New insights into the structure-performance relationships of Ce-based catalysts for synthesis of organic carbonates using CO$_2$

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M. Sc. Iuliia Prymak
geboren am 18.05.1987 in Charkiw, Ukraine

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Gutachter:

1. Gutachter:
PD Dr. habil. Evgenii V. Kondratenko
Leibniz-Institut für Katalyse e.V., Universität Rostock

2. Gutachter:
Prof. Dr. Angelika Brückner
Leibniz-Institut für Katalyse e.V., Universität Rostock

Datum der Einreichung: 14.05.2019
Datum der Verteidigung: 12.11.2019
Declaration

I declare that the work presented in this thesis entitled "New insights into the structure-performance relationships of Ce-based catalysts for synthesis of organic carbonates using CO₂" is original and carried out by myself to obtain the doctoral degree at the Leibniz Institute for Catalysis e.V., Rostock, Germany, under the guidance of my supervisors PD Dr. habil. Andreas Martin (2011-2015, retired), PD Dr. habil. Evgenii V. Kondratenko (2015-2019, Department "Catalyst Discovery and Reaction Engineering", group "Reaction Mechanisms", Group leader) and Dr. Venkata Narayana Kalevaru (2011-2019, Department "Bioinspired Homo- & Heterogeneous Catalysis", Group "Gas Phase Oxidations", Group leader). I further declare that this thesis has not been submitted, either wholly or in part, to any academic institution for the award of any other degree or qualifications.

Rüsselsheim, 14.05.2019
Iuliia Prymak
Dedicated to my lovely husband Dimitri and our son Mark....
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Abstract

Carbon dioxide is a non-toxic, abundant and low-cost C1 feedstock. Its chemical utilization in various organic syntheses is certainly very attractive from both economic and environmental points of view, because CO2 is one of the most prominent greenhouse gases, being responsible for global warming. In this regard, this thesis is focused on a couple of industrially important catalytic reactions, where CO2 and C1-C2 alcohols (methanol or ethanol) are used as reactants to produce more valuable products, e.g. dimethyl carbonate (DMC) or diethyl carbonate (DEC). However, the one-step synthesis of organic carbonates from CO2 and alcohols is thermodynamically difficult and hence the yield of desired product reported so far is relatively low (~2%). Therefore, the aim of this study is to achieve the maximal thermodynamically possible yield of dialkyl carbonate by various means such as (i) by applying high pressure conditions (80-180 bar) in the temperature range 80-180 °C, (ii) developing efficient catalyst compositions, iii) using continuous flow system.

Literature survey reveals that ZrO2, CeO2 and their solid solutions are effective catalysts for the direct production of organic carbonates due to the presence of both acidic and basic sites on its surface, which consist of coordinatively unsaturated metal cations M4+, oxide anions O2− and hydroxyl groups. In order to further investigate the potential of CeO2-based catalysts, the effects of (i) surface modifications with phosphoric acid, (ii) doping of second metal, i.e. Hf4+, Zr4+, Ti4+, (iii) calcination temperature and iv) various synthesis methods on the yield of dialkyl carbonate were explored in detail. Catalytic performance of these solids was first checked in batch runs (stainless steel autoclave) for the formation of DMC from methanol and CO2 and then in a continuous-mode operation using a plug-flow reactor (PFR) for the formation of DEC from ethanol and CO2. The CeₓM₁₋ₓO₂ (M = metal) catalysts exhibited significant differences in their performance mainly depending on (i) their Ce : M ratio, (ii) the different acid–base characteristics and phase composition, (iii) ability to form monodentate methoxy intermediates.

The catalysts containing 80 mol% Ce and 20 mol% Zr exhibited the most efficient performance (YDMC = 0.24% and YDEC = 0.7%), which could be attributed to a good balance between the basic and acidic sites on its surface. The DMC yield was successfully improved further from 0.24% to 1.6% by phosphate modification of Ce₀.₈Zr₀.₂O₂ (P/Zr = 0.12).
Zusammenfassung


Die Literaturrecherche ergab, dass $ZrO_2$, $CeO_2$ und deren Mischkristalle als effektive Katalysatoren für die direkte Synthese von organischen Carbonaten verwendet werden können, da sie sowohl saure als auch basische Zentren an ihrer Oberfläche aufweisen, die aus den koordinativ ungesättigten Metallkationen $M^{4+}$, Oxidanionen $O^{2-}$ und Hydroxylgruppen bestehen. Um das Potenzial von $CeO_2$-basierten Katalysatoren weiter zu erforschen, wurde die Auswirkung von (i) Oberflächenmodifikationen mittels Phosphorsäure, (ii) Dotierung mit einem zweiten Metall, z.B. $Hf^{4+}$, $Zr^{4+}$, $Ti^{4+}$, (iii) der Kalzinierungstemperatur und (iv) von verschiedenen Synthesemethoden auf die Ausbeute von Dialkylcarbonat detaillierter untersucht. Die katalytische Effektivität dieser Festkörper wurde zuerst durch die Bildung von DMC aus Methanol und $CO_2$ in Eintopfsynthesen (Edelstahlautoklav) und dann durch eine Durchflusssynthese von DEC aus Ethanol und $CO_2$ im Plug-Flow-Reaktor (PFR) getestet. Die $Ce_xM_{1-x}O_2$-Katalysatoren ($M =$ Metall) zeichneten sich durch signifikante Unterschiede in ihrer Leistung aus, hauptsächlich abhängig von (i) dem $Ce : M$ Verhältnis, (ii) den unterschiedlichen sauren und basischen Eigenschaften und der Phasenzusammensetzung, (iii) der Fähigkeit einzähnige Methoxy-Liganden als Zwischenprodukte zu bilden.
Die Katalysatoren, die 80 mol% Ce und 20 mol% Zr enthielten, wiesen das effizienteste Ergebnis ($Y_{DMC} = 0.24\%$ und $Y_{DEC} = 0.7\%$) auf, welches durch ein ausgewogenes Gleichgewicht zwischen den basischen und sauren Zentren auf deren Oberfläche erklärt werden konnte. Die Ausbeute an DMC wurde durch die Phosphat-Modifikation von $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ (P/Zr = 0.12) erfolgreich von 0.24 % auf 1.6 % erhöht.
## List of Abbreviations, Acronyms and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABF</td>
<td>Annular Bright Field</td>
</tr>
<tr>
<td>atm.</td>
<td>Atmospheric Pressure [101.325 kPa]</td>
</tr>
<tr>
<td>a</td>
<td>Lattice Constant [nm]</td>
</tr>
<tr>
<td>→</td>
<td>Arrow Indicated Stationary Isothermal Treatment of the Samples</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmet–Teller</td>
</tr>
<tr>
<td>b</td>
<td>Lattice Constant [nm]</td>
</tr>
<tr>
<td>BJH</td>
<td>Barret–Joyner–Halenda</td>
</tr>
<tr>
<td>CP</td>
<td>Critical Parameters</td>
</tr>
<tr>
<td>CO₂-TPD</td>
<td>Temperature Programmed Desorption of Carbon Dioxide</td>
</tr>
<tr>
<td>c</td>
<td>Lattice Constant [nm]</td>
</tr>
<tr>
<td>D</td>
<td>Crystallite Size [nm]</td>
</tr>
<tr>
<td>Dᵣ</td>
<td>Reactor Diameter [mm]</td>
</tr>
<tr>
<td>dₚ</td>
<td>Particle Diameter [mm]</td>
</tr>
<tr>
<td>d</td>
<td>Average Pore Diameter [nm]</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl Carbonate</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl Carbonate</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethyl Ether</td>
</tr>
<tr>
<td>DEE</td>
<td>Diethyl Ether</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>EDXS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>ε</td>
<td>Microstrain [%]</td>
</tr>
<tr>
<td>etc.</td>
<td>Et Cetera</td>
</tr>
<tr>
<td>e.g.</td>
<td>Exempli Gratia</td>
</tr>
<tr>
<td>et al.</td>
<td>Et Alii</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>EDXS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transformation Infrared Spectroscopy</td>
</tr>
<tr>
<td>FIZ Karlsruhe</td>
<td>Fachinformationszentrum Karlsruhe</td>
</tr>
<tr>
<td>GWP</td>
<td>Global Warming Potential</td>
</tr>
</tbody>
</table>
GHG | Greenhouse Gas
---|---
GC | Gas Chromatography
HAADF | High-Angle Annular Dark Field
IPCC | Intergovernmental Panel on Climate Change
i.e. | Id Est
ICDD | International Centre of Diffraction Data
ICP-OES | Inductive Coupled Plasma Optical Electron Spectroscopy
ICSD | Inorganic Crystal Structure Database
JCPDS | Joint Committee on Powder Diffraction Standards
K | Kelvin
LHSV | Liquid Hourly Space Velocity \([L_{\text{liq.}} \text{kg}_{\text{cat.}}^{-1} \text{h}^{-1}]\)
M | Motor Octane Number
MeOH | Methanol
mol% | Molar Percentage
MS | Molecular Sieve
N.W. Europe | Northwest Europe
nm | Nanometer
NIST | National Institute of Standards and Technology
NH\textsubscript{3}-TPD | Temperature Programmed Desorption of Ammonia
\(p_{\text{cr}}\) | Critical pressure [bar]
\(p\) | Pressure [bar]
PFR | Plug-Flow Reactor
PSRK | Predictive Soave-Redlich-Kwong
\(\rho\) | Density \([\text{g cm}^{-3}]\)
\(\rho_{\text{cr}}\) | Critical Density \([\text{g cm}^{-3}]\)
RT | Room Temperature \([\degree \text{C}]\)
R | Research Octane Number
R-OH | Alcohol
\(\sigma\) | Standard Deviation [%]
SSA | Specific Surface Area \([\text{m}^2 \text{g}^{-1}]\)
STEM | Scanning Transmission Electron Microscopy
Sc | Supercritical
TEM | Transmission Electron Microscopy
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature Programmed Reduction</td>
</tr>
<tr>
<td>( \tau )</td>
<td>Contact Time ([s])</td>
</tr>
<tr>
<td>( T_{\text{max}} )</td>
<td>Maximal Temperature ( [^\circ\text{C}] )</td>
</tr>
<tr>
<td>( T_c )</td>
<td>Calcination Temperature ( [^\circ\text{C}] )</td>
</tr>
<tr>
<td>( T_D )</td>
<td>Drying Temperature ( [^\circ\text{C}] )</td>
</tr>
<tr>
<td>( t )</td>
<td>Time ([\text{h}])</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature ( [^\circ\text{C}] )</td>
</tr>
<tr>
<td>( T_{\text{cr}} )</td>
<td>Critical Temperature ( [^\circ\text{C}] )</td>
</tr>
<tr>
<td>U.S.</td>
<td>United State</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>VLE</td>
<td>Vapor-Liquid Equilibrium</td>
</tr>
<tr>
<td>( V )</td>
<td>Volume of the Unit Cell ([\text{nm}^3])</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight Percentage</td>
</tr>
<tr>
<td>( x )</td>
<td>Molar Fraction</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>( Y )</td>
<td>Yield ([%])</td>
</tr>
</tbody>
</table>
Structure of the thesis

The thesis is composed of seven chapters on the basis of motivation and objectives, state-of-the-art, catalyst preparation methods applied, characterization techniques used, modification of catalyst compositions and their catalytic results.

Chapter 1 contains a general introduction on carbon dioxide properties and its applications in the chemical industry followed by a brief description of the organic carbonates, their properties and applications. In addition, effective catalysts used so far for the synthesis of dialkyl carbonate are described together with the operation conditions and catalyst performance. The use of different dehydrating agents in order to increase dialkyl carbonate yield will also be shortly discussed. Furthermore, the motivation and the objective of the current study are also presented.

Chapter 2 summarizes the experimental procedures including solids preparation methods, basic principles and applications of different characterization techniques, description of the reaction setups and of evaluation of catalyst performance for the direct carboxylation of alcohols with carbon dioxide to dialkyl carbonates.

Chapter 3 deals with the results and discussion about the effect of Ce/Zr ratio in Ce_xZr_{1-x}O_2 and surface modification of Ce_{0.8}Zr_{0.2}O_2 by phosphoric acid on the catalytic performance for the direct synthesis of dimethyl carbonate (DMC) from methanol and CO_2 using stainless steel autoclave. These catalysts are characterized by N_2-adsorption (BET-SA), XRD, ICP-OES, TEM, in situ FTIR, NH_3-TPD as well as CO_2-TPD.

Chapter 4 demonstrates the data obtained from the catalytic tests for the direct synthesis of diethyl carbonate (DEC) from ethanol and CO_2 under continuous-flow conditions over different Ce_xZr_{1-x}O_2 catalysts. The optimization of reaction conditions is also described in this chapter. The catalysts were characterized with the help of various physico-chemical methods mentioned above.

Chapter 5 describes the influence of second metal in Ce_{0.8}M_{0.2}O_2 catalyst, where M is a metal (Hf^{4+}, Ti^{4+}), on the catalytic performance for direct synthesis of DEC from ethanol and CO_2. Catalyst characterization using the techniques listed above is also studied.
Chapter 6 explores the influence of synthesis parameters on the catalytic performance for the continuous production of DEC from CO$_2$ and ethanol, along with the solid state characterization to derive structure-performance correlations.

Finally, the main conclusions of this thesis are reviewed in Chapter 7, together with outlook for future research on the direct synthesis of organic carbonates from CO$_2$ and alcohols.
# Table of contents

1. General Introduction and Literature Overview ................................................................. 1

1.1. Carbon dioxide ............................................................................................................. 2

1.1.1. Chemical and physical properties of carbon dioxide ........................................... 2

1.1.2. World greenhouse gas emissions (GHG) ............................................................... 3

1.1.3. Utilization of CO₂ ............................................................................................... 5

1.2. Organic carbonates ....................................................................................................... 6

1.2.1. Physical and chemical properties of dimethyl carbonate (DMC) and diethyl carbonate (DEC) ..................................................................................... 6

1.2.2. Application of DMC and DEC ........................................................................... 6

1.2.3. Production of DMC and DEC ............................................................................ 7

1.3. State of the art: Carboxylation of alcohols ................................................................. 10

1.3.1. Suitable catalysts for DMC synthesis ............................................................... 10

1.3.2. Suitable catalysts for DEC synthesis ................................................................ 11

1.3.3. Thermodynamic restrictions ......................................................................... 12

1.3.4. Phase behavior of the CO₂ + EtOH system ...................................................... 13

1.4. Motivation and objectives of the thesis ...................................................................... 15

2. Experimental section: Preparation, testing and characterization methods ................. 18

2.1. Catalyst preparation ................................................................................................... 19

2.1.1. Chemicals ......................................................................................................... 19

2.1.2. Citrate complexation method ............................................................................ 19

2.1.2.1. CeₓZr₁₋ₓO₂ solids ............................................................................................... 19

2.1.2.2. Ce₀.₈Ti₀.₂O₂ solids ............................................................................................. 20

2.1.2.3. Ce₀.₈Hf₀.₂O₂ solids ............................................................................................ 20

2.1.3. Ce₀.₈Zr₀.₂O₂ solid solutions prepared by co-precipitation ................................. 20

2.1.4. CeₓZr₁₋ₓO₂ via oxalate gel co-precipitation method ........................................... 21
2.1.5. Phosphated Ce$_x$Zr$_{1-x}$O$_2$: co-precipitation and wet impregnation .......... 22

2.2. Catalyst characterization ............................................................................................ 23

2.2.1. Thermogravimetric analysis (TGA) ................................................................. 23

2.2.2 Nitrogen adsorption: BET and BJH methods ................................................... 23

2.2.3 X-ray diffraction studies (XRD) ....................................................................... 24

2.2.4 Inductively coupled plasma optical emission spectroscopy (ICP-OES) ........ 25

2.2.5 X-ray photoelectron spectroscopy (XPS) ......................................................... 25

2.2.6 Transmission electron microscopy (TEM) ....................................................... 25

2.2.7 Temperature-programmed reduction (TPR) using H$_2$ as the reduction agent .. 26

2.2.8 Temperature programmed desorption (TPD) using NH$_3$ as basic probe and CO$_2$ as acidic probe ................................................................. 26

2.2.9 Fourier Transform Infrared Spectroscopy (FTIR) ............................................ 27

2.3. Experimental system and catalytic tests ..................................................................... 27

2.3.1. Continuous flow reactor ................................................................................... 27

2.3.2. Batch reactor ..................................................................................................... 29

2.3.3. Analysis: Gas chromatography ......................................................................... 30

2.3.3.1. Continuous reaction .......................................................................................... 30

2.3.3.2. Batch reaction ................................................................................................... 31

3. Ce-Zr mixed oxide catalysts and surface modified Ce$_{0.8}$Zr$_{0.2}$O$_2$ for the direct synthesis of dimethyl carbonate from methanol and CO$_2$ ..................................................................................... 32

3.1. Ce-Zr mixed oxide catalysts for the direct synthesis of dimethyl carbonate from methanol and carbon dioxide ................................................................................ 33

3.1.1. Catalysts characterization ................................................................................. 33

3.1.2. Catalytic results ................................................................................................ 39

3.2. Surface modified Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst for direct synthesis of dimethyl carbonate from methanol and CO$_2$ ................................................................................. 41

3.2.1. Catalysts characterization ................................................................................. 41

3.2.2. Catalytic results ................................................................................................ 48
3.3. Summary .................................................................................................................... 49

4. Continuous synthesis of diethyl carbonate from ethanol and CO₂ over CeₓZr₁₋ₓO₂ 
(x = 0, 0.2, 0.5, 0.8, 1) catalysts .......................................................................................... 52

4.1. An effective CeₓZr₁₋ₓO₂ catalysts for the continuous synthesis of DEC from CO₂ 
and ethanol : effect of varying reaction conditions ............................................................ 53

4.1.1. Catalysts characterization ................................................................................. 53

4.1.2. Catalytic results: effect of Ce/Zr ratio, temperature and pressure on catalytic 
performance .................................................................................................................. 60

4.1.3. Catalytic results and materials properties affecting the catalyst activity ......... 62

4.2. Impact of calcination temperature on catalytic properties of Ce₀.₈Zr₀.₂O₂ solids ..... 64

4.2.1. Catalysts characterization ................................................................................. 64

4.2.2. Catalytic results and material properties affecting the activity .................... 71

4.3. Effect of LHSV and ratio of EtOH : CO₂ on catalytic performance ..................... 73

4.4. Conclusions ................................................................................................................ 74

5. Effect of second metal in Ce₀.₈M₀.₂O₂ catalysts on the catalytic activity towards 
DEC synthesis from ethanol and CO₂ ................................................................................. 76

5.1. Catalyst characterization ............................................................................................ 77

5.2. Catalytic results .......................................................................................................... 83

5.3. Conclusions ................................................................................................................ 85

6. Influence of synthesis parameters on catalytic performance of Ce₀.₈Zr₀.₂O₂ in the 
production of diethyl carbonate from ethanol and CO₂ ....................................................... 86

6.1. Catalyst characterization ............................................................................................ 87

6.3. Conclusions ................................................................................................................ 94

7. Summary and Outlook ......................................................................................................... 95

7.1. Ce-Zr mixed oxide catalysts and surface modified Ce₀.₈Zr₀.₂O₂ for the direct 
synthesis of dimethyl carbonate from methanol and CO₂ ............................................. 95

7.2. Continuous synthesis of diethyl carbonate from CO₂ and ethanol over 
CeₓZr₁₋ₓO₂ (x = 0, 0.2, 0.5, 0.8, 1) catalysts .............................................................. 96
7.3. Effect of second metal in $\text{Ce}_{0.8}\text{M}_{0.2}\text{O}_2$ catalysts on the catalytic activity towards
DEC synthesis from ethanol and CO$_2$ ................................................................. 98

7.4. Influence of synthesis methods on catalytic performance of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ in the
production of diethyl carbonate from ethanol and CO$_2$ ........................................... 98

7.5. Outlook ................................................................................................................. 99

8. References .................................................................................................................. 101
Chapter 1

1. General Introduction and Literature Overview

Chapter 1 comprises a thorough literature survey on production of organic carbonates with a special emphasis on technologies of dimethyl carbonate and diethyl carbonate synthesis. It starts with a short description of the physical and chemical properties of carbon dioxide and its applications in chemical industries. The main focus is put on direct synthesis of organic carbonates via carboxylation of alcohols and effective heterogeneous catalysts. Moreover, various drawbacks of this reaction, such as thermodynamic limitations and hydrolysis of products, are also discussed. Physical and chemical properties as well as industrial applications of these carbonates are also introduced and discussed (Scheme 1). The motivation and main objectives of the thesis are given at the end.

![Scheme 1. Important properties of organic carbonates for industrial uses.](image-url)
1. General Introduction and Literature Overview

1.1. Carbon dioxide

1.1.1. Chemical and physical properties of carbon dioxide

Carbon dioxide (CO$_2$) is a non-toxic, abundant and relatively cheap C$_1$ feedstock. It is a major greenhouse gas, however it is considered as a substitute to phosgene currently used for large-scale DMC synthesis [1, 2]. The oxidation number of carbon in CO$_2$ is +IV. For chemical conversion of CO$_2$, a substantial input of energy, effective reaction conditions and active catalysts are typically required because CO$_2$ is a highly thermodynamically and kinetically stable molecule. However, CO$_2$ has a strong affinity towards electron-donating reagents and thus, rapidly reacts with basic compounds, like ammonia. CO$_2$ is used for various industrial applications: chemicals, pharmaceuticals, foodstuffs, beverage, healthcare, laboratories and analysis (mobile phase in supercritical chromatography), safety (CO$_2$ for fire extinguishers) [3]. Selected physical and chemical properties of CO$_2$ are summarized in Table 1.1.

Table 1.1. Physical and chemical properties of CO$_2$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>44.01</td>
<td>g·mol$^{-1}$</td>
</tr>
<tr>
<td>Gas density at 273 K and 1 atm.</td>
<td>1.977</td>
<td>kg·m$^{-3}$</td>
</tr>
<tr>
<td>Liquid density at 293 K and 56 atm.</td>
<td>770</td>
<td>kg·m$^{-3}$</td>
</tr>
<tr>
<td>Solid density at 195 K and 1 atm.</td>
<td>1562</td>
<td>kg·m$^{-3}$</td>
</tr>
<tr>
<td>Triple point at 5.1 atm.</td>
<td>-56.5</td>
<td>°C</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>31.04</td>
<td>°C</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>72.85</td>
<td>bar</td>
</tr>
<tr>
<td>Critical density</td>
<td>468</td>
<td>kg·m$^{-3}$</td>
</tr>
</tbody>
</table>

The physical state of CO$_2$ changes with temperature and pressure. As shown in Figure 1.1a, CO$_2$ has three states: solid, liquid and gas. However, at temperatures and pressures above the critical point ($T_{cr} = 31.1$°C, $p_{cr} = 73.8$ bar), CO$_2$ behaves as a supercritical fluid. Under these conditions, CO$_2$ is in a single phase with both liquid and gas properties. Carbon dioxide has no liquid state at pressures below 5.1 atm. At atmospheric pressure and temperatures below −78.5 °C gaseous CO$_2$ is converted into a solid and the solid sublimes directly to a gas above −78.5 °C. Liquid CO$_2$ is formed only at pressures and temperatures above 5.1 atm. and above -56.6 °C. The density of CO$_2$ varies with temperature and pressure (Figure. 1.1b). At critical pressure, its compressibility is maximized, and small changes in temperature can lead to big changes in CO$_2$ local density and its solubility [4]. Supercritical
CO₂ is an important commercial and industrial solvent due to its role in chemical extraction in addition to its low toxicity and environmental impact.

Figure 1.1. (a) Phase diagram for CO₂ and (b) Variation of density as a function of temperature and pressure (reprinted from the Annex of IPCC [5]).

1.1.2. World greenhouse gas emissions (GHG)

Carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) are some of the major greenhouse gases (GHG) with a large global warming potential (GWP). GWP is a measure of the radiative forcing of a unit mass of a given greenhouse gas in atmosphere integrated over a selected time horizon, relative to that of CO₂ (Table 1.2). Thus, if a molecule has a longer atmospheric lifetime than CO₂ its GWP will increase with the timescale considered. CO₂ has a GWP of 1 over all time periods.

Table 1.2. GWP values of various greenhouse gases [6].

<table>
<thead>
<tr>
<th>Gas</th>
<th>Lifetime (year)</th>
<th>Global warming potential</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20-yr</td>
</tr>
<tr>
<td>CO₂</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>CH₄</td>
<td>12</td>
<td>72</td>
</tr>
<tr>
<td>N₂O</td>
<td>114</td>
<td>289</td>
</tr>
</tbody>
</table>

Figure 1.2a represents a relative fraction of anthropogenic greenhouse gases originating from eight categories of sources, as estimated by the Emission Database for Global Atmospheric Research version 3.2 [7]. Anthropogenic emissions are emissions related with human activities including combustion of fossil fuels, deforestation, livestock etc. Global annual emissions of CO₂, CH₄ and N₂O in 2017 were 73%, 18%, and 6%, respectively.
Figure 1.2b shows changes in the global emissions of CO₂ in the period of time from 1995-2017. 2017 was an outstanding year in which emissions increased by 1.2% and reached 37.1 gigatonnes (Gt). The largest producers of energy-related CO₂ emissions in 2017, based on their share of global energy-related CO₂ emissions, were: China, U.S., India, Russia, Brazil and Japan (Figure 1.2b (inset)). China was the biggest emitter of CO₂ that accounted for around 25% of global CO₂ emissions.

It is a well-known fact that greenhouse gases are responsible for global climate change. There are some key issues related to GHG control and utilization: energy economics, policy regulations, environmental protections and global climate change. Carbon dioxide is today’s greenhouse gas number one (73% of total emissions). A continuous temperature increase on the Earth (1.2 °C since 1850), caused by increased CO₂ concentration in the atmosphere, results in melting of arctic Sea ice, increased forest fires, rising sea levels, loss of animal habitat, spreading of tropical diseases and more frequent and severe storms [12, 13].

Figure 1.3 shows three main pathways for utilizing of CO₂:
· Conversion of CO₂ into fuels
· Utilization of CO₂ as a feedstock for synthesis of chemicals
· Non-conversional use of CO₂
1. General Introduction and Literature Overview

1.1.3. Utilization of CO₂

In 2003 the global market for merchant CO₂, measured by the amount of CO₂ sold in the market, was estimated to be $3.2 billions [15]. Thus, CO₂ conversion into various useful chemical products is very attractive from both economic and environmental points of view.

The main processes for CO₂ conversion and application in the chemical industry are:

- CO₂ hydrogenation to various compounds, depending upon the catalysts used and reaction conditions applied
  - CO₂ + 3H₂ → CH₃OH + H₂O, ΔH²⁷³ = -49.5 kJ/mol: low conversion resulting in high volume of recycled gases, 5 Mt/year of methanol, important petrochemicals in industry [16, 17].
  - CO₂ + H₂ → HCOOH, ΔH²⁷³ = -31.6 kJ/mol: reactant for electrochemical fuel cells [18].
  - CO₂ + H₂ ↔ CO + H₂O, ΔH²⁷³ = +41.19 kJ/mol: provides a synthetically valuable CO from cheap CO₂ [19].
- Dry reforming of methane (CH₄ + CO₂ → 2CO + 2H₂, ΔH²⁷³ = +247.3 kJ/mol) gives syngas [20].
- Synthesis of urea (CO₂ + 2NH₃ → CO(NH₂)₂ + H₂O, ΔH²⁷³ = -134 kJ/mol) is the largest-volume industrial example of converting CO₂, 146 Mt of urea/year [21].
- Production of salicylic acid (C₆H₅OH + CO₂ → C₇H₆O₃, ΔH²⁷³ = -90.1 kJ/mol), which is used for making Aspirin, 170 kT/year of salicylic acid.
1. General Introduction and Literature Overview

Obviously, many reactions for CO$_2$ conversion involve positive change in enthalpy and thus they are endothermic in nature. In addition, there are many other methodologies to transform carbon dioxide into various commercially important products, for instance, transformation of CO$_2$ into cyclic carbonates by cycloaddition with epoxides [22, 23] or glycols [23] and via oxidative carboxylation of olefins with CO$_2$ [23], synthesis of ethanol (70 Mt/year) from CO$_2$ and H$_2$ [24] etc. Among different approaches, direct synthesis of organic carbonates from alcohols and CO$_2$ [25, 26] is gaining huge interest in recent times due to their high commercial significance. Efforts have been made to produce fuel additives from CO$_2$ without using hydrogen source. For instance, dimethyl carbonate (DMC) from methanol and CO$_2$ [23, 27, 28] or diethyl carbonate (DEC) from ethanol and CO$_2$ [29-31] were found to be effective fuel additives.

1.2. Organic carbonates

1.2.1. Physical and chemical properties of dimethyl carbonate (DMC) and diethyl carbonate (DEC)

Dialkyl carbonates are low toxic, non-corrosive and readily biodegradable [32]. They are useful intermediates for manufacture of polycarbonates through a non-phosgene process [33]. Among different approaches, direct synthesis of organic carbonates from alcohols and CO$_2$ [25, 26] is gaining huge interest in recent times due to commercial significance of organic carbonates. For instance, dimethyl carbonate (DMC) from methanol and CO$_2$ [23, 27, 28] or diethyl carbonate (DEC) from ethanol and CO$_2$ [29-31] are two challenging examples of CO$_2$ utilization. Some properties of DEC and DMC are summarized in Table 1.3.

1.2.2. Application of DMC and DEC

The catalytic synthesis of DMC is currently studied intensively owing to wide applications of this chemical such as solvent [34], raw material for production of polycarbonate resins [35], electrolyte solvent [36, 37] and in pharmacy [38]. In contrast, DEC the second homologue in short-chain dialkylcarbonate family played only a negligible role, although DEC is also used as a raw material for production of polycarbonates [39], as solvent and intermediate for various pharmaceuticals [40, 41], as solvent for polyamides, polyacrylonitriles and diphenoxy resins in the synthetic fiber industry, as solvent for cellulose ethers, synthetic and natural resins in the textile printing and dyeing industry, as paint remover and as electrolyte in lithium ion batteries [42]. CH$_3$-/C$_2$H$_5$- and -CO- functional groups in the DMC / DEC molecules,
respectively, are suited for alkylation and carboxylation making a green substitution of phosgene, dimethyl sulfate/methyl iodide and ethyl/methyl halides possible [32, 34, 43, 44]. Furthermore, DMC and DEC contain 53.3 and 40.6 wt.% of oxygen, respectively, and thus can be used as an additive to diesel fuel due to their high octane booster power (Table 1.3) [34] to improve the performance of gasoline combustion. Engine tests show that 5 wt% DEC in diesel fuel can reduce particulate emissions by up to 50% [45]. DMC and DEC have more oxygen content per volume than methyl tert-butyl ether (MTBE, 18.2%). Moreover, the use of MTBE as an oxygen-containing fuel additive has a negative environmental impact.

### Table 1.3. Selected properties of DEC and DMC [46].

<table>
<thead>
<tr>
<th>Property</th>
<th>DEC</th>
<th>DMC</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>(C₃H₅O)₂CO</td>
<td>(CH₃O)₂CO</td>
<td></td>
</tr>
<tr>
<td>Molar mass</td>
<td>118.13</td>
<td>90.08</td>
<td>g·mol⁻¹</td>
</tr>
<tr>
<td>Density</td>
<td>0.975</td>
<td>1.069-1.073</td>
<td>g·cm⁻³</td>
</tr>
<tr>
<td>Boiling point</td>
<td>126-128</td>
<td>90</td>
<td>°C</td>
</tr>
<tr>
<td>Melting point</td>
<td>-43</td>
<td>4</td>
<td>°C</td>
</tr>
<tr>
<td>Flash point</td>
<td>33</td>
<td>17</td>
<td>°C</td>
</tr>
<tr>
<td>Blending octane (R+M)/2*</td>
<td>104-106</td>
<td>103-116</td>
<td></td>
</tr>
<tr>
<td>Toxicity</td>
<td>Mildly toxic</td>
<td>Slightly toxic</td>
<td></td>
</tr>
<tr>
<td>Oral acute toxicity (rats)</td>
<td>LD₅₀ = 1.57</td>
<td>LD₅₀ = 13.8</td>
<td>g·kg⁻¹</td>
</tr>
</tbody>
</table>

*R is the research octane number and M stands for motor octane number

### 1.2.3. Production of DMC and DEC

The world-wide production of DMC in 1993 was estimated to be 0.1 Mt per year [47, 48], in 1997 was estimated around 0.06 Mt/year and in 2006 to be 0.1-0.15 Mt/year [49]. The global consumption of DMC is majorly driven by including polycarbonate industry (51%), solvent (24%) and other (25%). Hence, global market size for dimethyl carbonate was valued over 410 million USD and its compound general growth rate is expected to exceed 5% by 2024 [50]. In a contrast, DEC production capacity is estimated to be much lower [51]. The demand of DMC/DEC is much higher than the production and hence lots of efforts have been done in order to find a sustainable route to produce DMC in large scale.
1. General Introduction and Literature Overview

**Scheme 1: Phosgenation**

\[
2 \text{ROH} + \text{Cl}_2 \rightarrow \text{CO}_2 + 2 \text{HCl}
\]

**Drawbacks**
- acid waste, corrosive, toxic, co-production of salt

**Advantages**
- pure products with high yields

**Producer**
- Bayer (Germany)

Up to beginning of the 1980s, dialkyl carbonates were mainly produced by the Bayer company developed a process on the basis of the reaction of alcohols with phosgene in the presence of sodium hydroxide (Scheme 1) [52-54]. However, the main disadvantages of this route are the use of poisonous gas (phosgene) and co-production of large amounts of salt in a subsequent neutralization step.

