photoelectron might lose a fraction of its kinetic energy during this interaction, which is then observed as these extra signals in the XP spectra. As the binding energy depend on the surface state and the device used for the measurement, the apparatus must be calibrated beforehand. Generally, an additional element is used for calibration of the signals, as it is the case for the ionization of adsorbed C 1s peak at 285 eV. Finally, the charge of the measured material is generally compensated during the measurement, as the sample is continuously losing electrons. For this purpose, external electrons and/or Ar^+ are used.

Experimentally, a small amount (~ 10 mg) of selected *ex situ* reduced catalyst was deposited on a stainless-steel holder with conductive double-sided adhesive carbon tape and inserted in a ESCALAB 220iXL (ThermoFisher Scientific) spectrophotometer. The signal of C 1s core level at 284.8 eV (C-C and C-H bonds) was used to calibrate the detectors. The measurements were performed with charge compensation using a flood electron system combining low energy electrons and Ar^+ ions ($p_{\text{Ar}} = 1.10^{-7}$ mbar). For quantification, the peaks were deconvoluted with Gaussian-Lorentzian curves using the software Unifit 2021. The peak areas were normalized by the transmission function of the spectrometer and the element specific sensitivity factor of Scofield [279].

7.1.9 Electronic paramagnetic resonance spectroscopy (EPR)

This characterization method was used to study the oxidation state of the active Ni species, the same as for the identification of structural defects in the powder catalysts, e.g., oxygen vacancies, after applying different pre-treatments (specified below) and magnetic fields (within the microwave energy region).

This technique studies the transitions between magnetic levels of unpaired electrons of certain nuclei provoked after applying an external magnetic field (B_0) of known frequency. In this sense, each electron

has a defined magnetic moment ($m_s = +1/2$ or $-1/2$) and spin quantum number ($s = 1/2$), thus, applying a magnetic field of appropriate energy would force the electrons to align themselves with respect to the applied magnetic field. For example, the alignment can be parallel or anti-parallel (i.e., spin-up or spin-down, respectively) vs. the applied magnetic field, having both possibilities a discrete value of energy (described by Eq. S11) [280].

$$E = m_s g_e \mu_B B_0 \quad (\text{Eq. S11})$$

Being m_s : magnetic moment of the electron ($m_s = +1/2$ or $-1/2$), g_e : free electron's g-factor = 2.0023 (no units), μ_B : Bohr magneton ($9.27401 \cdot 10^{-28}$ J/G) and B_0 : applied magnetic field (G).

Thus, the transition between these magnetic states occurs when the energy of the applied magnetic field matches the energy of $\Delta E = g_e \mu_B B_0$. However, other charged nuclei like ions or other unpaired electrons in the surroundings of the electron under study also possess intrinsic magnetic fields, thus, these can alter the magnetic properties of the system [281]. Consequently, the latter interaction gives rise to many other magnetic levels, thus, more magnetic transitions can take place and be recorded in the EPR spectra, augmenting its complexity. Such magnetic interaction between the nuclei and the electrons depends on their position and relative orientation vs. the magnetic field of the measured electron, therefore, this interaction is called anisotropic. The latter anisotropic interaction gives rise to the fine structure of the EPR spectra, i.e., several absorption lines at different (but close) B_0 with different intensity. After a certain time, the electrons promoted to higher energy values return to the ground level by releasing the excess of energy, which is known as 'relaxation'. The unpaired electrons of some metals (for example, Ni) have very short relaxation times, thus, the measurements have to be performed at low temperature (-173 °C) to produce meaningful EPR spectra [282].

Consequently, by swiping the strength of the applied magnetic field (at low temperature), a compendium of signals is recorded at different B_0 values, which are basically fingerprints of the different chemical species present in the sample. By doing so, the values of B_0 at which the absorption took place provides valuable information regarding the oxidation states of the absorbing species (for example, Ni^+ or Ni^{3+}), the coordination of complexes, or to the presence of oxygen vacancies, among others [282].

As a side note, due to the importance of the maximum value of the absorption in the EPR spectra at certain B_0 , the first derivative of the absorption spectra was plotted against the applied B_0 . Consequently, 'EPR intensity' (graph displayed in chapter 4.2) refers to the first derivative of the absorption, and not to the absorption intensity itself. Finally, the g value can be calculated by using Eq. S11, as all other parameters are constant and known at a specific absorption maximum.

Experimentally, approximately 7 mg of catalyst were diluted with 30 mg of quartz and loaded into a home-made quartz plug-flow reactor (3.0 mm inner diameter and 0.5 mm wall thickness). The reactor was placed in an X-band cw-spectrometer ELEXSYS 500-10/12 (Bruker) with a microwave power of 6.3 mW, a modulation frequency of 100 kHz, and modulation amplitude up to 5 G. The reactor was connected to a gas-dosing device with mass flow controllers (Bronkhorst) at the inlet and a quadrupole mass spectrometer (Omnistar, Pfeiffer Vacuum GmbH) at the outlet, for online product analysis. Thus, for the pre-heating experiments, the catalyst was firstly heated under Ar (25 mL/min) to 300 °C for 90 min, followed by cooling down (under Ar) for low temperature measurements (at 25 °C and -173 °C, respectively). Then, the *in situ* reduced measurements were done after reducing at 300 °C for 30 min with 100% H_2 (25 mL/min), followed by cooling down under H_2 for low temperature measurements (at 25 °C and -173 °C, respectively).

7.2 Description of the setup used to perform the experiments, representative chromatograms obtained using the developed separation method and investigation of the activation conditions on the reforming performance (sections 3.3 and 3.3.1)

The gases used for the catalyst pre-treatment and different reforming and regeneration tests were dosed using calibrated mass flow controllers (MFC, Brooks and Bronkhorst High-Tec), while deionized water was fed using a calibrated Shimadzu HPLC pump (model LC-20AT).

All the catalytic activity tests were performed in fixed-bed quartz reactors (length = 20.2 cm, volume = 14.1 mL, inner diameter = 9.6 mm) using an isolated electrical furnace (Applied Tests Systems Inc., max. temperature 1000 °C). The temperature was monitored using a thermocouple embedded in a quartz guide tube placed in the middle of the catalyst bed, which consisted of 50 mg of catalyst powder (sized < 180 µm) diluted with 2 g (1:40) of inert quartz sized between 0.5 – 0.8 mm. Two quartz wool plugs (20 mg each) sandwiched each extreme of the catalyst bed.

The setup was connected to an on-line Shimadzu GC-2030 (previously calibrated for all reactants using test gases and H₂O) to analyze feed and product gases during operation in real time. The GC was equipped with two analytical lines, two barrier discharge ionization detectors (BID) and three columns: Shimadzu RT-Plot-U-BOND (30 m × 0.53 mm × 20 µm) and a switchable combination of Shimadzu RT-Molsieve 5A (30 m × 0.53 mm × 50 µm) to separate H₂, N₂, H₂S, Ar, O₂, N₂, CH₄ and CO in line 1, and Shimadzu Volatile Amine (30 m × 0.32 mm × 5 µm) to separate CO₂, NH₃, H₂O in line 2. Helium was used as a carrier gas. Sampling was performed every 15 min during the tests without H₂O or NH₃, while sampling every 29 min was done during tests with these 2 compounds. The gas lines, GC in- and outlet, valves, sample loop, etc., were heated to T > 120 °C using additional heating devices (heating bands and oven in the GC sample loop chamber) to avoid water condensation.

