

Catalysis for Hydrogen Storage and Release Mediated by Carbon Dioxide and Its Analogs

Cumulative Dissertation

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And from this day forward, I'm going to stop doing everything my sister does.

For Dr. Nicola V. M. Stein

Statement of Authorship

I hereby confirm that I have written the present work by myself and without outside assistance. No aids or sources other than those specified by me have been used. All passages taken from the works consulted, whether in substance or verbatim, have been duly acknowledged as such.

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Rostock, 18.07.2025

Carolin A. M. Stein

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1. Introduction

“Without the low operating costs, high efficiency, high reliability, and great durability of diesel engines, it would have been impossible to reach the extent of globalization that now defines the modern economy.”^[1]

Newcomen’s invention of the steam engine in 1712^[2] ignited the Industrial Revolution. Coal, a solid energy carrier that has stored solar power in the Earth’s crust for millions of years, was converted into machine power. In the late 19th and early 20th centuries, oil and gas supplanted coal, fueling economic growth and driving the development of the internal combustion engine. In 1885, Benz introduced the first car.^[3] Today, around 83 million vehicles are sold annually (2022), 86% of which are powered by gasoline or diesel, emitting greenhouse gases.^[4]

It is not only transportation: Sources of CO₂ emissions include energy production (73.2 %), industrial processes (5.2 %), and deforestation (18.4 %, Figure 1).^[5] The global energy demand has increased radically, from $5 \cdot 10^{12}$ kWh/year (1860) to $1.2 \cdot 10^{14}$ kWh/year today – more than double the Earth's renewable capacity.^[6] Consequently, CO₂ emissions are climbing rapidly.

The Earth's overall temperature is expected to rise by more than 1.5 °C in the 21st century. Only through drastic changes can global warming be mitigated. The Paris Agreement (2015) aims to limit global warming to below 2 °C. This requires a fundamental overhaul of how we generate, distribute, and use energy worldwide.

Reducing CO₂ emissions from the energy sector can be achieved by transitioning to renewable energy sources. However, these sources are intermittent. To ensure a continuous electricity supply, energy storage solutions are crucial. Hydrogen is a versatile storage medium: it can be used as a chemical feedstock, be combusted for heat generation, or converted back into electricity. Its ability to be stored long-term in tanks or underground caverns makes it one of the few green technologies capable of seasonal energy storage.^[7]

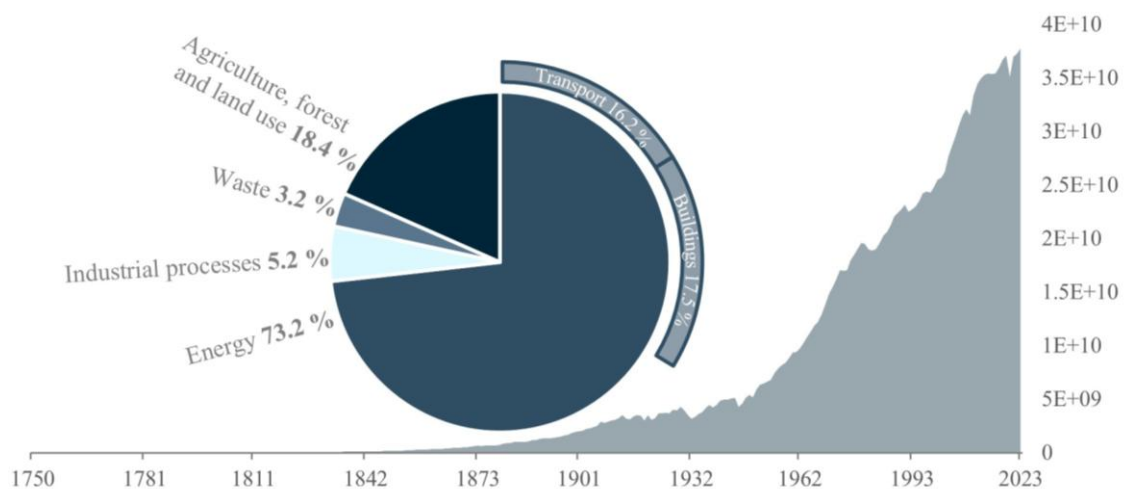


Figure 1. Overview of global greenhouse gas emissions: Global greenhouse gas emissions by sector, as of 2016 (left).^[5] Annual CO₂ emissions by world regions from 1750 to 2023 (right).^[8]