**Scheme 2: Oxidative carbonylation of alcohols**

\[
2 \text{ROH} + \text{CO} + 0.5 \text{O}_2 \rightarrow \text{RO} = \text{C} - \text{OR} + \text{H}_2\text{O}
\]

**Drawbacks**
- corrosive, flammable, toxic

**Advantages**
- high yields of products

**Producer**
- ENIChem (Italy)

To fulfil the growing market demand, new synthetic technologies were developed on the basis of CO or CO\(_2\), which were used as phosgene substitutes. As a result, a new industrial process was developed at ENICchem (1983), which is based on the oxidative carbonylation of alcohols over metal catalysts such as copper- or palladium-based solids (Scheme 2) [55, 56].

**Scheme 3: Carbonylation of alkyl nitrite**

\[
2 \text{ROH} + 2 \text{NO} + 0.5 \text{O}_2 \rightarrow \text{RO} = \text{C} - \text{OR} + 2 \text{NO}
\]

**Drawbacks**
- Combination of three reagents (EtOH/MeOH, NO and O\(_2\))- highly exothermic and explosive under certain reaction conditions; methyl/ethyl nitrite is highly reactive; not environmentally friendly process-formation of NO

**Advantages**
- without deactivation of catalyst

**Producer**
- UBE (Japan)
Nowadays, dialkyl carbonates are mainly produced via oxidative carbonylation of alcohols in both gaseous and liquid phase in the presence of Cu-based catalysts (Versalis/Lummus technology, China and N.W. Europe location bases). However, this process uses an explosive gas mixture (CO/O₂) under certain reaction conditions.

**Scheme 4: Transesterification of cyclic carbonate**

- **Drawbacks**: explosive, unfavorable equilibrium
- **Advantages**: environmentally friendly synthetic route, ethylene glycol as by-product
- **Current producer**: Asahi technology (USA)

In addition, several other routes are applied like carbonylation of alkyl nitrite (UBE, 1983) using Pd/carbon catalysts (Scheme 3) [57-59], transesterification of ethylene carbonate with alcohols in the presence of Sn, Zr and Ti complexes (Scheme 4) [60, 61] or transesterification of urea with alcohols using metal oxide catalysts like ZnO (Scheme 5) [62, 63]

**Scheme 5: Transesterification of urea**

- **Drawbacks**: unfavorable equilibrium
- **Advantages**: environmentally friendly and atom efficient, NH₃ can be recycled for the preparation of urea
- **Current producer**: CDT technology

Since the 1980s, alternative routes to form linear carbonates via direct carboxylation of alcohols in liquid as well as in gaseous phase have been reported [27, 64-69]. The direct synthesis of organic carbonates from CO₂ and alcohols represents one of the proposed favorable processes (Scheme 6). The one-step synthesis of dialkyl carbonates from CO₂ and alcohols allows CO₂ to be viewed as non-toxic, non-flammable, non-corrosive and abundant feedstock. This route will be deeply discussed in the next sections.
1.3. **State of the art: Carboxylation of alcohols**

### 1.3.1. Suitable catalysts for DMC synthesis

Until now, a wide range of catalytic systems had been studied for direct synthesis of DMC from methanol and CO₂ (see Table A1.2). For instance, group IV- and V-metal alkoxides (e.g. Nb, Ta, V, Ti) [70-72], organometallic compounds such as n-Bu₂Sn(OCH₃)₂ [73-77] and (MeO)₂ClSi(CH₂)₃SnCl₃ [78], K₂CO₃ in presence of C₂H₅I as co-reactant [79], CH₃OK in presence of CH₃I [80], Keggin type heteropoly compounds with different countercations, like Co or Fe, and addenda atoms, like W or Mo [81-84], basic zeolites [85], metal oxides [67, 86, 87], mixed metal oxides [28, 66, 88, 89] and supported catalysts (Cu-Fe/SiO₂, CeO₂/Al₂O₃, Cu-Ni/graphite, CuCl₂/AC, Rh/ZSM-5) [46, 90-92]. Among those catalysts, ZrO₂, CeO₂ and their mixtures showed very promising performance [65, 93, 94]. The catalytic activity of CeₓZr₁₋ₓO₂ solid solutions is adjustable through tuning the acid-base characteristics with varying Ce/Zr ratios. Moreover, due to the different charges and ionic radii of Ce⁴⁺ (0.097 nm) and Zr⁴⁺ (0.084 nm) cations, the acid strength of mixed oxides may change. For instance, Zr⁴⁺ with the smaller ionic radius exhibits a more acidic nature than Ce⁴⁺ in CeₓZr₁₋ₓO₂ solid solutions [95]. However, a concentration balance between the basic and acidic centers on the catalyst’s surface is also known to be crucial in the direct synthesis of DMC [82, 83]. In order to further promote these key properties Ikeda et al. performed surface modifications of ZrO₂ with phosphoric acid [96]. The authors claimed that both ZrO₂ and ZrO₂/H₃PO₄ had Lewis acid sites (Zr⁴⁺), whereas only ZrO₂/H₃PO₄ had weak Brønsted acid sites. From the reaction mechanism proposed by Ikeda et al. they claimed that in the last step of DMC formation, activation of MeOH was more favorable on the Brønsted acid sites than on the Lewis acid sites. In the research group of Wu et al. V₂O₅ catalyst was also modified by phosphoric acid and applied for DMC synthesis [97]. The results showed an increase in DMC yield with increasing P/V ratio. Such improved catalytic performance was also attributed to the formation of weak Brønsted acid sites by interaction between V and P. In the case of ZrO₂/H₃PO₄ catalyst, the Brønsted acid sites on ZrO₂/H₃PO₄ were responsible for methanol
activation. Another well-known method to enhance the surface acidity is the modification with sulfate ions (super acidic catalyst) [98]. However, it is known that the catalytic activity of unmodified Ce_xZr_{1-x}O_2 is reduced to some extent by the presence of strong acid sites on the surface of the catalysts [99].

1.3.2. Suitable catalysts for DEC synthesis

Based on the results shown in Tables A1.1, A1.2 and A1.3, it is obvious that only a few efforts are being made to develop suitable catalysts for the direct synthesis of DEC from ethanol and carbon dioxide. However, the majority of these efforts were focused mainly on batch processes. According to the Tables A1.1 and A1.2, attempts to use continuous processes for DEC production from ethanol are very rare. In addition, the synthesis of DEC certainly allows CO_2 to be used as a valuable and renewable relatively low-cost feedstock. Until now, a wide range of heterogeneous catalytic systems have been studied for this reaction. For instance, CeO_2 [99-105], K_2CO_3-C_2H_5I [30], CeO_2/SBA-15 [102], Nb_2O_5/CeO_2 [106], Cu-Ni/AC [31], Ce-H-MCM-41 [29], Cu-Cl [107], CeO_2-ZrO_2 are some of the most widely used catalyst compositions so far. In addition, several homogeneous catalysts such as KI/EtONa [72] and metal tetra-alkoxides [70, 72] were found to be effective for one-pot DEC synthesis. Among them, literature reports indicate that Ce-Zr-O solids are most effective catalysts [94, 99, 100]. The catalytic activity of Ce-Zr-O towards DEC production was ascribed to the presence of acid-base sites on the surface, which consist of coordinatively unsaturated metal cations M^{4+} (Lewis acid-electron acceptors), lattice oxygen O^{2-} (Lewis base-electron donors) and hydroxyl groups probably acting as Brønsted basic centers during water formation [27, 99]. It has been proposed that dissociation of adsorbed ethanol leads to the formation of ethoxide group on the acid sites of the catalyst accompanied by a proton release, which reacts with a surface hydroxyl group to produce water. CO_2 is then inserted into the M-O bond of the C_2H_5O-M species to produce the reaction intermediate m-C_2H_5OCOO-M. This process is facilitated by interactions of C and O atoms with Lewis acid-base pairs, i.e. O^{2-}-M^{4+}-O^{2-}. Monoethyl carbonate species react with activated ethanol on the acid sites of the catalyst to produce DEC [87, 108, 109]. It was suggested that high selectivity to DEC is due to rapid conversion of the ethoxide species to ethyl carbonate species under high CO_2 pressure.
1.3.3. Thermodynamic restrictions

In spite of the obvious environmentally-friendly synthesis route, some additional difficulties of the direct synthesis of carbonate esters from alcohols and CO\(_2\) also need to be taken into account. For instance, the activation of carbon dioxide is very difficult due to the fact that CO\(_2\) is highly thermodynamically stable and kinetically inert. In addition, direct synthesis of dialkyl carbonates from alcohols and CO\(_2\) shows some thermodynamic (equilibrium) limitations and therefore the yields of DEC and DMC to be achieved are expected to be relatively low in the absence of dehydrating agent. Thermodynamically possible yield of dialkyl carbonate is in a range of 1-2\%, depending on reaction temperature and pressure. The formation of H\(_2\)O as a by-product shifts the equilibrium towards the reactants side. Several studies described some ways to overcome this problem (Table A1.3), e.g. usage of certain chemical reagents or absorbents for instance butylene oxide [29, 88, 102], benzonitrile [110], acetals or ketals [71, 76, 78, 79, 94], acetonitrile [104] and also inorganic absorbents like zeolites [77], might be helpful to remove H\(_2\)O from the product stream during the course of the reaction. The use of acetals as dehydrating agents over Bu\(_2\)Sn(OMe)\(_2\) catalyst leads to high yield of DMC (\(Y_{DMC} = 70\%\)), however high CO\(_2\) pressure (2000 bar) is required in order to avoid side reactions [25]. Choi et al. used inorganic dehydrating agent and reached high DMC yield (~50\%) by removing the water with molecular sieve 3A in an external cooled loop [77]. However, this route has not been explored due to an extra consumption of energy for cooling the loop. Alternatively, Dibenedetto et al. [106] used a polymeric organic membrane PERVAP 1211 to remove the water formed during the reaction. Unfortunately, this effort was not successful due to problem that the reaction mixture cannot be directly separated as DEC passes through the membrane since it is permeable at concentrations above 0.3\%. Nevertheless, in the work of Li et al. [89] three types of supported membranes (mesoporous silica, polyimide silica and polyimide-titania hybrid membrane) were applied for the synthesis of dimethyl carbonate (DMC) from methanol and CO\(_2\). Even though, the use of such membranes considerably improved DMC formation, however, the capability of dehydration at high pressure and temperature was reported to be very low.
1.3.4. Phase behavior of the CO₂ + EtOH system

Carbon dioxide has a low critical temperature (T_{cr} = 31.04 °C) and pressure (p_{cr} = 72.9 bar). However, the addition of alcohols to CO₂ causes a variation of the critical properties T_{cr}, p_{cr}, ρ_{cr} and of phase diagram of the resultant CO₂-alcohol mixture. For instance, the addition of 4.8 mol% MeOH to CO₂ causes an increase of T_{cr} of CO₂-MeOH by 39% and an increase of P_{cr} by a factor of 2.2, compared to pure CO₂. [111]. Since the present study was mainly focused on diethyl carbonate synthesis, the phase behavior of CO₂ + EtOH system at different temperatures and pressures is further described in detail. The critical points (p_{cr}, T_{cr}) for the C₂H₅OH-CO₂ binary system were studied by various researchers in the past, such as by Backer [112], Takishima [113], Lim [114], Yeo [115] and Galicia-Luna et al. [116, 117]. As can be seen in Fig. 1.4a, the supercritical region for C₂H₅OH-CO₂ binary system is reached maximum near 160 bar and temperature in a range of 120-160 °C when initial CO₂ molar fraction in such system is between 0.7 and 0.9. Moreover, the larger the ethanol concentration in the feed mixture, the higher the required temperature to reach the critical point is. Based on such reports, I suppose that these trends are still valid for quaternary system, due to the low amounts of DEC (predicted x~0.004 at reaction equilibrium) and H₂O (predicted x~0.004 at reaction equilibrium). One can also expect that above 160 bar the reaction mixture might be in the liquid or supercritical state, depending upon the system temperature. Based on the literature [68, 106], in order to reach a higher ethanol conversion with respect to using liquid ethanol pressurized by CO₂ the use of supercritical conditions is required. I supposed that under supercritical conditions, EtOH and CO₂ are in a single phase and the effect of solubility-dependent concentration of CO₂ in the liquid phase is cancelled out. Cai et al. [118] and Leino et al. [26] showed in their theoretical studies for DMC synthesis that the relatively high DMC formation had been partly attributed to the fact that reaction becomes thermodynamically favourable as the system pressure increases. The experimental data are confirmed that an increase in the pressure from 45 bar to 200 bar improved the yield of DMC from 0.14 mol% to 0.20 mol%, respectively, at relatively low reaction temperature of 170 °C.
1. General Introduction and Literature Overview

Figure 1.4. (a) Critical parameters for CO\textsubscript{2}-C\textsubscript{2}H\textsubscript{5}OH mixture reported by several authors: 1-[116], 2-[115], 3-[112], 4-[119], 5-[114], 6-[113] (reprinted from [111]). *CP- supercritical parameters of pure components; (b) Ethanol and CO\textsubscript{2} concentrations in the C\textsubscript{2}H\textsubscript{5}OH-CO\textsubscript{2} system in vapor-liquid equilibria at: p = 140 bar, T = 80, 100, 120, 140, 180 °C and molar EtOH : CO\textsubscript{2} = 30 : 70.

A group contribution equation of state called PSRK (Predictive Soave-Redlich-Kwong) [120] has been applied to describe vapor-liquid equilibrium (VLE) of quaternary mixture, containing C\textsubscript{2}H\textsubscript{5}OH-CO\textsubscript{2}-C\textsubscript{5}H\textsubscript{10}O\textsubscript{3}-H\textsubscript{2}O. VLE were measured at 80, 100, 120, 140, 180 °C and at high pressure (80-200 bar). The general form of SRK (Soave-Redlich-Kwong) equation can be written as follows:

\[ P = \frac{RT}{(V - b)} + \frac{a}{V(V + b)} \alpha(T) \]  

(Equation 1.1)

The calculation of thermodynamic parameters under the temperatures 80-180 °C and the pressures 80-200 bar is used to predict the maximum DEC yields under selected reaction conditions (Table 1.4). It is noted, that in the C\textsubscript{2}H\textsubscript{5}OH-CO\textsubscript{2}-C\textsubscript{5}H\textsubscript{10}O\textsubscript{3}-H\textsubscript{2}O system vapor-liquid two phases exist.

Table 1.4. Maximal thermodynamically possible DEC yields at equilibrium for several reaction conditions at a constant molar ratio of EtOH : CO\textsubscript{2} of 30 : 70.

<table>
<thead>
<tr>
<th>T→</th>
<th>80</th>
<th>140</th>
<th>180</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>p↓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.8</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>100</td>
<td>0.6</td>
<td>0.9</td>
<td>0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>120</td>
<td>0.5</td>
<td>0.8</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>150</td>
<td>0.5</td>
<td>0.6</td>
<td>0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>180</td>
<td>0.5</td>
<td>0.5</td>
<td>0.1</td>
<td>0.6</td>
</tr>
</tbody>
</table>
To illustrate the effect of temperature on the concentration of ethanol and CO$_2$, mole fractions of ethanol and CO$_2$ in gas and liquid phase at 140 bar are plotted in Figure 1.4b. It clearly seen, that ethanol concentrated in liquid phase and as temperature increases, the highest attainable ethanol concentration increases. These results are in a good agreement with those published by J. S. Lim [114]. He described a high pressure vapour-liquid equilibrium for CO$_2$-C$_2$H$_5$OH system with a wide range of ethanol concentration and found the similar effect of temperature on the ethanol concentration.

1.4. Motivation and objectives of the thesis

The global warming from the emission of greenhouse gases has received worldwide interest in the recent years. Among several greenhouse gases, CO$_2$ contributes over 72% to global warming due to its huge emission amount over 37 Gt CO$_2$ per year. This is also indicated by increased atmospheric CO$_2$ concentration, which has risen from about 280 ppm (1850) to 411 ppm (February 2019). The utilization of CO$_2$ to produce various commercially important chemicals over heterogeneous catalysts is one of the efficient pathways to reduce CO$_2$ emissions, since the CO$_2$ is not only just a greenhouse gas, but also an important source of carbon in industry.

Among different chemicals that can be produced from CO$_2$ conversion, organic carbonates are special class of chemicals with high oxygen content that are used in various sectors. The traditional route to produce organic carbonates is to use the extremely toxic phosgene (Bayer process). In terms of safety and environment concerns, the replacement of hazardous phosgene route by CO$_2$ is highly concerned, encouraged and also attracted the scientific interest. The organic carbonates, such as dimethyl carbonate (DMC) and diethyl carbonate (DEC), are used as raw materials in a wide range of chemical reactions, for instance, as a precursor to synthesize polycarbonates, as electrolytes in lithium batteries and as solvent due to their high solubilizing power, exhibit relatively low toxicity and having suitable boiling point to be removed by vaporization. Furthermore, DEC/DMC can be used as an additive to diesel fuel due to their high oxygen content (40.6% for DEC and 53.3% for DMC) and high octane booster power ((R + M)/2 = 105, where R is the research octane number and M stands for motor octane number) to improve the performance of gasoline combustion.

The direct production of organic carbonates via reaction of CO$_2$ and alcohols is certainly attractive and promising way due to the conversion of CO$_2$ into valuable chemicals and is
"green" chemical process with many advantages. However, the amount of CO2 consumption for generated chemicals is relatively small (only 110 Mt/y of CO2 converted into organic and inorganic compounds) and is not enough to consume most of CO2 produced. Therefore, there is a real need to convert CO2 into various industrially important products, such as DMC and DEC.

However, there are three major problems of this reaction: i) thermodynamic limitations, ii) catalyst deactivation and iii) hydrolysis of the desired products by formed water. Therefore, achieving high yield of target product is difficult / very low (~1-2%) without water elimination during the course of the reaction. Within the project "Innovative homogen- und heterogenkatalysierte Reaktionen zur chemischen Umwandlung von CO2", the main task of our research group was developing effective catalysts and identifying suitable reaction conditions for the direct and continuous synthesis of dialkyl carbonates from CO2 and C1-C2 alcohols (methanol and ethanol). Water-removal approaches using inorganic membranes for the direct carboxylation of alcohols were designed and tested by other research group under the same project but with another Ph.D. student.

Thus, the main objective of the present study in general is to improve the yield of dialkyl carbonates from CO2 and alcohols by means of developing i) effective catalyst compositions, ii) optimizing reaction conditions, iii) identifying key properties of the catalysts (e.g. acid-base functions, reducibility etc.), iv) ultimately establishing structure-performance relationships as required for tailored catalyst design. In particular, for direct and continuous synthesis of DEC the main goal is to evaluate the potential of catalysts in a continuous mode using a plug-flow reactor (PFR) to increase the DEC yield under suitable reaction conditions.

Pure CeO2, ZrO2 and mixed Ce-Zr oxides are generally reported to be the most effective catalysts in the formation of dialkyl carbonates due to the presence of both acidic and basic sites in these solids. Even though Ce-Zr oxides are known from the literature, tuning their acid-base properties, their suitable modifications by means of different dopants and exploring their potential towards the desired reaction are still missing in the literature. With this background, we are motivated to systematically tune their catalytic properties by various means, e.g. by varying preparative methods, tuning Ce/Zr ratios, application of different dopants, varying calcination temperatures etc. and check their influence on the catalytic performance. As mentioned above, catalytic properties of various CeO2-ZrO2 solid solutions can be adjusted through the ratio of Ce/Zr. Therefore, Ce_xZr_1-xO2 catalysts with different Ce/Zr ratios were synthesized in the frame of this work. Moreover, the effect of promoting of
CeO$_2$-ZrO$_2$ with an acidic compound, e.g. phosphoric acid, was also investigated with the purpose to check if the yield of DMC can be increased through accelerating DMC formation step.

In order to achieve the above mentioned goals, this thesis focuses on the following aspects:

i) to synthesize and apply Ce$_x$Zr$_{1-x}$O$_2$ catalysts with different Ce content for the one-pot synthesis of organic carbonates from CO$_2$ and alcohols and find out optimum Ce content.

ii) to perform surface modifications of previously optimized Ce-Zr-O composition (e.g. Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst) with a phosphoric acid and also to investigate the effect of such modification through varying P-contents in Ce$_{0.8}$Zr$_{0.2}$O$_2$ with the aim to identify efficient catalyst composition for direct synthesis of DMC from CO$_2$ and methanol.

iii) to gain deeper insights into the key catalytic properties, the catalysts were characterized by means of various physico-chemical techniques such as N$_2$ physisorption, ICP-OES, BET, XRD, XPS, H$_2$-TPR, TEM, In situ FTIR, NH$_3$- and CO$_2$-TPD. The obtained results were related to catalytic activity towards dialkyl carbonates production.

iv) to design continuous flow system and to determine optimal reaction conditions for direct DEC synthesis from CO$_2$ and ethanol, i.e. to investigate the effect of each parameter (e.g. temperature, pressure, EtOH : CO$_2$ ratios and LHSV) on DEC yield.
Chapter 2

2. Experimental section: Preparation, testing and characterization methods

Chapter 2 represents the detailed procedure for the preparation of $\text{Ce}_x\text{M}_{1-x}\text{O}_2$ materials: various Ce/M ratios, preparation methods, surface modification etc. The necessary theoretical background of different characterization methods is also given. The experimental set-ups and reaction procedures are described in detail.
2. Experimental section: Preparation, testing and characterization

2.1. Catalyst preparation

2.1.1. Chemicals

For catalyst preparation Ce(NO$_3$)$_3$·6H$_2$O (99.5%, Acros), ZrO(NO$_3$)$_2$·xH$_2$O (99%, technical grade), ZrCl$_2$·8H$_2$O (99.5%, Sigma-Aldrich), anhydrous hafnium nitrate ((Hf(NO$_3$)$_4$, Sigma-Aldrich, 99.9%), titanium tetrachloride (99.9% TiCl$_4$, Aldrich), oxalic acid-dihydrate (98% C$_2$O$_4$H$_2$·2H$_2$O, Alfa Aesar), phosphoric acid (85% H$_3$PO$_4$, Roth), nitric acid (65% HNO$_3$, Roth), citric acid (99% C$_6$H$_8$O$_7$, Sigma-Aldrich) and aqueous ammonium hydroxide (25%, Roth) were used. All used solvents were of analytical grade.

2.1.2. Citrate complexation method

2.1.2.1. Ce$_x$Zr$_{1-x}$O$_2$ solids

For the correct calculation of the specific Ce$_x$Zr$_{1-x}$O$_2$ stoichiometries the determination of x in ZrO(NO$_3$)$_2$·xH$_2$O is absolutely essential. x was calculated from the thermal decomposition of the Zr precursor studied by TG under air. x was calculated with ~4. Hence, the molar composition was ZrO(NO$_3$)$_2$·4H$_2$O. The detailed explanation is given in Appendix (section A2.1). Ce$_x$Zr$_{1-x}$O$_2$ solids with x = 0, 0.2, 0.5, 0.8 or 1.0 (catalysts for Chapter 4) were prepared by a citric acid complexation method according to Alifanti et al. [121]. ZrO(NO$_3$)$_2$·4H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O in desired quantities were dissolved in deionized water yielding a 0.1 M solution (Table 2.1).

<table>
<thead>
<tr>
<th>Catalyst Code</th>
<th>Code</th>
<th>Ce(NO$_3$)$_3$·6H$_2$O (g)</th>
<th>ZrO(NO$_3$)$_2$·4H$_2$O (g)</th>
<th>C$_6$H$_8$O$_7$ (g)</th>
<th>Drying (T$_d$/h)</th>
<th>Calcination (T$_c$/atm./t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>C-citrate</td>
<td>15.5</td>
<td>-</td>
<td>7.5</td>
<td>70 °C/16h</td>
<td>450 °C/air/3h</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$</td>
<td>C80Z-citrate</td>
<td>15.5</td>
<td>2.7</td>
<td>9.4</td>
<td>70 °C/16h</td>
<td>450,700, 1000 °C/air/3h</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$</td>
<td>C80Z-1*</td>
<td>15.5</td>
<td>2.7</td>
<td>9.4</td>
<td>70 °C/16h</td>
<td>700 °C/air/3h</td>
</tr>
<tr>
<td>Ce$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>C50Z-citrate</td>
<td>15.5</td>
<td>10.8</td>
<td>15.1</td>
<td>70 °C/16h</td>
<td>450 °C/air/3h</td>
</tr>
<tr>
<td>Ce$<em>{0.2}$Zr$</em>{0.8}$O$_2$</td>
<td>C20Z-citrate</td>
<td>15.5</td>
<td>43.3</td>
<td>37.7</td>
<td>70 °C/16h</td>
<td>450 °C/air/3h</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Z-citrate</td>
<td>-</td>
<td>43.3</td>
<td>30.2</td>
<td>70 °C/16h</td>
<td>450 °C/air/3h</td>
</tr>
</tbody>
</table>

*C$_2$H$_5$OH was used as a solvent during preparation instead of H$_2$O

Citric acid was added in 10 mol% excess for complete complexation of metal cations. The mixture was stirred at room temperature for 2 hours. The excess solvent was removed on a
rotary evaporator. The obtained solid was dried overnight (16 h) under vacuum at 70 °C. The precursors were calcined at 450 °C for 3 h in air (heating rate of 2 K min⁻¹, air flow of 60 mL min⁻¹). In total five different CeₓZr₁₋ₓO₂ catalysts with varying Ce contents of 0, 20, 50, 80, 100 mol% were prepared and they are denoted as Z-citrate (pure zirconia), C20Z-citrate, C50Z-citrate, C80Z-citrate and C-citrate (pure ceria), respectively. Another batch of C80Z-citrate was calcined in air separately at 700 or 1000 °C for 3 h.

2.1.2.2. Ce₀.₈Ti₀.₂O₂ solids

The Ce₀.₈Ti₀.₂O₂ catalyst was prepared by citrate complexation method in analogy to section 2.1.2.1. Cerium nitrate hexahydrate and titanyl nitrate (Table 2.2) were used as Ce and Ti precursors. Based on the fact that titanyl nitrate is not commercially available, TiO(NO₃)₂ [122] was prepared and used as precursor for Ce₀.₈Ti₀.₂O₂ (See Appendix A2.2).

Table 2.2. Pure TiO₂ and Ce₀.₈Ti₀.₂O₂ catalysts prepared by citrate complexation method.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Code</th>
<th>Ce(NO₃)₃·₆H₂O (g)</th>
<th>TiO(NO₃)₂ (g)</th>
<th>C₆H₈O₇ (g)</th>
<th>Drying (T่อ/t)</th>
<th>Calcination (Tᵥ/atm./t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₀.₈Ti₀.₂O₂</td>
<td>C80T-citrate</td>
<td>7.7</td>
<td>0.4</td>
<td>4.1</td>
<td>70 °C/16h</td>
<td>700 °C/air/3h</td>
</tr>
<tr>
<td>TiO₂</td>
<td>T-citrate</td>
<td>-</td>
<td>8.5</td>
<td>20</td>
<td>70 °C/16h</td>
<td>700 °C/air/3h</td>
</tr>
</tbody>
</table>

2.1.2.3. Ce₀.₈Hf₀.₂O₂ solids

The Ce₀.₈Hf₀.₂O₂ catalyst was prepared by citrate complexation method using the procedure described in section 2.1.2.1. Cerium nitrate hexahydrate and anhydrous hafnium nitrate were used as Ce and Hf precursors (Table 2.3).

Table 2.3. Pure HfO₂ and Ce₀.₈Hf₀.₂O₂ catalysts prepared by citrate complexation method.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Code</th>
<th>Ce(NO₃)₃·₆H₂O (g)</th>
<th>Hf(NO₃)₂ (g)</th>
<th>C₆H₈O₇ (g)</th>
<th>Drying (T่อ/t)</th>
<th>Calcination (Tᵥ/atm./t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₀.₈Hf₀.₂O₂</td>
<td>C80H-citrate</td>
<td>15.49</td>
<td>3.8</td>
<td>9.4</td>
<td>70 °C/16h</td>
<td>700 °C/air/3h</td>
</tr>
<tr>
<td>HfO₂</td>
<td>H-citrate</td>
<td>-</td>
<td>8.5</td>
<td>6.1</td>
<td>70 °C/16h</td>
<td>700 °C/air/3h</td>
</tr>
</tbody>
</table>

2.1.3. Ce₀.₈Zr₀.₂O₂ solid solutions prepared by co-precipitation

Ce₀.₈Zr₀.₂O₂ (catalyst used in Chapter 6) was prepared by a co-precipitation method with aqueous solutions of ZrOCl₂·8H₂O (0.1M) and Ce(NO₃)₃·6H₂O (0.36M) using aqueous
ammonium hydroxide (6 vol.%) as a precipitating agent (Table 2.4) [99]. pH value during this procedure (addition of NH₄OH) was controlled to be about 10. The resultant precipitate was collected and washed with deionized water until Cl⁻ species were no longer detectable as AgCl precipitate via titration with AgNO₃ solution. The product precipitate was dried at 120 °C overnight and calcined at 700 °C for 3 hours in air (heating rate of 2 K min⁻¹, air flow of 60 mL min⁻¹).

Table 2.4. Ce₀.₈Zr₀.₂O₂ catalyst prepared by co-precipitation method.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Code</th>
<th>Ce(NO₃)₃•6H₂O (g)</th>
<th>ZrOCl₂•8H₂O (g)</th>
<th>Drying (T/°C/t)</th>
<th>Calcination (T/atm./t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₀.₈Zr₀.₂O₂</td>
<td>C80Z</td>
<td>15.49</td>
<td>2.9</td>
<td>120 °C/16h</td>
<td>700 °C/air/4hr</td>
</tr>
</tbody>
</table>

2.1.4. CeₓZr₁₋ₓO₂ via oxalate gel co-precipitation method

The preparation of CeₓZr₁₋ₓO₂ solids (with x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) was carried out by an oxalate gel co-precipitation method (catalysts for Chapter 3) [123]. For each synthesis, following two solutions were prepared: i) desired amounts of Ce(NO₃)₃•6H₂O and ZrO(NO₃)₂•4H₂O were dissolved in 65 ml of ethanol and ii) 6 g of oxalic acid in 48 ml of ethanol (1M solution) (Table 2.5).

Table 2.5. List of CeₓZr₁₋ₓO₂ catalysts prepared by oxalate gel co-precipitation method.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Code</th>
<th>Ce(NO₃)₃•6H₂O (g)</th>
<th>ZrO(NO₃)₂•4H₂O (g)</th>
<th>Drying (T/°C/t)</th>
<th>Calcination (T/atm./t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>Cpreci</td>
<td>4.3</td>
<td>-</td>
<td>70 °C/16h</td>
<td>600 °C/air/4hr</td>
</tr>
<tr>
<td>Ce₀.₈Zr₀.₂O₂</td>
<td>C80Zpreci</td>
<td>17.4</td>
<td>3.03</td>
<td>70 °C/16h</td>
<td>600 °C/air/4hr</td>
</tr>
<tr>
<td>Ce₀.₆Zr₀.₄O₂</td>
<td>C60Zpreci</td>
<td>6.5</td>
<td>3.03</td>
<td>70 °C/16h</td>
<td>600 °C/air/4hr</td>
</tr>
<tr>
<td>Ce₀.₄Zr₀.₆O₂</td>
<td>C40Zpreci</td>
<td>2.9</td>
<td>3.03</td>
<td>70 °C/16h</td>
<td>600 °C/air/4hr</td>
</tr>
<tr>
<td>Ce₀.₂Zr₀.₈O₂</td>
<td>C20Zpreci</td>
<td>1.1</td>
<td>3.03</td>
<td>70 °C/16h</td>
<td>600 °C/air/4hr</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Zpreci</td>
<td>-</td>
<td>3.03</td>
<td>70 °C/16h</td>
<td>600 °C/air/4hr</td>
</tr>
</tbody>
</table>

Solution (ii) was added dropwise under vigorous stirring to solution (i) until complete precipitation. The obtained precipitate was stirred for additional 2 hours, filtered and dried overnight (16 h) at 70 °C. Afterwards, the received powders were calcined at 600 °C for 4 hours (heating rate of 1.67 K min⁻¹, air flow of 100 mL min⁻¹). The received CeₓZr₁₋ₓO₂ catalysts were denoted as Zpreci (pure zirconia), C20Zpreci, C40Zpreci, C60Zpreci, C80Zpreci (40, 60, 80 mol% Ce) and Cpreci (pure ceria).
2.1.5. Phosphated Ce$_x$Zr$_{1-x}$O$_2$: co-precipitation and wet impregnation

Ce$_{x}$Zr$_{1-x}$O$_2$/H$_3$PO$_4$ (x = 0.8) solid solutions were prepared in two steps according to previously reported protocols [96, 124]. First, Ce-Zr hydroxide were prepared at room temperature from ethanolic solutions of ZrO(NO$_3$)$_2$•4H$_2$O and Ce(NO$_3$)$_3$•6H$_2$O in desired quantities using aqueous ammonium hydroxide (6 vol.%) as precipitating agent (Table 2.6). pH value at the end of the procedure was about 9. The resultant precipitate was washed three times with deionized water and then dried at 120 °C for 12 hours.