A schematic representation of the setup used for conducting the catalytic tests and representative chromatograms obtained using the developed separation method are displayed in Figure A 1 a-b, respectively.

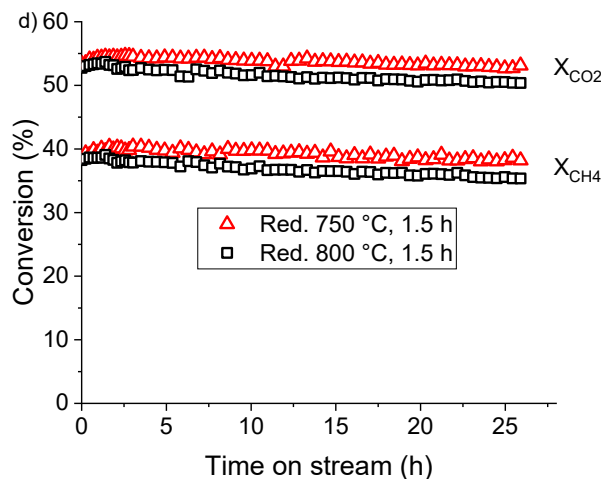
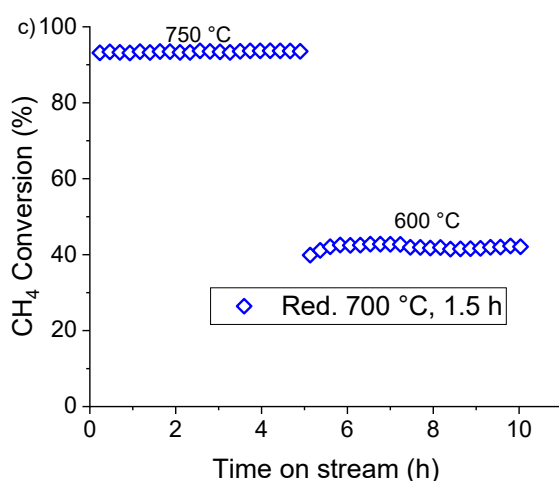
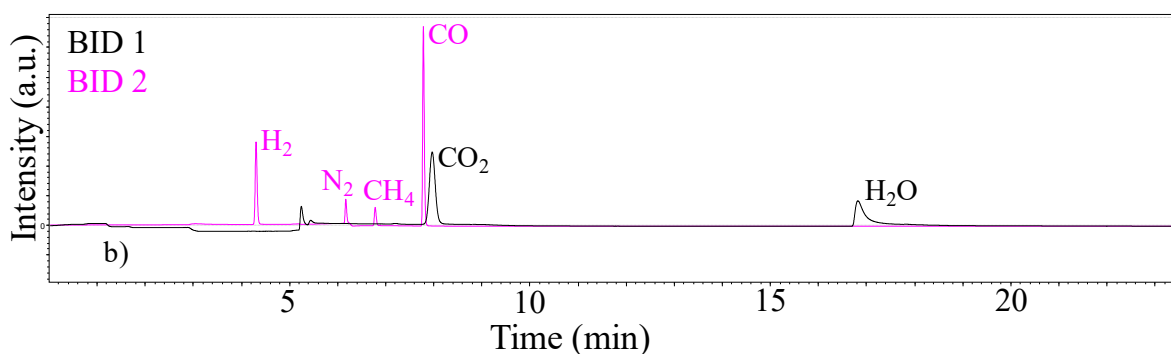
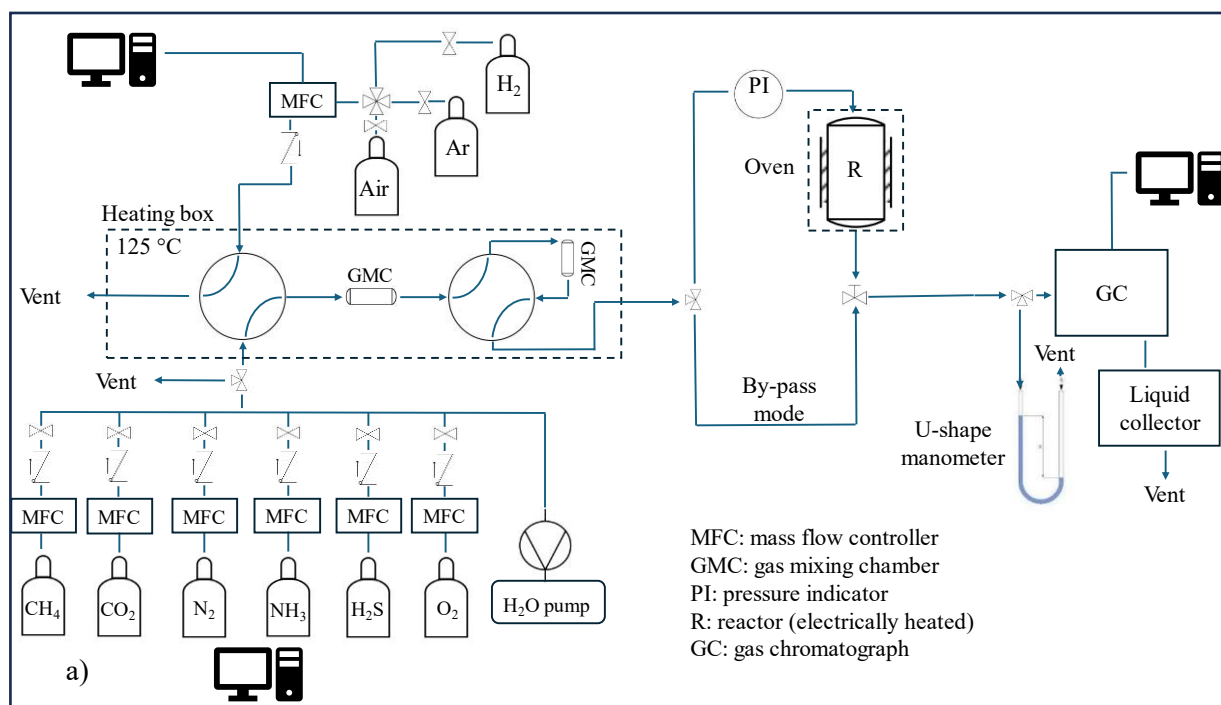


Figure A 1. a) Schematic representation of the setup used throughout this work. b) Overlay of representative chromatograms obtained using the developed separation method for target reforming reactants and products. The black chromatogram was recorded in detector BID 1 (after separation using Shimadzu Volatile Amine for polar compounds), while the pink chromatogram was recorded in detector BID 2 (after separation using Shimadzu RT-Molsieve 5A for permanent gases and less polar compounds). c) X_{CH_4} at 600 °C and 750 °C after activation at $T_{\text{red}} = 700$ °C with 50 mL/min H_2 for 1.5 h and d) X_{CH_4} and X_{CO_2} at 600 °C after activation at $T_{\text{red}} = 750$ °C (red triangles) and $T_{\text{red}} = 800$ °C (black squares) with 50 mL/min H_2 for 1.5 h over TOS. Reaction conditions: catalyst: Ni(CA-5.5)/S2, $\text{CH}_4/\text{CO}_2/\text{N}_2 = 45:45:10$ vol.%, $p = 1$ bar, $m_{\text{cat}} = 50$ mg, GHSV = 170 L/(g_{cat}·h).