1.1 A Short History of Hydrogen

In the Middle Ages, Paracelsus noted a gas evolution when iron is dissolved in “spirit of vitriol”.^[9] The separation and identification of the molecule hydrogen dates back to 1671, when Boyle produced the gas in an experiment with iron and sulfuric acid. He noted that the gas is inflammable but can be burned when air is added.^[10] Almost a century later (1766), Cavendish generated hydrogen over mercury and defined it for the first time as a distinct element. He described the gas as “inflammable air from metals” and did not recognize its actual source, namely the acid.^[11] During the late 1770s, he conducted experiments with electric discharges in hydrogen-oxygen mixtures and observed the production of water. In 1783, Lavoisier finally identified the nature of the gas and gave it its current name, composed of the Greek words “hydro” for water and “genes” for forming. Meanwhile, human transportation was demonstrated using hydrogen in hot-air balloons and hydrogen-filled gas balloons.^[9]

The lightest known element is also the most abundant gas in the universe, accounting for 70-80 % of the matter in the visible universe.^[12] The gas is colorless, odorless, non-toxic, and highly combustible. Hydrogen contains about three times the energy per weight as gasoline and is already fueling our world. The energy emitted from the sun and other stars comes from hydrogen fusion. The sun is mostly made of hydrogen in its plasma state; its hydrogen supply is estimated to last for another 5 billion years.^[9,13]

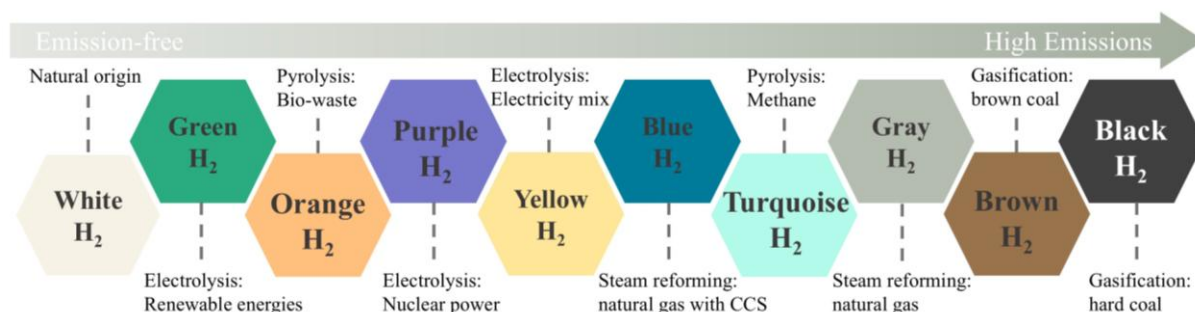
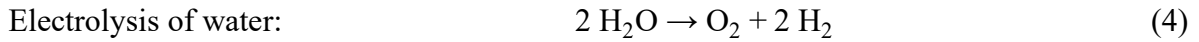
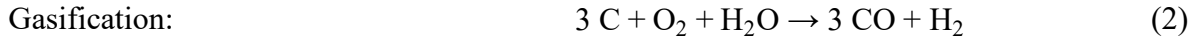


Figure 2. Classification of hydrogen based on its production method and the emission intensity.^[14] CCS stands for carbon capture and storage.

Despite its abundance in the universe, hydrogen makes up only about 1% of the geosphere. There are few natural sources (white hydrogen, Figure 2), and producing hydrogen in its elemental form is cumbersome. Industry uses thermochemical conversion of fossil fuels, such as steam reforming (blue and gray hydrogen, Figure 2; Eq. 1) and gasification (brown and black hydrogen, Figure 2; Eq. 2). These processes are comparably cheap and produce syngas, a mixture mainly composed of CO and H₂, which is then converted to hydrogen through the water-gas shift (WGS) reaction (Eq. 3). Although carbon capture and storage (CCS) can reduce CO₂ emissions significantly,^[15] the state-of-the-art industrial pathways still contribute substantially to global CO₂ emissions.^[14]

Alternatively, hydrogen can be generated from water *via* electrolysis (Eq. 4). The first demonstration dates back to 1800, when Nicholson and Carlisle split water by applying an electric current, making water the first substance to be electrolyzed.^[13] Depending on the electricity source, the colors of hydrogen can be classified further (green, purple, yellow, Figure 2). Green hydrogen is generated solely from renewable energy sources.