**Table 2.6. Ce-Zr precursor prepared by precipitation method.**

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Ce(NO$_3$)$_3$•6H$_2$O (g)</th>
<th>ZrO(NO$_3$)$_2$•4H$_2$O (g)</th>
<th>Drying (T$_D$/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ce$<em>{0.8}$Zr$</em>{0.2}$)OH</td>
<td>17.4</td>
<td>3.03</td>
<td>120 °C/12h</td>
</tr>
</tbody>
</table>

Ce$_{0.8}$Zr$_{0.2}$O$_2$/H$_3$PO$_4$ catalysts were prepared by impregnation of 0.06M aqueous H$_3$PO$_4$ on Ce-Zr hydroxides with different P/Zr ratios of 0.03 (C80ZP-1), 0.12 (C80ZP-2), 0.3 (C80ZP-3) (Table 2.7).

**Table 2.7. List of Ce$_x$Zr$_{1-x}$O$_2$ catalysts treated with H$_3$PO$_4$.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Code</th>
<th>V of 0.06M H$_3$PO$_4$ (mL) for 1g of Zr</th>
<th>P/Zr</th>
<th>Drying (T$_D$/t)</th>
<th>Calcination (T$_c$/atm./t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$/H$_3$PO$_4$</td>
<td>C80ZP-1</td>
<td>6.5</td>
<td>0.03</td>
<td>120 °C/3h</td>
<td>600 °C/air/4h</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$/H$_3$PO$_4$</td>
<td>C80ZP-2</td>
<td>26</td>
<td>0.12</td>
<td>120 °C/3h</td>
<td>600 °C/air/4h</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$/H$_3$PO$_4$</td>
<td>C80ZP-3</td>
<td>65</td>
<td>0.3</td>
<td>120 °C/3h</td>
<td>600 °C/air/4h</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$/H$_3$PO$_4$</td>
<td>C80ZP*</td>
<td>26</td>
<td>0.12</td>
<td>120 °C/3h</td>
<td>600 °C/air/4h</td>
</tr>
</tbody>
</table>

* Post-treated sample

To investigate the effect of post–treatment, 0.06M aqueous H$_3$PO$_4$ (P/Zr=0.12) was introduced directly to calcined Ce$_{0.8}$Zr$_{0.2}$O$_2$ at 600 °C/air/4h (denoted as C80ZP*). All treatments were performed under stirring for 1 hour at room temperature. The excess liquid was removed under vacuum on a rotavapor, the residue was dried for 3 hours at 120 °C and finally calcined at 600 °C for 4h (1.67 K min$^{-1}$, airstream of 100 mL min$^{-1}$).
2. Experimental section: Preparation, testing and characterization

2.2. Catalyst characterization

2.2.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is used to evaluate the thermal stability of materials and to determine the fraction of volatile components (e.g. moisture) during heating process. TGA has been performed in the temperature range between 27 and 1000 °C using a Netzsch STA 449F3 instrument. The heating rate was 10 K min⁻¹. The measurements were carried out in synthetic air (80 mL min⁻¹). 60 mg of the each sample was used for the analysis.

2.2.2. Nitrogen adsorption: BET and BJH methods

Physical adsorption of nitrogen is widely used for the determination of overall surface area and pore size distribution of various porous solids. The specific surface area is estimated by measuring the amount of adsorbed nitrogen at -196°C across a wide range of relative pressures. In present work the surface areas (SA) calculated according to the BET equation (Equation 2.1) and pore volumes of the samples obtained from BJH equation (Equation 2.2) were experimentally determined using a NOVA 4200e device (Quantachrome Instruments).

\[
S_{BET} = \frac{V_m N_A A_m}{22414 W}
\]  
(Equation 2.1)

\[
r_k = \frac{-2\sigma V}{RT \ln\left(\frac{P}{P_0}\right)}
\]  
(Equation 2.2)

\(V_m = \) the monolayer volume at STP conditions (mL)
\(N_A = \) Avogadro constant (6.022 x 10²³ mol⁻¹)
\(A_m = \) effective cross-sectional area of one adsorbate molecule (0.162 nm² for N₂)
\(22414 = \) volume occupied by 1 mole of the adsorbate gas at STP (mL)
\(W = \) the amount of the sample tested (grams).

 Prior to each nitrogen sorption measurement, the samples were evacuated at 200 °C for 2 h to remove gases and vapours that may have become physically adsorbed on the surface during preparation and storage.
2. Experimental section: Preparation, testing and characterization

2.2.3 X-ray diffraction studies (XRD)

X-ray diffraction is used to determine the crystal structure, phase composition, lattice parameters, crystallite size and microstrain of solids. X-ray diffraction (XRD) studies described and discussed in Sections 4.1 and 5 were carried out on a X’Pert Pro diffractometer (Panalytical, Almelo, Netherlands) with CuKα radiation (λ = 1.5418 Å, 40 kV, 40 mA) and an X’Celerator RTMS detector. The phase composition of the samples was determined using the program suite WinXPOW by STOE & CIE with inclusion of the Powder Diffraction File PDF2 of the ICDD (International Centre of Diffraction Data). An average crystallite size (D) was calculated using Scherrer equation [125]:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

(Equation 2.3)

\( \lambda \) = X-ray wavelength (1.54 Å for CuKα radiation)

K = Scherrer’s constant of proportionality taken as 0.94

\( \beta \) = full width at half maximum of the peak

\( \Theta \) = the diffraction angle

The detailed XRD analysis, recorded on a Bruker D8 Advance instrument in Bragg-Brentano mode with Cu Kα radiation (1.54 Å, 40 kV and 40 mA) using a silicon single crystal as sample holder to minimize scattering, was described and discussed in sections 3, 4.2 and 6. For better homogenization, the dried powder samples were redispersed in ethanol and coated on a silicon surface. XRD patterns were recorded in the range from 5 to 90° 20 with a step of 0.01° 20 at a counting time of 0.6 s. For qualitative phase analysis with a Diffrac.Suite EVA V1.2 from Bruker the pattern of monoclinic ZrO₂ (#78-0047), tetragonal ZrO₂ (#79-1764), and cubic CeO₂ phase (#78-0694) from the ICDD database were used as references. Rietveld refinement with the program package TOPAS 4.2 from Bruker or Rietveld Quantitative Analysis was performed to determine the lattice parameters, the substitution in the unit cells, the weight amount of crystalline phases, the crystallographic density, the average crystallite sizes and microstrain. The breadth and position of diffraction peak can be affected by the defective crystal structure. This deviation from the crystallinity is caused by the lattice distortion due to the microstrain. The defects producing microstrains are dislocations, grain, sinter stresses and grain boundaries etc. The width of the diffraction peaks can vary due to the size of crystallite and crystalline defects. Thus, both microstrain and
crystallite size lead to peak broadening. The peak broadening due to microstrain ($\varepsilon$) changes as

$$B(2\theta) = 4\varepsilon \frac{\sin \theta}{\cos \theta}$$  \hspace{1cm} (Equation 2.4)

compared to peak broadening due to crystallite size

$$B(2\theta) = \frac{K\lambda}{D \cos \theta}$$  \hspace{1cm} (Equation 2.5)

For each Rietveld refinement, the instrumental correction as determined with a standard powder sample LaB6 from NIST (National Institute of Standards and Technology) as standard reference material (SRM 660b; a(LaB6)=4.15689 Å) was taken into account.

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

For the determination of the elemental composition, a Varian 715-ES ICP-OES was used. Approximately 10 mg of the sample was mixed with 8 mL of aqua regia and 2 mL hydrofluoric acid. The acid digestion was performed in a microwave-assisted sample preparation system "MULTIWAVE PRO" from Anton Paar at ~200 °C and ~50 bar pressure. The data analysis was performed on the Varian 715-ES software "ICP Expert".

2.2.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), also known as ESCA (electron spectroscopy for chemical analysis), is used to determine the composition of the catalysts in the near-surface-region due to shifts in the binding energies. XPS tests were carried out using a VG ESCALAB 220iXL instrument with monochromatic AlK$\alpha$ radiation ($E = 1486.6$ eV). The samples were fixed by using a double adhesive carbon tape on a stainless steel sample holder. The peaks were fitted by Gaussian–Lorentzian curves following a Shirley background subtraction.

2.2.6 Transmission electron microscopy (TEM)

Transmission Electron Microscopy (TEM) provides information on position of atoms in crystalline sample, morphology (size, shape, distributions) and elemental composition. TEM
investigations were carried out at 200 kV with an aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS). The aberration corrected STEM imaging (High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF)) were done with a spot size of approximately 0.13 nm, a convergence angle of 30–36° and collection semi-angles for HAADF and ABF of 90–170 mrad and 11–22 mrad, respectively. The microscope is equipped with a JED-2300 (JEOL) energy-dispersive X-ray-spectrometer (EDXS) for chemical analysis. Samples were prepared by depositing without any pre-treatment on a holey carbon supported Cu-grid (mesh 300) and transferred to the microscope.

2.2.7 Temperature-programmed reduction (TPR) using H_2 as the reduction agent

Temperature programmed reduction (TPR) is a useful technique to obtain information on the reducibility of solid oxide materials. TPR profiles were recorded in a temperature range from RT to 800 °C at a heating rate of 5 K min⁻¹ on a Micromeritics AC2920 instrument. This instrument mainly consists of a fixed-bed reactor in a furnace and a thermal conductivity detector (TCD) for determination of gas composition. The temperature of reaction is controlled by thermocouple located in the catalyst bed. The H_2 concentration in a gas stream is monitored continuously using TCD with a linear temperature ramp of e.g. 5 K min⁻¹. The obtained TPR profiles are used to determine an overall amount of H_2 consumed and temperature of maximal H_2 consumption. Prior to TPR measurements, all the samples were pretreated with 5% H_2/Ar at room temperature for 10 min. For each H_2-TPR experiment 0.1-0.2 g of powder is used.

2.2.8 Temperature programmed desorption (TPD) using NH_3 as basic probe and CO₂ as acidic probe

Temperature programmed desorption (TPD) techniques are important methods for determination of acidic and basic properties (strength and number of acid-base sites) of catalyst. In this method, acidic (e.g. carbon dioxide) or basic molecular probes (e.g. ammonia) are adsorbed on the basic or acidic sites of solids, respectively. TPD of ammonia (TPD-NH₃) or carbon dioxide (TPD-CO₂) were carried out in a homemade apparatus consisting of a gas flow system, a high temperature oven and a quartz reactor. For determination of overall concentration of acid sites and their distribution, the samples (0.1–0.2 g) were treated in nitrogen at 400 °C for 30 min to remove moisture and cooled down to 100 °C in He of high
purity (6.0) prior to NH$_3$ adsorption, which was carried out at 100 °C for 30 min in a flow of 5% NH$_3$/He. Afterwards, the TPD-NH$_3$ experiments were carried out from 100 to 450 °C in He flow (50 cm$^3$ min$^{-1}$) with a heating rate of 10 K min$^{-1}$. The reaction temperature was continuously controlled by a thermocouple placed inside the catalyst bed. Desorption of NH$_3$ was monitored and evaluated by a thermal conductivity detector (TCD, GOW-Mac Instrument Co.). For determination of basic properties, the sample (0.2 g) was treated in He (50 mL min$^{-1}$) at 500 °C with a heating rate of 10 K min$^{-1}$ for 15 min (for the removal of adsorbed water) and cooled down to 100 °C in He (50 mL min$^{-1}$) prior to CO$_2$ adsorption, which was carried out at 100 °C for 90 min in a flow of 1.2% CO$_2$–He mixture. Afterwards, the TPD-CO$_2$ experiments were carried out in He flow (50 mL min$^{-1}$) at 100 °C for 30 min (for removal of physisorbed CO$_2$). After cooling to 70 °C for 10 min, the sample was heated up to 800 °C at a rate of 10 K min$^{-1}$ in a helium flow (50 mL min$^{-1}$). The analysis of the effluent gases was performed by Quadrupole mass spectrometer (Balzers Omnistar).

### 2.2.9 Fourier Transform Infrared Spectroscopy (FTIR)

*In situ* FTIR spectroscopy is widely used to study surface properties of solid samples through the adsorption of probe molecules and to characterize/identify reaction intermediates on its surfaces. In this work methanol and carbon dioxide were selected as probe molecules since they are the feed components in the studied reaction. *In situ* FTIR measurements were carried out in transmission mode on a Bruker Tensor 27 spectrometer equipped with a heatable and evacuable homemade reaction cell with CaF$_2$ windows connected to a gas-dosing and evacuation system. The powder was pressed into self-supporting wafer with a diameter of 20 mm and a weight of 50 mg. Before MeOH/CO$_2$ adsorption, the samples were pretreated in synthetic air by heating up to 400 °C for 10 min, cooled down to 170 °C and a spectrum was recorded. Then MeOH/CO$_2$ (saturator, RT; 50 mL min$^{-1}$ CO$_2$) was adsorbed at this temperature for 30 min. After adsorption the cell was flushed with He (50 mL min$^{-1}$) for 10 min and the adsorbate spectrum was recorded.

### 2.3. Experimental system and catalytic tests

#### 2.3.1. Continuous flow reactor

Continuous operation is used in large-scale industrial processes. In a general procedure, the reactants are delivered continuously into the reactor at a constant flow and reaction products
and non-reacted reactants are collected at the outlet. Moreover, the rate of reaction and the concentration of reactants and reaction products change across the catalyst bed.

Diethyl carbonate from ethanol and carbon dioxide was synthesized in continuous flow reactor. The experimental setup is schematically shown in Scheme 2.1. It mainly consists of a high pressure reactor (plug flow reactor, inner volume = 32 mL, inner diameter = 12.7 mm, max. pressure = 200 bar), equipped with an oil heated jacket (max. temperature = 220 °C); high pressure pumps, relief valves, product collector and flow-meter. All tubings and fittings were made from stainless steel 316L (Swagelok).

![Scheme 2.1](image)

**Scheme 2.1.** Schematic diagram of the experimental set up used for diethyl carbonate synthesis from ethanol and carbon dioxide.

In a standard procedure, the reactor was packed layer-by-layer: 27 g of corundum (size: 1 to 1.25 mm), 1 g of catalyst (size: 1 to 1.25 mm fraction), 27 g of corundum (Figure 2.1b). The catalyst was pressed and sieved in the particle size range of 1-1.25 mm. Such range was taken based on operation conditions published by C. Perego and S. Peratello [126]: the reactor diameter (D) must be minimum 10 catalyst particle diameter (d_p) \( \Rightarrow \frac{D}{d_p} > 10 \).
2. Experimental section: Preparation, testing and characterization

Figure 2.1. (a) Digital image of the experimental set up used and (b) Dimensions of plug-flow reactor (PFR).

A Gilson-pump with a thermostatic kit was employed to feed liquid CO₂ (99.9%, Air Liquide) to the reactor at a flow rate of 0.6 mL min⁻¹ (Figure 2.1a). A Shimadzu-HPLC pump was used in order to independently control the flow of ethanol of 0.1 mL min⁻¹ (99.9%, H₂O ≤ 0.1%, Roth). The molar ratio of EtOH : CO₂ was kept constant during the reaction. Three different molar ratios EtOH : CO₂ were used: 1 : 9, 1 : 6 and 1 : 3. The mixture of ethanol and liquid CO₂ (from a dip tube cylinder) were passed through a tube that was filled with molecular sieve type 3A and placed before the reactor to adsorb H₂O, if any is in the used ethanol. The molecular sieve dehydration technology was used to produce anhydrous EtOH. The filter with pore diameter of 0.5 µm was placed in order to avoid a discharge of catalyst with flowing reagents. The system pressure was controlled by two manually regulated relief valves in series. The first one was set to the desired reaction pressure while the second one was set to approximately 5-10 bar less. Such modification was applied to reduce a possible rapid pressure drop and to allow a more constant flow. Moreover, the second relief valve was covered by an external heating to avoid freezing of humidity. To provide the desired set pressure three different spring kits were used separately: purple (51.7 to 103 bar), orange (103 to 155) and brown (155 to 206 bar). Afterwards, the liquid phase was separated from the gas phase in a cold trap placed at the exit of the reactor outlet.

2.3.2. Batch reactor

Batch reactor operation is economical and simple way for small production rates. In a general procedure, the batch reactor is filled with reactants and under the reaction conditions they
convert into products. However, in comparison to continuous process the rate of batch reaction and reactant concentration depend on time. The reactant concentration falls down as shown in Figure 2.2a. Therefore, for the same reactor volume, the batch reaction would give lower conversions than continuous.

Carboxylation of methanol was performed in a stainless steel autoclave with an inner volume of 25 mL (Figure 2.2b). In a standard procedure 10 mL (247 mmol) of methanol and 50 mg of catalyst were added into the autoclave. The reactor was purged by filling and releasing 10 bar of CO$_2$ three times at room temperature. Further, liquid CO$_2$ was introduced into the reactor to reach 15 bar. Afterwards the autoclave was heated to 170 °C.

![Figure 2.2](image.png)

**Figure 2.2.** (a) Influence of time on the concentration of reactants in a batch reactor used for dimethyl carbonate synthesis from methanol and carbon dioxide and (b) Digital image of batch reactor with external heating jacket.

An external jacket was used for heating the reactor. When the desired temperature was achieved, the autoclave was further purged with liquid CO$_2$ to 65 bar and magnetically stirred constantly at 600 rpm during the reaction time. After 1 h of reaction the autoclave was rapidly cooled down in an ice bath to room temperature and the residual gas was immediately released.

### 2.3.3. Analysis: Gas chromatography

#### 2.3.3.1. Continuous reaction

The feed components and the reaction products were analyzed off-line by a gas chromatograph (GC-2014, Shimadzu) using a capillary column (CP-PoraBOND Q, 10m x 0.53mm x 10µm). The column outlet was connected to a methanizer (NiO catalyst) for conversion of CO$_2$ into methane, detected by a Flame Ionization Detector (FID). The temperature of the column was held at 45 °C for 3 min, then increased to 160 °C at a rate of
15 K min\(^{-1}\) and held for 6.5 min. The yield of diethyl carbonate (\(Y_{\text{DEC}}\), mol\%) is defined as molar amount of diethyl carbonate per initial molar amount of taken ethanol.

\[
Y(\text{DEC}) = \frac{\text{mole amount of DEC formed}}{\text{mole amount of EtOH taken}/2} \times 100\% \tag{Equation 2.6}
\]

The standard deviation (\(\sigma\)) is 0.001 mmol of DEC which is 0.6 %. It was calculated as

\[
\sigma = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \tag{Equation 2.7}
\]

\(n\) = number of GC measurements made
\(x_i\) = each measurement result (mmol of DEC)
\(\bar{x}\) = mean value of measurement results (mmol of DEC)

2.3.3.2. Batch reaction

Liquid products were analyzed off-line by gas chromatography using a GC HP6890 equipped with an HP-1 capillary column (length 50 m). The yield of DMC (\(Y_{\text{DMC}}\), mol\%) was calculated on the basis of methanol fed.

\[
Y(\text{DMC}) = \frac{\text{mole amount of DMC formed}}{\text{mole amount of MeOH taken}/2} \times 100\% \tag{Equation 2.8}
\]
Chapter 3

3. Ce-Zr mixed oxide catalysts and surface modified Ce$_{0.8}$Zr$_{0.2}$O$_2$ for the direct synthesis of dimethyl carbonate from methanol and CO$_2$

Chapter 3 presents the results about the influence of (i) Ce content in Ce$_x$Zr$_{1-x}$O$_2$ solids and (ii) surface modification of Ce$_{0.8}$Zr$_{0.2}$O$_2$ on catalyst performance in the direct dimethyl carbonate synthesis from methanol and CO$_2$. Different Ce-Zr precursors were prepared by a co-precipitation method and calcined at 600 °C. Phosphate surface groups on Ce$_{0.8}$Zr$_{0.2}$O$_2$ solids were generated by treating Ce-Zr-hydroxide precursors and Ce-Zr mixed oxides ($T_c = 600$ °C) with phosphoric acid. Catalysts were thoroughly characterized by N$_2$-adsorption (BET-SA), XRD, TEM, in situ FTIR, NH$_3$-TPD as well as CO$_2$-TPD. The materials obtained were tested towards the formation of dimethyl carbonate from methanol and carbon dioxide at 170 °C and 65 bar for 1 h using a batch reactor.
3. Ce-Zr mixed oxide catalysts and surface modified Ce_{0.8}Zr_{0.2}O_{2} for the direct synthesis of dimethyl carbonate from methanol and CO₂

3.1. Ce-Zr mixed oxide catalysts for the direct synthesis of dimethyl carbonate from methanol and carbon dioxide

3.1.1. Catalysts characterization

**BET surface area**

The specific surface areas (SSA), pore volumes and pore diameters of pure metal oxides (C_{\text{prec}} and Z_{\text{prec}}) and mixed metal oxides (C_{20}Z_{\text{prec}}, C_{40}Z_{\text{prec}}, C_{60}Z_{\text{prec}} and C_{80}Z_{\text{prec}}) are summarized in Table 3.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>x in Ce_{x}Zr_{1-x}O_{2}</th>
<th>BET-SA (m² g⁻¹)</th>
<th>Pore V (cm³ g⁻¹)</th>
<th>Average pore d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z_{\text{prec}}</td>
<td>0.0</td>
<td>25</td>
<td>0.13</td>
<td>3.7</td>
</tr>
<tr>
<td>C_{20}Z_{\text{prec}}</td>
<td>0.2</td>
<td>71</td>
<td>0.19</td>
<td>4.0</td>
</tr>
<tr>
<td>C_{40}Z_{\text{prec}}</td>
<td>0.4</td>
<td>92</td>
<td>0.24</td>
<td>3.7</td>
</tr>
<tr>
<td>C_{60}Z_{\text{prec}}</td>
<td>0.6</td>
<td>73</td>
<td>0.11</td>
<td>3.7</td>
</tr>
<tr>
<td>C_{80}Z_{\text{prec}}</td>
<td>0.8</td>
<td>46</td>
<td>0.13</td>
<td>4.0</td>
</tr>
<tr>
<td>C_{\text{prec}}</td>
<td>1.0</td>
<td>45</td>
<td>0.18</td>
<td>3.7</td>
</tr>
</tbody>
</table>

The surface areas and pore volumes of the unmodified samples vary between 25 and 92 m² g⁻¹ and between 0.11 and 0.24 cm³ g⁻¹, respectively. The highest values were obtained for a Ce_{0.8}Zr_{0.2}O_{2} sample with 40% cerium. On the basis of average pore diameters varying between 3.7 to 4.0 nm, it can be concluded that all samples are mesoporous. For the C_{80}Z_{\text{prec}} catalyst, the crystallite sizes were in a good agreement with the values obtained by transmission electron microscopy (see Figure 3.5). Furthermore, the size of individual nanoparticle (visible by TEM) and the crystallite size (calculated by XRD) confirmed that the nanoparticles were not twinned.

**X-ray powder diffraction analysis (XRD)**

In the present study the structural assignment was performed using V-curves where the volumes of the substituted unit cells for cubic (Ce_{x}Zr_{1-x})O_{2} (Fm3m space group) and tetragonal (Zr_{x}Ce_{1-x})O_{2} (P4_{2}/nmc space group) phases were taken from the ICSD database (FIZ Karlsruhe, see Figure 3.2). Therefore, the lattice volume is related to the respective molar compositions in the Ce_{x}Zr_{1-x}O_{2} mixed oxides. The obtained phase compositions from V-curves were in a good agreement with those determined using the Rietveld method (program package TOPAS 4.2 from Bruker). Figure 3.1 shows the diffractograms of
Ce$_x$Zr$_{1-x}$O$_2$ with different Ce/Zr ratios. The results show that ceria is stabilized in the fluorite structure, whereas both monoclinic (71 wt%) and tetragonal phases (29 wt%) were identified in bare ZrO$_2$.

Figure 3.1. Diffractograms for Ce$_x$Zr$_{1-x}$O$_2$ catalysts. Phase composition: ■ cubic CeO$_2$ (JCPDS 01-078-0694), ◆ tetragonal ZrO$_2$ (JCPDS 01-079-1764), ○ monoclinic ZrO$_2$ (JCPDS 01-078-0047). Inset: ▲ t-Ce$_{0.26}$Zr$_{0.74}$O$_2$, ◆ t-Ce$_{0.45}$Zr$_{0.55}$O$_2$, ♦ t-Ce$_{0.91}$Zr$_{0.09}$O$_2$, △ t-Ce$_{0.5}$Zr$_{0.5}$O$_2$, ♣ c-Ce$_{0.93}$Zr$_{0.07}$O$_2$, □ t-Ce$_{0.62}$Zr$_{0.38}$O$_2$.

In case of mixed metal oxides, the substitution of Ce$^{4+}$ (ionic radius 0.097 nm) with relatively smaller Zr$^{4+}$ (ionic radius 0.084 nm) led to a shrinkage of resulted lattice (smaller inter-plane distance $d$ and lattice constant) and as a consequence to a shift of peak reflections to higher diffraction angles, according to the Bragg’s law ($2dsin\theta = n\lambda$, where $d$ is the spacing between the planes in the lattice, $\theta$ is the diffraction angle, $n$ is an integer and $\lambda$ is the wavelength of incident X-ray wavelength) [127, 128]. The lattice constants ($a$ and $c$) were slightly changed after addition of zirconium into ceria. A distinct decrease in lattice parameters $a$ and $c$ occurred upon incorporation of increasing amount of Zr$^{4+}$ (≥ 60 mol%) into CeO$_2$. The crystallite sizes of the Ce$_x$Zr$_{1-x}$O$_2$ samples are varied between 7 and 15 nm calculated from diffractograms by using the Scherrer equation $D_{\text{XRD}} = K\lambda / \beta\cos\theta$ [125] (Table 3.2). It was found that the C20Z$^{\text{prec}}$ and C40Z$^{\text{prec}}$ mixed oxides exhibited homogeneous solid solutions with 100 wt% of tetragonal Ce$_{0.26}$Zr$_{0.74}$O$_2$ and Ce$_{0.45}$Zr$_{0.55}$O$_2$ structure, respectively (see Table 3.2). However, for samples with Ce content ≥ 60 mol% (C60Z$^{\text{prec}}$ and C80Z$^{\text{prec}}$) additional XRD reflexes were observed.
Table 3.2. Effect of Ce content and surface modification on crystallite size (D) and lattice constants of Ce$_x$Zr$_{1-x}$O$_2$ solid solutions. The crystallographic density ($\rho$) and microstrain ($\varepsilon$) for each phase were also calculated.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Rietveld method</th>
<th>V-curve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crystal phase</td>
<td>$\rho$ (g cm$^{-3}$)</td>
</tr>
<tr>
<td>Z$^{\text{prec}}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C20Z$^{\text{prec}}$</td>
<td>100% t- Ce$<em>{0.36}$Zr$</em>{0.64}$O$_2$</td>
<td>6.65</td>
</tr>
<tr>
<td>C40Z$^{\text{prec}}$</td>
<td>100% t- Ce$<em>{0.57}$Zr$</em>{0.43}$O$_2$</td>
<td>6.90</td>
</tr>
<tr>
<td>C60Z$^{\text{prec}}$</td>
<td>68% c- Ce$<em>{0.95}$Zr$</em>{0.05}$O$_2$</td>
<td>7.20</td>
</tr>
<tr>
<td></td>
<td>32% t- Ce$<em>{0.73}$Zr$</em>{0.27}$O$_2$</td>
<td>7.20</td>
</tr>
<tr>
<td>C80Z$^{\text{prec}}$</td>
<td>76% c- Ce$<em>{0.95}$Zr$</em>{0.05}$O$_2$</td>
<td>7.13</td>
</tr>
<tr>
<td></td>
<td>24% t- Ce$<em>{0.78}$Zr$</em>{0.22}$O$_2$</td>
<td>7.20</td>
</tr>
<tr>
<td>C80ZP-2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C$^{\text{prec}}$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
It was proven that these two samples were not homogeneous in nature and were composed of two different phases, i.e. a tetragonal phase with lower content of Ce with respect to nominal composition (t-Ce$_{0.5}$Zr$_{0.5}$O$_2$ for C60Z$^{\text{prec}}$ and t-Ce$_{0.62}$Zr$_{0.38}$O$_2$ for C80Z$^{\text{prec}}$) and ii) a cubic phase with higher Ce concentration in regard to nominal composition (c-Ce$_{0.9}$Zr$_{0.09}$O$_2$ for C60Z$^{\text{prec}}$ and t-Ce$_{0.93}$Zr$_{0.07}$O$_2$ for C80Z$^{\text{prec}}$). Alifanti et al. [121] and Yao-Matsuo et. al [129] also found that at low cerium contents homogeneous solid solutions can be obtained during sol-gel synthesis while an increase in Ce content led to an appearance of two separate phases: a cubic CeO$_2$ and cubic Ce$_{0.5}$Zr$_{0.5}$O$_2$.

![Figure 3.2.](image)

**Figure 3.2.** (a) Volume of the unit cells of the cubic (Ce$_x$Zr$_{1-x}$)O$_2$ phase as a function of Ce content and (b) Tetragonal (Zr$_x$Ce$_{1-x}$)O$_2$ phase as a function of the Zr content.

The phase composition of Ce$_x$Zr$_{1-x}$O$_2$ solids determined by applying V-curves is summarized in Table 3.2. In case of C60Z$^{\text{prec}}$, it was composed of 68 wt% of cubic Ce$_{0.9}$Zr$_{0.09}$O$_2$ and 32 wt% of tetragonal Ce$_{0.5}$Zr$_{0.5}$O$_2$ phases. The C80Z$^{\text{prec}}$ sample showed well-defined diffraction peaks corresponding to 76 wt% of cubic Ce$_{0.93}$Zr$_{0.07}$O$_2$ and a few less intense peaks due to 24 wt% of tetragonal Ce$_{0.62}$Zr$_{0.38}$O$_2$ phase. Additionally, the lattice volume for the substituted tetragonal and cubic phase was determined. According to Vegard’s law, the replacement of Ce$^{4+}$ cation (0.097 nm) with smaller Zr$^{4+}$ cation (0.084 nm) leads to a shrinkage of CeO$_2$ lattice. Hence, with increasing content of incorporated Zr atoms into CeO$_2$ lattice the corresponding volume and the crystallographic densities (so called density of the unit cell) decreased. Calculated microstrain (Equation 2.4) in the crystal lattice of the Ce$_x$Zr$_{1-x}$O$_2$ solid solutions is also presented in Table 3.2. The microstrain is the lattice distortion inside a grain due to the incorporation of Zr$^{4+}$ into CeO$_2$. The microstrain in polycrystalline material appears when small grains deformed in different ways so that the defects (dislocations) could not move in the whole sample volume. This situation leads to
peak broadening. The microstrain of mixed Ce-Zr oxides decreased with zirconium addition into CeO₂. Such doping effect of Zr⁴⁺ into CeO₂ is well described by R. Si et al. [130]. Those authors reported that the high lattice strain level in CeₓZr₁₋ₓO₂ solid solutions was related to the large density of oxygen defects including pure oxygen vacancy and vacancy-interstitial oxygen defects in the crystal lattice. Therefore, the zirconium content affects the concentration of oxygen defects and thus resulted in lattice strain in the CeₓZr₁₋ₓO₂ solid solutions.

**Elemental analysis by Inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray photoelectron spectroscopy (XPS)**

Bulk and surface atomic ratios of Ce/Zr determined from ICP and XPS measurements of CeₓZr₁₋ₓO₂ samples are shown in Table 3.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ce/Zr nominal</th>
<th>Bulk composition (ICP)</th>
<th>Surface composition (XPS)</th>
<th>EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce/Zr</td>
<td>Ce/Zr</td>
<td>Ce/Zr</td>
<td></td>
</tr>
<tr>
<td>C20Z⁰⁰%</td>
<td>0.25</td>
<td>0.27</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>C40Z⁰⁰%</td>
<td>0.66</td>
<td>0.79</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>C60Z⁰⁰%</td>
<td>1.5</td>
<td>1.9</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>C80Z⁰⁰%</td>
<td>4</td>
<td>5.5</td>
<td>4.25</td>
<td>2.4, 24.1, 12.6⁴</td>
</tr>
</tbody>
</table>

⁴ Figure 3.5a', Ce/Zr molar ratios on labelled areas

The measured ratios were compared with the nominal ones assuming that the metals have been uniformly distributed within the Ce-Zr-O system. The counterparts of C60Z⁰⁰% and C80Z⁰⁰% possessed the nearly nominal Ce/Zr surface atomic ratios of 1.44 and 4.25, respectively. However, at lower Ce contents (samples C40Z⁰⁰% and C20Z⁰⁰%) the surface Ce/Zr ratio is significantly reduced. Such migration of Zr from the bulk to the surface was also noticed by other research groups, who indicated a decrease in the Ce/Zr ratio for Ce₀.₇Zr₀.₃O₂, Ce₀.₅Zr₀.₅O₂ and Ce₀.₃Zr₀.₇O₂ [131].
Acid-base properties: Temperature-programmed desorption (TPD) of NH₃ and CO₂

Temperature-programmed desorption of NH₃ was used to evaluate acidic properties (total number of acidic sites and their distribution) of the Ce-Zr mixed oxides. The amount of desorbed ammonia, expressed as µmol of NH₃ per square meter and per gram of catalyst, was taken as a measure of the total acidity of the catalysts (Table 3.4).