Finally, the impacts of the activation conditions on the DRM activity and stability are discussed. As introduced in section 3.3.1, lower reduction temperatures compared to those measured with H₂-TPR were used for activating all reforming catalysts. Considering that the developed materials were highly competitive in DRM vs. many other samples reported in the literature (see chapters 4.1, 4.2 and 4.3), it was demonstrated that the developed activation procedures were highly efficient. Through this approach, particle sintering is arguably prevented due to the lower activation temperatures used, which ultimately prolongs the reforming activity over TOS.

The catalyst Ni(CA-5.5)/S2 was used to develop the activation procedures, as it displayed very high T_{red} and excellent catalytic performance (the reader is referred to sections 4.1.2.1 and 4.1.2.2 for further details). Firstly, lack of activity was recorded at $T = 600\text{ }^{\circ}\text{C}$ after reducing the catalysts at $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h with H₂ (not shown). The original idea was to screen the catalysts from low to high temperatures, however, all catalysts were inactive for DRM after this activation protocol. Alternatively, and by keeping the $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h, the order of the reaction temperature was inverted, i.e., the screening started from high ($T = 750\text{ }^{\circ}\text{C}$) to low temperatures ($T = 600\text{ }^{\circ}\text{C}$), which led to high activity at both consecutive temperatures (see Figure A 1 c).

Secondly, as the long-term runs were performed at low temperature ($T = 600\text{ }^{\circ}\text{C}$), we wanted to avoid exposing the catalysts to the reaction conditions for 5 h at $T = 750\text{ }^{\circ}\text{C}$ to prevent particle sintering. The material was then reduced at higher temperatures for shorter times (1.5 h) with H₂ before the long-term tests at $T = 600\text{ }^{\circ}\text{C}$. Interestingly, reducing the catalyst at $T_{\text{red}} = 750\text{ }^{\circ}\text{C}$ for 1.5 h led to a more active and stable material, than by reducing it at $T_{\text{red}} = 800\text{ }^{\circ}\text{C}$ for the same time (see Figure A 1 d). It could be argued that higher T_{red} fostered agglomeration of more Ni sites, which negatively affected the catalyst stability. The reasons behind catalyst deactivation and their link to the different reduction temperatures were not investigated in detail through catalyst characterization, but these were evaluated on a catalytic basis instead. Thus, to appropriately activate the developed catalysts for low temperature DRM, a high temperature step ($T = 750\text{ }^{\circ}\text{C}$) with: i) H₂ for 1.5 h or ii) with the reaction conditions for 5 h was needed.

Obviously, lower activation temperatures did not reduce all Ni²⁺ species; however, high and stable activity were reached anyways. The role of Ni⁰/Ni²⁺ on the reforming activity and stability should be further investigated.

7.3 Analysis of solutions used to prepare the catalysts of Group II (section 4.1.2)

The formation of different complexes in solution depends on the nature of metals and ligands selected, as well as the preparation conditions used. By following the discussion provided in section 4.1.2, different Ni complexes are expected to form at the different preparation pH chosen.

The impregnation solutions prepared at the different pH were analyzed with UV-vis spectrophotometry (see Figure A 2). The electronic spectra of the samples showed two main bands in the studied region: at wavelengths of 350 – 420 nm (high energy band) ascribed to the electronic transition ${}^3\text{A}_{2g}({}^3\text{F}) \rightarrow {}^3\text{T}_{1g}({}^3\text{P})$ and at 550 – 800 nm (middle energy band) due to ${}^3\text{A}_{2g}({}^3\text{F}) \rightarrow {}^3\text{T}_{1g}({}^3\text{F})$ transition, as expected for d⁸ transition elements in an octahedral field [283-285]. The high energy band displayed a shift towards lower wavelengths (from $\lambda \sim 395\text{ nm}$ at $\text{pH} < 2$ to $\lambda \sim 380\text{ nm}$ at $\text{pH} = 9$) when the pH was higher than 2, indicating the formation of complexes other than $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. At the same time, its intensity increased when the pH was raised. On the other hand, the shape and position of the middle energy band (560 – 800 nm) were strongly distorted when changing the conditions. The spectra of the solutions prepared at $\text{pH} = 1 - 2$ matched accordingly with the spectra of the reference Ni²⁺ aqueous solution. For these samples, a broad flat band with small humps at 650 and 720 nm was observed, which remained unchanged at both pH values, indicating that the complex nature ($[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$) did not change. By increasing the pH to 4, both the main band (650 nm) and the shoulder (720 nm) experienced a slight red shift to $\lambda \sim 655\text{ nm}$ and $\lambda \sim 727\text{ nm}$, respectively. The overall absorbance also increased, which suggested the formation of possibly more absorptive $[\text{Ni}(\text{HCA})(\text{H}_2\text{O})_4]$, $[\text{Ni}(\text{CA})(\text{H}_2\text{O})_4]^-$ and $[\text{Ni}(\text{HCA})(\text{CA})(\text{H}_2\text{O})_2]^{3-}$ complexes. Moreover, there were substantial differences between the spectra

recorded at pH = 4 and 5.5. At both pH, the main band at 650 nm was observed, in line with the formation of $[\text{Ni}(\text{CA})(\text{H}_2\text{O})_4]^-$ in high concentrations, but the shoulder centered at $\lambda \sim 720$ nm decreased its intensity for pH 5.5, which might be due to the lower concentration of $[\text{Ni}(\text{HCA})(\text{H}_2\text{O})_4]$, which turned $[\text{Ni}(\text{CA})(\text{H}_2\text{O})_4]^-$ the predominant species. Moreover, the presence of the complex $[\text{Ni}(\text{CA})_2(\text{H}_2\text{O})_2]^{4-}$ (absent at pH = 4) might have contributed to the recorded spectroscopic differences. Finally, at pH = 9, the absorbance increased further caused by the competitive formation of other Ni-CA and Ni-NH₃ complexes absent at acidic impregnation pH values.

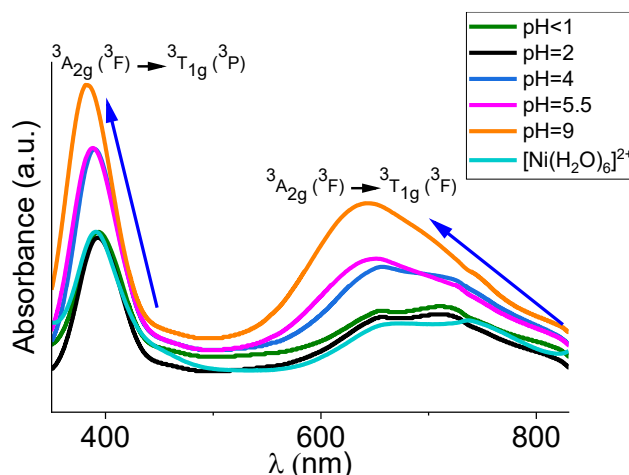


Figure A 2. UV-Vis spectra measured for the preparation solutions of catalysts of Group II.