Vice versa, hydrogen can react with oxygen to generate water and electricity – a fuel cell. The forerunner of such a device was presented in 1839 as a “gas voltaic battery” by Sir Grove.^[16] The term “fuel cell” was first introduced in 1889 by Mond and Langer, who attempted to build a practical device that utilized hydrogen from coal gas and air. Nevertheless, interest in this technology declined after the invention of the first dynamoelectric generator. This device enabled the generation of electric energy from any mechanical energy source.^[9,13]

1.2 Storing Renewable Energy in the Hydrogen Cycle

Rising CO₂ levels are drastically affecting the world’s climate. The transition from fossil fuels to renewable energies can significantly reduce global emissions, which is why the EU launched the “European Green Deal” to become the first climate-neutral continent by 2050.^[17] Over the past two decades, improvements in efficiency and production scale have drastically reduced the costs of renewables, making them increasingly competitive with fossil fuels.^[17] Beyond emission reductions, renewable energy technologies diversify the energy supply, enhance energy security through local production (independence from oil- and natural gas-producing countries), support decentralized and resilient systems, and create new jobs, thereby boosting local economies.^[19]

These benefits are reflected in the growing share of renewables across electricity, heat, and transportation. Germany obtained 53 % of its electricity from renewable energy sources (RES) in 2023 – this corresponds to 273.2 billion kWh of generated electricity and amounts to 197 million tons of avoided CO₂-equivalent emissions.^[20] Wind (onshore: 43 %, offshore: 9 %) and solar (23 %) power are the most common technologies. Table 1 provides an overview of a wide range of technologies for electricity production that utilize various natural forces.^[19]

Despite many advantages, RES are fluctuating. Their intermittent availability originates from the dependence on weather conditions (Table 1). Solar energy, for example, is only available during clear daylight hours (Figure 3). However, the electrical grid requires a constant balance

between supply and demand. Variability in RES output can lead to frequency deviations or even blackouts. These limitations create a problem, as the timing of high energy supply often does not align with actual demand. For this reason, efficient energy storage that captures excess energy during periods of high generation (green areas in Figure 3) and releases it during periods of low production is a key component of an economy based on renewable energy sources.^[14]

Table 1. Renewable energy technologies for electricity production, their intermittency and fluctuation characteristics.^[19]

Energy source	Technology	Intermittency	Fluctuation
Wind	Wind turbines (onshore and offshore)	High	Wind speed and weather patterns
Solar	Photovoltaic solar energy conversion	High	Limited to daylight and affected by cloud cover
	Solar thermal energy conversion		
Biomass	Combustion	Low	Uses stored organic material
	Gasification/power production		
Water	Hydropower	Moderate	Seasonal water flow variations
Geothermal	Geothermal power	Low	Constant heat source
Marine	Tidal energy	Moderate	Predictable
	Wave energy		Wind speed and weather patterns
	Current energy		Wind speed and weather patterns
	Ocean thermal energy conversion		Constant
	Salinity gradient/osmotic energy		Weather-driven river discharge and salinity gradient

Electricity Generation from Renewables vs. Electricity Demand – Germany, Week 34/2024