Table 3.4. Acidic and base characteristics of the CeₓZr₁₋ₓO₂ samples. Tₘₐₓ (NH₃) and Tₘₐₓ (CO₂) stand for temperature of maximal NH₃ and CO₂ desorption, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total basicity (CO₂-TPD)</th>
<th>Total acidity (NH₃-TPD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂ desorbed (µmol g⁻¹)</td>
<td>CO₂ desorbed (µmol m⁻²)</td>
</tr>
<tr>
<td>Zprec</td>
<td>80</td>
<td>3.2</td>
</tr>
<tr>
<td>C20Zₚprec</td>
<td>90</td>
<td>1.3</td>
</tr>
<tr>
<td>C40Zₚprec</td>
<td>120</td>
<td>1.3</td>
</tr>
<tr>
<td>C60Zₚprec</td>
<td>100</td>
<td>1.4</td>
</tr>
<tr>
<td>C80Zₚprec</td>
<td>100</td>
<td>2.2</td>
</tr>
<tr>
<td>Cₚprec</td>
<td>90</td>
<td>2.0</td>
</tr>
</tbody>
</table>

NH₃-TPD profiles of the CₓZr₁₋ₓO₂ samples are presented in Figure 3.3a. The intensity of desorption peaks considerably increased after incorporation of zirconium atoms into the ceria lattice leading to an increase in total concentration of acid sites as reported elsewhere [132]. The highest number of acidic sites was observed for pure ZrO₂ (Zₚprec, 4.4 µmol m⁻²), whereas the lowest one was found for pure CeO₂ (Cₚprec, 0.07 µmol m⁻²). Pengpanich et al. [134] reported that Zr⁴⁺ exhibits more acidic nature than Ce⁴⁺ and incorporation of Zr⁴⁺ into CeO₂ lattice can promote the formation of acidic sites in resulted Ce-Zr-O solid solution. As in a present work, Zr⁴⁺ in CeO₂ increased the total amount of NH₃ desorbed from Ce-Zr-O solid solutions compared to pure CeO₂.

On the bases of broad NH₃-TPD profiles in Figure 3.3a, one can conclude that the tested samples possess acidic sites of different strength. The desorption peaks of NH₃ located at 100-200 °C, 200-400 °C and 400-450 °C can be assigned to weak, moderate and strong acid sites, respectively [133]. The Ce-Zr-O catalysts exhibit mainly weak (<200 °C) and moderate (200-400 °C) acid sites. However, the concentration and distribution of acid sites depend upon the Ce/Zr ratio.
3. Ce-Zr mixed oxide catalysts and surface modified Ce\textsubscript{0.8}Zr\textsubscript{0.2}O\textsubscript{2} for the direct synthesis of dimethyl carbonate from methanol and CO\textsubscript{2}

Figure 3.3. (a) NH\textsubscript{3}-TPD profiles of Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} catalysts, (b) CO\textsubscript{2}-TPD profiles of Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} solids.

In order to analyze basic properties of the Ce-Zr-O solids, CO\textsubscript{2}-TPD experiments were also carried out. CO\textsubscript{2} was used as an acidic probe molecule being able to adsorb on surface hydroxyls (forms hydrogen carbonate species) or oxygen ions (forms carbonate species) of metal oxides [134]. Figure 3.3b illustrates the CO\textsubscript{2}-TPD profiles obtained for different Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} solids. All Ce-Zr-O catalysts exhibit two broad desorption peaks of CO\textsubscript{2} thus indicating the presence of different types of basic sites such as weak (100-230 °C), moderate (230-500 °C) and strong (above 500 °C) basic sites [105, 135]. The total concentration of basic sites of Ce-Zr–O solid solutions, expressed as the amount of CO\textsubscript{2} desorbed per gram and per square meter of catalyst, is reported in Table 3.4. It can be found that pure ZrO\textsubscript{2} (3.2 µmol m\textsuperscript{-2}) has the highest concentration of basic sites, which markedly decreases upon addition of 20 mol% of cerium, then increases as Ce content is further increases up to 80 mol%. It was reported that chemical mixing can significantly change basic properties of given metal oxides [136]. As in this case, the incorporation of zirconium into ceria lattice had a direct influence on the basicity and acidity of parent oxides. Moreover, the contribution of strong basic sites to total basicity was more significant as Zr content in the Ce-Zr mixed oxides increased.

3.1.2. Catalytic results

Table 3.5 depicts the effect of Ce content in Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} catalysts on DMC yield. No DMC was formed over pure ZrO\textsubscript{2}. Catalytic properties of ZrO\textsubscript{2} are greatly enhanced upon its promoting with CeO\textsubscript{2}. It is evident from the results shown in Table 3.5 that the yield of DMC increases with increasing Ce content up to 60% and then remained constant (Y\textsubscript{DMC} ~ 0.24%). According to the literature, the equilibrium DMC yield was about 2% [137, 138].
Table 3.5. Influence of cerium content in Ce$_x$Zr$_{1-x}$O$_2$ catalysts on the yield of DMC (Reaction conditions: catalyst weight 50 mg, CH$_3$OH = 247 mmol, T = 170 °C, p = 65 bar, t = 1 h, 600 rpm).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x$ in Ce$<em>x$Zr$</em>{1-x}$O$_2$</th>
<th>Y–DMC (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z$^{\text{prec}}$</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>C20Z$^{\text{prec}}$</td>
<td>0.2</td>
<td>0.04</td>
</tr>
<tr>
<td>C40Z$^{\text{prec}}$</td>
<td>0.4</td>
<td>0.13</td>
</tr>
<tr>
<td>C60Z$^{\text{prec}}$</td>
<td>0.6</td>
<td>0.24</td>
</tr>
<tr>
<td>C80Z$^{\text{prec}}$</td>
<td>0.8</td>
<td>0.24</td>
</tr>
<tr>
<td>C$^{\text{pre}}$</td>
<td>1</td>
<td>0.24</td>
</tr>
</tbody>
</table>

No correlation between the DMC yield and BET-SA was found. In fact, the tetragonal Ce$_x$Zr$_{1-x}$O$_2$ phase was mainly formed in Z$^{\text{prec}}$, C20Z$^{\text{prec}}$ and C40Z$^{\text{prec}}$, whereas the cubic Ce$_x$Zr$_{1-x}$O$_2$ phase was predominant in C60Z$^{\text{prec}}$, C80Z$^{\text{prec}}$ and also in pure ceria (C$^{\text{pre}}$). Since the latter samples are significantly more active ($Y_{\text{DMC}} \sim 0.24\%$), it can be concluded that the most active phase for DMC formation is cubic Ce$_x$Zr$_{1-x}$O$_2$ (C60Z$^{\text{prec}}$, C80Z$^{\text{prec}}$, C$^{\text{pre}}$).

Previous studies deal with DMC synthesis from methanol and CO$_2$ [87, 124] reported that the acid-base properties play a crucial role in the target reaction. As described by Tomishige et al. [139], the presence of both acidic and basic sites is the key factor for activating methanol and CO$_2$ in the course of DMC synthesis. More precisely, a suitable combination of acidic and basic sites is responsible for controlling catalytic carboxylation of methanol over ZrO$_2$ catalysts. Tomishige et al. [87] further claimed that an equal number of neighboring acid-base sites is required for optimal catalyst performance. For the most active catalysts (e.g. C60Z$^{\text{prec}}$, C80Z$^{\text{prec}}$ and C$^{\text{pre}}$) towards DMC formation this is obviously not the case. Basic sites dominate on their surface (see Table 3.4).

Based on initial results (maximal DMC yields \( \sim 0.24\% \)), the CeO$_2$-ZrO$_2$ solid solution catalyst with a theoretical Ce/Zr ratio of 4 (C80Z$^{\text{prec}}$) was chosen and used in subsequent runs especially for modification with H$_3$PO$_4$ to boost the yield of DMC beyond 0.24%. The promoting effect of H$_3$PO$_4$ was then investigated by varying the P-contents in C80Z$^{\text{prec}}$ with the aim to identify efficient catalyst compositions for achieving enhanced DMC yields.
3. Ce-Zr mixed oxide catalysts and surface modified Ce$_{0.8}$Zr$_{0.2}$O$_2$ for the
direct synthesis of dimethyl carbonate from methanol and CO$_2$.

3.2. Surface modified Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst for direct synthesis of
dimethyl carbonate from methanol and CO$_2$.

3.2.1. Catalysts characterization

**BET surface area**

The specific surface area (SSA), pore volume and diameter of modified mixed metal oxides (CZ80ZP-1, C80ZP-2, C80ZP-3 and C80ZP*) are summarized in Table 3.6.

**Table 3.6.** Effect of surface modification on the textural properties of Ce$_{0.8}$Zr$_{0.2}$O$_2$ solids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x$ in Ce$<em>x$Zr$</em>{1-x}$O$_2$</th>
<th>P/Zr</th>
<th>$P_{\text{surf.}}$\textsuperscript{b} (mol%)</th>
<th>BET-SA (m$^2$ g$^{-1}$)</th>
<th>Pore V (cm$^3$ g$^{-1}$)</th>
<th>Average pore d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80ZP-1</td>
<td>0.8</td>
<td>0.03</td>
<td>0</td>
<td>73</td>
<td>0.11</td>
<td>3.7</td>
</tr>
<tr>
<td>C80ZP-2</td>
<td>0.8</td>
<td>0.12</td>
<td>5</td>
<td>63</td>
<td>0.09</td>
<td>4.3</td>
</tr>
<tr>
<td>C80ZP-3</td>
<td>0.8</td>
<td>0.30</td>
<td>34</td>
<td>74</td>
<td>0.10</td>
<td>3.7</td>
</tr>
<tr>
<td>C80ZP*\textsuperscript{a}</td>
<td>0.8</td>
<td>0.12</td>
<td>21</td>
<td>22</td>
<td>0.08</td>
<td>4.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}post-treated sample (H$_3$PO$_4$-addition to already calcined solid)

\textsuperscript{b}surface concentration of phosphorus measured by XPS, assuming that Ce+Zr+P=100%

The treatment of Ce-Zr hydroxides with H$_3$PO$_4$ provoked textural modifications. As a result, considerable changes in surface area and pore volume were observed. C80ZP-2 and C80ZP-1 with P concentration on the surface of 5 mol% and 0 mol%, respectively, showed differences in their specific surface areas. These results are in good agreement with those earlier reported by López Granados et al. [140] and Smitha et al. [141] where the effect of P loading on structural properties of CeO$_2$/H$_3$PO$_4$ and ZrO$_2$/H$_3$PO$_4$, in particular on specific surface area, was investigated. It was found that with low amount of phosphorus (2.5 mL of H$_3$PO$_4$ per gram of the hydroxide), surface area of CeO$_2$/H$_3$PO$_4$ and ZrO$_2$/H$_3$PO$_4$ slightly increased with respect to parent CeO$_2$ and ZrO$_2$, respectively. However, a further addition of P (5 mL of H$_3$PO$_4$) led to a decrease in surface area. Nonetheless, this tendency seems to be not valid for the C80ZP-3 (P = 34 mol%) solid, which demonstrated the highest specific surface area of 74 m$^2$ g$^{-1}$ among all phosphated Ce$_{0.8}$Zr$_{0.2}$O$_2$ samples. In case of the C80ZP* sample, where the phosphorus was incorporated into the calcined C80Z\textsuperscript{prec} catalyst, a significant loss of SA was found. However, the surface of post-treated C80ZP* sample contained less phosphorus (26 mol%) in comparison with the C80ZP-3 catalyst. The main reason for such decline of surface area might be the double calcination of C80ZP* solid at 600 °C, for four hours each time. It is well-known fact that long time calcination causes a
decrease in specific surface area of Ce-based oxides [142]. Therefore, it can be concluded that any change in surface behavior of C80ZP* occurred as a result of thermal treatment (indicated by the drop in SA).

**X-ray powder diffraction analysis (XRD)**

The XRD pattern of C80Zprec solid is presented in Figure 3.4. C80ZP-2 was selected for XRD analysis due to its improved catalytic activity towards DMC formation (see Table 3.10).

![Representative X-ray powder diffractograms with Rietveld refinement of the samples C80Zprec and C80ZP-2 with additionally highlighted tetragonal Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} phases.](image)

Unphosphated C80Zprec sample is composed of a tetragonal Ce-rich Ce\textsubscript{0.62}Zr\textsubscript{0.38}O\textsubscript{2} phase (24%) besides a cubic Ce\textsubscript{0.93}Zr\textsubscript{0.07}O\textsubscript{2} phase (76%). In contrast, the formation of a Zr-rich tetragonal Ce\textsubscript{0.22}Zr\textsubscript{0.78}O\textsubscript{2} phase (13%) and the cubic Ce\textsubscript{0.93}Zr\textsubscript{0.07}O\textsubscript{2} phase (87%) is observed in the phosphated C80ZP-2 sample (see Table 3.2). Crystalline P-containing phases were not detected in these phosphated samples.

**Elemental analysis by Inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray photoelectron spectroscopy (XPS)**

Bulk and surface atomic ratios (Ce/Zr and P/Zr) from ICP and XPS measurements of the three P-modified C80Zprec samples obtained after H\textsubscript{3}PO\textsubscript{4} pretreatment of a Ce-Zr hydroxide precursor (C80ZP1-3, P/Zr = 0.03-0.3) are reported in Table 3.7. In addition, the data of another P-doped catalyst are also included (C80ZP*) for comparative purposes.
Table 3.7. Comparison of the overall molar Ce/Zr and P/Zr ratios in the near-surface-region (as measured by XPS) with bulk composition (as measured by ICP) for modified Ce$_{0.8}$Zr$_{0.2}$O$_2$ solids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ce/Zr nominal</th>
<th>P/Zr nominal</th>
<th>Ce/Zr (ICP)</th>
<th>P/Zr (ICP)</th>
<th>Ce/Zr (XPS)</th>
<th>P/Zr (XPS)</th>
<th>Ce/Zr EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80ZP-1</td>
<td>4</td>
<td>0.03</td>
<td>4.6</td>
<td>0.04</td>
<td>3.76</td>
<td>n.d.$^a$</td>
<td></td>
</tr>
<tr>
<td>C80ZP-2</td>
<td>4</td>
<td>0.12</td>
<td>4.7</td>
<td>0.13</td>
<td>6.69</td>
<td>0.4</td>
<td>6.4, 20.6$^b$</td>
</tr>
<tr>
<td>C80ZP-3</td>
<td>4</td>
<td>0.3</td>
<td>4.6</td>
<td>0.47</td>
<td>2.13</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>C80ZP*</td>
<td>4</td>
<td>0.12</td>
<td>1.5</td>
<td>0.13</td>
<td>0.6</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

$^a$n.d. – not determined
$^b$Fig.3.5b, Ce/Zr molar ratios on labelled areas

Bulk and surface concentrations of P-modified C80Z$^{\text{pre}}$ (C80ZP1-3 and C80ZP*) catalyst components measured via ICP and XPS measurements, respectively, are reported in Table 3.7. The ICP results revealed a nearly constant Ce/Zr bulk ratio independent on the amount of H$_3$PO$_4$ added to the Ce-Zr hydroxide precursor. From the near-surface region compositions (XPS), a maximum of Ce-enrichment was found on the surface of C80ZP-2. These findings are in good agreement with those reported by Atribak et al. [143]. Since the solubility constant of Zr(OH)$_4$ is lower than that of Ce(OH)$_3$ ($2\times10^{-48}$ and $1.5\times10^{-20}$, respectively), a faster precipitation of Zr(OH)$_4$ during the co-precipitation of Ce$^{3+}$ and Zr$^{4+}$ occurs. Therefore, the nuclei of particles will be rich in Zr and outer part will have a Ce-enrichment while the overall compositions obtained by ICP confirmed Ce/Zr ratios very close to the theoretical values. XPS did not detect the phosphorus on the surface of C80ZP-1 (nominal ratio P/Zr = 0.03). Most probably the concentration of P is below the detection limit of XPS technique. On the other hand, C80ZP-3 exhibited Zr-rich surface at phosphorus concentration of 34 mol%. López Granados et al. [140] also observed such a decrease in Ce concentration with increasing amount of incorporated P in CeO$_2$/H$_3$PO$_4$ sample. The surface P/Zr ratio of C80ZP-2 was found to be 0.4 and this value is three times higher than its corresponding bulk value (0.13). Comparing ICP and XPS data, it is suggested that P is an important component for tuning catalytic performance and it is mainly concentrated in the near-surface-region of Ce-Zr mixed oxides. In contrary, the post-treated (P-addition to a calcined solid) C80ZP* sample exhibits low concentration of Ce and high concentration of Zr in the near-surface-region compared to the others. Obviously, the H$_3$PO$_4$ treatment of an already calcined catalyst causes Ce-leaching and, therefore, an overall enrichment in Zr. Moreover, the near-surface...
concentration of P is much higher (more than three times) than the best C80ZP-2 catalyst. It can be assumed that P remained on the surface (probably formation of monolayer) and did not go deeper into the bulk during impregnation of already calcined samples.

**Transmission electron microscopy (TEM)**

HAADF-STEM images of C80Z\textsuperscript{prec} and C80ZP-2 are shown in Figure 3.5. They revealed nanosized irregular particles densely agglomerated in two cases. The particles sizes of C80Z\textsuperscript{prec} and C80ZP-2 are in the range of 7-15 nm in good agreement to the calculated crystallite sizes from XRD (see Table 3.2).

![Figure 3.5](image)

**Figure 3.5.** HAADF-STEM images of (a), (a’) C80Z\textsuperscript{prec} and (b), (b’) C80ZP-2. EDX analysis of the Ce/Zr molar ratio: (a’) 1 = 2.4, 2 = 24.1, 3 = 12.6; (b) 1 = 6.4, 2 = 20.6.

Energy dispersive X-Ray analysis (EDX) was used to get information about local composition. EDX results from a relatively large region (0.1-0.3 µm) confirmed that the distribution of cerium and zirconium concentrations within the selected region is also different (labelled areas in Figure 3.5). In C80Z\textsuperscript{prec} the Ce-enrichment is represented by the formation of Ce-rich Ce\textsubscript{0.93}Zr\textsubscript{0.07}O\textsubscript{2} phase. In case of C80ZP-2, EDX results confirmed the presence of Ce-rich as well as Zr-rich regions. In C80ZP-2 the Ce/Zr molar ratios from EDX measurements exceeded to a greater extent the Ce/Zr ratios obtained from ICP-OES.
3. Ce-Zr mixed oxide catalysts and surface modified Ce$_{0.8}$Zr$_{0.2}$O$_2$ for the direct synthesis of dimethyl carbonate from methanol and CO$_2$

measurements (Table 3.7). Obviously, the treatment of Ce-Zr-hydroxides with H$_3$PO$_4$ solutions provoked textural modifications.

**Acid-base properties: Temperature-programmed desorption (TPD) of NH$_3$ and CO$_2$**

Temperature-programmed desorption (TPD) of NH$_3$ is a suitable characterization technique to estimate the total acidity of the catalysts (Table 3.8).

**Table 3.8.** Acidic and base characteristics of the P-modified C80Z samples. T$_{\text{max}}$ (NH$_3$) and T$_{\text{max}}$ (CO$_2$) stand for temperature of maximal NH$_3$ and CO$_2$ desorption, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total basicity (CO$_2$-TPD)</th>
<th>Total acidity (NH$_3$-TPD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO$_2$ desorbed (µmol g$^{-1}$)</td>
<td>CO$_2$ desorbed (µmol m$^{-2}$)</td>
</tr>
<tr>
<td>C80ZP-1</td>
<td>35.4</td>
<td>0.5</td>
</tr>
<tr>
<td>C80ZP-2</td>
<td>30</td>
<td>0.5</td>
</tr>
<tr>
<td>C80ZP-3</td>
<td>6.1</td>
<td>0.1</td>
</tr>
<tr>
<td>C80ZP*</td>
<td>48</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The obtained NH$_3$-TPD profiles of the surface modified Ce-Zr mixed oxides are displayed in (Figure 3.6a). Depending on desorption temperature range the presence of acid sites can be classified as weak, moderate and strong [67]. P-modified solids exhibit mainly weak (<200 °C) and moderate (200-400 °C) acid sites. However, the concentration and distribution of acidic sites depend upon the Ce/Zr ratio and P-modification.

**Figure 3.6.** (a) NH$_3$-TPD profiles of P-modified Ce$_{0.8}$Zr$_{0.2}$O$_2$ solids (b) CO$_2$-TPD profiles of P-modified Ce$_{0.8}$Zr$_{0.2}$O$_2$ solids.
Figure 3.6b shows CO\(_2\)-TPD profiles of P-modified Ce\(_{0.8}\)Zr\(_{0.2}\)O\(_2\) mixed oxides. The C80ZP1-3 samples exhibit CO\(_2\) desorption at around 151 °C that indicates the presence of only weak basic sites (<230 °C), whereas this feature is distinctly reduced for C80ZP-3. This suggests that P-modification from hydroxide derived catalyst suppresses the concentration of both moderate and strong basic sites which is not the case for C80ZP*.

**Fourier Transform Infrared Spectroscopy (FTIR)**

In order to further analyze the surface properties (hydroxyl groups and possible carbonate surface species) of C80Z\(^{\text{prev}}\) and C80ZP-2, *in situ* FTIR analysis using synthetic air (400 °C) was performed. The corresponding FTIR spectra of the pretreated samples at 170 °C are shown in Figure 3.7a.

Figure 3.7. (a) *In situ* FTIR spectra of C80Z\(^{\text{prev}}\) and C80ZP-2 recorded at 170 °C after pretreatment in synthetic air at 400 °C (b) *In situ* FTIR of C80Z\(^{\text{prev}}\) and C80ZP-2 recorded after 30 min exposure to MeOH/CO\(_2\) at 170 °C and subsequent flushing with He.

Compared to C80Z\(^{\text{prev}}\), the C80ZP-2 catalyst shows additional bands at 3671 cm\(^{-1}\) (\(\nu_{\text{Zr-OH}}\)) and 3510 cm\(^{-1}\), besides a band at 3649 cm\(^{-1}\) (\(\nu_{\text{Ce-OH}}\)). A band at 3649 cm\(^{-1}\) can be assigned to a \(\nu_{\text{OH}}\) band from a cerium hydroxide phase [145]. In addition, the \(\nu_{\text{C-H}}\) bands at 2935, 2844, and 2723 cm\(^{-1}\) in C80Z\(^{\text{prev}}\) are due to formate species [146, 147], the respective \(\nu_{\text{as}}/\nu_{\text{s}}\)COO\(^{-}\) bands that appear at 1546 and 1372/1358 cm\(^{-1}\). For C80ZP-2 sample these formate bands are missing. Instead, bands at 1542/1523 cm\(^{-1}\) and 1253/1220 cm\(^{-1}\) appeared. These bands pointed to surface bidentate carbonate species, which could be resulted from oxidation of formate species [148].

For possible correlation of DMC formation from methanol and CO\(_2\) with specific adsorbates species, *in situ* FTIR experiments were performed in which MeOH/CO\(_2\) gas mixtures were adsorbed exemplarily on C80Z\(^{\text{prev}}\) and C80ZP-2 solids at 170 °C. Under these conditions...
conditions both catalysts are also active in the conversion of CO₂ with methanol. The corresponding spectra are shown in Figure 3.7b. Methanol can be adsorbed in a dissociative form over the catalyst surface thus giving methoxy species. The bands in the νC-H region around 2940, 2915, and 2810 cm⁻¹ are due to C-H stretching vibrations of methoxy species, whereas the bands in the frequency range of 1200-1000 cm⁻¹ can be assigned to νC-O vibrations [149]. Based on the νC-O band positions, it is possible to estimate the nature of surface methoxides. Hence, the bands at 1150 and 1100 cm⁻¹ are assigned to monodentate methoxy species, whereas the bands around 1050/1030 cm⁻¹ are related to bidentate methoxy species adsorbed on Zr⁴⁺ or/and Ce⁴⁺ [144, 150]. Depending upon the band positions of the monodentate methoxy species it is possible to distinguish between Ce⁴⁺-OCH₃ (1103 cm⁻¹) [150] and Zr⁴⁺-OCH₃ (1148 cm⁻¹) [144]. The FTIR spectrum of C80Zprec is characterized by a strong band of Ce⁴⁺-OCH₃ and only a weak band of Zr⁴⁺-OCH₃ species. Moreover, the latter is essentially more intensive over C80ZP-2. For C80Zprec the bands due to formate species at 1546 and 1372/1358 cm⁻¹ (not shown on Figure 3.7) disappeared, instead, the bands in the range of 1600-1300 cm⁻¹ were found due to carbonate species most probably resulted from oxidation of both methoxy and formate species.

Table 3.9. Surface properties of the unmodified C80Zprec and P-modified C80ZP-2 samples examined by MeOH/CO₂ (FTIR) and pyridine adsorption (Py-IR).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Methoxy formation</th>
<th>Lewis acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intensity ratio νC-O³⁄₄⁻¹ Zr⁴⁺⁻¹</td>
<td>Band intensity 1440 cm⁻¹ (pyridine ads.)</td>
</tr>
<tr>
<td>C80Zprec</td>
<td>40 / 1</td>
<td>15.9</td>
</tr>
<tr>
<td>C80ZP-2</td>
<td>2 / 1</td>
<td>30.5</td>
</tr>
</tbody>
</table>

³⁄₄рыво Ratio of νC−O band intensities (~1100 cm⁻¹ and 1150 cm⁻¹), normalized to BET-SA
²⁄₄рыво Band intensity ×10⁻³ (1440 cm⁻¹), normalized to BET-SA

When comparing the FTIR spectra of pure C80Zprec and P-modified C80ZP-2, it is obvious that the overall intensities of the methoxy bands on the surface of C80ZP-2 decreases. However, the intensity ratio of the Ce⁴⁺/Zr⁴⁺-OCH₃ bands changes dramatically by H₃PO₄ modification in favor of Zr⁴⁺-OCH₃ (Table 3.9). This goes well along with an increasing Lewis acidity (Py-IR, Figure A3.1.3) caused by higher percentage of unsaturated surface Zr⁴⁺ cations in the modified C80ZP-2 sample. A possible correlation between the adsorbates species and catalyst performance is discussed in next section.
3.2.2. Catalytic results

Table 3.10 compares the DMC yields obtained over three P-modified C80ZP samples obtained from H₃PO₄ pretreatment of Ce-Zr hydroxide precursors with varying P/Zr ratios (C80ZP1-3). Furthermore, the DMC yield of another catalyst (C80ZP*) is also shown. Note that the C80ZP* catalyst was prepared by post-treatment of C80Zₚᵢᵣₑ with H₃PO₄. Ce-Zr precursor was modified initially by H₃PO₄ keeping the ratio of P/Zr=0.03 (C80ZP-1). However, this catalyst didn’t show any enhancement in DMC yield (0.24%) with respect to unmodified C80Zₚᵢᵣₑ. Nevertheless, in further attempts the P-content in the total catalyst was optimized by means of varying P/Zr ratios (P/Zr = 0.12 and 0.3). With this intention, Ce₀.₈Zr₀.₂O₂ solid was modified with varying P-contents at varying stages. For instance, phosphorous is added to both uncalcined as well as calcined (post treated) samples and checked its influence on the catalytic performance and in particularly on the yield of DMC.

**Table 3.10.** Influence of the different P/Zr ratios in Ce₀.₈Zr₀.₂O₂/H₃PO₄ catalysts on the yield of DMC (Reaction conditions: catalyst weight 50 mg, CH₃OH = 247 mmol, T = 170 °C, p = 65 bar, t = 1 h, 600 rpm).

<table>
<thead>
<tr>
<th>Sample</th>
<th>P/Zr</th>
<th>Y–DMC (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80ZP-1</td>
<td>0.03</td>
<td>0.24</td>
</tr>
<tr>
<td>C80ZP-2</td>
<td>0.12</td>
<td>1.62</td>
</tr>
<tr>
<td>C80ZP-3</td>
<td>0.3</td>
<td>0.11</td>
</tr>
<tr>
<td>C80ZP*</td>
<td>0.12</td>
<td>0.004</td>
</tr>
</tbody>
</table>

In contrast to the unmodified C80Zₚᵢᵣₑ, the phosphoric acid treated sample C80ZP-2 showed an extraordinary increase in the yield of DMC reaching ~ 1.62%, which is nearly four times higher than that for the unmodified C80Zₚᵢᵣₑ sample. The BET-SA increased for all P-modified C80ZP samples compared to their parent C80Zₚᵢᵣₑ solid. The surface composition is also altered to a certain extent. In fact, there is a clear enrichment of Ce in the P-modified C80ZP-2 sample compared to its parent C80Zₚᵢᵣₑ solid. From adsorption spectra of MeOH/CO₂ mixture, the decrease of the overall intensities of the methoxy bands for C80ZP-2 could be found. However, the intensity ratio of the Ce⁴⁺/Zr⁴⁺-OCH₃ bands changes dramatically by H₃PO₄ modification in favor of Zr⁴⁺-OCH₃ (Table 3.9). An increasing Lewis acidity in the modified C80ZP-2 sample is also observed. CO₂- and NH₃-TPD results confirmed that the total basicity decreased by modification while the overall acidity did not change dramatically (Table 3.8). Based on the work of Tomishige et al. [87] intermediate methoxy carbonate species are easily formed over ZrO₂ catalysts by reaction of adsorbed...
monodentate methoxy species with CO₂. It can be concluded that the favored formation of Zr⁴⁺-OCH₃ species is responsible for the increased yield of DMC over C80ZP-2 catalyst.

The yield of DMC significantly increases with increasing P/Zr ratio and reaches a maximum at composition of P/Zr=0.12 (C80ZP-2; Y_{DMC} = 1.62%). A further increase in the P/Zr ratio to 0.3 resulted in a significant decrease in the DMC yield. Ikeda et al. [124] reported similar findings for the ZrO₂/H₃PO₄ system: catalysts with low P/Zr ratio (0.025-0.1) were more effective for DMC formation compared to un-phosphated ZrO₂. A considerably lower DMC yield (0.004 mol%) was obtained over the post-treated C80ZP*. A similar effect of post-treatment was also observed in phosphated zirconia catalysts by other researchers [96], where the active sites were formed by the interaction between H₃PO₄ and Zr hydroxides during catalyst preparation. XPS results suggest that post-treated sample C80ZP* has high content of P (21 mol%) concentrated on its surface and high surface acidic characteristics of resulting solids. In contrast, on the surface of pretreated C80ZP-2 solid, the concentration of P was lower (5 mol%) than on post-treated sample with identical nominal P content. Thus, the presence of high concentration of acid sites on CZ80P* surface (4.5 µmol NH₃ m⁻²) could be responsible for lower catalytic activity towards DMC. As a conclusion i) the method of H₃PO₄ treatment plays an important role and ii) a certain amount of phosphorus in the C80Z^{pre} catalyst (P/Zr=0.12) is essential for proper catalytic activity.

3.3. Summary

The effects of Ce content in Ce-Zr mixed oxides and their surface functionalization with phosphoric acid on the DMC yield in liquid phase carboxylation of methanol were investigated. DMC was not formed over pure ZrO₂ catalyst. However, the yield of DMC is greatly affected by the introduction of Ce⁴⁺ into ZrO₂, thus it was enhanced from 0.04% over C20Z^{pre} to 0.24% over C60Z^{pre} and remained the same over C80Z^{pre} and C^{pre}. Tetragonal CeₓZr₁₋ₓO₂ phase was mainly formed by the high Zr content (x ≤ 0.4), whereas the cubic CeₓZr₁₋ₓO₂ phase was predominant at higher Ce proportion (x > 0.4). To explore acid-base properties, TPD analysis was performed. CO₂ was desorbed in a broad temperature range (100-800 °C) and three types of basic sites were suggested to present on the surface of CeₓZr₁₋ₓO₂ materials: weak, moderate and strong. CeₓZr₁₋ₓO₂ solids with high Zr content exhibited high concentration of CO₂ desorption, predominantly strong. NH₃-TPD profiles of all CeₓZr₁₋ₓO₂ catalysts are characterized by a broad NH₃ desorption peak with a maximum at 200 °C. Both weak and medium strength acidic sites were identified. Pure ZrO₂ showing poor
catalytic performance had the highest concentration of acidic sites (4.4 µmol m\(^{-2}\)). The DMC formation is greatly depends on the presence of both acid-base sites on the surface of catalyst, since this reaction is catalyzed simultaneously by acidic and basic sites. Based on mechanism of DMC formation proposed by Tomishige et al. [87], CO\(_2\) is activated on basic sites to form CO\(_2^-\) ions, whereas MeOH is activated at both acidic and basic sites to form a methyl and methoxy species, respectively. In order to realize the high DMC yield simultaneous activation of both MeOH and CO\(_2\) is required. Furthermore, nearly equal amount of acidic and basic sites is efficient for DMC formation. In a case when one kind of active sites exceeds the other on the surface of catalyst, only an activation of one reactant is dominant. In this work the presence of strong acidic and/or basic sites has a negative effect on the DMC formation. This suggests that temperature at with CO\(_2\) and NH\(_3\) desorbed from catalyst surface during TPD analyses is related to the activation of CO\(_2\) and MeOH. The higher is desorption temperature during TPD the lower is DMC yield. In the present study the Ce\(_{x}\)Zr\(_{1-x}\)O\(_2\) catalyst with the acid-basic sites of weak to medium strength (100-400 °C) was favorable for DMC formation, since DMC is catalyzed at temperature of 170 °C and does not involve the temperature region of strong acidity/basicity (400-600 °C). C\(_60\)Z\(_{\text{prec}}\), C\(_80\)Z\(_{\text{prec}}\), C\(_{\text{prec}}\) catalysts having the right balance of the weak and moderate acid/base sites showed high DMC yield.