7.4 Calculated fractions of complexes formed (using CA, Gly, TA or DTPA) during the preparation of catalysts of Group III (section 4.1.3)

To calculate the speciation of different complexes, the preparation conditions at two stages of the impregnation were considered. These were performed considering the initial preparation pH (determined by sole addition of the different acidic complexing agents in aqueous solution) and at the pH measured after 16 h of impregnation (determined by hydrolysis of MgO and formation of $\text{Mg}(\text{OH})_2$). The fractions of metal complexes formed at the different conditions for CA, Gly, TA and DTPA were calculated using Visual MINTEQ 3.1 software [198] and are displayed in Table A 1-4, respectively.

Table A 1. Calculated distributions of the different species in the precursor solution for the system Ni-CA using Visual MINTEQ 3.1 software [198]. $[\text{Ni}^{2+}] = 0.014 \text{ M}$, $[\text{CA}] = 0.021 \text{ M}$, $[\text{NO}_3^-] = 0.028 \text{ M}$, $[\text{Mg}^{2+}] = 0.006 \text{ M}$, $I \approx 0.1 \text{ M}$ (ionic strength, calculated as $\frac{1}{2}\sum(c_i z_i^2)$, being c_i : the molar concentration of the considered specie, and z_i : its ionic charge). Republished with permission from [199]. Copyright 2024 Elsevier.

pH = 1.91			pH = 9.00		
Component	% of total concentration	Species name	Component	% of total concentration	Species name
Citrate ³⁻	0.022	MgH ₂ -citrate ⁺	Citrate ³⁻	1.502	Citrate ³⁻
	0.021	H-citrate ²⁻		49.955	Ni-citrate ⁻
	6.961	H ₂ -citrate ⁻		31.831	Ni-(citrate) ₂ ⁴⁻
	87.749	H ₃ -citrate		16.705	Mg-citrate ⁻
	0.602	NiH-citrate	Ni ²⁺	1.059	Ni ²⁺
	4.436	NiH ₂ -citrate ⁺		0.064	NiOH ⁺
	90.105	Ni ²⁺		0.039	Ni(OH) ₂ (aq)
Ni ²⁺	2.329	NiNO ₃ ⁺		0.028	NiNO ₃ ⁺
	0.903	NiH-citrate		74.933	Ni-citrate ⁻
	6.653	NiH ₂ -citrate ⁺		23.873	Ni-(citrate) ₂ ⁴⁻
NO ₃ ⁻	98.835	NO ₃ ⁻	NO ₃ ⁻	99.986	NO ₃ ⁻
	1.165	NiNO ₃ ⁺		0.014	NiNO ₃ ⁺
Mg ²⁺	99.248	Mg ²⁺	Mg ²⁺	44.237	Mg ²⁺
	0.019	MgH-citrate		0.08	MgOH ⁺
	0.733	MgH ₂ -citrate ⁺		55.683	Mg-Citrate ⁻

Table A 2. Calculated distributions of the different species in the precursor solution for the system Ni-Gly using Visual MINTEQ 3.1 software [198]. $[\text{Ni}^{2+}] = 0.014 \text{ M}$, $[\text{Gly}] = 0.021 \text{ M}$, $[\text{NO}_3^-] = 0.028 \text{ M}$, $[\text{Mg}^{2+}] = 0.0044 \text{ M}$, $I \approx 0.1 \text{ M}$ (ionic strength, calculated as $\frac{1}{2}\sum(c_i z_i^2)$, being c_i : the molar concentration of the considered specie, and z_i : its ionic charge).

pH = 2.00			pH = 9.00		
Component	% of total concentration	Species name	Component	% of total concentration	Species name
Glycine ⁻	1.096	MgH-glycine ²⁺	Glycine ⁻	0.242	Glycine ⁻
	27.325	H-glycine (aq)		5.531	Ni-glycine(OH) ₂ ³⁻
	71.57	H ₂ -glycine ²⁺		0.124	Mg-(glycine) ⁺
Ni ²⁺	97.578	Ni ²⁺	Ni ²⁺	0.166	H-glycine (aq)
	2.408	NiNO ₃ ⁺		0.011	MgH-glycine ²⁺
	0.014	Ni-glycine ⁺		28.117	Ni-glycine ⁺
NO ₃ ⁻	98.796	NO ₃ ⁻	Ni ²⁺	65.809	Ni-(glycine) ₂ (aq)
	1.204	NiNO ₃ ⁺		3.625	Ni ²⁺
Mg ²⁺	94.77	Mg ²⁺	Mg ²⁺	2.766	Ni-glycine(OH) ₂ ³⁻
	5.23	MgH-glycine ²⁺		1.864	NiOH ⁺
				0.124	Ni(OH) ₂ (aq)
			NO ₃ ⁻	0.089	NiNO ₃ ⁺
				42.175	Ni-glycine ⁺
				49.357	Ni-(glycine) ₂ (aq)
			Mg ²⁺	99.956	NO ₃ ⁻
				0.044	NiNO ₃ ⁺
				96.662	Mg ²⁺
				0.592	Mg-glycine ⁺
				2.693	MgOH ⁺
				0.053	MgH-glycine ²⁺

Table A 3. Calculated distributions of the different species in the precursor solution for the system Ni-TA using Visual MINTEQ 3.1 software [198]. $[\text{Ni}^{2+}] = 0.014 \text{ M}$, $[\text{TA}] = 0.021 \text{ M}$, $[\text{NO}_3^-] = 0.028 \text{ M}$, $[\text{Mg}^{2+}] = 0.006 \text{ M}$, $I \approx 0.1 \text{ M}$ (ionic strength, calculated as $\frac{1}{2}\sum(c_i z_i^2)$, being c_i : the molar concentration of the considered specie, and z_i : its ionic charge). Republished with permission from [199]. Copyright 2024 Elsevier.

pH = 1.89			pH = 9.00		
Component	% of total concentration	Species name	Component	% of total concentration	Species name
Tartrate ²⁻	0.059	Tartrate ²⁻	Tartrate ²⁻	42.858	Tartrate ²⁻
	0.012	Mg-tartrate		6.646	Mg-tartrate
	0.467	MgH-tartrate ⁺		50.495	Ni-Tartrate
	8.371	H-tartrate ⁻	Ni ²⁺	21.594	Ni ²⁺
	89.404	H ₂ -tartrate		1.299	NiOH ⁺
	0.305	Ni-Tartrate		0.79	Ni(OH) ₂ (aq)
	1.384	NiH-Tartrate ⁺		0.01	Ni(OH) ₃ ⁻
Ni ²⁺	95.013	Ni ²⁺		0.563	NiNO ₃ ⁺
	2.454	NiNO ₃ ⁺		75.743	Ni-Tartrate
	0.457	Ni-Tartrate	NO ₃ ⁻	99.718	NO ₃ ⁻
	2.076	NiH-Tartrate ⁺		0.282	NiNO ₃ ⁺
NO ₃ ⁻	98.773	NO ₃ ⁻	Mg ²⁺	77.705	Mg ²⁺
	1.227	NiNO ₃ ⁺		22.154	Mg-Tartrate
Mg ²⁺	98.404	Mg ²⁺		0.141	MgOH ⁺
	0.038	Mg-Tartrate			
	1.557	MgH-Tartrate ⁺			