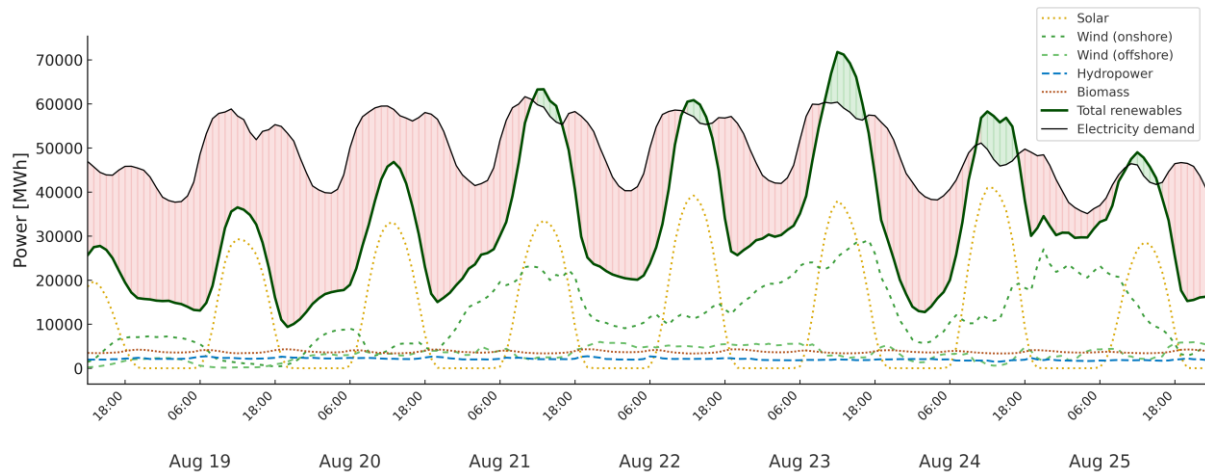


Figure 3. Electricity generation from various renewable energy technologies and demand in Germany for the week 34/2024.^[21] Own illustration, created with ChatGPT.^[22]

Batteries are among the most widespread storage systems, offering high round-trip efficiency (< 90 %). They store electric energy from RES *via* reversible electrochemical reactions and enable decentralized, short-term storage.^[23] Nevertheless, they have technical shortcomings: limited lifespan, reliance on critical raw materials, high weight, temperature sensitivity, and environmental concerns from production and recycling, such as hazardous waste and greenhouse gases emissions.^[14,24]

Alternatively, excess electric energy from RES can be stored chemically, e.g., in hydrogen *via* electrolysis of water, where the molecule H_2O is split electrochemically into its components, hydrogen (H_2) and oxygen (O_2). Electrolysis is an established technology that produces high-purity hydrogen. The only impurities are water ($> 5 \text{ ppm}$)^[25] and oxygen ($\sim 800 \text{ ppm}$)^[26]. Considering technical losses, systems today have an efficiency of approximately 82 %.^[9] Hydrogen, with a gravimetric energy density (GED) of 33 kWh/kg, exceeds gasoline (12.0 kWh/kg) and diesel fuel (11.9 kWh/kg) by more than a factor of two.^[27] The storage and use of electrical energy in hydrogen form the foundation of the “hydrogen economy” (Figure 4),^[7] a concept introduced in 1955 by Justi, where hydrogen is used as a secondary energy carrier.^[13] The cycle includes the production of hydrogen, its storage and release, and finally the energy release from hydrogen. Hydrogen is regarded as the most suitable candidate for large-scale and long-term storage of renewable energy due to its versatility across various uses. It can serve as an energy vector, analogous to fossil fuels, through combustion. Alternatively, it can be employed in fuel cells to generate electricity, with water as the only by-product. Additionally, hydrogen is a commodity gas and a feedstock for many industrial applications.^[28]

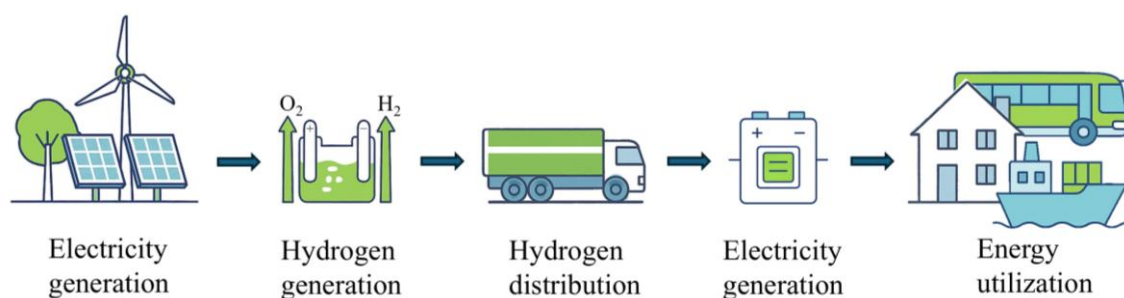


Figure 4. Schematic of the hydrogen economy: production of green hydrogen via water electrolysis powered by renewable energy; distribution of hydrogen; conversion of hydrogen e.g. in a fuel cell; and finally, utilization of the energy. Own illustration, created with ChatGPT.^[22]