The effect of surface phosphated Ce-Zr mixed oxides on the carboxylation of methanol was investigated. Phosphate modification of Ce-Zr precursors resulted in a noticeable promotion of catalytic performance compared to their corresponding unmodified C\(_{80}\)Z\(_{\text{prec}}\). Structural and textural changes were noticed in P-modified C\(_{80}\)Z\(_{\text{prec}}\) solids. BET-surface area increased for all samples after the P-modifications. As revealed by XRD, after phosphoric acid treatment the phase composition and crystallite size were also changed leading to Ce-rich cubic and Zr-rich tetragonal Ce\(_x\)Zr\(_{1-x}\)O\(_2\) nanophases with intimate contact on the nanoscale but they do not exhibit the primary influence on DMC yield. The high DMC yield was related to the changed surface properties. The ICP and XPS studies revealed that the bulk P/Zr ratio was much lower than the surface P/Zr ratio indicating the concentration of P mostly on the surface. Moreover, surface enrichment of Ce is also noticed with P-modification, which also promoted the catalytic performance.

In subsequent efforts on the optimization of P/Zr ratios, the yield of DMC over C\(_{80}\)ZP-2 (P/Zr = 0.12) was further enhanced to 1.62%. The acid treatment caused a decrease of moderate and strong basic sites and an increase of Lewis acidic sites from most likely unsaturated surface Zr\(^{4+}\) cations that are responsible for an enhanced ability to form
monodentate methoxy species as an intermediate of the catalytic cycle. Besides, the effect of P-addition to an already calcined C80Z\textsuperscript{prec} sample was investigated. It was found that the introduction of phosphate ions on the surface of calcined C80Z\textsuperscript{prec} (post-treatment) caused a decrease of DMC formation compared to its addition on uncalcined samples. This result also suggests that the amount of P and its addition at a suitable stage during their preparation is crucial for tuning the catalytic properties of Ce-Zr-O solids and also to improve the yield of DMC to a considerable extent.
Chapter 4

4. Continuous synthesis of diethyl carbonate from ethanol and CO₂ over CeₓZr₁₋ₓO₂ (x = 0, 0.2, 0.5, 0.8, 1) catalysts

Chapter 4 deals with preparation of CeₓZr₁₋ₓO₂ (x = 0, 0.2, 0.5, 0.8 and 1.0) materials by a citrate method and their characterization by various techniques such as N₂-adsorption (BET-SA), XRD, XPS, ICP-OES, TEM, H₂-TPR, NH₃- and CO₂-TPD. In addition, the potential of such materials is evaluated for the direct synthesis of diethyl carbonate (DEC) from ethanol and CO₂ under continuous-flow conditions in a plug-flow reactor (PFR). According to the thermodynamic data, the reaction is favourable at low temperatures but high pressures. Thus, catalytic experiments were carried out at temperatures in the range between 80 and 180 °C and at pressures between 80 and 180 bar.
4. Continuous synthesis of diethyl carbonate from ethanol and CO₂ over CeₓZr₁₋ₓO₂ (x = 0, 0.2, 0.5, 0.8, 1) catalysts

4.1. An effective CeₓZr₁₋ₓO₂ catalysts for the continuous synthesis of DEC from CO₂ and ethanol: effect of varying reaction conditions

4.1.1. Catalysts characterization

**BET surface area**

CeₓZr₁₋ₓO₂ catalysts were prepared by citrate complexation method from Ce(NO₃)₃•6H₂O and ZrO(NO₃)₂•4H₂O by addition of citric acid as a chelating agent. Table 4.1 compares the surface areas, average pore sizes, pore volumes and crystalline size between pure CeO₂ or ZrO₂ and CeₓZr₁₋ₓO₂ catalysts. BET surface areas were found to depend on the content of Ce in the catalysts. In a case of pure oxides, C-citrate (CeO₂) shows much lower SA compared to Z-citrate (ZrO₂). As a result, the surface area of prepared Ce–Zr mixed oxides was established to decrease with increasing Ce content due to the poor resistivity of cerium-rich solids against sintering as claimed elsewhere [151].

<table>
<thead>
<tr>
<th>Sample</th>
<th>x in CeₓZr₁₋ₓO₂</th>
<th>BET-SA (m² g⁻¹)</th>
<th>Average pore d (nm)</th>
<th>Total pore V (cm³ g⁻¹)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-citrate</td>
<td>0</td>
<td>88</td>
<td>2.8</td>
<td>0.069</td>
<td>3.8</td>
</tr>
<tr>
<td>C20Z citrate</td>
<td>0.2</td>
<td>79</td>
<td>2.8</td>
<td>0.060</td>
<td>4.6</td>
</tr>
<tr>
<td>C50Z-citrate</td>
<td>0.5</td>
<td>57</td>
<td>4.2</td>
<td>0.064</td>
<td>4.8</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>0.8</td>
<td>42</td>
<td>6.2</td>
<td>0.076</td>
<td>6.0</td>
</tr>
<tr>
<td>C-citrate</td>
<td>1.0</td>
<td>27</td>
<td>5.3</td>
<td>0.036</td>
<td>9.0</td>
</tr>
</tbody>
</table>

The size of crystallites of Ce₀.₁₈Zr₀.₈₂O₂, Ce₀.₅Zr₀.₅O₂ and Ce₀.₇₅Zr₀.₂₅O₂ as well as the volume of pores of the corresponding mixed solids were found to vary in a narrow range from 4.6 to 6.0 nm and from 0.060 to 0.076 cm³ g⁻¹, respectively. These two parameters are however dependent upon Ce content in the system. Pure ZrO₂ possesses the smallest crystallite size of 3.8 nm and the highest pore volume of 0.069 cm³ g⁻¹, whereas CeO₂ exhibits the largest crystallite size of 9 nm and the lowest pore volume of 0.036 cm³ g⁻¹ in the range of mixed oxides. In addition, it was found that mesopores are present in all CeₓZr₁₋ₓO₂ samples. The mixture of zirconium and cerium suppresses the crystal growth during catalyst preparation and enhances the stability of mixed oxides, compared to their parent oxides. It well-known that thermal stability and redox nature of pure CeO₂ is limited because of the decrease of SA at higher calcination temperature due to nucleation and growth of crystallites.
of ceria within the pore [152, 153]. As was reported by Hori et al. [154], the addition of Zr⁴⁺ into ceria can improve these properties.

**X-ray diffraction (XRD)**

XRD patterns of different CeₓZr₁₋ₓO₂ catalysts are shown in Figure 4.1. Reflexes in the XRD pattern of the sample C-citrate can be attributed to the cubic CeO₂ phase [29, 155]. After zirconium loading into CeO₂, the main reflexes of this phase shift to higher diffraction angles due to changes of unit cell parameters and lattice deformation [156-158]. This shift can be attributed to a progressive substitution of Ce⁴⁺ (ionic radius 0.097 nm) with smaller Zr⁴⁺ (ionic radius 0.084 nm) [127, 128, 159].

![XRD patterns of CeₓZr₁₋ₓO₂ catalysts. Phase composition: + cubic CeO₂ (JCPDS 65-5923), * tetragonal ZrO₂ (JCPDS 79-1769). Inset: ■ c-Ce–Zr–O mixed phase (c-Ce₀.₇₅Zr₀.₂₅O₂ (JCPDS 28-271)), ● t-Ce–Zr–O mixed phase (t-Ce₀.₁₈Zr₀.₈₂O₂ (JCPDS 80-785), t-Ce₀.₅Zr₀.₅O₂ (JCPDS 38-1436)).](image)

In accordance to the work of Yashima et al. [160], the phase transitions occurring in CeₓZr₁₋ₓO₂ depend on their composition. The cubic single CeₓZr₁₋ₓO₂ (C50Z-citrate and C80Z-citrate) phase is formed at and above 50 mol% of Ce, while below 50 mol%, a tetragonal CeₓZr₁₋ₓO₂ (e.g. C20Z-citrate) phase is appeared [127, 158, 161]. There is no evidence for phase segregation in wide range of composition. For pure ZrO₂ (Z-citrate) the diffraction patterns can be assigned to the tetragonal ZrO₂ structure [155].
Elemental analysis by Inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray photoelectron spectroscopy (XPS)

Table 4.2 compares the bulk and surface atomic ratios of Ce/Zr determined from ICP and XPS measurements of Ce$_x$Zr$_{1-x}$O$_2$ samples. It can be observed, that the Ce/Zr surface ratios for all mixed oxides are significantly lower than the corresponding bulk ratios indicating on the clear enrichment of zirconium in the near-surface-region. However, the surface Ce/Zr ratio for Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst is in very close agreement with the nominal value. The similar decrease in surface Ce/Zr ratio for Ce$_x$Zr$_{1-x}$O$_2$ solids was observed in previous Chapter 3 that indicated on the migration of zirconium from the bulk to the surface.

### Table 4.2. Comparison of molar Ce/Zr ratios in the near-surface-region (as measured by XPS) with bulk composition (as measured by ICP) for Ce$_x$Zr$_{1-x}$O$_2$ solids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ce/Zr ratio</th>
<th>Ce/Zr ratio (XPS)</th>
<th>Ce/Zr ratio (ICP)</th>
<th>Ce/Zr ratio (EDX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80Z-citrate</td>
<td>4</td>
<td>3.9</td>
<td>5.34</td>
<td>3.9, 6.1*</td>
</tr>
<tr>
<td>C50Z-citrate</td>
<td>1</td>
<td>0.7</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>C20Z-citrate</td>
<td>0.25</td>
<td>0.11</td>
<td>0.41</td>
<td></td>
</tr>
</tbody>
</table>

*Selected areas for the calculation of Ce/Zr are labelled on Figure 4.3

**Transmission electron microscopy (TEM)**

TEM (Transmission Electron Microscopy) studies were performed on the pure oxides C-citrate and Z-citrate as well on C80Z-citrate in order to get more insight into elemental composition and particle size. The TEM images are displayed in Figure 4.3 revealing nanometer sized particles. The particle size of CeO$_2$ is about 8 nm, which is quite close to the crystallite size calculated from Scherrer equation (9 nm). In case of C80Z-citrate particle, the size of about 5 nm was determined. As for the pure individual oxides, Ce-Zr-O particles are also not uniform in shape.

EDX results for C80Z-citrate catalyst confirmed that the distribution of cerium and zirconium concentrations within the selected region is not uniform. In 2a(1) region the molar Ce/Zr ratio was found to be 3.9 which is close to nominal one, whereas 2a(2) region represented Ce-enrichment with Ce/Zr molar ratio of 6.1.
Continuous synthesis of diethyl carbonate from ethanol and CO₂ over CeₓZr₁₋ₓO₂ (x = 0, 0.2, 0.5, 0.8, 1) catalysts

Temperature-programmed reduction (TPR) by H₂

The redox properties of the CeₓZr₁₋ₓO₂ solids were investigated by means of temperature-programmed reduction (TPR) experiments using a feed (50 mL min⁻¹) with 5 vol% H₂ in Ar. Figure 4.4 displays the TPR profiles of the CeₓZr₁₋ₓO₂ catalysts with the various temperature regions of catalyst reduction.

It is known that cerium can exist in CeₓZr₁₋ₓO₂ solid solutions as Ce³⁺ and Ce⁴⁺ ions while zirconium exists as Zr⁴⁺ only [162]. Pure CeO₂ (C-citrate) has a high oxygen storage/release capacity compared to pure ZrO₂ [163], since ceria can store the oxygen in aerobic conditions and release the oxygen in anaerobic conditions in order to satisfy its stoichiometry [164]. These redox properties can strongly be enhanced when Zr⁴⁺ cations are introduced into the CeO₂ lattice owing to improving oxygen ion mobility in the modified Ce-Zr-O lattice. The substitution of Ce⁴⁺ (radius 0.097nm) with the smaller Zr⁴⁺ cation (radius 0.084 nm) causes shrinking of the CeO₂ fluorite-type lattice, formation of structural defects and alteration of surrounded oxygen [136, 162, 165]. Moreover, the presence of Zr⁴⁺ in CeO₂ decreases the surface reduction temperature of Ce⁴⁺ and also increases the total amount of reduced cerium.
The reduction process of pure CeO₂ (C-citrate) is well-known to occur in two steps. The first region is located between 350 and 600 °C with T_max of around 452 °C and second region starts from 600 °C with T_max of around 792 °C. The low-temperature peak is related to the removal of surface lattice oxygen of CeO₂, while the high-temperature signal at 792 °C is caused by the removal of bulk lattice oxygen [166]. The small peak centered at 224 °C was associated with the reduction of the outermost layer of Ce⁴⁺ (surface reduction) [163]. The reduction of pure ZrO₂ was negligible (small peak at 582 °C). However, the incorporation of Zr⁴⁺ to CeO₂ promoted the reduction of pure CeO₂. In contrast to the TPR profile for pure CeO₂, the mixed CeₓZr₁₋ₓO₂ oxides show a main broad reduction feature in the region between 500–530 °C with different T_max values. Based on results obtained by de Rivas _et al._ [167, 168], the addition of Zr⁴⁺ to CeO₂ causes a reduction of surface and bulk in one step at moderate temperatures. In addition, some H₂ consumption can be observed at higher temperatures for C80Z-citrate and C50Z-citrate, but to a lower extent than for CeO₂. Furthermore, the position of surface reduction peak shifted from 452 to 508 °C with increasing of zirconium content. It was found that the extent of the reduction was the highest for C50Z-citrate sample. In addition, the weak peak at 360 °C can be attributed to the reduction of Ce⁴⁺ located in a different chemical environment, such as subsurface region [169].

Figure 4.4. H₂-TPR profiles of different CeₓZr₁₋ₓO₂ solids. (→: indicates isothermal treatment of the samples at 800 °C for 2 h).

In addition, the total amount of hydrogen consumed by the catalysts and T_max values are summarized in Table 4.3. An increase in the H₂ uptake from 1.15 mmol g⁻¹ for pure ceria (C-citrate) to 1.793 mmol g⁻¹ for C50Z-citrate provides hints to an enhanced reducibility of
CeO$_2$ caused by the addition of Zr$^{4+}$ to CeO$_2$ [167]. Obviously the H$_2$ consumption progressively reduces with increase in zirconium content above 50 mol%. For pure ZrO$_2$ (Z-citrate) the H$_2$ consumption was only 0.192 mmol g$^{-1}$. This result indicates that under the conditions applied the Zr$^{4+}$ cations are hardly reduced.

**Table 4.3.** H$_2$ uptake and temperature of maximal hydrogen consumption ($T_{\text{max}}$) during TPR runs for Ce$_x$Zr$_{1-x}$O$_2$ solids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H$_2$-uptake (mmol g$^{-1}$)</th>
<th>$T_{\text{max}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-citrate</td>
<td>0.192</td>
<td>582</td>
</tr>
<tr>
<td>C20Z-citrate</td>
<td>0.704</td>
<td>508</td>
</tr>
<tr>
<td>C50Z-citrate</td>
<td>1.793</td>
<td>530</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>1.482</td>
<td>503</td>
</tr>
<tr>
<td>C-­citrate</td>
<td>0.015, 0.271, 0.869</td>
<td>224, 452, 792</td>
</tr>
</tbody>
</table>

**Acid-base properties: Temperature-programmed desorption (TPD) of NH$_3$ and CO$_2$**

The total concentration and the strength of acidic sites on the surface of Ce$_x$Zr$_{1-x}$O$_2$ solids were determined by NH$_3$-TPD (i.e. expressed as the amount of NH$_3$ desorbed per gram and per square meter of catalyst) and given in Table 4.4.

**Table 4.4** Acid-base characteristics of Ce$_x$Zr$_{1-x}$O$_2$ solids. $T_{\text{max}}$ (NH$_3$) and $T_{\text{max}}$ (CO$_2$) stand for temperature of maximal NH$_3$ and CO$_2$ desorption, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NH$_3$ desorbed ($\mu$mol g$^{-1}$ / $\mu$mol m$^{-2}$)</th>
<th>$T_{\text{max}}$ (NH$_3$) (°C)</th>
<th>CO$_2$ desorbed ($\mu$mol g$^{-1}$ / $\mu$mol m$^{-2}$)</th>
<th>$T_{\text{max}}$ (CO$_2$) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-citrate</td>
<td>185 / 2.1</td>
<td>230</td>
<td>112 / 1.3</td>
<td>168, 584</td>
</tr>
<tr>
<td>C20Z-citrate</td>
<td>130 / 1.7</td>
<td>210, ~450</td>
<td>235 / 3.0</td>
<td>171, 570</td>
</tr>
<tr>
<td>C50Z-citrate</td>
<td>118 / 2.1</td>
<td>220, ~450</td>
<td>117 / 2.1</td>
<td>168, 637</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>94 / 2.2</td>
<td>220</td>
<td>104 / 2.5</td>
<td>163, 618</td>
</tr>
<tr>
<td>C-­citrate</td>
<td>34 / 1.3</td>
<td>200</td>
<td>52 / 1.9</td>
<td>149, 589</td>
</tr>
</tbody>
</table>

The acidic properties of the solids are strongly affected by the presence of zirconium in the lattice of CeO$_2$ [170], since pure ZrO$_2$ and CeO$_2$ have different lattice potentials and incorporation of one oxide matrix into the other cause a generation of new surface acidic sites in the solid solution as per Kung’s model [131, 171]. From Table 4.4 it is evident that pure ZrO$_2$ (Z-citrate) is more acidic (i.e. 2.1 $\mu$mol NH$_3$ m$^{-2}$) than pure CeO$_2$ (C-citrate). It can be seen that the total acidity was the lowest for solid C-citrate (1.3 $\mu$mol NH$_3$ m$^{-2}$), which is
4. Continuous synthesis of diethyl carbonate from ethanol and CO₂ over CeₙZr₁₋ₙO₂ (ₙ = 0, 0.2, 0.5, 0.8, 1) catalysts

However considerably improved upon addition of 20 mol% of zirconium, then decreases as Zr content is further increased up to 80 mol%. C80Z-citrate exhibits the highest amount of NH₃ desorbed from its surface (2.2 µmol NH₃ m⁻²). Based on literature [131], the acidic sites are located more in the interior of pores, leading to more physisorption of NH₃. As in the present case, C80Z-citrate possessed the highest pore volume of 0.076 cm³ g⁻¹ compared to other CeₙZr₁₋ₙO₂ samples.

Figure 4.5 shows the NH₃-TPD profiles of the CeₙZr₁₋ₙO₂ solids. It can be seen, that these solids possess acidic sites of different strength. The desorption peaks of TPD profiles located at 100 –200 °C, 200 –400 °C and 400 – 450 °C can be assigned to weak, moderate and strong acid sites, respectively [67]. Both the weak and moderate acid sites were observed for all catalysts. However, the strong acid sites with characteristic desorption temperature of about 450 °C were observed in Z-citrate, C20Z-citrate and C50Z-citrate solids only.

![Figure 4.5](image)

**Figure 4.5.** (a) NH₃-TPD profiles and (b) CO₂-TPD profiles of CeₙZr₁₋ₙO₂ solids.

In order to investigate the effect of Ce content on basic properties, CO₂-TPD experiments were also studied. CO₂-TPD profiles of the CeₙZr₁₋ₙO₂ solids are shown in Figure 4.5b. CeₙZr₁₋ₙO₂ solids possess basic sites of different types with weak (100-230 °C), moderate (230–500 °C) and strong (above 500 °C) strengths [105, 135]. All Ce-based catalysts exhibit two broad desorption peaks at different temperatures: the low temperature peak was attributed to weak and moderate basic sites, while the high temperature peak was ascribed to strong basic sites.

Table 4.3 lists the amount of CO₂ desorbed during temperature programmed desorption measurements of different CeₙZr₁₋ₙO₂ solids. It can be seen, that the total concentration of CO₂ desorption from sample Z-citrate is very low (1.3 µmol m⁻²). The basic properties of mixed oxides are improved as the Zr content is increased up to 80 mol%. Among all prepared
mixed oxides, C20Z-citrate exhibited the highest concentration of basic sites (3.0 µmol m\(^{-2}\)), mostly centered in the region of strong basicity (2.9 µmol m\(^{-2}\) which is 98% of total basic sites concentration). By comparison the NH\(_3\) - and CO\(_2\)-TPD results, the acid-base properties of pure oxides, i.e. CeO\(_2\) and ZrO\(_2\), can be significantly modified by their chemical mixing. As the result, mixed Ce\(_x\)Zr\(_{1-x}\)O\(_2\) catalysts possess both acidic and basic sites of different types. Interestingly the acid-to-base site ratio was about 1 for C80Z-citrate and C50Z-citrate catalysts, which seemed to be optimum for improved catalytic properties.

4.1.2. Catalytic results: effect of Ce/Zr ratio, temperature and pressure on catalytic performance

The present work was focused on transferring the knowledge from batch-reactor approaches to a continuous-flow operation. Thus the contact time of the reagents with the catalyst is a very important parameter to achieve the highest possible DEC yield and space-time-yield as well. From the tests performed over the C80Z-citrate catalyst (T\(_c\) = 700 °C) at 140 °C and 140 bar and described in Section 4.2, a total flow rate of 42 L\(_{\text{liq.}}\) kg\(_{\text{cat}}\) \(-1\) h\(^{-1}\) (\(\tau = 68.6\) s, highest Y\(_{\text{DEC}}\) obtained) was identified and selected for the present section. The ratio of EtOH : CO\(_2\) = 1 : 6 was selected for further experiments, since an increase in this ratio leads to a decrease in the DEC yield (see Figure 4.13). The effect of R-OH : CO\(_2\) feed ratio on equilibrium conversion of C\(_1\)-C\(_2\) alcohols was already discussed in literature [172-174]. It was found that the larger is concentration of C\(_1\)-C\(_2\) alcohol in the feed mixture, the higher the temperature (up to the critical temperature of pure R-OH, 240 °C) required for conducting the target reaction. Moreover, a decrease of R-OH : CO\(_2\) feed ratio favours the equilibrium C\(_1\)-C\(_2\) alcohols conversion.

Figure 4.6 shows the influence of total reaction pressure (p = 80, 110, 140 or 180 bar) and temperature (T = 80, 100, 120, 140, 160 or 180 °C) on DEC formation over C-citrate, C80Z-citrate, C50Z-citrate, C20Z-citrate and Z-citrate catalysts under continuous-flow conditions in a plug flow reactor (tubular reactor). Figure 4.6 shows the influence of pressure and temperature on DEC yield obtained over different Ce\(_x\)Zr\(_{1-x}\)O\(_2\) catalysts. An increase in DEC yield was determined upon pressure rise up to 140-160 bar depending on Ce content in Ce\(_x\)Zr\(_{1-x}\)O\(_2\) solid solutions. A further pressure increase up to 180 bar led to a decline in DEC production. Based on phase equilibrium data which are available in the literature [112, 114-117], it was found that supercritical region for C\(_2\)H\(_5\)OH-CO\(_2\) binary system was reached maximum near 160 bar and temperature in a range of 120-160 °C when initial CO\(_2\) molar
fraction in such system was between 0.7 and 0.9. It was supposed that these trends are still valid for quaternary system, due to the low amounts of DEC (predicted \( x \approx 0.004 \) at reaction equilibrium) and H\(_2\)O (predicted \( x \approx 0.004 \) at reaction equilibrium). One can also expect that above 160 bar the reaction mixture might be in the liquid or supercritical state, depending upon the system temperature. According to the findings of Hou et al. [175] dialkyl carbonate production increased with increasing pressure in the two–phase region, and decreased with pressure in the supercritical region (one phase region).

![Figure 4.6](image_url)

**Figure 4.6.** Effect of reaction pressure and temperature on the yield of DEC over different Ce\(_x\)Zr\(_{1-x}\)O\(_2\) catalysts. Reaction conditions: catalyst weight 1 g, EtOH : CO\(_2\) = 1 : 6, 1 h time-on-stream, LHSV = 42 L\(_{\text{liq.}}\) kg\(_{\text{cat.}}^{-1}\) h\(^{-1}\), \( \tau = 68.6 \) s.

The effect of reaction temperature on the desired reaction is more complicated. The yield of DEC gradually increased with reaction temperature up to 140 °C and then dropped to lower values at higher temperatures for C-citrate, C80Z-citrate and C50Z-citrate. Based on the fact that that carboxylation of alcohols is an exothermic reaction, from thermodynamic point of view high reaction temperature is unfavourable for organic carbonates formation [99, 105]. The DEC yield of pure ZrO\(_2\) (Z-citrate) and C20Z-citrate slowly increased with rising temperature in the pressure region of 140-160 bar and reached the highest value of 0.4% at 180 °C. The highest DEC yield over C50Z-citrate (0.48%) and C80Z-citrate (0.5%) catalysts
were achieved at pressure of 160 and 140 bar and temperature of 160 and 140 °C, respectively.

4.1.3. Catalytic results and materials properties affecting the catalyst activity

According to literature [94, 176], DMC and DEC formation over pure CeO₂ and CeₓZr₁₋ₓO₂ catalysts had been related to its specific surface areas. In this work, the BET-SA of the CeₓZr₁₋ₓO₂ solids increased with Zr content and reached a maximum value for pure ZrO₂ (Z-citrate). Although C₈₀Z-citrate (42 m² g⁻¹) and C₅₀Z-citrate (57 m² g⁻¹) have lower BET-SA in contrast to other CeₓZr₁₋ₓO₂ catalysts, they exhibited higher DEC yields. Thus, a relation between DEC formation and BET-SA could not be established in the present study. Possible reasons for higher performance of C₈₀Z-citrate and C₅₀Z-citrate solids compared to other Ce/Zr ratios could be related to their different surface composition, crystal structure and acid–base properties. A tetragonal phase was found to be predominant in the solids with Ce content below 50 mol%, whereas the cubic structure was formed for Ce-rich samples (e.g. Ce ≥ 50 mol%). Based on catalytic results, it can be established that the most active phase for DEC formation was cubic CeₓZr₁₋ₓO₂ (C-citrate, C₈₀Z-citrate, C₅₀Z-citrate). This result is in good agreement with previous works where pure CeO₂ [99] and mixed oxides such as Ce₀.₆Zr₀.₄O₂ [28] and Ce₀.₅Zr₀.₅O₂ [93] existed in cubic phase were the most active catalysts in direct DEC/DMC batch syntheses. The introduction of Zr into the cubic CeO₂ lattice remarkably affects the amount of oxygen vacancies and the basic properties of the materials therewith [167]. Postole et al. [131] claimed that the maximum number of oxygen species, which act as basic sites in the calorimetric experiments, is observed on the surface of CeₓZr₁₋ₓO₂ sample with high zirconium content. It is due to distortion of CeO₂ lattice by insertion of Zr⁴⁺, which allowed for easier removal of lattice oxygen. Besides, from XPS results (Table 4.2) a clear enrichment of Zr in the near-surface-region of all samples was found. Interestingly, such enrichment is much more pronounced in case of C₈₀Z-citrate and C₅₀Z-citrate samples. Moreover, the total number of acidic sites in CeₓZr₁₋ₓO₂ catalysts also depended on Zr content, which consequently led to different catalytic behaviour. Table 4.5 compares acidic properties of CeₓZr₁₋ₓO₂ catalysts reported by different authors. As in this work, the strength and the total concentration of acidic sites increase upon addition of zirconium. In addition, the high concentration of strong acidic sites 57% and 60% of total acidity was found for CeₓZr₁₋ₓO₂ samples with x = 0.5 and 0.15, respectively. These results
are in good agreement with the results obtained in this work, since only CeₙZr₁₋ₙO₂ catalysts with x = 0.5 and 0.2 possess strong acidic sites 15% and 7% of total acidity, respectively.

Table 4.5. Comparison of total acidity of catalysts with literature reports.

<table>
<thead>
<tr>
<th></th>
<th>This work</th>
<th>Postole et al. [131]</th>
<th>de Rivas et al. [167]</th>
<th>Gutiérrez-Ortiz et al. [177]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>NH₃ µmol m⁻²</td>
<td>Composition</td>
<td>NH₃ µmol m⁻²</td>
<td>Composition</td>
</tr>
<tr>
<td>CeO₂</td>
<td>1.3</td>
<td>Ce₀.₇Zr₀.₃O₂</td>
<td>2.0</td>
<td>Ce₀.₈Zr₀.₂O₂</td>
</tr>
<tr>
<td>Ce₀.₈Zr₀.₂O₂</td>
<td>2.2</td>
<td>Ce₀.₅Zr₀.₅O₂</td>
<td>2.4</td>
<td>Ce₀.₅Zr₀.₅O₂</td>
</tr>
<tr>
<td>Ce₀.₅Zr₀.₅O₂</td>
<td>2.1</td>
<td>Ce₀.₂Zr₀.₈O₂</td>
<td>2</td>
<td>Ce₀.₁₅Zr₀.₈₅O₂</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>2.1</td>
<td>ZrO₂</td>
<td>4.1</td>
<td>ZrO₂</td>
</tr>
</tbody>
</table>

As reported in literature [99, 124], the DEC yield over CeₙZr₁₋ₙO₂ is reduced to some extent in the presence of strong acid–base sites on the surface of the catalysts. As in the present study, pure ZrO₂ (Z-citrate) and C20Z-citrate possessing stronger strength of acid-base sites in comparison to other CeₙZr₁₋ₙO₂ catalysts showed rather poor performance. C80Z-citrate catalyst with Ce content of 80 mol% exhibits weak to medium strength of acidic sites seems to be a good balance between the acidity and DEC formation.

According to the results discussed above, the DEC yield was primarily related to the amount of acidic and basic sites on the Ce–Zr–O surface. Both C80Z-citrate and C50Z-citrate have shown nearly an equal amount of acidic and basic sites and the highest catalytic performance as well. These results are in a good agreement with Tomishige et al. [87] who claimed that an equal number of neighbouring acidic and basic sites is required for optimal catalyst performance, whereas they found such an effect in the direct synthesis of DMC over ZrO₂ catalysts.

In addition, CO₂ activation needs to be evaluated in a systemic manner, since it is the most difficult part of the reaction. Based on the reaction mechanism proposed by Wada et al. [66] for the formation of DMC over Cu–CeO₂ catalyst, the CO₂ adsorption was related to oxidation state of surface cerium (H₂-TPR results). It was assumed that oxygen vacancies can adsorb CO₂. The reduction in H₂ and/or by the presence of Cu sites in catalysts lead to the increase the population of O vacancies. In case of CeₙZr₁₋ₙO₂ solid solutions investigated in the present study, an addition of Zr⁴⁺ into the CeO₂ lattice caused a distortion in the ceria
lattice resulting in an increase in lattice oxygen mobility and also in an increase of the number of anion vacancies on Ce-Zr-O surface [167]. These surface oxygen anions act as basic sites, which were confirmed by CO2-TPD analysis (Table 4.4). An improved catalytic performance was achieved on C50Z-citrate and C80Z-citrate solids compared to pure CeO2 most probably due to significantly increased adsorption of CO2 on their surface.

Since C80Z-citrate showed the highest Y_{DEC} at possibly lowest temperatures and pressures, this solid was used to check its long-term stability. The reaction was performed at 140 °C, 140 bar for 20 hours over C80Z-citrate. It was found that the formation of DEC slightly increased with reaction time and levelled off after 6 hours (Y_{DEC} = 0.55%), probably because the active catalytic species forms gradually.

4.2. Impact of calcination temperature on catalytic properties of Ce_{0.8}Zr_{0.2}O_{2} solids

Next, the influence of calcination temperature of catalyst precursor compounds on DEC formation was studied. It is a well-known fact that thermal treatment produces significant textural and structural changes. Among various catalysts tested, C80Z-citrate (80 mol% Ce and 20 mol% Zr) sample was found to be active. Therefore, it was further used in subsequent investigations. The catalyst precursor was calcined at three different temperatures (i.e. 450, 700 and 1000 °C) in air for 3 hours and examined under optimized conditions (140 °C and 140 bar). Such results are discussed below in a systematic way.

4.2.1. Catalysts characterization

**BET surface area**

Table 4.5 presents the specific BET-SAs, geometrical SAs, pore volumes and average pore sizes of C80Z-citrate samples in dependence on the calcination temperatures applied. The results reveal that an increase in calcination temperature up to 1000 °C caused a significant decrease in the surface area, which was related to changes in pore structure and crystallite size. The calculated geometrical surface areas from S_{XRD} = 6/ρd of Ce_{0.8}Zr_{0.2}O_{2} solids significantly differ from the BET-SA. Dobrosz-Gómez *et al.* [178] explained this fact based on difference in calculations. For S_{XRD} calculations, the diffraction peaks of crystallites with initial Ce-Zr solid solution composition were used, while for S_{BET} all particles in the sample were taking in account. Moreover, he claimed that solid solution may contain small
4. Continuous synthesis of diethyl carbonate from ethanol and CO₂ over CeₓZr₁₋ₓO₂ (x = 0, 0.2, 0.5, 0.8, 1) catalysts

Agglomerates and grain boundary interfaces which are not available to N₂ gas during the BET analysis. The total pore volumes and the average pores sizes based on the BJH method are also displayed in Table 4.5. An increase in pore size is observed for samples calcined at 700 and 1000 °C. The high temperature treatment leads to the destruction of the small pores and to an increase in the size of the remaining pores. The average pore diameters of all C80Z-citrate catalysts irrespective of calcination temperature are in the mesoporous range.

**Table 4.5.** Effect of calcination temperature on the textural properties of Ce₀.₈Zr₀.₂O₂ catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_c (°C)</th>
<th>BET-SA a (m² g⁻¹)</th>
<th>XRD-SA b (m² g⁻¹)</th>
<th>Average pore d (nm)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80Z-citrate</td>
<td>450</td>
<td>42</td>
<td>143</td>
<td>6.2</td>
<td>0.076</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>700</td>
<td>37</td>
<td>85</td>
<td>8.9</td>
<td>0.095</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>1000</td>
<td>11</td>
<td>19</td>
<td>15.7</td>
<td>0.049</td>
</tr>
</tbody>
</table>

a Specific BET surface area  
b Geometrical surface area calculated from S_XRD = 6/ρd.