Table A 4. Calculated distributions of the different species in the precursor solution for the system Ni-DTPA using Visual MINTEQ 3.1 software [198]. $[\text{Ni}^{2+}] = 0.014 \text{ M}$, $[\text{DTPA}] = 0.021 \text{ M}$, $[\text{NO}_3^-] = 0.028 \text{ M}$, $[\text{Mg}^{2+}] = 0.02 \text{ M}$, $I \approx 0.1 \text{ M}$ (ionic strength, calculated as $\frac{1}{2}\sum(c_i z_i^2)$, being c_i : the molar concentration of the considered specie, and z_i : its ionic charge). Republished with permission from [199]. Copyright 2024 Elsevier.

pH = 1.00			pH = 9.00		
Component	% of total concentration	Species name	Component	% of total concentration	Species name
DTPA ⁵⁻	0.154	Ni ₂ -DTPA ⁻	DTPA ⁵⁻	0.037	NiH-DTPA ²⁻
	1.649	NiH-DTPA ²⁻		66.63	Ni-DTPA ³⁻
	34.246	H ₇ -DTPA ²⁺		0.296	MgH-DTPA ²⁻
	52.77	H ₆ -DTPA ⁺		33.037	Mg-DTPA ³⁻
	10.351	H ₅ -DTPA	Ni ²⁺	0.055	NiH-DTPA ²⁻
	0.817	H ₄ -DTPA ⁻		99.945	Ni-DTPA ³⁻
	0.013	H ₃ -DTPA ²⁻	NO ₃ ⁻	100	NO ₃ ⁺
Ni ²⁺	94.621	Ni ²⁺	Mg ²⁺	58.717	Mg ²⁺
	2.444	NiNO ₃ ⁺		0.107	MgOH ⁺
	0.462	Ni ₂ -DTPA ⁻		0.366	MgH-DTPA ²⁻
	2.473	NiH-DTPA ²⁻		40.81	Mg-DTPA ³⁻
NO ₃ ⁻	98.778	NO ₃ ⁻			
	1.222	NiNO ₃ ⁺			
Mg ²⁺	100	Mg ²⁺			

7.5 Structure, chemical and electronic surface properties, and morphology of catalysts of Group III (section 4.1.3.1)

Using different chelating agents during preparation did not provoke modifications in the catalysts' crystalline structure detectable using XRD, as evidenced by the almost identical diffractograms of the *ex situ* reduced catalysts of Group III (see Figure A 3). Thus, only the support's phases (MgO and MgAl₂O₄) were identified in these catalysts. The lack of reflexes associated to Ni phases was ascribed to any or combination of the following factors: i) incorporation of Ni into the support's parental phases, ii) formation of NiO-MgO (which have almost identical crystalline structure), iii) low Ni content, and/or iv) very fine distribution of Ni species mediated by the chelating agents used in the preparation.

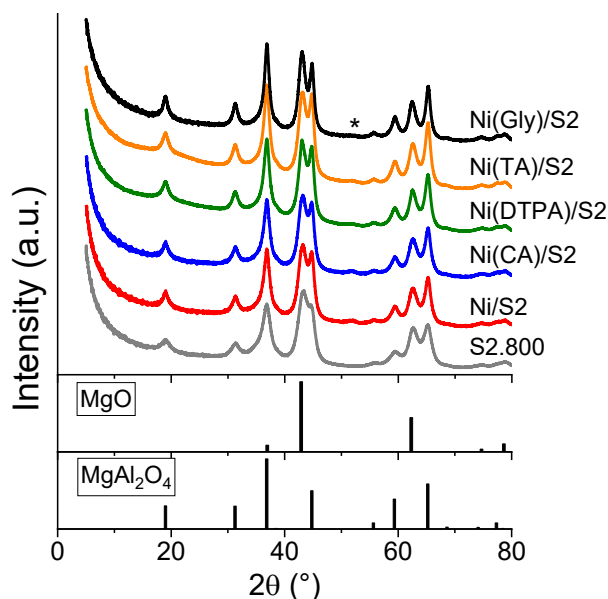


Figure A 3. Diffractograms of *ex situ* reduced catalysts (at $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h) of Group III. Legend: “*”: metallic Ni^0 (cubic, ICDD: 00-004-0850). Republished with permission from [199]. Copyright 2024 Elsevier.

However, the different chelating agents impacted on the distribution of the active surface Ni^0 sites and their interaction with the support. Thus, the electronic properties of surface Ni species and the resulting interaction with the support were modified according to the ligand used during preparation (see Figure A 4), the same as the concentration of surface Ni species (see section 4.1.3.1). Thus, it was found that the sample that showed the highest BE of $\text{Ni}_{3/2}^0$ photoelectrons (i.e., $\text{Ni}(\text{TA})/\text{S2}$) also displayed the highest reduction temperature (thus, strongest MSI; see Figure 4-15) among the series, which indicated good agreement between both characterization techniques.

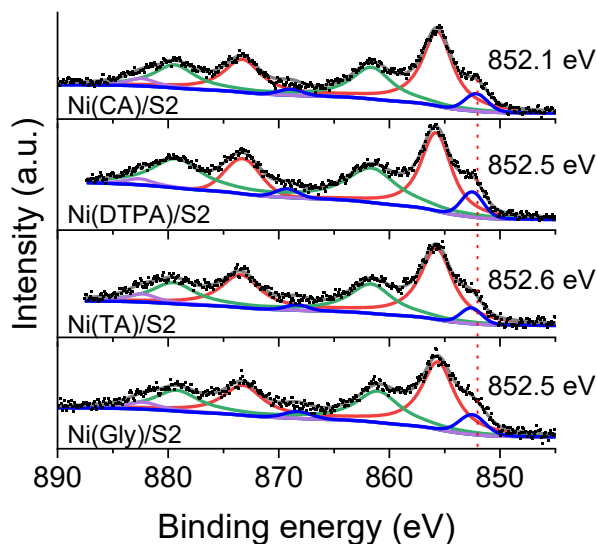


Figure A 4. XP spectra of *ex situ* reduced (at $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h) $\text{Ni}(\text{CA})/\text{S2}$, $\text{Ni}(\text{DTPA})/\text{S2}$, $\text{Ni}(\text{TA})/\text{S2}$ and $\text{Ni}(\text{Gly})/\text{S2}$. Republished with permission from [199]. Copyright 2024 Elsevier.

Additionally, the morphology and distribution of Ni particles of the *ex situ* reduced catalysts (at $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h) were investigated using TEM (see Figure A 5). As discussed in section 4.1.3.1, the catalysts prepared using different chelating agents showed similar features to those of the catalysts of Group II (see section 4.1.2.1 for more details), which was corroborated by imaging the *ex situ* reduced catalysts of Group III using TEM-HAADF.