Despite their importance for balancing supply and demand, energy storage systems cause significant conversion losses. Hydrogen production, compression, transportation, and reconversion through a fuel cell can lower the overall round-trip efficiency to below 40 %.^[29] In contrast, direct use of renewable electricity, e.g. in electric vehicles, can achieve total efficiencies above 80 %.^[30] Therefore, direct utilization should be prioritized whenever feasible, with storage mainly used to manage temporal fluctuations.

1.3 Concepts for Hydrogen Storage

Mission Innovation rates hydrogen as one of the most important sectors for achieving decarbonization by 2050.^[31] In response, the EU launched the European Clean Hydrogen Alliance.^[27] Interest in hydrogen is fueled by its high GED suitability for long-distance transportation, long-term storage, and compatibility with existing infrastructure.^[32] However, several hurdles remain: H_2 has a low volumetric energy density (VED; 5.6 MJ/L at 700 bar), is combustible, volatile, and exhibits the lowest minimum ignition energy, the widest flammability

range, and the highest diffusivity of any known fuel (Table 2).^[33] A well-functioning hydrogen economy requires the energy-efficient, safe, and environmentally friendly production, distribution, storage, and utilization of H₂. Hydrogen storage can help overcome some of these issues.^[34]

Traditionally, hydrogen is stored *via* physical methods (Figure 5, left) such as compression to 700 bar (ca. 40 gH₂/L), liquefaction or cryogenic storage (20 K, ca. 70 gH₂/L).^[35] All of these techniques are energy-intensive (using 30-40% of the energy content), costly, and require specialized high-pressure tanks, which raises safety concerns.^[40]

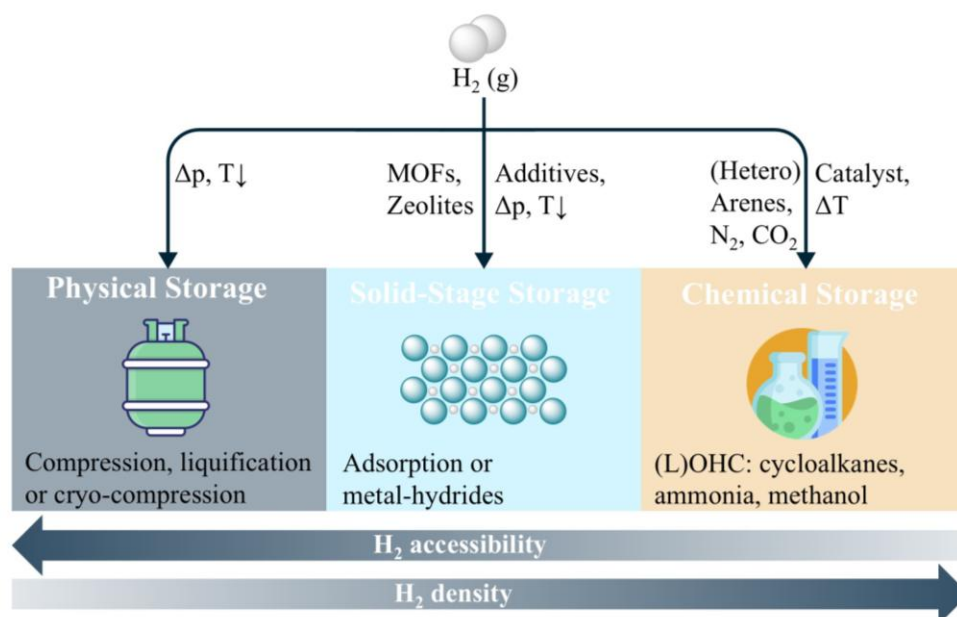


Figure 5. Different storage possibilities for green hydrogen and their storage/synthesis conditions.^[37–39]