**X-ray diffraction (XRD)**

Figure 4.7a shows the XRD patterns of the C80Z-citrate catalysts. XRD results revealed the formation of single cubic fluorite phase with space group *Fm-3m* in all three cases [179]. No phase segregation was detected. The structural assignment was performed using V-curve (Figure 4.7b). Thus, the lattice volume was related to the respective atomic compositions in the CeₓZr₁₋ₓO₂ solid solution. C80Z-citrate shows 100% cubic Ce₀.₈₅Zr₀.₁₅O₂ phase in all three cases (450, 700 and 1000 °C).

![XRD patterns of C80Z-citrate calcined at 450, 700 and 1000 °C; (b) Volume of the unit cell of the cubic (CeₓZr₁₋ₓ)O₂ as function of the Ce content.](image)

**Figure 4.7.** (a) XRD patterns of C80Z-citrate calcined at 450, 700 and 1000 °C; (b) Volume of the unit cell of the cubic (CeₓZr₁₋ₓ)O₂ as function of the Ce content.
The obtained C80Z-citrate materials are of nanocrystalline nature that is confirmed by the calculation of crystallite size using the Scherrer equation applied to the XRD line broadening [125] (Table 4.6). For the quantitative analysis (Rietveld) the whole diffractogram including the calculated crystallite size in the 20 region from 5-90° was refined. The values are average values for all "visible" reflection peaks of a phase, which appear in the mentioned 20 region and for this calculation the width of peak is required. By the separation of the peaks I would consider anisotropic effects in the size. The diffraction peaks become sharper with increasing calcination temperature from 450 to 700 °C due to crystallite growth (6→10 nm), while at 1000 °C sintering effect is even more pronounced (10 to 45 nm). This observation is in a good agreement with the results from the BET measurements (see Table 4.5).

**Table 4.6.** Effect of calcination temperature on crystallite size, lattice constant, lattice volume and crystallographic density of C80Z-citrate samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tc (°C)</th>
<th>Crystal phase</th>
<th>a (nm)</th>
<th>V (nm³)</th>
<th>D (nm)</th>
<th>ρ (g cm⁻³)</th>
<th>ε (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80Z-citrate</td>
<td>450</td>
<td>Cubic fluorite</td>
<td>0.538</td>
<td>0.156</td>
<td>6</td>
<td>7.01</td>
<td>0.40</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>700</td>
<td>Cubic fluorite</td>
<td>0.538</td>
<td>0.156</td>
<td>10</td>
<td>7.02</td>
<td>0.26</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>1000</td>
<td>Cubic fluorite</td>
<td>0.539</td>
<td>0.156</td>
<td>45</td>
<td>7.00</td>
<td>0.12</td>
</tr>
</tbody>
</table>

The line widths of the Bragg’s peaks can vary due to the size of crystallite and crystalline defects originating from microstrain. Thus, both microstrain and crystallite size lead to peak broadening (Equation 2.4). With progressing thermal treatment (700 and 1000 °C) the microstrain decreased due to ordering of the atoms in the crystal lattice and decreasing concentration of defects [180] (Table 4.6). The lattice parameter (a), lattice volume (V) and crystallographic density (ρ) are almost not affected by the calcination temperature.

**Elemental analysis by Inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray photoelectron spectroscopy (XPS)**

XPS and ICP were used to investigate the effect of calcination temperature on the surface and bulk atomic ratios of Ce/Zr in C80Z-citrate solids. The results of the XPS and ICP measurements are presented in Figure 4.8. The surface and bulk atomic Ce/Zr ratios for C80Z-citrate samples calcined at 450 and 700 °C are almost equal to the theoretical atomic ratio of 4.0. However, a decrease in surface Ce to Zr atomic ratio was observed for samples
calcined at 1000 °C due to the migration of Zr from the bulk to the surface during ageing process. Fan et al. [181] explained such decline in the Ce/Zr ratio by the reorganization of phases with different Zr composition under high calcination temperature, forming a so-called "shell–core" structure with the high-Zr composition phase in the outer sphere of the particles.

![Graph showing XPS and ICP measurements](image)

**Figure 4.8.** Comparison of the relative Ce and Zr concentrations in the near-surface-region as measured by XPS with bulk composition (ICP) for C80Z-citrate calcined at 450, 700 and 1000 °C.

**Transmission electron microscopy (TEM)**

Figure 4.9 presents TEM images of C80Z-citrate calcined at three different temperatures: 450, 700 and 1000 °C. It can be seen that nanosized particles of C80Z-citrate were obtained under the three calcination temperatures. The particle size of Ce$_{0.8}$Zr$_{0.2}$O$_2$ calcined at 450 and 700 °C increased from approximately 5 to 10 nm. A more significant increase in the particle size of Ce$_{0.8}$Zr$_{0.2}$O$_2$ up to 50 nm was observed in samples calcined at 1000 °C. The size of nanoparticle from TEM image is in a good agreement with an average crystallite size calculated from XRD patterns. In addition, via TEM investigation an intergrowth of the single crystallites was detected. In spite of thermal resistivity due to the presence of zirconium in the ceria lattice, the effect was found to be low at 1000 °C. A well separated particle morphology and grain boundary was observed for C80Z-citrate samples calcined at 450 and 700 °C (Figure 4.9a and 4.9b). In a case of C80Z-citrate calcined at 1000 °C, a significant aggregation of crystallites was found (Figure 4.9c).
Figure 4.9. TEM micrographs of C80Z-citrate solids calcined at different temperatures: (a)-(a’) 450 °C; (b)-(b’) 700 °C; (c)-(c’) 1000 °C.

**Temperature-programmed reduction (TPR) by H₂**

Temperature-programmed reduction (TPR) using a feed with 5 vol% H₂ in Ar was applied to study the effect of calcination temperature on the reduction properties of C80Z-citrate catalyst. Figure 4.10 depicts the TPR profiles of the C80Z-citrate catalyst calcined at 450, 700 and 1000 °C.

Figure 4.10. H₂-TPR profiles of C80Z-citrate solids calcined at 450, 700 and 1000 °C.

According to the literature low-temperature (T ≤ 550 °C) reduction process accounts for reduction of surface oxygen, whereas high-temperature (T > 550 °C) reduction corresponds to the reduction of bulk oxygen [166, 182-186]. Wang et al. [133] claimed that the coordinately unsaturated surface lattice oxygen ions can be easily removed in low temperature region
(T ≤ 550 °C), whereas bulk oxygen requires to be transported to the surface before its removal. Thus bulk reduction takes place at higher temperatures (T > 550 °C). The reduction profile of C80Z-citrate calcined at 450 °C is characterized by two peak at 503 °C (70% of total area) and at higher temperature (634 °C, 30%). Further increase in calcination temperature caused a shift of the reduction peak to higher T. For C80Z-citrate (700 °C) and C80Z-citrate (1000 °C) samples the reduction process also involves two steps. First region is 350-600 °C with T_max around 509 (60% of total area of reduction peaks, C80Z-700 °C) and 539 °C (53% of total area, C80Z-1000 °C), second region started at 600 °C with T_max 665 (C80Z-700 °C) and 715 °C (C80Z-1000 °C). Moreover, a good relationship between the BET surface area and H₂ consumption from the first peak was found. It is evident that high surface area of C80Z-citrate calcined at 450 °C (SA: 42 m² g⁻¹, H₂-uptake from the first peak: 1.0 mmol g⁻¹) sample favours reduction at lower temperature compared to the counterparts sintered at 700 (37 m² g⁻¹, 0.9 mmol H₂ g⁻¹) and 1000 °C (11 m² g⁻¹, 0.6 mmol H₂ g⁻¹). According to the literature, a linear relationship was obtained between the BET surface area and the H₂-uptake during the low-temperature reduction using experimental data determined by Trovarelli et al. [184, 187, 188] and the values predicted by the method of Johnson and Mooi [189]. For the bulk reduction, the temperature of reduction gradually became higher and the area of peaks progressively became relatively larger (30%→40%→47%) with the increase of calcination temperature.

The hydrogen consumption expressed as the amount of H₂ per gram of catalyst is summarized in Table 4.7. A decrease in the amount of H₂ consumed by surface lattice oxygen with an increase in calcination temperature of C80Z-citrate can be related to a temperature-induced decrease in BET-SA as suggested in [190]. Thermal treatments strongly affect redox behaviour of C80Z-citrate solid solution and reduce H₂-uptake at lower reduction temperatures [182, 191].

### Table 4.7. H₂ uptake and temperature of maximal hydrogen consumption (T_max) during TPR runs for C80Z-citrate catalysts calcined at 450, 700 and 1000 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_c (°C)</th>
<th>H₂ uptake (mmol g⁻¹)</th>
<th>T_max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80Z-citrate</td>
<td>450</td>
<td>1.482</td>
<td>503, 634</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>700</td>
<td>1.441</td>
<td>509, 665</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>1000</td>
<td>1.196</td>
<td>539, 715</td>
</tr>
</tbody>
</table>
4. Continuous synthesis of diethyl carbonate from ethanol and CO₂ over CeₓZr₁₋ₓO₂ (x = 0, 0.2, 0.5, 0.8, 1) catalysts

**Acid-base properties: Temperature-programmed desorption (TPD) of NH₃ or CO₂**

Temperature-programmed desorption (TPD) of ammonia or carbon dioxide was applied for determining the concentration of acidic or basic sites. The temperature, at which desorption occurred, indicates the strength of adsorption, whereas the amount of desorbed probe molecules represent the concentration of acidic or basic sites on the surface of C80Z-citrate. NH₃-TPD profiles for C80Z-citrate samples calcined at 450, 700 and 1000 °C are shown in Figure 4.11a. Two C80Z-citrate samples (450 and 700 °C) exhibit a broad desorption profile. It reveals the presence of different types of acid sites mostly concentrated in region of moderate acidity. However, a slight shift in desorption temperature towards lower T was found in C80Z-citrate calcined at 700 °C. Such shift of desorption peak was attributed to a decrease in the strength of acidic sites. The solid calcined at 1000 °C has completely lost acidic sites and hence there is absolutely no adsorption of NH₃ over this sample.

Figure 4.11a shows CO₂-TPD profiles of C80Z-citrate calcined at 450, 700 and 1000 °C. It can be clearly seen that the total amount of CO₂ desorbed from C80Z-citrate 450 °C is very high compared to other two samples. Furthermore, this sample exhibited two large peaks at different temperatures indicating that different types of basic sites are present with weak (100-230 °C), moderate (230-500 °C) and strong (above 500 °C) strength [105, 135]. Compared to C80Z-citrate 450 °C, the intensity of the peak with T_max at 174 °C for C80Z-citrate 700 °C decreased gradually indicating a drop in the concentration of basic sites. Moreover, C80Z-citrate 700 °C does not possess strong basic sites. As shown in Table 4.7, high calcination temperature provoked crystal growth along with a decrease in the specific surface area. This seemed to be a probable reason for the decline in the concentration of both
Continuous synthesis of diethyl carbonate from ethanol and CO$_2$ over Ce$_x$Zr$_{1-x}$O$_2$ ($x = 0, 0.2, 0.5, 0.8, 1$) catalysts

Acidic and basic sites on the surface of C80Z-citrate 1000 °C. The similar behaviour for Ce$_{0.33}$Zr$_{0.67}$O$_2$ was described by Tomishige et al. [135]. They claimed that both acidity and basicity decreased for material calcined at high temperature (1000 °C). It has been speculated that the surface on Ce-Zr-O catalysts calcined at low temperatures (400 °C) has more roughness and more coordinatively unsaturated cations and anions thereby yielding a higher acidity. Similar effect of calcination temperature on acidic properties of zirconia was also reported by Bolis et al. [192] It was assumed that by increasing temperature the elimination of coordinatively unsaturated zirconium ions located at the corners of crystals takes place.

The total concentration of acidic and basic sites on C80Z-citrate samples treated at 450, 700 and 1000 °C has been evaluated and is given in Table 4.8. Compered to C80Z-citrate 450 °C, the peak intensities in TPD profiles of NH$_3$ and CO$_2$ for C80Z-citrate 700 °C dropped significantly. This intensity drop was attributed to an overall loss of the total number of acid-base sites with increasing calcination temperatures. The decrease in concentration of acid-base sites, preferentially strong, was in accordance with the surface thermal treatment. Almost no NH$_3$ and CO$_2$ were desorbed from C80Z-citrate calcined at 1000 °C indicating negligible number of acidic and basic sites on it.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ (°C)</th>
<th>Total acidity (NH$_3$-TPD)</th>
<th>Total basicity (CO$_2$-TPD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{NH}_3$-desorbed ($\mu$mol g$^{-1}$ / $\mu$mol m$^{-2}$)</td>
<td>Peak max (°C)</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>450</td>
<td>94 / 2.2</td>
<td>220</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>700</td>
<td>41 / 1.1</td>
<td>205</td>
</tr>
<tr>
<td>C80Z-citrate</td>
<td>1000</td>
<td>0 / 0</td>
<td>-</td>
</tr>
</tbody>
</table>

### 4.2.2. Catalytic results and material properties affecting the activity

Figure 4.12 compares DEC yield obtained over C80Z-citrate catalysts under continuous-flow conditions at 140 bar and 140 °C. The effect of pressure and temperature on the catalytic performance [193, 194] was described in previous paragraph 4.1. The pressure of 140 bar and temperature of 140 °C were selected for further tests, since the highest DEC yield was achieved under these reaction conditions. Tomishige et al. [65] applied similar catalysts for the carboxylation of methanol to DMC and claimed that high calcination temperature for
Ce$_{0.2}$Zr$_{0.8}$O$_2$ catalysts is more favourable for DMC formation even though the BET surface area was considerably reduced after thermal treatment. Consequently, the Ce$_{0.2}$Zr$_{0.8}$O$_2$ catalyst calcined at 1000 °C despite its much lower surface area exhibited the highest performance in case of $Y_{DMC} = 0.8\%$. The authors speculated that the surface structure and properties, especially acidity and basicity, are modified with a high temperature of calcination. Keeping this aspect in mind, I tried to apply the same logic and extended such treatment to my catalysts but for the DEC synthesis. The intention is also to elucidate the correlation between DEC formation and catalyst properties such as BET-SA, crystalline structure, redox properties, adsorption of NH$_3$ and CO$_2$ using the present C80Z solid.

Figure 4.12 presents the DEC yield as a function of the calcination temperature of C80Z-citrate catalyst precursor. The yield increased with catalyst calcination temperature only up to 700 °C and then decreased at 1000 °C. Consequently, the DEC formation over C80Z-citrate samples is very dependent on catalyst calcination temperature [195]. However, somewhat different results were obtained compared to the studies of Tomishige et al. related to DMC synthesis [65].

![Figure 4.12](image)

**Figure 4.12.** Effect of calcination temperature on the yield of DEC over C80Z-citrate catalysts. Reaction conditions: catalyst weight 1 g, EtOH : CO$_2$ = 1 : 6, 1 h-on-stream, LHSV = 42 L$_{\text{liq.}}$ kg$_{\text{cat.}}^{-1}$ h$^{-1}$, $\tau = 68.6$ s.

XRD results reveals that C80Z-citrate solids had cubic crystal structure and the phase composition did not change strongly with rising calcination temperature, though crystallite size became larger on the sample calcined at higher temperature. A decrease of BET-SA from 42 m$^2$ g$^{-1}$ ($T_c = 450$ °C) to 11 m$^2$ g$^{-1}$ ($T_c = 1000$ °C) caused by the high temperature treatment. However, no correlation between BET surface area and DEC formation could be found. The yield of DEC can be related to changes of the strength of acidic and basic sites. C80Z-citrate
calcined at 450 °C possesses higher acidity and basicity than the other two samples. In addition, the presence of strong basic sites in C80Z-citrate calcined at 450 °C has a rather negative effect on the DEC formation. Based on these results, it can be concluded that the active sites of C80Z-citrate solids were the weak and moderate acid-base sites that are present on the surface of the catalysts calcined at 700 °C. In case of C80Z-citrate calcined at 1000 °C, poor performance was observed, which may be attributed to the very low number of acid-base sites. Wang et al. [99] observed a similar effect of calcination temperature (400, 600, 800 and 1000 °C) on acid-base behaviour of Ce0.07Zr0.93O2 catalysts. Over pure CeO2 and Ce0.07Zr0.93O2 calcined at 800 °C the highest DEC yield (0.16 and 0.11%) was obtained. It was claimed that the Ce-Zr-O solid solutions calcined at lower temperature has more surface roughness while high temperatures lead to more plain surfaces. As a result, more coordinatively unsaturated cations and anions on rough surfaces possess higher number of acidic sites and hence higher DEC yield.

4.3. Effect of LHSV and ratio of EtOH : CO2 on catalytic performance

As seen above, superior catalytic performance could be achieved with C80Z-citrate calcined at 700 °C. In subsequent tests, the effect of different EtOH : CO2 ratios and different LHSVs on the target reaction was investigated. The results of these studies are illustrated in Figure 4.13a and 4.13b.

![Figure 4.13](image)

**Figure 4.13.** Effect of (a) EtOH : CO2 ratios and (b) LHSV’s on DEC yield over C80Z-citrate calcined at 700 °C. Reaction conditions: catalyst weight 1 g, 1 h-on-stream, T = 140 °C, p = 140 bar.

The yield of DEC was observed to maintain at around 0.7 % within EtOH : CO2 ratios ranging from 1 : 9 to 1 : 6 and then decreased considerably with a further increase in the ratio to 1 : 3. As a result, with rise in concentration of ethanol in the feed mixture, the DEC yield
4. Continuous synthesis of diethyl carbonate from ethanol and CO₂ over CeₓZr₁₋ₓO₂ (x = 0, 0.2, 0.5, 0.8, 1) catalysts decreased. In this case, an increase in concentration of ethanol requires to apply the higher reaction temperature (up to the critical temperature of pure EtOH, Tₜₜ = 241 °C) in order to reach equilibrium DEC yield. On the whole, a EtOH : CO₂ ratio of 1 : 6 was found to be somewhat better. Moreover, up to a LHSV of 42 Lₗq kg⁻¹ cat⁻¹ h⁻¹ (τ = 68.6 s) an increase in the DEC yield up to Yₐ = 0.7% was observed. A further increase in LHSV, e.g. 62 Lₗq kg⁻¹ cat⁻¹ h⁻¹ (τ = 46.5 s), caused a drastic drop of the DEC yield (Yₐ = 0.1%). The total CO₂–EtOH flow greatly influences on the contact time. Very low CO₂-EtOH flow was found to be effective for this continuous reaction mode, since the longer is the contact time, the higher the conversion of EtOH can be achieved.

In order to get better assessment of DEC formation over C₈₀Z-citrate, the predictive Soave–Redlich–Kwong equation was used to calculate the equilibrium DEC yield of ~0.8% under similar reaction conditions T = 120 °C and p = 140 bar (see Table 1.4b). In sum, a continuous process for the direct formation of DEC from carbon dioxide and ethanol can be operated at a near equilibrium level.

4.4. Conclusions

CeₓZr₁₋ₓO₂ catalysts were applied for the direct synthesis of DEC from EtOH and CO₂ under continuous-flow conditions. The Ce : Zr ratio displayed a considerable effect on the catalytic performance. As a result, for Zr-rich catalysts higher reaction temperature regimes is required in comparison with Zr-lean catalysts. CeₓZr₁₋ₓO₂ solid solutions with x ≥ 0.5 showed better catalytic performance than the catalysts with x < 0.5. Furthermore, the reaction pressure, temperature, EtOH : CO₂ and LHSV are also crucial parameters for improving the catalytic performance.

NH₃- and CO₂-TPD results revealed that the concentration of acidic and basic sites was the lowest for pure ceria, but markedly increased upon addition of Zr. The highest amount of desorbed NH₃ was found on pure zirconia due to its acidic nature. H₂-TPR results showed that the introduction of Zr into the CeO₂ lattice remarkably enhanced the amount of oxygen vacancies due to the formation of Ce³⁺ species. These additional adsorption sites lead to a significant increase in Yₐ by cubic CeₓZr₁₋ₓO₂ solid solutions instead of pure CeO₂. The Ce : Zr ratio is helpful to tune the acid–base properties, reducibility, surface vacancies, phase composition of the solids and hence the catalytic properties as well. C₈₀Z-citrate and C₅₀Z-citrate solids with equal concentration of acidic and basic sites (1 : 1) exhibited better DEC yields compared to other catalysts tested.
In addition, the influence of calcination temperature on structural, textural, surface and catalytic properties of Ce$_{0.8}$Zr$_{0.2}$O$_2$ mixed oxides was studied. The synthesis of DEC from ethanol and CO$_2$ was studied at 140 °C and 140 bar over Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalysts calcined at 450, 700 and 1000 °C. XRD results confirmed the presence of cubic fluorite phase in all three cases. C$_{80}$Z-citrate calcined at 450 °C exhibited the highest concentration of acidic and basic sites, especially strong. High-temperature treatment caused a decrease in the concentration and the strength of acidic and basic sites on C$_{80}$Z-citrate catalysts. It was supposed that high calcination temperature leads to more plain surfaces and less coordinatively unsaturated cations and anions. C$_{80}$Z-citrate calcined at 700 °C seems to have good balance between acidity/basicity that probably leads to the observed improved performance. For C$_{80}$Z-citrate calcined at 1000 °C the acid-base concentration and strengths significantly drops to a very low level. It showed a negative effect on the key catalytic properties for DEC synthesis. A high DEC yield (0.7%) could be achieved with C$_{80}$Z-citrate calcined at 700 °C. This catalyst was tested at 140 °C and 140 bar at a EtOH : CO$_2$ ratio of 1 : 6 at a LHSV of 42 L$_{\text{liq}}$ kg$_{-\text{cat}}^{-1}$ h$^{-1}$ (τ = 68.6 s). Hence, it is possible to run the reaction continuously at the near equilibrium level (Y$_{\text{DEC}}$ = 0.8%) applying suitable contact time.
Chapter 5

5. Effect of second metal in Ce\textsubscript{0.8}M\textsubscript{0.2}O\textsubscript{2} catalysts on the catalytic activity towards DEC synthesis from ethanol and CO\textsubscript{2}

Chapter 5 describes the effect of introduction of isovalent Hf\textsuperscript{4+} and Ti\textsuperscript{4+} guest cations into host CeO\textsubscript{2} lattice on the DEC formation from ethanol and CO\textsubscript{2} over this novel catalytic system. Pure CeO\textsubscript{2} (C-citrate), HfO\textsubscript{2} (H-citrate), TiO\textsubscript{2} (T-citrate) and Ce-Ti (C80T-citrate), Ce-Hf (C80H-citrate) mixed oxides (80:20 mole ratio based on metal) were prepared by a citrate complexation method, calcined in air at 700 °C for 3 h and characterized by N\textsubscript{2}-adsorption, XRD, ICP-OES, XPS, TEM, H\textsubscript{2}-TPR, NH\textsubscript{3}- & CO\textsubscript{2}-TPD. Catalytic experiments were carried out under continuous-flow conditions in a plug-flow reactor at 140 bar and at 140 °C.
Cerium oxide (CeO$_2$) based solids are effective catalysts for producing DEC from ethanol and CO$_2$ due to the presence of both acidic and basic sites. The replacement of cerium ions (0.097 nm) by other smaller cations, such as Ti$^{4+}$ (0.069 nm), Hf$^{4+}$ (0.078 nm) or Zr$^{4+}$ (0.084 nm) is expected to improve those properties compared to pure CeO$_2$. In spite of the similarities in structure and stoichiometry of the corresponding metal oxides (metallic ions in the same Group IV), they possess differences in metal-oxygen bond strengths, which depend on their crystalline ionic radii. The Ce-M-O (M = Hf, Ti) is an efficient catalyst for the direct synthesis of DEC from ethanol and CO$_2$ due to the presence of M-OH hydroxyl groups and coordinately unsaturated M$^{4+}$O$_2$-sites that act as Lewis acid-base pairs on its surface. The present chapter describes the effect of introduction of Hf$^{4+}$ and Ti$^{4+}$ cations into ceria lattice on the performance of resulted Ce-M-O catalyst for the direct synthesis of DEC from ethanol and CO$_2$. The catalytic properties of CeO$_2$ doped with Zr$^{4+}$ were already described in details in Chapter 4. The results showed that 20 mol% of Zr doped ceria catalyst yielded DEC at the equilibrium level of $Y_{\text{DEC}} \sim 0.7\%$ at 140 °C and 140 bar at a EtOH : CO$_2$ ratio of 1 : 6 at a LHSV of 42 L liq kg$^{-1}$ cat$^{-1}$ h$^{-1}$. This catalyst has good balance between acidity/basicity that probably leads to the observed improved performance.

5.1. Catalyst characterization

**BET surface areas**

The specific surface area, average pore diameter and total pore volume of Ce$_{0.8}$M$_{0.2}$O$_2$ catalysts and their individual metal oxides are summarized in Table 5.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET-SA (m$^2$ g$^{-1}$)</th>
<th>Average pore d (nm)</th>
<th>Total pore V (cm$^3$ g$^{-1}$)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-citrate</td>
<td>30</td>
<td>3</td>
<td>0.10</td>
<td>26</td>
</tr>
<tr>
<td>H-citrate</td>
<td>12</td>
<td>8</td>
<td>0.04</td>
<td>12</td>
</tr>
<tr>
<td>C80H-citrate</td>
<td>38</td>
<td>6</td>
<td>0.11</td>
<td>7</td>
</tr>
<tr>
<td>T-citrate</td>
<td>15</td>
<td>28</td>
<td>0.14</td>
<td>26</td>
</tr>
<tr>
<td>C80T-citrate</td>
<td>29</td>
<td>13</td>
<td>0.08</td>
<td>6</td>
</tr>
</tbody>
</table>

Pure HfO$_2$ exhibits the lowest surface area (12 m$^2$ g$^{-1}$) compared to CeO$_2$ and TiO$_2$. Upon incorporating 20 mol% of Hf into CeO$_2$, the surface area of the resulting mixed oxides increased to 38 m$^2$ g$^{-1}$. A similar effect was also observed by Biswas [196] and Masui [197].
The specific surface area and pore volume of the Ti-containing counterpart were slightly lower than those of bare CeO₂, i.e. 30 versus 29 m² g⁻¹ and 0.10 versus 0.08 cm³ g⁻¹, respectively.

**X-ray diffraction (XRD)**

Figure 5.1 shows the XRD patterns of Ce₀.₈M₀.₂O₂ mixed oxides. The XRD patterns of pure CeO₂, HfO₂ and TiO₂ are also included for comparative purposes. The crystal phases of all these materials were identified through a comparison with the corresponding JCPDS files. The reflection peaks at 2Θ = 28.6, 33.19, 47.57, 56.43, 59.23, 69.49 and 79.11° correspond to the fluorite cubic CeO₂ phase (JCPDS 65-5923).

![XRD pattern](image)

**Figure 5.1.** XRD patterns of Ce₀.₈M₀.₂O₂ catalysts (M = Hf, Ti). Phase composition: ▲ c-Ce₀.₈Hf₀.₂O₂ (ICDD 04-006-1933), ■ cubic CeO₂ (JCPDS 65-5923). Inset: a) * tetragonal TiO₂ (rutile, JCPDS 89-4920), b) ◆ monoclinic HfO₂ (JCPDS 78-49).

In case of pure HfO₂, the most intensive diffraction peaks at 2Θ = 24.43, 28.22, 31.55, 34.45, 35.46 and 50.54° are characteristic for monoclinic HfO₂ phase. The addition of 20 mol% of Hf into CeO₂ lattice led to a shift of reflection peaks towards higher 2Θ values compared to pure CeO₂. The diffraction peaks at 2Θ = 29.01, 33.49, 48.07, 57.14, 59.82, 70.39 and 77.99° represent the cubic Ce₀.₈Hf₀.₂O₂ phase (ICDD-04-006-1933). The XRD pattern of pure TiO₂ catalyst consists of the most intensive reflexes at 2Θ = 27.48, 36.07, 39.19, 41.22, 54.33, 56.51 and 68.98° which are representative for the tetragonal (rutile) TiO₂ phase. These findings are in a good agreement with those reported in literature [198] where transformation of anatase to rutile is thermodynamically possible above 500 °C. Even in case of mixed oxides, the diffractogram of the C80T-citrate provides typical patterns of cubic
CeO₂ and a few less intensive reflexes at 36.07 and 54.33° due to the rutile TiO₂ phase. Thus, phase segregation for Ce₀.₈Ti₀.₂O₂ into CeO₂ and TiO₂ was detected, confirming that Ti⁴⁺ was not homogeneously incorporated into the CeO₂ lattice.

The crystallite size of pure and mixed oxides calculated using Scherrer equation [125] is summarized in Table 5.1. As was reported earlier, pure CeO₂ exhibited poor thermostability [199] and hence high-temperature treatment (700 °C) caused a crystallite growth (26 nm). However, the presence of Hf⁴⁺ in ceria hinders the crystallite growth resulting in the formation of smaller crystallites (7 nm). XRD pattern of T-citrate confirms high crystallinity of TiO₂ (26 nm). In contrast, Ce₀.₈Ti₀.₂O₂, where the cubic CeO₂ structure predominated along with the tetragonal TiO₂ (rutile) is composed of crystallites of 6 nm. Compared to CeO₂ (26 nm), such decrease in crystallite size is attributed to the presence of the TiO₂ rutile phase in C₈₀T-citrate, which restrained the growth of CeO₂ crystallite. As a conclusion, the incorporation of Hf⁴⁺ and Ti⁴⁺ into CeO₂ lattice leads to an increase in BET-SA and the formation of smaller crystallite size in comparison to their individual metal oxides.

**Elemental analysis determined by Inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray photoelectron spectroscopy (XPS)**

Selected surface and bulk composition of Ce₀.₈M₀.₂O₂ solids is reported in Table 5.2. From ICP analysis it can be seen clearly, that cerium mostly concentrated in the bulk of Ce-M-O solid solutions. Consequently, the XPS studies indicate surface enrichment of promoter metal (Hf, Ti) in all catalysts. Similar results were previously reported by Fang et al. [200], where the surface region of CeO₂-TiO₂ with high Ce content > 0.7 is enriched with Ti⁴⁺.

**Table 5.2.** Surface and bulk composition of Ce₀.₈M₀.₂O₂ catalysts as determined by XPS and ICP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk composition (ICP)</th>
<th>Surface composition (XPS)</th>
<th>EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce (mol%)</td>
<td>M (mol%)</td>
<td>Ce/M</td>
</tr>
<tr>
<td>C80H-citrate</td>
<td>75</td>
<td>25</td>
<td>3</td>
</tr>
<tr>
<td>C80T-citrate</td>
<td>79</td>
<td>21</td>
<td>3.8</td>
</tr>
</tbody>
</table>
Transmission electron microscopy (TEM)

TEM was applied to investigate the morphology and elemental composition of Ce$_{0.8}$M$_{0.2}$O$_2$ catalysts. Selected micrographs of different Ce-M mixed oxides are shown in Figure 5.2. It is clearly seen that C80H-citrate is composed of nano-sized particles in the range of 8-10 nm, which are distributed uniformly (Figure 5.2(1a)). However, C80T-citrate represents some regions with different shapes and sizes of particles (Figure 5.2(2)). EDX analysis confirmed the presence of Ti-rich region (2c(1)) with very low Ce content as well as Ce-rich region (2c(2)). Using EDX results, it was possible to distinguish Ce- and Ti-rich regions. Ce-rich area exhibits large with well-defined boundaries particles whose size exceeds 10 nm.

![Figure 5.2. TEM images of (1a, 1b, 1c) C80H-citrate and (2a, 2b, 2c) C80T-citrate. EDX analysis of the Ce/Ti molar ratio: (2c) area 1 = 1.1, area 2 = 14.9.]

Temperature-programmed reduction (TPR) by H$_2$

Figure 5.3 demonstrates the profiles of H$_2$ upon temperature-programmed reduction of Ce$_{0.8}$M$_{0.2}$O$_2$ mixed oxides as well as their individual metal oxides. Two peaks of H$_2$ consumption were identified for pure CeO$_2$: the first at low temperature (475 °C) was attributed to the removal of surface lattice oxygen, while the second at 744 °C was assigned to the removal of bulk lattice oxygen [169, 201]. The H$_2$-TPR profile for rutile TiO$_2$ is
characterized by a maximum at 563 °C, whereas the maximal H$_2$ consumption over HfO$_2$ was achieved at 758 °C. Thus, among all pure oxides, HfO$_2$ is the most difficult oxide to be reduced.