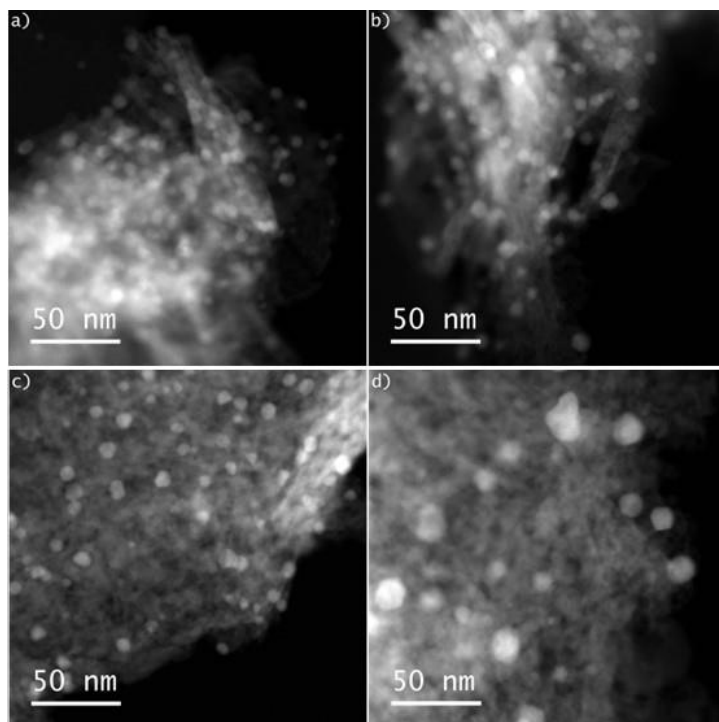


Figure A 5. TEM-HAADF micrographs of *ex situ* reduced (at $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h): a) Ni(CA)/S2, b) Ni(TA)/S2, c) Ni(Gly)/S2 and d) Ni(DTPA)/S2. Republished with permission from [199]. Copyright 2024 Elsevier.

7.6 Chemical and electronic properties of catalysts of Group IV (section 4.1.4.1)

The surface properties of the promoted catalysts (Group IV) *ex situ* reduced (at $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h) were analyzed using XPS (spectra displayed in Figure A 6). Basically, the electronic properties of surface Ni species, the same as Ni surficial concentration were modified according to the additional metal(s) included during preparation. See section 4.1.4.1 for a deeper discussion regarding the surface composition and electronic properties of these catalysts.

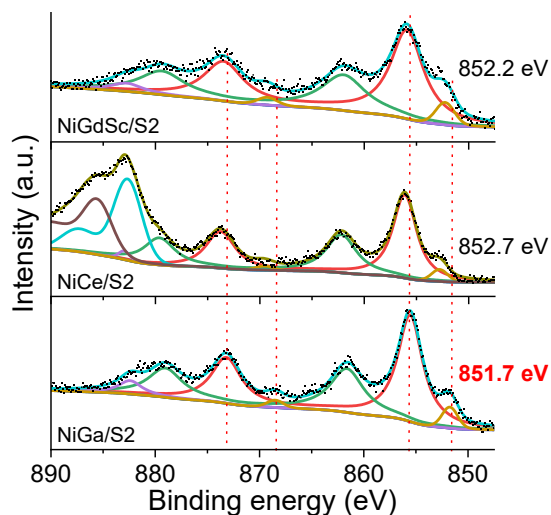


Figure A 6. XP spectra of *ex situ* reduced (at $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h) NiGa/S2, NiCe/S2 and NiGdSc/S2.

7.7 Morphology of spent NiLaGa/S2 after 25 h TOS in DRM (section 4.1.4.3)

As discussed in section 4.1.4.3, not only La single sites, but also La agglomerates were observed using TEM-HAADF in the recovered spent catalyst NiLaGa/S2 after 25 h TOS in DRM (see Figure A 7). The red arrows were inserted in the previous image to highlight the agglomerated La species.

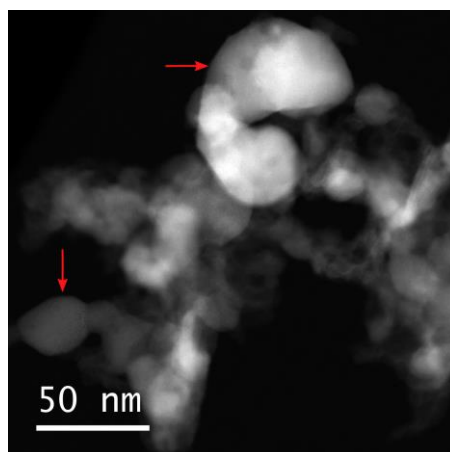


Figure A 7. TEM-HAADF micrograph of spent NiLaGa/S2 after 25 h TOS in DRM. The red arrows highlight the agglomerated La particles. Reaction conditions: $T_{\text{red}} = 700\text{ }^{\circ}\text{C}$ for 1.5 h, $\text{CH}_4/\text{CO}_2/\text{N}_2 = 45:45:10$ vol.%, $p = 1$ bar, $T = 600 - 750\text{ }^{\circ}\text{C}$, $m_{\text{cat}} = 50$ mg, $\text{GHSV} = 170\text{ L}/(\text{g}_{\text{cat}}\cdot\text{h})$.

7.8 Distribution of Ni species on Ni(CA-5.5)/S2 according to TEM-EDX (section 4.2.3.3)

The catalyst Ni(CA-5.5)/S2-R700 (*ex situ* reduced at $700\text{ }^{\circ}\text{C}$ for 1.5 h) showed Ni nanoparticles mostly supported on Mg-rich domains (see Figure A 8), which contrasted to a somehow preferential deposition of Ni sites on Al-rich domains in Ni(CA-5.5)/WI.800-R700 (see Figure 4-32). According to XPS (see section 4.2.3.2), the catalysts Ni(CA-5.5)/S2-R700 and Ni(CA-5.5)/WI.800-R700 displayed different chemistry (i.e., surface ratio $\text{Mg}/\text{Al} = 1.7$ and 1.0 , respectively) and electronic properties at their surface. The different surface chemical and electronic environments of both catalysts most likely influenced the deposition of the Ni sites in different ways during the preparation and activation.