The incorporation of isovalent almost non-reducible cations such as Hf$^{4+}$ and Ti$^{4+}$ into CeO$_2$ can improve its redox properties. It can be ascribed to the smaller ionic radii of Hf$^{4+}$ (0.078 nm) and Ti$^{4+}$ (0.069 nm) in comparison with that of Ce$^{4+}$ (0.097 nm) that compensated for volume expansion and facilities the formation of oxygen vacancies. Subsequently, it leads to higher mobility of lattice oxygen inside Ce-M-O solid solution [202]. C80H-citrate demonstrates one reduction peak at T$_{\text{max}}$ 554 °C and small shoulder at ~800 °C. In contrast with pure CeO$_2$, the position of surface reduction peak moved towards higher temperature in the presence of Hf$^{4+}$. Moreover, the H$_2$-uptake for C80H-citrate is greatly increased at low temperature indicating high reduction degree of the catalyst. These obtained results are in a good agreement with earlier reports where the reducibility of ceria was enhanced when it was mixed with Hf to form a solid solution [203, 204]. The H$_2$-TPR profile of the C80T-citrate catalyst is very broad with several maxima, attributing to the removal of surface and bulk lattice oxygen. C80T-citrate sample shows highest H$_2$-uptake (1.928 mmol g$^{-1}$) in a wide temperature range. According to Fang et al. [205], among different Ce$_{x}$Ti$_{1-x}$O$_2$ tested, Ce$_{0.8}$Ti$_{0.2}$O$_2$ solid solution exhibited the best reducibility. In addition, the surface enrichment (XPS results) of Hf$^{4+}$ and Ti$^{4+}$ in C80H-citrate and C80T-citrate, respectively, is responsible for the high surface reduction degree of corresponding mixed oxides compared to CeO$_2$.  

Figure 5.3. H$_2$-TPR profiles of Ce$_{0.8}$M$_{0.2}$O$_2$ mixed oxides and their parent pure oxides (→: indicates stationary treatment of sample at 800 °C for 2 h).
Table 5.3. H₂ uptake and temperature of maximal hydrogen consumption (T_max) during TPR runs for Ce₀.₈M₀.₂O₂ solids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_max (°C)</th>
<th>H₂ uptake (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>475, 744</td>
<td>1.249</td>
</tr>
<tr>
<td>HfO₂</td>
<td>758</td>
<td>0.064</td>
</tr>
<tr>
<td>C80H</td>
<td>554</td>
<td>1.532</td>
</tr>
<tr>
<td>TiO₂</td>
<td>563</td>
<td>0.232</td>
</tr>
<tr>
<td>C80T</td>
<td>560, 598, 699, 786</td>
<td>1.928</td>
</tr>
</tbody>
</table>

Acid-base properties: Temperature-programmed desorption (TPD) of NH₃ and CO₂

Temperature-programmed desorption (TPD) of NH₃ used as a probe molecule was employed to investigate surface acidity of Ce₀.₈M₀.₂O₂ catalysts. The total concentration of acid sites, expressed as the amount of NH₃ desorbed per gram and per square meter of catalyst, is present in Table 5.4.

Table 5.4. Acid-base characteristics of Ce₀.₈M₀.₂O₂ where M = Hf, Ti. T_max (NH₃) and T_max (CO₂) stand for temperature of maximal NH₃ and CO₂ desorption, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NH₃ desorbed (µmol g⁻¹ / µmol m⁻²)</th>
<th>T_max (NH₃) (°C)</th>
<th>CO₂ desorbed (µmol g⁻¹ / µmol m⁻²)</th>
<th>T_max (CO₂) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80H-citrate</td>
<td>60 / 1.6</td>
<td>191</td>
<td>49 / 1.3</td>
<td>158, 607, 785</td>
</tr>
<tr>
<td>C80T-citrate</td>
<td>0 / 0</td>
<td>-</td>
<td>9 / 0.3</td>
<td>152, 360, 790</td>
</tr>
</tbody>
</table>

No NH₃ was desorbed from C80T-citrate catalyst, thus indicating the absence of acidic sites able to adsorb ammonia above 100 °C. However, the NH₃-TPR profile of C80H-citrate is characterized by a broad peak with a maximum at 191 °C (Figure 5.4a) which is in the range of weak to moderate strength of acidity. It was suggested that differences in both acidic and basic sites can be attributed to the various fractions of crystal phases along with the crystallite sizes of catalyst. Temperature-programmed desorption (TPD) of CO₂ is used to evaluate the number and the strength of basic sites on Ce₀.₈M₀.₂O₂ surface. The obtained CO₂-TPD profiles are shown in Figure 5.4b. The profile of the C80H-citrate catalyst consists of a broad peak between 50 and 500 °C with a maximum at 158 °C and additionally of lower intensive peaks at higher temperatures, which are characteristic of strong acidic sites. In case of C80T-citrate, CO₂ desorption takes place in a broad temperature range with maxima at 152, 360 and 790 °C. The obtained results suggest that structural (crystal phase) and textural (specific SA)
changes in $\text{Ce}_{0.8}\text{M}_{0.2}\text{O}_2$ solids caused by the introduction of either Hf or Ti into CeO$_2$ can modify surface basicity making it either weaker or stronger in comparison to pure CeO$_2$.

![Figure 5.4](image)

Figure 5.4. (a) NH$_3$-TPD profiles and (b) CO$_2$-TPD profiles of Ce$_{0.8}\text{M}_{0.2}\text{O}_2$ catalysts (M = Hf, Ti).

The total amount of CO$_2$ desorbed from the surface of Ce$_{0.8}\text{M}_{0.2}\text{O}_2$ samples in the temperature range of 50-800 °C is shown in Table 5.4. The concentration of CO$_2$ desorbed from C80H-citrate is 1.3 µmol m$^{-2}$ and from C80T-citrate is 0.3 µmol m$^{-2}$.

5.2. Catalytic results

Figure 5.5 demonstrates the effect of Ce$^{4+}$ substitution with isovalent cations such as Hf$^{4+}$ and Ti$^{4+}$ in CeO$_2$ lattice on the yield of DEC. In addition, pure oxides were also tested. The DEC yield over pure CeO$_2$ (C-citrate) is about 0.5%, while over HfO$_2$ (H-citrate) DEC formation was negligible (the yield of 0.04%). In case of pure TiO$_2$, no DEC was formed over pure TiO$_2$. In a case of Ce-M-O solid solution, 20 mol% of Hf$^{4+}$ doped ceria (C80H-citrate) resulted in higher DEC yield than 20 mol% of Ti$^{4+}$ doped ceria (C80T-citrate). The reason for improved catalytic activity of C80H-citrate catalyst in comparison with C80T-citrate might be rooted from the difference in their textural, structural and acid-base properties, which can affect the interaction between catalyst surface and the adsorbed reactants. BET-SAs of C80H-citrate and C80T-citrate are 38 and 29 m$^2$ g$^{-1}$, respectively. However, for carboxylation of ethanol C80T-citrate catalyst was almost not active. Thus, no relationship between specific surface area and DEC formation was found. XRD was performed to correlate the crystalline phase structure and catalytic properties of these solids for carboxylation of ethanol. XRD patterns show the formation of single cubic Ce$_{0.8}\text{Hf}_{0.2}\text{O}_2$ phase, whereas the diffractogram of the C80T-citrate sample exhibits typical patterns of cubic CeO$_2$ and a few less intensive peaks due to rutile TiO$_2$ phase. Based on XRD results, it was suggested that C80H-citrate possesses
reactive Ce-rich crystal planes. TEM reveals the formation of nanocrystalline mixed solution with particle size of 8-10 nm when Hf$^{4+}$ is incorporated into ceria lattice. C80T-citrate sample represents both Ce-rich and Ti-rich nanocrystals.

**Figure 5.5.** Effect of second metal in CeO$_2$ on the catalytic performance towards DEC formation. Reaction conditions: catalyst amount 1g, $T_c = 700 \, ^\circ C$, EtOH : CO$_2$ = 1 : 6, $p = 140$ bar, $T = 140 \, ^\circ C$, 1 hour-on-stream, LHSV = 42 $L_{liq}^{-1} \cdot kg_{cat}^{-1} \cdot h^{-1}$, $\tau = 68.6 \, s$.

The NH$_3$- and CO$_2$-TPD results reveal the presence of acid-base sites on C80H-citrate sample. No NH$_3$ was desorbed from C80T-citrate catalyst, whereas CO$_2$-TPD experiments showed only a small amount of CO$_2$ desorbed from C80T-citrate. However, C80H-citrate sample demonstrates the high amount of desorbed CO$_2$ in high temperature region. Previous reports [94, 206] have shown that weak to medium acidity is required to produce carbonates such as DEC and DMC over solid catalysts. Combining the NH$_3$- and CO$_2$-TPD results together, it was noted that C80H-citrate possesses both acidic and basic sites. The simultaneous presence of them on the surface is required for DEC synthesis. Especially, when acidic and basic functions are well balanced in terms of site concentrations, two-points of adsorption of reactants (ethanol and CO$_2$) occur: ethanol interacts with acid M$^{4+}$ sites (Lewis acid) to form ethoxide groups and basic O$^{2-}$ sites (Lewis base) is required to activate CO$_2$. In a situation where the amount of one kind of active sites is much higher than the other, only the activation of one reactant is dominated, which can in turn lead to reduced performance of the catalysts. Such observation was also reported to be unfavorable in the DEC/DMC formation [207].
5.3. Conclusions

A Ce$_{0.8}$Hf$_{0.2}$O$_2$ solid solution was successfully synthesized by citrate complexation method. The XRD results proved the formation of homogeneous Ce-Hf-O solid material without any phase segregation, while Ce$_{0.8}$Ti$_{0.2}$O$_2$ catalyst was composed of cubic CeO$_2$ and rutile TiO$_2$. Hence Hf$^{4+}$ cations were fully inserted into CeO$_2$. Ce-based samples demonstrated relatively high specific surface areas in the range of 29-38 m$^2$ g$^{-1}$ and crystallite size in 6-10 nm range. Surface areas were found to depend on the nature of metal incorporated into ceria. Furthermore, the redox properties and acidity characteristics are also considerably affected by the kind of doped metal. The different performance of Ce$_{0.8}$M$_{0.2}$O$_2$ catalyst towards DEC formation was assigned to its varying acid-base properties. C80T-citrate catalyst exhibited poor catalytic performance, which was attributed to the absence of acidic sites on its surface. C80H-citrate with high number of acid-base sites showed the high DEC yield. Such difference in acid-base properties could be related to difference in the geometric arrangement of cations and anions of the various crystallographic planes exposed at the surface of CeO$_2$, TiO$_2$ and Ce$_{0.8}$Hf$_{0.2}$O$_2$ crystallites. In conclusion, the bimetal catalysts (C80H-citrate and C80T-citrate) exhibited better catalytic performance than individual metals (HfO$_2$ and TiO$_2$). However compared to pure CeO$_2$, C80H-citrate possessed the high concentration of strong basic sites with characteristic desorption temperatures of 680 and 785 °C which is responsible for its lower DEC yield.
6. Influence of synthesis parameters on catalytic performance of Ce$_{0.8}$Zr$_{0.2}$O$_2$ in the production of diethyl carbonate from ethanol and CO$_2$

Chapter 6 addresses different preparation routes of Ce$_{0.8}$Zr$_{0.2}$O$_2$ solids. Ce-Zr-O catalysts were prepared by two methods: co-precipitation and citrate complexation. The synthesis methods greatly affected textural, structural and acid-base properties of Ce-Zr-O solids. The influence of Ce$_{0.8}$Zr$_{0.2}$O$_2$ physico-chemical properties on catalytic performance in DEC formation from CO$_2$ and ethanol is also thoroughly discussed.
Chapter 6 is focused on the influence of different synthesis methods of \( \text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2 \) on its catalytic performance in synthesis of diethyl carbonate from ethanol and \( \text{CO}_2 \). According to the literature \([160, 208-213]\), the physico-chemical properties of Ce-Zr-O material largely depend on preparation methods. Thus, two different methods were applied for preparation of \( \text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2 \) solid solutions such as co-precipitation \([99]\) and citrate complexation methods \([121]\) using water (already discussed in Chapter 4) and ethanol as solvents. Co-precipitation method using ammonia as precipitating agent is the most common method for the preparation of Ce-Zr solid solution \([214, 215]\). Applying this synthesis route, mixed metal oxides with relatively high specific surface area are formed \([216]\). Citrate complexation method is also well-known method for preparation of Ce-Zr mixed oxides. According to this method, highly dispersed and homogeneously distributed solid solutions are formed. Usually for this method a complexing agent is required.

### 6.1. Catalyst characterization

**BET surface areas**

Selected textural properties such as BET surface area, total pore volume and average pore diameter of differently prepared \( \text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2 \) materials are summarized in Table 6.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method of preparation</th>
<th>BET-SA ((\text{m}^2\text{ g}^{-1}))</th>
<th>Total pore V ((\text{cm}^3\text{ g}^{-1}))</th>
<th>Average pore d ((\text{nm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80Z-1</td>
<td>Citrate (solvent: ( \text{C}_2\text{H}_5\text{OH} ))</td>
<td>46</td>
<td>0.057</td>
<td>4.2</td>
</tr>
<tr>
<td>C80Z-2</td>
<td>Co-precipitation (solvent: ( \text{H}_2\text{O} ))</td>
<td>51</td>
<td>0.103</td>
<td>7.7</td>
</tr>
</tbody>
</table>

The material prepared by co-precipitation method (C80Z-2) possesses higher surface area and total pore volume than its counterpart prepared by citrate complexation method (C80Z-1) despite the fact that the former material is composed of larger crystallites (15 nm versus 10 nm). It might be due to the use of \( \text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} \) as a Zr precursor and high pH of mixed solution \((\geq10)\) which prevented the collapse of the porous network during drying and calcination (detailed explanation in works of Yoo \textit{et al.} \([217]\) and Hudson \textit{et al.} \([218]\)).
X-ray diffraction (XRD)

The XRD patterns of two Ce$_{0.8}$Zr$_{0.2}$O$_2$ samples are depicted in Figure 6.1. They are characterized by reflections at 2\(\Theta\) of 28.69, 33.23, 47.68, 56.49, 59.25, 69.70, 77.01, 79.26 and 88.82\(^\circ\), which correspond to the cubic Ce$_{0.75}$Zr$_{0.25}$O$_2$ (PDF number 00-28-0271) structure with a space group \(Fm-3m\). No reflexes corresponding to any ZrO$_2$ structure were found. However, additional reflexes at 2\(\Theta\) of 30.20 and 50.08\(^\circ\) were identified in the XRD pattern of C80Z-2 catalyst and can be ascribed to a Zr-rich phase. On the basis of the database of powder diffraction patterns, this phase is the tetragonal Ce$_{0.16}$Zr$_{0.84}$O$_2$ (Pdf number 00-038-1437) phase with phase group \(P4_2/nmc\). Nevertheless, the major crystal phase in C80Z-2 is cubic Ce$_{0.75}$Zr$_{0.25}$O$_2$.

![XRD patterns of Ce$_{0.8}$Zr$_{0.2}$O$_2$ prepared by citrate complexation (C80Z-1) and co-precipitation (C80Z-2) methods.](image)

**Figure 6.1.** XRD diffraction patterns of Ce$_{0.8}$Zr$_{0.2}$O$_2$ prepared by citrate complexation (C80Z-1) and co-precipitation (C80Z-2) methods.

The calculated crystal sizes using Scherrer equation [125] are shown in Table 6.2. For sample prepared by citrate method, the crystal size is 10 nm. C80Z-2, where two phases were found, exhibits the Ce$_{0.75}$Zr$_{0.25}$O$_2$ crystal with 15 nm in size and Ce$_{0.16}$Zr$_{0.84}$O$_2$ with 6 nm. It can be noted that the Ce-Zr crystal size changes according to the concentration of Zr, being larger at high Ce content. In addition, the structural assignment was also performed using V-curves (Figure 6.2). Therefore, the lattice volume was related to the respective atomic compositions in the Ce$_x$Zr$_{1-x}$O$_2$ solid solution. In case of C80Z-1, the cubic Ce$_{0.87}$Zr$_{0.13}$O$_2$ phase is the only identified phase. It means that Ce and Zr ions were homogeneously distributed in the Ce-Zr powder. C80Z-2 exhibits both Ce-rich Ce$_{0.89}$Zr$_{0.11}$O$_2$ and Zr-rich Ce$_{0.17}$Zr$_{0.83}$O$_2$ phases.
6. Influence of synthesis parameters on catalytic performance of Ce$_{0.8}$Zr$_{0.2}$O$_2$ in the production of diethyl carbonate from ethanol and CO$_2$

![Figure 6.2. Volume of the unit cell of the cubic (Ce$_x$Zr$_{1-x}$)O$_2$ as function of the (a) Ce content and tetragonal (Zr$_x$Ce$_{1-x}$)O$_2$ phase as function of the (b) Zr content.](image)

The phase composition of Ce$_x$Zr$_{1-x}$O$_2$ solids determined by applying V-curves is summarized in Table 6.2. The C80Z-1 sample shows 100% of cubic Ce$_{0.87}$Zr$_{0.13}$O$_2$ phase. In case of C80Z-2, 90% of cubic Ce$_{0.89}$Zr$_{0.11}$O$_2$ and 10% of tetragonal Ce$_{0.17}$Zr$_{0.83}$O$_2$ phases are present. The obtained phase compositions from V-curves are in a good agreement with those defined by the Rietveld method (program package TOZr.PAS 4.2 from Bruker).

**Table 6.2.** Effect of preparation methods on crystallite size and lattice parameters of C80Z samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal phase</th>
<th>a nm</th>
<th>c nm</th>
<th>V nm$^3$</th>
<th>ρ g cm$^{-3}$</th>
<th>ε %</th>
<th>D nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80Z-1</td>
<td>100% c-Ce$<em>{0.87}$Zr$</em>{0.13}$O$_2$ (Pdf number 00-028-0271)</td>
<td>0.539</td>
<td>-</td>
<td>0.157</td>
<td>7.03</td>
<td>0.30</td>
<td>10</td>
</tr>
<tr>
<td>C80Z-2</td>
<td>90% c-Ce$<em>{0.89}$Zr$</em>{0.11}$O$_2$ (Pdf number 00-028-0271)</td>
<td>0.539</td>
<td>-</td>
<td>0.157</td>
<td>7.05</td>
<td>0.21</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>10% t-Ce$<em>{0.17}$Zr$</em>{0.83}$O$_2$ (Pdf number 00-038-1437)</td>
<td>0.363</td>
<td>0.53</td>
<td>0.069</td>
<td>6.42</td>
<td>0.11</td>
<td>6</td>
</tr>
</tbody>
</table>

It can be concluded that the use of co-precipitation route for Ce$_{0.8}$Zr$_{0.2}$O$_2$ synthesis resulted in phase segregation: the major phase is cubic Ce-rich phase with the composition Ce$_{0.89}$Zr$_{0.11}$O$_2$ and the minor phase is tetragonal Zr-rich phase with composition Ce$_{0.17}$Zr$_{0.83}$O$_2$. These observations prove that homogeneous solid solution is difficult to obtain by co-precipitation method, since Ce and Zr precursors have different rates of precipitation.
Elemental analysis by Inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray photoelectron spectroscopy (XPS)

XPS and ICP studies were used to determine the elemental composition in the near-surface-region and in the bulk of Ce$_{0.8}$Zr$_{0.2}$O$_2$ samples, respectively. Table 6.3 compares the surface Ce and Zr atomic concentration with bulk composition. It could be seen that C80Z-2 shows the formation of solid solution with a bulk composition almost equal to nominal. In case of C80Z-1, the Ce-enrichment is observed in the bulk of Ce-Zr-O, which corresponds to composition obtained from V-curve (Figure 6.2a). The surface concentration of Ce species is lower than in the bulk in both cases. On the basis of these results it can be concluded that the bulk and surface compositions of Ce$_{0.8}$Zr$_{0.2}$O$_2$ differ and also depend strongly on preparation method.

Table 6.3. Surface and bulk elemental composition of Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalysts measured by XPS and ICP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk composition (ICP)</th>
<th>Surface composition (XPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce (mol%)</td>
<td>Zr (mol%)</td>
</tr>
<tr>
<td>C80Z-1</td>
<td>87.7</td>
<td>12.3</td>
</tr>
<tr>
<td>C80Z-2</td>
<td>82.8</td>
<td>17.2</td>
</tr>
</tbody>
</table>

Transmission electron microscopy (TEM)

Selected TEM images of two Ce$_{0.8}$Zr$_{0.2}$O$_2$ samples are illustrated in Figure 6.3. C80Z-1 reveals an agglomerated structure, the particles with 10 nm in size are found. C80Z-2 is composed of particles with irregular size and shape (5-15 nm).

Figure 6.3. TEM images of Ce$_{0.8}$Zr$_{0.2}$O$_2$ solid solution synthesized by various methods: C80Z-1 (1a, 1b) and C80Z-2 (2a, 2b).

As evidenced by XRD, such broad distribution in the size is due to the presence of two different crystallite phases, i.e. cubic Ce$_{0.86}$Zr$_{0.14}$O$_2$ and tetragonal Ce$_{0.17}$Zr$_{0.83}$O$_2$ with crystallite
size of 15 and 6 nm, respectively. Based on these observations, it can be concluded that nanosized particles were obtained in samples prepared both by co-precipitation and citrate methods. In summary, the co-precipitation method can be used to produce well crystalline powder, whereas the citrate route - homogeneous material with agglomerated particles.

**Temperature-programmed reduction (TPR) by H$_2$**

Redox properties of the two Ce$_{0.8}$Zr$_{0.2}$O$_2$ materials were determined by temperature programmed reduction (TPR) using a feed consisting of 5 vol% H$_2$ in Ar. Figure 6.4 depicts the obtained TPR profiles.

![Figure 6.4: H$_2$-TPR profiles of Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalysts prepared by different methods.](image)

The reduction of C80Z-1 and C80Z-2 samples occurs in two temperature regions. The first peak between 400 and 635 °C is ascribed to the removal of surface lattice oxygen whereas the second peak is associated with removal of bulk lattice oxygen [166]. In general, both the surface and bulk reduction processes occur easier for C80Z-1 than for C80Z-2 as concluded from the temperature of maximal H$_2$ consumption (Figure 6.4 and Table 6.4).

**Table 6.4.** H$_2$ uptake and temperature of maximal hydrogen consumption (T$_{max}$) during TPR runs for C80Z solids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak max (°C)</th>
<th>H$_2$–uptake (mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80Z-1</td>
<td>501, 677</td>
<td>1.396</td>
</tr>
<tr>
<td>C80Z-2</td>
<td>556, 787</td>
<td>1.114</td>
</tr>
</tbody>
</table>
The total H₂ consumption, expressed as mmol of hydrogen per gram of catalyst, and different T_max are summarized in Table 6.4. C80Z-2 synthesized by co-precipitation method shows lower H₂ uptake than C80Z-1 most probably due to the presence of tetragonal Zr-rich phase which is, in general, hardly reduced [166, 219, 220].

**Acid-base properties: Temperature-programmed desorption (TPD) of NH₃ and CO₂**

Temperature-programmed desorption tests using NH₃ as basic molecule were applied for characterization of material acidity. Using this method, it was possible to determine the total number and the strength of acidic sites. The obtained NH₃-TPD profiles of C80Z-1 and C80Z-2 are given in Figure 6.5a. The observed desorption peaks are in the temperature range of 100-450 °C: the broad peaks at T_max of 205 °C and 190 °C correspond to weak and moderate acid sites, while others at higher temperatures (394 and ~450 °C) are assigned to strong acidity.

![Figure 6.5.](image)

The total acidity estimated from the peak area under NH₃-TPD curve and different T_max are summarized in Table 6.5. The C80Z-2 derived by co-precipitation method exhibits much higher concentration of acidic sites (1.7 µmol NH₃ m⁻²) than that prepared by citrate complexation method (0.54 µmol NH₃ m⁻²). Moreover, the contribution of strong acidity to total acidity is more significant for C80Z-2. It can be explained by the higher concentration of Zr atoms on surface of C80Z-2 than on C80Z-1 (revealed by XPS). It is already known fact, that ZrO₂ is more acidic than CeO₂ [170] and excess of Zr⁴⁺ amount on C80Z-2 surface leads to an increase in the surface acidity of resulted solid in contrast to C80Z-1 [177, 217].
Table 6.5. Acid-base characteristics of C80Z solids prepared by two different methods. $T_{\text{max}}$ (NH$_3$) and $T_{\text{max}}$ (CO$_2$) stand for temperature of maximal NH$_3$ and CO$_2$ desorption, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NH$_3$ desorbed (µmol g$^{-1}$/m$^2$)</th>
<th>$T_{\text{max}}$ (NH$_3$) (°C)</th>
<th>CO$_2$ desorbed (µmol g$^{-1}$/m$^2$)</th>
<th>$T_{\text{max}}$ (CO$_2$) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80Z-1</td>
<td>25 / 0.54</td>
<td>190, 394</td>
<td>39 / 0.85</td>
<td>155, 794</td>
</tr>
<tr>
<td>C80Z-2</td>
<td>80 / 1.7</td>
<td>200, ~450</td>
<td>45 / 0.88</td>
<td>155, ~365, ~650</td>
</tr>
</tbody>
</table>

Additionally, temperature programmed desorption of carbon dioxide (CO$_2$-TPD) was used to estimate the basicity of Ce$_{0.8}$Zr$_{0.2}$O$_2$ solids by determining the total number and the strength of surface basic sites (Table 6.5). C80Z-2 (0.88 µmol CO$_2$ m$^{-2}$) catalyst exhibits somewhat higher concentration of basic sites than C80Z-1 (0.85 µmol CO$_2$ m$^{-2}$) sample. Figure 6.5b shows the broad CO$_2$-TPD profiles (Figure 6.5b) for both C80Z-1 and C80Z-2 catalysts with desorption peaks at 155 °C and a few shoulders at 365, 650 and 794 °C. Hence, these solid solutions represent weak, moderate and strong basic sites. However, C80Z-2 catalyst reveals the higher amount of CO$_2$ desorbed at 650 and 794 °C corresponded to strong basicity. The difference in basicity and acidity of Ce$_{0.8}$Zr$_{0.2}$O$_2$ prepared by two different methods was ascribed to various specific SA and concentration of Zr$^{4+}$ on their surface.

6.2. Catalytic results and materials properties affecting the catalyst performance

The texture and crystal structure of Ce-Zr mixed oxides were affected by preparation methods. C80Z-1 and C80Z-2 catalysts showed quite similar specific surface areas of 46 and 51 m$^2$ g$^{-1}$. Since C80Z-1 catalyst with lower specific surface area (46 m$^2$ g$^{-1}$) exhibited higher DEC yield (0.68 mol% vs. 0.6 mol%) than C80Z-2 with higher surface area (51 m$^2$ g$^{-1}$), there is no relationship between BET-SA and DEC yield. The crystal structures of resulted C80Z were greatly depended on synthesis route. Using co-precipitation method, non-homogeneous solid material was formed. XRD results of C80Z-2 revealed the co-existence of two crystal phases: 90% of cubic Ce$_{0.89}$Zr$_{0.11}$O$_2$ and 10% of tetragonal Ce$_{0.17}$Zr$_{0.83}$O$_2$. C80Z-1 solid solutions using citrate route showed a single cubic Ce-Zr-O phase: 100% cubic Ce$_{0.87}$Zr$_{0.13}$O$_2$. From H$_2$-TPR results, it was evident that the surface oxygen ions were more easily removable in samples prepared by citrate method. From NH$_3$- and CO$_2$-TPD results, it was found that all samples possess both acidic and basic sites. The highest concentration of strong acid-base
sites with characteristic desorption temperature of about 400 and 500 °C were observed in C80Z-2 solid only.

The effect of acidity/basicity ratio on catalytic performance is shown in Table 6.6. The catalytic results reveal that the higher this ratio, the lower is the DEC yield indicating the negative effect of high concentration of acidic sites, especially strong. However, over C80Z-1 with n(NH3)/n(CO2) = 0.6 the formation of DEC slightly increased. The preparation method was an important parameter since it defines the crystalline phase, specific surface area and consequently the redox and acid-base behavior of Ce-Zr mixed oxides.

**Table 6.6.** Correlation of molar ratios n\textsubscript{NH3}/n\textsubscript{CO2} with DEC yield. (Reaction conditions: catalyst weight 1g, T\textsubscript{c} = 700 °C, EtOH : CO\textsubscript{2} = 1 : 6, p = 140 bar, T = 140 °C, 1 hour-on-stream, LHSV = 42 L\textsubscript{liq.}/kg\textsubscript{cat}•h, τ = 68.6 s). *Standard deviation is 0.6%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation method</th>
<th>Y-DEC (mol%)*</th>
<th>n(NH\textsubscript{3}) / n(CO\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C80Z-1</td>
<td>citrate complexation</td>
<td>0.68</td>
<td>0.6</td>
</tr>
<tr>
<td>C80Z-2</td>
<td>co-precipitation</td>
<td>0.60</td>
<td>1.9</td>
</tr>
</tbody>
</table>

6.3. **Conclusions**

The effective catalyst properties such as crystallite size, porosity, homogeneity, redox and acid-base properties were found to depend on the preparation method of Ce\textsubscript{0.8}Zr\textsubscript{0.2}O\textsubscript{2} samples. All the obtained Ce-Zr solid solutions were mesoporous materials confirming by the average pore size in a range of 4-9 nm. Co-precipitation technique applied for the synthesis of C80Z-2 resulted in higher BET-SA in contrast with C80Z-1 prepared by citrate complexation method. Using co-precipitation method, the phase-segregated Ce-Zr samples were obtained, while single c-Ce\textsubscript{0.75}Zr\textsubscript{0.25}O\textsubscript{2} phase was formed in material prepared by citrate method. It is clearly indicated that Ce and Zr ions were homogeneously distributed in Ce-Zr-O powder. TPD results revealed the presence of high concentration of acidic and basic sites, especially strong, on the surface of C80Z-2. It caused to the lower DEC yield in comparison with C80ZP-1 catalyst. Reduction degree, concentration and strength of acid-base sites were influenced by preparation method and recognized as important parameters in increase of DEC yield over Ce-Zr-O catalyst. Between the two methods applied, the citrate derived Ce\textsubscript{0.8}Zr\textsubscript{0.2}O\textsubscript{2} was effective catalyst for DEC synthesis.
Chapter 7

7. Summary and Outlook

This chapter summarizes the results obtained in the frame of this thesis, provides some conclusions and an outlook for future research on the direct synthesis of organic carbonates, such as DMC and DEC, from alcohols and CO₂.

7.1. Ce-Zr mixed oxide catalysts and surface modified Ce₀.₈Zr₀.₂O₂ for the direct synthesis of dimethyl carbonate from methanol and CO₂

The influence of Ce-content in CeₓZr₁₋ₓO₂ materials and their surface functionalization with phosphoric acid on the DMC yield in liquid phase carboxylation of methanol was investigated. The effectiveness of CeₓZr₁₋ₓO₂ catalyst for DMC synthesis was ascribed to the co-existence of acid–base sites on its surface. Basic sites are required to activate MeOH and CO₂ and the acidic sites are required to supply methyl groups from MeOH in the last step of the reaction. DMC yield over CeₓZr₁₋ₓO₂ catalysts was found to depend strongly on cerium content. DMC was not formed over pure ZrO₂ catalyst, while it was significantly enhanced after cerium introduction into ZrO₂. Thus DMC yield increased from 0.04% over C20Z prep to 0.24% over C60Z prep and remained the same over C80Z prep and C prep. Different physico-chemical characterization studies such as N₂ physisorption, XRD, TEM, XPS, NH₃- and CO₂-TPD were performed to elucidate the effect of Ce content in CeₓZr₁₋ₓO₂ solid solution on DMC yield. The crystal structure of CeₓZr₁₋ₓO₂ with high Ce proportion (x ≥ 0.6) was cubic with negligible amount of tetragonal phase, whereas CeₓZr₁₋ₓO₂ high Zr content (x < 0.6) showed single phase of the tetragonal structure. Based on CO₂-TPD results, it was suggested that all CeₓZr₁₋ₓO₂ contained basic sites of three different strengths: weak, moderate and strong. However, CeₓZr₁₋ₓO₂ solids with x < 0.6 possessed a high concentration of strong basic sites, confirming that the high content of zirconium greatly enhanced the strength of basic sites. NH₃-TPD revealed the presence of both weak and medium strength acidic sites on all CeₓZr₁₋ₓO₂ catalysts. Pure ZrO₂ showing poor catalytic performance had the highest concentration of acidic sites (4.4 μmol m⁻²). It was assumed that C60Z prep, C80Z prep, C prep catalysts having the right balance of the weak and moderate acid/base sites showed high DMC yield.
The surface of Ce$_{0.8}$Zr$_{0.2}$O$_2$ was modified by phosphoric acid in order to promote acid-base properties. Different P-content in Ce$_{0.8}$Zr$_{0.2}$O$_2$ was investigated with the aim to identify efficient catalyst compositions for achieving enhanced DMC yields. In subsequent efforts on the optimization of P/Zr ratios, the yield of DMC enhanced from 0.24 % over C80Z$^{\text{prec}}$ to 1.62 % over C80ZP-2 (P/Zr = 0.12). The phosphate treatment has caused remarkable changes in phase composition of C80Z$^{\text{prec}}$ leading to Ce-rich cubic and Zr-rich tetragonal Ce$_x$Zr$_{1-x}$O$_2$ phases. Specific surface properties such as surface composition (P/Zr ratios) and acid-base properties were established to be crucial for achieving high DMC yield. The modification by H$_3$PO$_4$ caused a decrease in the concentration moderate and strong basic sites and an increase in the concentration of Lewis acidic sites from most likely unsaturated surface Zr$^{4+}$ cations which are responsible for an enhanced ability to form monodentate methoxy species which further converted to the methyl carbonate species (reaction intermediate for DMC formation) under high CO$_2$ pressure. In addition, the introduction of phosphate ions on the surface of calcined C80Z$^{\text{prec}}$ (C80ZP*, P/Zr = 0.12) was studied. Such modification caused a decrease of DMC formation ($\gamma_{\text{DMC}} = 0.004\%$) compared to its addition on uncalcined samples. It was concluded that any thermal treatment, especially double, led to the surface changes, indicating by the drop in BET-SA and by increase in the concentration of strong acidic and basic sites.

### 7.2. Continuous synthesis of diethyl carbonate from CO$_2$ and ethanol over Ce$_x$Zr$_{1-x}$O$_2$ ($x = 0, 0.2, 0.5, 0.8, 1$) catalysts

Different catalyst composition and reaction variables, e.g. reaction temperature, molar ratio of reactants, reaction pressure, reaction time, LHSV, were evaluated for the continuous synthesis of diethyl carbonate from CO$_2$ and EtOH. With the knowledge of suitable reaction conditions and catalyst active species, it was possible to reach maximum possible amount of DEC, i.e. at the equilibrium level. Since this route shows high thermodynamic limitations, the acid-base catalyst is required to activate CO$_2$ and EtOH. Ce$_x$Zr$_{1-x}$O$_2$ catalyst was applied for DEC synthesis due to its unique acid-base bifunctional properties. Ce$_x$Zr$_{1-x}$O$_2$ solids were prepared by citrate complexation method and calcined at 450 °C/3h/air. Catalytic performance of the catalysts was evaluated towards the synthesis of DEC from ethanol and CO$_2$ in a broad range of pressures (80-180 bar) and temperatures (80-180 °C). The Ce proportion has shown a considerable influence on DEC formation. The results revealed that the SSA, crystal structure, redox properties as well as acid-base characteristics of the solids are strongly influenced by the content of Ce in the catalysts, which in turn showed a clear impact on the catalytic
performance. C80Z-citrate solid, exhibited a single Ce$_{0.75}$Zr$_{0.25}$O$_2$ phase of cubic structure and right concentration of acidic and basic sites (2.2 : 2.5) of weak and moderate strength, showed the best catalytic performance compared to all other Ce-Zr mixed catalysts.

Next, the effect of reaction temperature and pressure on DEC formation was investigated over C-citrate, C80Z-citrate, C50Z-citrate, C20Z-citrate and Z-citrate catalysts in continuous running plug flow reactor. An increase of DEC yield was observed with pressure rise upto 140-160 bar depending Ce-Zr-O composition, beyond which it showed some adverse effect on the yield of DEC. Temperature also revealed positive effect on DEC yield, which increased from 0.06 to 0.5% with rise of temperature from 80 to 140 °C. But a further increase in temperature to 180 °C again caused a decrease in the DEC formation due to thermodynamic reasons. The highest yield of DEC obtained over C80Z-citrate was 0.52% at 140 °C and at 140 bar. This obtained DEC yield was still lower that thermodynamically possible $Y_{\text{DEC}}$ of 0.8% at similar reaction conditions.

In order to explore catalyst on-stream stability, the DEC reaction was performed at 140 °C, 140 bar for 20 hours over the C80Z-citrate catalyst. The experimental results revealed that the formation of DEC slightly increased with reaction time and levelled off after 6 hours ($Y_{\text{DEC}} = 0.55\%$). This result indicates that equilibrium was not established for the formation of DEC from ethanol and CO$_2$.

In subsequent runs, the influence of the calcination temperature on the phase composition and other properties of the best catalyst (C80Z-citrate) were studied. These characterizations were explored to check its impact on DEC formation. The C80Z-citrate catalyst precursors were calcined at three different temperatures (i.e. 450, 700 and 1000 °C) in air for 3 hours and tested at temperature of 140 °C and pressure of 140 bar. The structural and surface changes were related to alterations of the Ce-Zr-O crystallite size, reducibility, and/or acid-base properties. The increase in the crystallite size of Ce$_{0.75}$Zr$_{0.25}$O$_2$ leading to decrease of BET-SA and concentration of acid-base sites was observed with increasing the calcination temperature. Among the three calcination temperatures, the sample calcined at 700 °C further improved the yield of DEC to 0.7%. On the whole, C80Z-citrate calcined at 700 °C exhibited a good balance between acidity/basicity (1.1 : 0.8) and crystallite size (10 nm) variation that led to the observed improved performance.

Since this chapter has focused on continuous process for the synthesis of DEC from CO$_2$ and ethanol, the total flow rate of reagents was very important parameter to achieve a high DEC yield. Therefore, the effect of LHSV on catalytic performance was investigated.
C80Z-citrate catalyst calcined at 700 °C was tested at constant temperature (140 °C) and pressure (140 bar) but different total flow rates: 17, 42 and 62 L\textsubscript{liq} kg\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1}. It was found that an increase of CO\textsubscript{2}-EtOH flow rate up to 42 L\textsubscript{liq} kg\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} favored the DEC formation. However, further increase of total flow rate caused to dramatic drop of Y\textsubscript{DEC}. Based on this finding, a flow rate of 42 L\textsubscript{liq} kg\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} was selected for the further catalytic tests because it enables maximum space-time-yield.

7.3. Effect of second metal in Ce\textsubscript{0.8}M\textsubscript{0.2}O\textsubscript{2} catalysts on the catalytic activity towards DEC synthesis from ethanol and CO\textsubscript{2}

The effect of introduction of isovalent M\textsuperscript{4+} (where M\textsuperscript{4+} is either Hf\textsuperscript{4+} or Ti\textsuperscript{4+}) guest cations into host ceria lattice (Metal : Ce molar ratio of 20 : 80) and its influence on DEC yield was investigated. The ceria doped with M\textsuperscript{4+} resulted in different crystallite size, redox and acid-base properties compared to pure CeO\textsubscript{2}, since the substitution of Ce\textsuperscript{4+} (ionic radius 0.097 nm) with smaller M\textsuperscript{4+} (Hf\textsuperscript{4+} or Ti\textsuperscript{4+} with ionic radii of 0.078 and 0.069 nm, respectively) led to the structural modifications of the fluorite-type lattice of ceria. XRD pattern of C80H-citrate showed the formation of cubic Ce\textsubscript{0.8}Hf\textsubscript{0.2}O\textsubscript{2} phase, whereas C80T-citrate sample provided typical patterns of cubic CeO\textsubscript{2} with a few less intensive peaks due to rutile phase, indicating a limited solubility of Ti\textsuperscript{4+} in the ceria matrix. C80H-citrate and C80T-citrate exhibited the better redox properties than their parent metal oxides. C80H-citrate contained the higher concentration of weak and moderate acid sites than pure CeO\textsubscript{2}. However, the number of basic sites did not change considerably after doping of Hf\textsuperscript{4+}. No NH\textsubscript{3} was desorbed from C80T-citrate, indicating the absence of acid sites. It was suggested that various crystal structure of Ce\textsubscript{0.8}M\textsubscript{0.2}O\textsubscript{2} affected the properties of both surface M\textsuperscript{4+} and O\textsuperscript{2−} ions forming acid–base pairs. On the whole, the 20 mol% of Hf doped ceria (i.e. C80H-citrate) catalyst gave the higher DEC yield (0.45%) compared to C80T-citrate catalyst (0.02%).

7.4. Influence of synthesis methods on catalytic performance of Ce\textsubscript{0.8}Zr\textsubscript{0.2}O\textsubscript{2} in the production of diethyl carbonate from ethanol and CO\textsubscript{2}

Finally, with aim to improve the efficient catalyst properties for DEC synthesis, two different methods were applied for preparation of Ce\textsubscript{0.8}Zr\textsubscript{0.2}O\textsubscript{2} solid solutions such as co-precipitation and citrate complexation methods. Citrate complexation method provided a homogeneous nanocrystalline Ce\textsubscript{0.8}Zr\textsubscript{0.2}O\textsubscript{2} solid solution, whereas co-precipitation method resulted in
relatively high specific surface area \( \text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2 \). From NH\(_3\)-TPD experiments was found that C80Z-2 prepared by co-precipitation method had much higher concentration of acid sites, especially strong, compared to C80Z-1 prepared by citrate method. The distribution of basic sites on C80Z-1 and C80Z-2 surfaces was almost the same. However, C80Z-2 demonstrated more basic character than C80Z-1 that leaded to its lower catalytic activity compared to C80Z-2. As a conclusion, the catalysts prepared by different methods possess different crystal phase and surface properties that affected the catalyst performance.

7.5. **Outlook**

This work presents the preparation, thorough characterization and evaluation of Ce-based catalysts for the direct synthesis of dialkyl carbonates from \( \text{CO}_2 \) and \( \text{C}_1\text{-C}_2 \) alcohols (methanol and ethanol). Since a possible high yield (close to equilibrium yield) of dialkyl carbonate was achieved in the present study, future works should continue tests in a continuous-flow reactor under reaction conditions of \( p = 140 \) bar, \( T = 140 ^\circ \text{C} \), \( \text{R-OH} : \text{CO}_2 = 1 : 6 \) over Ce-Zr-O catalysts.

Despite the high yields of DMC and DEC over CeO\(_2\)-ZrO\(_2\) and CeO\(_2\)-ZrO\(_2\)/H\(_3\)PO\(_4\) described in this work, the amount of DMC/DEC produced remains very low. This is due to the thermodynamic limitations. Therefore, the most powerful method to shift the reaction equilibrium towards the product side is the use of dehydrating agent to remove water. Inorganic agents, such as zeolites or MgSO\(_4\), can be used for this purpose. However, under high reaction temperature (140-180 \(^\circ\text{C}\)) it is difficult to adsorb water from the reaction mixture. It can be successfully done, using external loop with a fixed bed column (at room temperature) filled with zeolite 3A and circulating the reaction mixture through this loop. After the required time, the system should be depressurized and then the reaction products can be analyzed. Another, more attractive technology for water removal is membrane catalytic reactor. However, under reaction conditions applied in the present work it will difficult to remove water from the reaction mixture. In most cases, high reaction pressure will causes swelling of the membrane. The introduction of reactive dehydration agents, such as CH\(_3\)I, trimethyl phosphate, butylene oxide, acetal and *ortho* ester into reaction media can also increase the amount of the desired products. The big advantage of these dehydration systems is their ability to work at high reaction temperature (> 100 \(^\circ\text{C}\)) that was not possible with inorganic absorbents. However, they have many disadvantages: i) toxic and corrosive reactants; ii) formation of by-products that cause to difficulties in separation from DMC/DEC;
iii) side reaction and deactivation of catalyst. To overcome these drawbacks, the use of catalytic hydration system becomes very attractive method to remove the water from the reaction media. This means that dehydration reagents are hydrated by catalysts. In conclusion, the combination of Ce-Zr-O catalyst (acid-base properties) with catalytic dehydration system will increase the yield and selectivity of organic carbonates.
8. References

[54] I.E. Muskat, F. Strain, 2 379 250 (1945), PPG.
8. References

8. References

[125] P. Scherrer, Göttinger Nachrichten Gesell. 2 (1918) 98.
8. References

[164] Z.Y. M. Pudukudy, Der Pharma Chem. 6 (2014) 188.
# 9. Appendices

**Appendix A: List of supporting figures, tables and discussions**

## A1 State of the art: Carboxylation of alcohols

Table A1.1. Important studies related to carboxylation of ethanol to DEC.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Type of reaction</th>
<th>Conditions</th>
<th>DEC-Yield</th>
<th>Remarks</th>
<th>Year</th>
<th>[Reference]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$</td>
<td>Continuous</td>
<td>140, 140</td>
<td>n$<em>{\text{EtOH}}$ : n$</em>{\text{CO}_2}$ = 1 : 6</td>
<td>0.7</td>
<td>Acid-base bifunctional catalyst; Sc conditions.</td>
<td>2015 [100]</td>
</tr>
<tr>
<td>2. Nb$_2$O$_5$/CeO$_2$</td>
<td>Batch (4×parallel reactors, 10 cm$^3$)</td>
<td>135, 50</td>
<td>68.5</td>
<td>3</td>
<td>0.7</td>
<td>The presence of Nb ions in the CeO$_2$ lattice increased the total acidity, while the increase of basic sites was due to a distortion of CeO$_2$ lattice.</td>
</tr>
<tr>
<td></td>
<td>Continuous (100 cm$^3$)</td>
<td>135, 300</td>
<td>n$<em>{\text{EtOH}}$/n$</em>{\text{CO}_2}$ = 1/4</td>
<td>-</td>
<td>0.9</td>
<td>Under sc conditions, EtOH and CO$_2$ were in the single phase; the higher was pressure, the higher was conversion of EtOH into DEC.</td>
</tr>
<tr>
<td>3. Cu-Ni/AC</td>
<td>Continuous</td>
<td>90, 13</td>
<td>n$<em>{\text{EtOH}}$/n$</em>{\text{CO}_2}$ = 2</td>
<td>3</td>
<td>1.9</td>
<td>Molar ratio Cu:Ni=3:1; Cu-Ni bimetallic catalyst–activation of CO$_2$ at moderate T and p, ethanol through dissociative adsorption.</td>
</tr>
<tr>
<td>4. K$_2$CO$_3$–C$_2$H$_5$I</td>
<td>Batch (200 cm$^3$)</td>
<td>110, 80</td>
<td>856</td>
<td>5</td>
<td>46 (one-pot reaction)</td>
<td>Sc conditions; K$_2$CO$_3$ acted as base, C$_2$H$_5$I-co-reagent, PTC-phase transfer catalyst; possible: one- or two-steps reactions; the sc CO$_2$ acts as swelling solvent</td>
</tr>
<tr>
<td>K$_2$CO$_3$–C$_2$H$_5$I-PTC</td>
<td></td>
<td></td>
<td>1200</td>
<td>51 (two steps reaction)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Ce$<em>{0.07}$Zr$</em>{0.93}$O$_2$</td>
<td>Batch (100 cm$^3$)</td>
<td>140, 80</td>
<td>257</td>
<td>2</td>
<td>0.16</td>
<td>Catalytic performance was related to crystal structure and acid-base properties; catalyst was recyclable.</td>
</tr>
</tbody>
</table>
**Table A1.2.** Important studies related to carboxylation of methanol to DMC.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Type of reaction</th>
<th>Conditions</th>
<th>Y-DMC</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T (°C)</td>
<td>p (bar)</td>
<td>MeOH (mmol)</td>
</tr>
<tr>
<td>1. Ce₈Zr₂O₂/H₃PO₄</td>
<td>Batch (25 cm³)</td>
<td>170</td>
<td>65</td>
<td>247</td>
</tr>
<tr>
<td>2. Cu-CeO₂</td>
<td>Batch (120 cm³)</td>
<td>120</td>
<td>13</td>
<td>247</td>
</tr>
<tr>
<td>3. CeO₂</td>
<td>Batch (100 cm³)</td>
<td>140</td>
<td>50</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>Batch (70 cm³)</td>
<td>130</td>
<td>60</td>
<td>192</td>
</tr>
<tr>
<td>4. Ce₅Zr₀.₄O₂</td>
<td>Batch (30 cm³)</td>
<td>170</td>
<td>65</td>
<td>247</td>
</tr>
<tr>
<td></td>
<td>Continuous</td>
<td>150</td>
<td>18</td>
<td>n₂MeOH/n₂CO₂ =1</td>
</tr>
<tr>
<td></td>
<td>Batch (70 cm³)</td>
<td>110</td>
<td>210</td>
<td>192</td>
</tr>
<tr>
<td>5. Cu-Fe/SiO₂</td>
<td>Continuous</td>
<td>120</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>6. 5Ga₂O₃/Ce₀.₆Zr₀.₄O₂</td>
<td>Batch (75 cm³)</td>
<td>170</td>
<td>60</td>
<td>741</td>
</tr>
<tr>
<td>No.</td>
<td>Catalyst</td>
<td>Conditions</td>
<td>TON</td>
<td>Yield</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>------------</td>
<td>-----</td>
<td>-------</td>
</tr>
<tr>
<td>7.</td>
<td>CeO$_2$/Al$_2$O$_3$</td>
<td>Continuous (4×parallel reactor, 20 cm$^3$)</td>
<td>135</td>
<td>50</td>
</tr>
<tr>
<td>8.</td>
<td>Sn/SBA-15</td>
<td>Batch (100 cm$^3$)</td>
<td>240</td>
<td>180</td>
</tr>
<tr>
<td>9.</td>
<td>Ce$<em>x$Ti$</em>{1-x}$O$<em>2$/H$<em>3$PW$</em>{12}$O$</em>{40}$</td>
<td>Batch (100 cm$^3$)</td>
<td>170</td>
<td>50</td>
</tr>
<tr>
<td>10.</td>
<td>Cu-Ni/V$_2$O$_5$-SiO$_2$</td>
<td>Continuous, photo-reactor, UV irradiation</td>
<td>120</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Continuous</td>
<td>140</td>
<td>6</td>
</tr>
<tr>
<td>11.</td>
<td>n-Bu$_2$Sn(OMe)$_2$</td>
<td>Batch (125 cm$^3$)</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Batch (20 cm$^3$)</td>
<td>180</td>
<td>300</td>
</tr>
<tr>
<td>12.</td>
<td>V$_2$O$_5$/H$_3$PO$_4$</td>
<td>Continuous</td>
<td>140</td>
<td>6</td>
</tr>
<tr>
<td>13.</td>
<td>ZrO$_2$</td>
<td>Batch (30 cm$^3$)</td>
<td>170</td>
<td>60</td>
</tr>
<tr>
<td>14.</td>
<td>ZrO$_2$/H$_3$PO$_4$</td>
<td>Batch (70 cm$^3$)</td>
<td>130</td>
<td>60</td>
</tr>
</tbody>
</table>
Table A1.3. DMC and DEC syntheses using dehydration agents.

<table>
<thead>
<tr>
<th>Organic carbonate</th>
<th>Catalyst</th>
<th>Dehydrating agent</th>
<th>Type of reaction</th>
<th>Conditions</th>
<th>Yield</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T (°C)</td>
<td>p (bar)</td>
<td>R-OH (mmol)</td>
</tr>
<tr>
<td>1. DEC</td>
<td>KI/EtONa</td>
<td>Ethylene oxide (45 mmol)</td>
<td>Batch (150 cm³)</td>
<td>170</td>
<td>30</td>
<td>680</td>
</tr>
<tr>
<td>2. DMC</td>
<td>CeO₂</td>
<td>2- Cyanopyridine (100 mmol)</td>
<td>Batch (190 cm³)</td>
<td>120</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>DEC</td>
<td>Butylene oxide (19 mmol)</td>
<td>Batch (300 cm³)</td>
<td>180</td>
<td>90</td>
<td>314</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. DEC</td>
<td>CeO₂/SBA-15</td>
<td>Butylene oxide (19 mmol)</td>
<td>Batch (300 cm³)</td>
<td>180</td>
<td>90</td>
<td>314</td>
</tr>
<tr>
<td>5. DEC</td>
<td>16 wt% Ce-H-MCM-41</td>
<td>Butylene oxide (19 mmol)</td>
<td>Batch (300 cm³)</td>
<td>170</td>
<td>45</td>
<td>314</td>
</tr>
<tr>
<td>6. DEC</td>
<td>none</td>
<td>Polymeric organic membrane PERVAP 1211</td>
<td>Continuous</td>
<td>80</td>
<td>1</td>
<td>Feed rate 10 mL min⁻¹</td>
</tr>
<tr>
<td>7. DMC</td>
<td>CeO₂</td>
<td>Benzonitrile (200 mmol)</td>
<td>Batch (190 cm³)</td>
<td>5</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>8. DEC</td>
<td>DMC</td>
<td>Acetonitrile (300 mmol)</td>
<td>Batch (190 cm³)</td>
<td>150</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>9. DMC</td>
<td>CeO₂</td>
<td>Acetonitrile (300 mmol)</td>
<td>Batch (190 cm³)</td>
<td>150</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>10. DMC</td>
<td>CuCl</td>
<td>N,N'-Dicyclohexylcarbodiimide (2.47 mmol)</td>
<td>Batch (70 cm³)</td>
<td>65</td>
<td>50</td>
<td>247</td>
</tr>
<tr>
<td>11. DMC</td>
<td>Cu-KF/MgSiO</td>
<td>none</td>
<td>Batch</td>
<td>130</td>
<td>100</td>
<td>nᵦMeOH/nᵦCO₂ = 5.9</td>
</tr>
<tr>
<td>No.</td>
<td>Reactants</td>
<td>Molecular Sieve</td>
<td>Reaction Conditions</td>
<td>Sc CO₂</td>
<td>Remarks</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----------</td>
<td>----------------</td>
<td>--------------------</td>
<td>--------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>Polyimide-silica hybrid membrane supported on the TiO₂/K-M ceramic tubes</td>
<td></td>
<td>n₃MeOH/nCO₂ = 2.4</td>
<td>8.8</td>
<td>conditions (silicon rubber, max 5 bar); hybrid membranes had excellent thermal and hydrophilic properties.</td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>Polyimide-titania hybrid membrane supported on the TiO₂/K-M ceramic tubes</td>
<td></td>
<td>n₃MeOH/nCO₂ = 2.4</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DMC Bu₂Sn(OMe)₂ Molecular sieve 3A (15 g)</td>
<td>Batch (20cm³) with internal recycle</td>
<td>180</td>
<td>300</td>
<td>100</td>
<td>72</td>
</tr>
</tbody>
</table>
9. Appendices

A2. Catalyst synthesis

A2.1. Citrate complexation method: Ce$_x$Zr$_{1-x}$O$_2$

For the correct calculation of the specific Ce$_x$Zr$_{1-x}$O$_2$ stoichiometries the determination of $x$ in ZrO(NO$_3$)$_2$·$x$H$_2$O is absolutely essential. $x$ was calculated from the thermal decomposition of the Zr precursor studied by TG under air. As shown in Figure A2.1.1, the TG curve had two stages of weight loss in the temperature range from r.t. to 405 °C. The first one starts at r.t. until ~178 °C while the second one took place above 178 °C and ends at ca. 405 °C. The weight loss of 25 wt.% at low temperature and 37 wt.% at higher temperature were caused by H$_2$O elimination and decomposition of nitrate precursor (ZrO(NO$_3$)$_2$)4•H$_2$O, respectively. Assuming that the first peak is due to the evolution of water, $x$ was calculated with ~4. Hence, the molar composition was ZrO(NO$_3$)$_2$•4H$_2$O. No weight loss was observed beyond 405 °C until 1000 °C.

![Figure A2.1.1. TG curve of thermal decomposition of ZrO(NO$_3$)$_2$·$x$H$_2$O under air.](image)

A2.2. Preparation of TiO(NO$_3$)$_2$ precursor for Ce$_{0.8}$Ti$_{0.2}$O$_2$ catalyst

Based on the fact that titanyl nitrate is not commercially available, TiO(NO$_3$)$_2$ [122] was prepared and used as precursor for Ce$_{0.8}$Ti$_{0.2}$O$_2$. Titanyl nitrate, TiO(NO$_3$)$_2$, was synthesized by the addition of a 6 vol.% solution of NH$_4$OH to titanium tetrachloride till a pH value of 11 was reached (Scheme A2.2.1).

\[
\text{TiCl}_4 + 2\text{NH}_4\text{OH} + \text{H}_2\text{O} \rightarrow \text{TiO(OH)}_2 + 2\text{NH}_4\text{Cl} + 2\text{HCl} \quad \text{(Scheme A2.2.1)}
\]

\[
\text{TiO(OH)}_2 + 2\text{HNO}_3 \rightarrow \text{TiO(NO}_3)_2 + 2\text{H}_2\text{O} \quad \text{(Scheme A2.2.2)}
\]
The synthesis was conducted at 0 °C under vigorous stirring. First, a white precipitate, TiO(OH)$_2$, was obtained (Scheme 2.2.1). The precipitate was washed several times with distilled water. Afterwards, 1M nitric acid was added to freshly precipitated TiO(OH)$_2$ until the final pH of mixed solution reached 1 (Scheme A2.2.2). Hydrothermally, the titanyl nitrate solution was treated at 80 °C for 3h and then dried at 100 °C for 24 hours. The amount of Ti in the solid was determined by ICP.

**Remark:** TiCl$_4$ is a fuming liquid and hydrolysis in the presence of moisture forms HCl gas and TiOCl$_2$. Therefore, TiO(OH)$_2$ is preferably prepared under ice-cold conditions.

**Table A2.1.1.** Preparation of TiO(NO$_3$)$_2$ precursor by treatment of TiO(OH)$_2$ by nitric acid.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>TiCl$_4$ (g)</th>
<th>6 vol.% NH$_4$OH (mL)</th>
<th>1M HNO$_3$ (mL)</th>
<th>Drying (T$_D$/t)</th>
<th>ICP (wt.% Ti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(NO$_3$)$_2$</td>
<td>38.6</td>
<td>200</td>
<td>150</td>
<td>100 °C/24h</td>
<td>53.8</td>
</tr>
</tbody>
</table>
A3 Catalyst characterization

A3.1. P-modified $\text{Ce}_{0.5}\text{Zr}_{0.2}\text{O}_2$ catalyst

![Graph showing nitrogen adsorption isotherms](image)

Figure A3.1.1. $\text{N}_2$ adsorption desorption isotherms (□ adsorption, ▭ desorption) and pore size distribution curves (inset) calculated from the desorption branch using the BJH method for unmodified C80Z$^{\text{prec}}$ and P-modified C80Z catalysts.

Table A3.1.1. $\text{H}_2$ uptake and temperature of maximal hydrogen consumption ($T_{\text{max}}$) during TPR runs for unmodified $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ and modified C80ZP-2 solids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak max (°C)</th>
<th>$\text{H}_2$–uptake (mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z^{\text{prec}}$</td>
<td>673</td>
<td>0.207</td>
</tr>
<tr>
<td>C20Z$^{\text{prec}}$</td>
<td>534</td>
<td>0.968</td>
</tr>
<tr>
<td>C40Z$^{\text{prec}}$</td>
<td>529</td>
<td>1.088</td>
</tr>
<tr>
<td>C60Z$^{\text{prec}}$</td>
<td>477, 712</td>
<td>1.435</td>
</tr>
<tr>
<td>C80Z$^{\text{prec}}$</td>
<td>447, 706</td>
<td>1.414</td>
</tr>
<tr>
<td>C80ZP-2</td>
<td>495, 703</td>
<td>1.103</td>
</tr>
<tr>
<td>C$^{\text{prec}}$</td>
<td>180, 454, 730</td>
<td>1.303</td>
</tr>
</tbody>
</table>
Figure A3.1.2 H₂-TPR profiles of unmodified CeₓZr₁₋ₓO₂ and P-modified C80ZP-2 solids.

Infrared spectroscopy of absorbed pyridine (Py-IR)

Pyridine adsorption studies were used to investigate the surface acid properties of unmodified C80Zᵖ管理和 P-modified C80ZP-2 samples. The Lewis acid site concentrations were calculated based on the intensity of the band at 1440 cm⁻¹ in the spectra recorded at 150 °C [229]. The measurements in transmission mode were carried out on a Bruker Tensor 27 FTIR spectrometer equipped with a heatable and evacuable homemade reaction cell with CaF₂ windows connected to a gas-dosing and evacuation system. The sample powders were pressed into self-supporting wafers with a diameter of 20 mm and a weight of 50 mg. Before pyridine adsorption, the samples were pretreated by heating in synthetic air up to 400 °C for 10 min, subsequent cooling to RT and evacuation (around 0.02 mbar). Pyridine was adsorbed at RT until saturation. Then the reaction cell was evacuated for removing physisorbed pyridine. The desorption of pyridine was followed by heating the sample in vacuum up to 400 °C and recording spectra every 50 K.

Py-IR results are shown in Figure A3.1.3. A significant increase of the intensity of the band at 1440 cm⁻¹ is observed for phosphated C80ZP-2 catalyst compared to un-phospated C80Zᵖ管理. These bands are assigned to Lewis acid sites.
Figure A3.1.3. Py-IR spectra of adsorbed pyridine at 150 °C on C80Z\textsuperscript{prec} and C80ZP-2 catalysts.

A3.2. \( \text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) catalysts: effect of Ce content

Figure A3.2.1. \( \text{N}_2 \) adsorption desorption isotherms (□ adsorption, ■ desorption) and pore size distribution curves (inset) calculated from the desorption branch using the BJH method for \( \text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) catalysts (\( T_c = 450 \) °C).
A3.3.  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ catalyst: effect of calcination temperature

Figure A3.3.1. $\text{N}_2$ adsorption desorption isotherms (□ adsorption, ■ desorption) and pore size distribution curves (inset) calculated from the desorption branch using the BJH method for C80Z-citrate catalysts calcined at 450, 700, 1000 °C.

A3.4.  $\text{Ce}_{0.8}\text{M}_{0.2}\text{O}_2$ catalyst: effect of second metal
**Figure A3.4.1.** $\text{N}_2$ adsorption-desorption isotherms (□ adsorption, ■ desorption) and pore size distribution curves (inset) calculated from the desorption branch using the BJH method for (a) pure CeO$_2$, HfO$_2$ and TiO$_2$ and (b) mixed oxides ($T_c = 700 ^\circ\text{C}$).

**A3.5. Ce}_{0.8}M_{0.2}O_2 catalyst: effect of preparation method**

**Figure A3.5.1.** $\text{N}_2$ isotherms (□ adsorption, ■ desorption) and the corresponding BJH pore size distribution curves (inset) of C80Z–1 and C80Z–2.
Appendix B

List of publications

1. Application of Ce,3Zr1−xO2 catalysts for the synthesis of diethyl carbonate from ethanol and carbon dioxide

2. Impact of calcination temperature on the catalytic properties of Ce-Zr-O solids in the direct synthesis of diethyl carbonate from ethanol and CO2.

3. Continuous synthesis of diethyl carbonate from ethanol and CO2 over Ce-Zr-O catalysts

4. Phosphate functionalization of CeO2-ZrO2 solid solutions for the catalytic formation of dimethyl carbonate from methanol and carbon dioxide
Conference contributions

1. Direct synthesis of diethyl carbonate from ethanol and carbon dioxide over Ce₅Zr₁₋ₓO₂ catalysts.
   I. Prymak, V. N. Kalevaru, P. Kollmorgen, S. Wohlrab, A. Martin

2. One-step synthesis of diethyl carbonate from ethanol and CO₂ using Ce-Zr-O catalysts.
   I. Prymak, V. N. Kalevaru, P. Kollmorgen, S. Wohlrab, A. Martin
   Workshop CaSuS Göttingen / LIKAT Rostock, Rostock, 16-18 September 2013 (poster).

3. Application of CeₓZr₁₋ₓO₂ catalysts for the synthesis of diethyl carbonate from ethanol and carbon dioxide.
   I. Prymak, V. N. Kalevaru, P. Kollmorgen, S. Wohlrab, A. Martin

4. Studies on Ce-Zr-O catalysts and their application for one-pot syntheses of diethyl carbonate from ethanol and CO₂.
   I. Prymak, V. N. Kalevaru, P. Kollmorgen, S. Wohlrab, A. Martin

5. Impact of calcination temperature on the catalytic properties of Ce-Zr-O solids in the direct synthesis of diethyl carbonate from ethanol and CO₂.
   I. Prymak, O. Prymak, V. N. Kalevaru, S. Wohlrab, A. Martin
Appendix C: Curriculum Vitae

Personal information

Full name: Iuliia Prymak
Date of birth: 18.05.1987
Place of birth: Charkiw, Ukraine
Nationality: Ukraine
Gender: Female
Marital status: Married
Email: iuliia.prymak@catalysis.de, prymak_julia@mail.ru
Phone number: +4917682463806

Academic Education

<table>
<thead>
<tr>
<th>Date</th>
<th>Institution</th>
<th>Position</th>
<th>Department</th>
<th>Supervisor(s)</th>
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<tbody>
<tr>
<td>4/2015-present</td>
<td>Leibniz Institute for Catalysis at University of Rostock, Germany</td>
<td>PhD student (guest) at Bioinspired Homo- &amp; Heterogeneous Catalysis</td>
<td></td>
<td>PD Dr. habil. E. Kondratenko, Dr. V. N. Kalevaru</td>
</tr>
<tr>
<td>5/2011-3/2015</td>
<td>Leibniz Institute for Catalysis at University of Rostock, Germany</td>
<td>PhD student at the Department of Heterogeneous Catalytic Processes</td>
<td></td>
<td>PD Dr. habil. A. Martin, Dr. V. N. Kalevaru</td>
</tr>
<tr>
<td>1/2010-4/2011</td>
<td>The state-owned enterprise &quot;Turboatom&quot; of Charkiw, Ukraine</td>
<td>Engineer at the Department of Radiography with X-rays and gamma rays</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5/2009</td>
<td>University of Duisburg-Essen, Germany</td>
<td>DAAD Scholarship holder (Leonard-Euler program) at the Department of Solid State Chemistry and Bio-Inorganic Chemistry</td>
<td>Supervisor: Prof. Dr. M. Epple</td>
<td></td>
</tr>
<tr>
<td>9/2008-6/2009</td>
<td>National University of Charkiw, Ukraine</td>
<td>Master at the Department of Solid-State Physics</td>
<td>Master Thesis &quot;Alterung von karbonisierter Hydroxylapitat Keramik bei Raumtemperatur&quot;</td>
<td></td>
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</tbody>
</table>
Supervisors: Prof. Dr. Z. Z. Zyman, Dr. M. V. Tkachenko

National University of Charkiw, Ukraine

Bachelor at the Department of Solid-State Physics

Bachelor Thesis "Untersuchung des Alterungsprozesses des karbonisierten Hydroxylapatits"

Supervisors: Prof. Dr. Z. Z. Zyman, Dr. M. V. Tkachenko