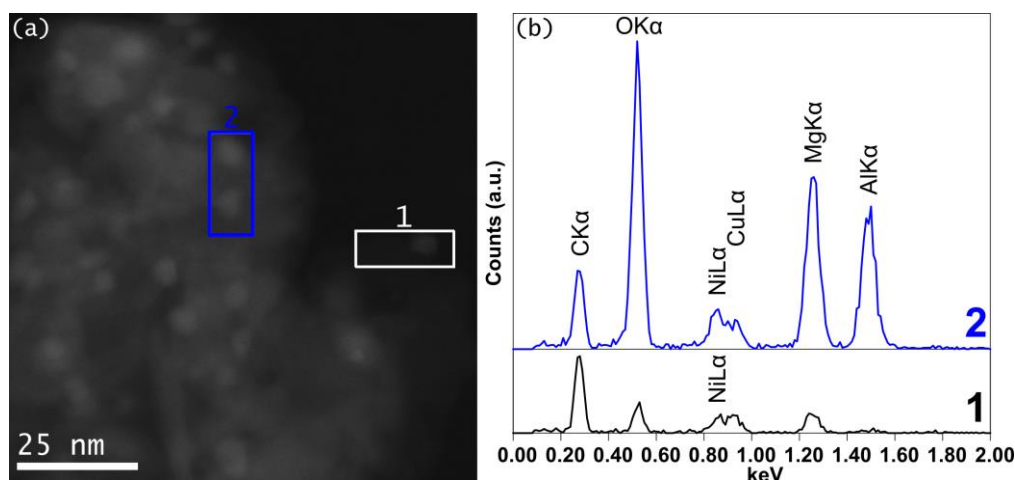


Figure A 8. a) TEM-HAADF micrograph of *ex situ* reduced Ni(CA-5.5)/S2-R700 and b) EDX spectra of the marked areas in a).

7.9 Oxidative regeneration of spent NiLaGa/WI.800-R800 catalyst (section 4.3.4)

Following the discussion provided in section 4.3.4, the spent catalyst NiLaGa/WI.800-R800 after different reaction regimes was reactivated using oxidative-reductive treatments at high temperatures ($800\text{ }^{\circ}\text{C}$). The oxidation step was monitored using GC by sampling the exhaust every 15 min, and the obtained chromatograms displayed the typical CO_2 peak (retention time = 7.97 min), which was formed during the oxidation of the coke deposits. Thus, the peak area of the formed CO_2 during oxidation decreased to zero over the 2 h of the oxidative treatment (see Figure A 9). Similar observations were done during oxidative treatment of the spent catalyst NiLaGa/WI.800-R800 after heavy coke deposition (see section 4.3.4.1), and after NH_3 (see section 4.3.4.2) and H_2S poisoning (see section 4.3.4.3.2). The

latter indicated that coke formation took place during all different tests, and that these coke deposits were successfully oxidized by using this regenerative treatment.

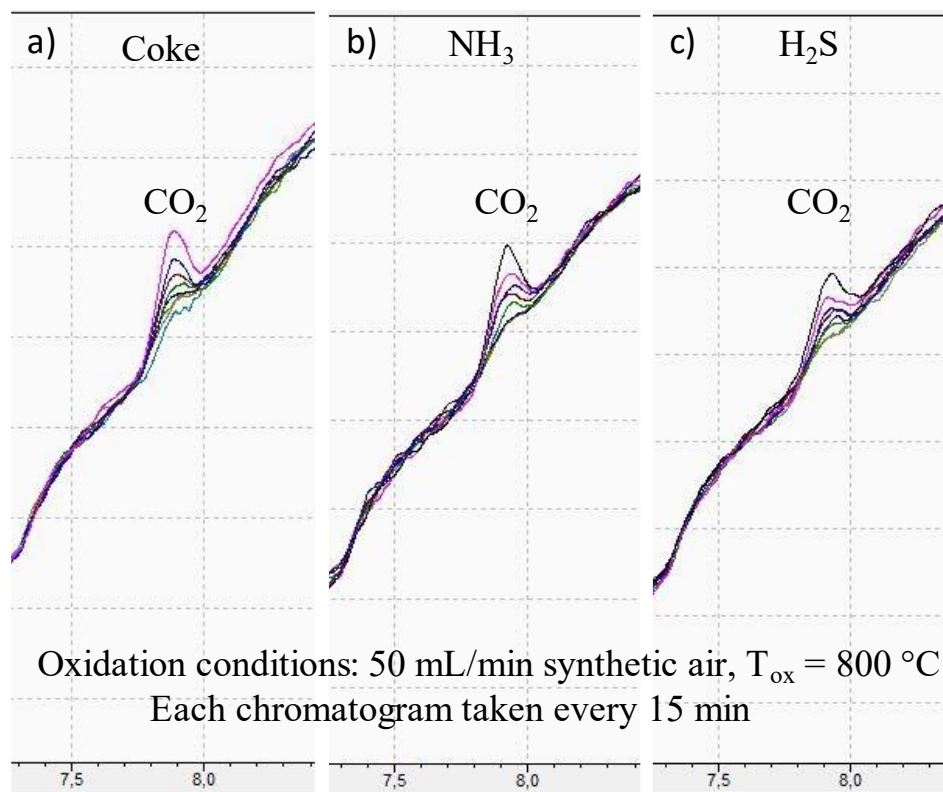


Figure A 9. Comparison of chromatograms collected during the oxidative regeneration of spent NiLaGa/WI.800-R800 after different treatments: a) after heavy coke deposition (see experiment description and reaction conditions in section 4.3.4.1), b) after NH_3 (see experiment description and reaction conditions in section 4.3.4.2), and c) after H_2S poisoning (see experiment description and reaction conditions in section 4.3.4.3.2).

7.10 Thermogravimetric analysis of S-poisoned NiLaGa/WI.800-R800 (section 4.3.4.3.1)

The S-poisoned NiLaGa/WI.800-R800 was analyzed using DTA-TGA under oxidative conditions to quantify the coke formed after 5 h TOS (3 h TOS under $\text{CH}_4/\text{CO}_2 = 2:1$ without H_2S + 2 h TOS under $\text{CH}_4/\text{CO}_2 = 2:1$ with 5 ppm H_2S) and to detect S-related species. Thus, the weight loss related to coke combustion ($m/z = 44$) was ca. 10% (see Figure A 10a), while no weight loss was related to any S-related specie (i.e., S: $m/z = 32$, HS : $m/z = 33$, SO : $m/z = 48$ and SO_2 : $m/z = 64$; see Figure A 10b).

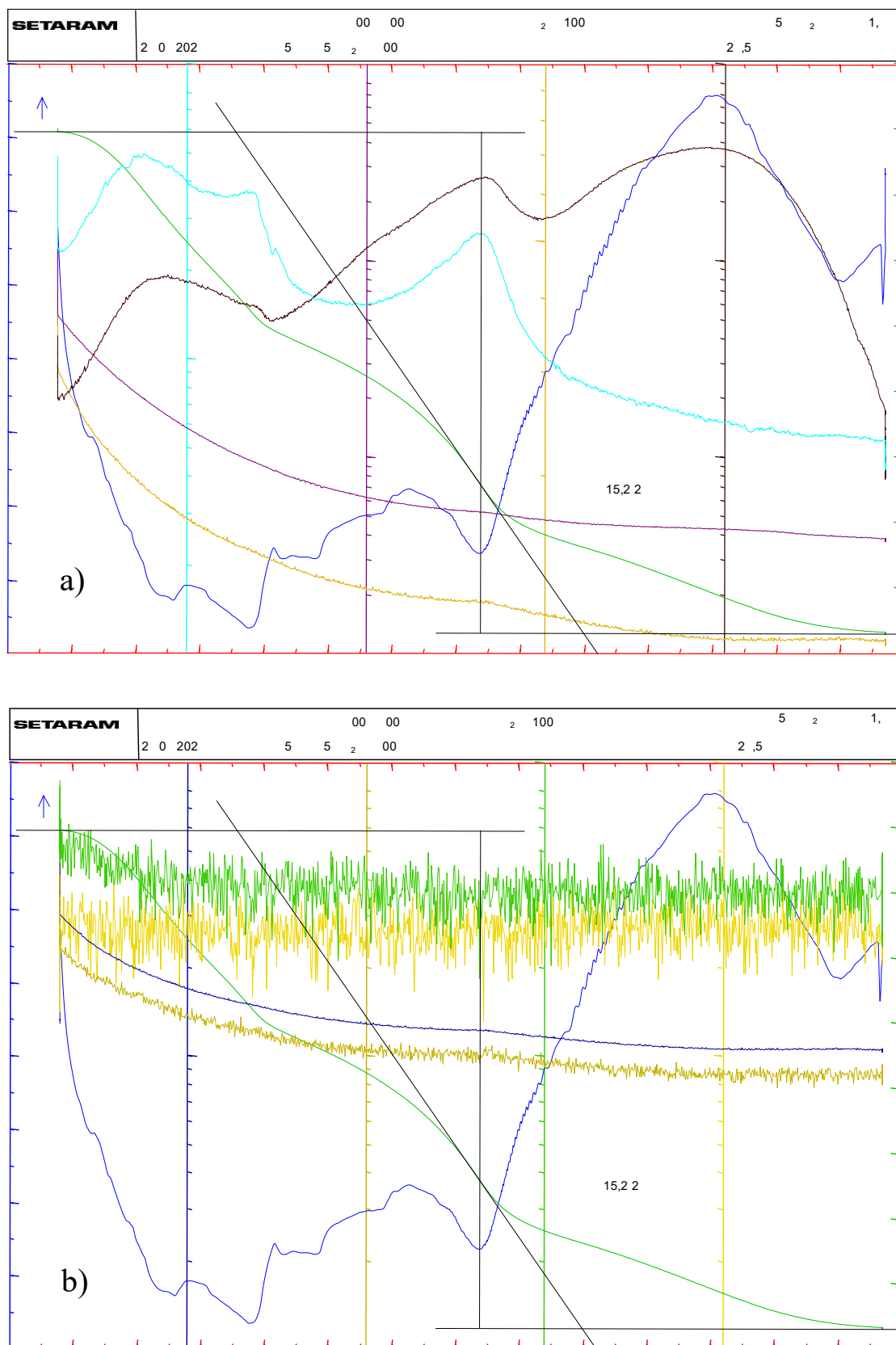


Figure A 10. Thermograms of spent NiLaGa/WI.800-R800 after 5 h TOS (3 h TOS under CH₄/CO₂ = 2:1 without H₂S + 2 h TOS under CH₄/CO₂ = 2:1 with 5 ppm H₂S). The following species were monitored using MS: in a) H₂O: m/z = 18, CO: m/z = 28, S: m/z = 32, CO₂: m/z = 44; in b) S: m/z = 32, HS: m/z = 33, SO: m/z = 48 and SO₂: m/z = 64. Oxidation conditions: 5 K/min, 5 vol.% O₂/He, m_{cat} = 29.56 mg.

7.11 Surface properties of S-poisoned NiLaGa/WI.800-R800 (section 4.3.4.3.1)

The low amount of S measured in the spent NiLaGa/WI.800-R800 after poisoning with 5 ppm H₂S (only 0.2 wt.% S) suggested that the massive activity drop in only 5 h TOS was due to surface poisoning of Ni⁰ active sites with S. Thus, XPS of the S-poisoned sample was performed. Unfortunately, no hints of S were measured at the catalyst's surface (only noise in the region of interest of S 2p and 2s photoelectrons, see Figure A 11a and b, respectively). The latter was ascribed to the very low amount of S deposited on the surface, which was below the detection limit of the XPS technique.

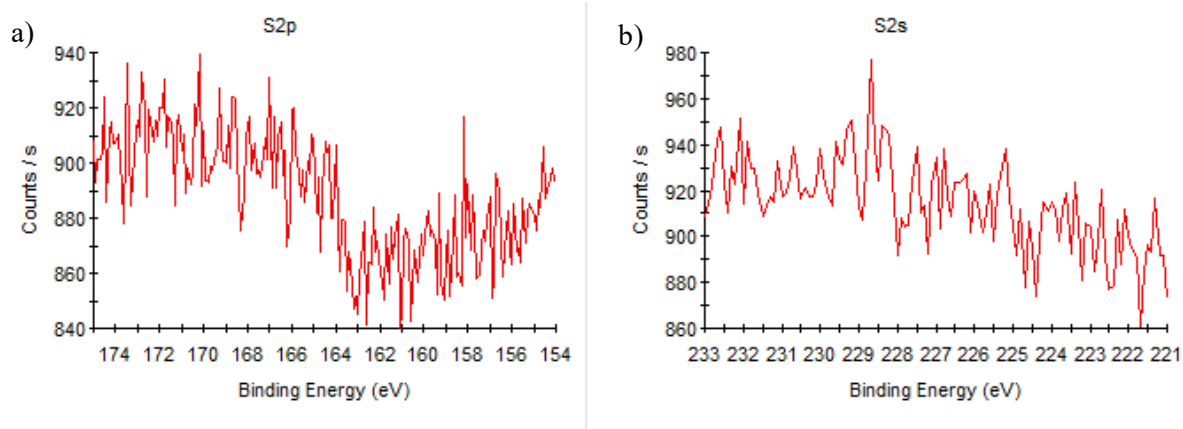


Figure A 11. XP spectra of S a) 2p and b) 2s photoelectrons of spent NiLaGa/WI.800-R800 after 5 h TOS. Reaction conditions: 3 h using: CH₄/CO₂/N₂ = 60:30:10 vol.%, p = 1 bar, T = 750 °C, m_{cat} = 50 mg, GHSV = 170 L/(g_{cat}·h), following by adding 5 ppm H₂S to the previous conditions for 2 h.

8. List of Publications Related to this Work and Contributions in Conferences

Publications

- (1) **S. Gonzalez**, et al., Impact of chelating agents on precursor formation and efficiency of Ni/MgO-Al₂O₃ catalysts in dry reforming of methane, Catal. Today, 2024 (429) 114475 – 114489
- (2) **S. Gonzalez**, et al., Study on the pH influence on preparation of Ni/MgO-Al₂O₃ catalysts assisted with citrate for dry reforming of methane, in preparation.

Oral Communications

- (1) **S. Gonzalez**,
Title: ‘Tuning Ni/MgO-Al₂O₃ catalysts via precursor complexation at different pH to boost the activity and stability for dry reforming of methane’

PREPA13 – 13th International Symposium on ‘Scientific Bases for the Preparation of Heterogeneous Catalysts’, Louvain-la-Neuve, Belgium, July 9th – 13th, 2023.

Posters

- (1) **S. Gonzalez**, H. Atia., N. Rockstroh, H. Lund, S. Bartling, S. Wohlrab, U. Armbruster
Title: ‘Boosting the catalyst stability and activity of Ni/MgO-Al₂O₃ with different complexing agents for dry reforming of methane’

15th European Congress on Catalysis, Prague, Czech Republic, August 27th – September 1st, 2023.