Physisorption onto materials with large internal surface areas, such as zeolites or metal-organic frameworks (MOFs) is a solid-state storage method (Figure 5, middle). MOFs can store and release H₂ at 100 bar and -196 °C, corresponding to a GED of up to 7.2 MJ/L. However, their synthesis is energy-demanding, and long-term operations is limited by air sensitivity and structural degradation.^[40,41]

Hydrogen can also be stored chemically *via* reversible (de)hydrogenation. Solid-state storage includes (complex) metal hydrides^[42] or metal alanates^[43]. Although hydrides have a high density, their weight and temperature sensitivity pose problems.^[44]

Liquid chemical storage media (Figure 5, right), also known as liquid organic hydrogen carriers (LOHC), enable the use of existing infrastructure for distribution and local storage. (Hetero)arenes, such as benzyl toluene, however, require high temperatures (150-300 °C) for hydrogen release. Moreover, many of the loaded and/or unloaded carrier molecules are classified as carcinogenic, toxic, flammable, or environmentally hazardous.^[45,46]

Table 2. Physical properties of various energy and hydrogen carriers.

Category	Carrier	Storage conditions	H ₂ [wt%]	VED [MJ/L]	GED [MJ/kg]	GHS	Ref
Fossil fuels	Diesel	ambient	-	36.0	41.4		[47]
	Gasoline	ambient	-	32.4	45.0		[47]
Hydrogen	H ₂ (g)	ambient	100	0.0108	120		[48]
	H ₂ (g)	350 bar	100	2.88	120		[33]
	H ₂ (g)	700 bar	100	4.68	120		[33]
	H ₂ (l)	-253 °C	100	8.28	120		[33]
	LiBH ₄	ambient	18.5	8.64	22.3		[33]
Metal hydrides	NaAlH ₄	ambient	7.5	10.08	9.0		[33]
	LiAlH ₄	ambient	10.6	12.60	12.6		[33]
	NaBH ₄	ambient	10.8	15.5	7.6		[33,49]
	AlH ₃	ambient	10.1	17.6	12.2		[33]
	MgH ₂	ambient	7.6	15.8	29.2		[49,50]
LOHCs	Cyclohexane	ambient	7.2	6.7	40.2		[45]
	Methyl-cyclohexane	ambient	6.2	5.8	40.6		[45]
	Decalin	ambient	7.3	7.8	-		[49]
Small molecules	Ammonia	10 bar, -34 °C	17.8	12.7	18.6		[49,51]
	Methane	ambient	25.1	13.0	29.9		[33]
	Ethanol	ambient	13.1	21.6	27.0		[47]
	Methanol	ambient	12.1	15.1	18.0		[47]
	Methyl formate	ambient	8.4	15.1	15.8		[52]
	Formic Acid ^[a]	ambient	4.4	6.4	5.2		[53]
	KHCO ₂ ^[b]	ambient	0.65	0.9	-		[45]

VED stands for volumetric energy density, GED for gravimetric energy density. [a] pure acid. [b] aqueous solution.

A different approach to liquid hydrogen storage involves the reversible hydrogenation of small molecules, such as nitrogen (N₂) or carbon oxides (CO_x), into carriers like ammonia, methanol, or methane. Compared to the LOHCs mentioned above, they are non-carcinogenic. CO₂ in particular is easy to handle, inexpensive, and can be sourced from industrial emissions. In this way, carbon dioxide can become an attractive resource. The concept of a hydrogen economy based on C₁ carriers can drive decarbonization beyond the energy sector.

1.4 Hydrogen Storage based on CO₂ and its Analogues

Hydrogen is the key to a low-carbon future. Jules Verne already envisioned water as the coal of the future in his novel from 1874, “The Mysterious Island”.^[36]

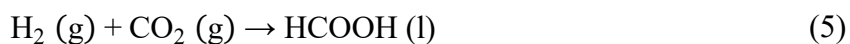
Promising liquid hydrogen carriers, such as ammonia or (hetero) arenes, face challenges including low hydrogen content, high energy demand, and environmental safety concerns (Table 2).

Despite its environmental impact, CO₂ is a renewable C₁ source for the production of bulk chemicals, such as methanol and formic acid (FA), thereby providing an opportunity to address the global issue of rising CO₂ levels.^[54] Given the low toxicity, mild reaction conditions for (de)hydrogenation, and good stability at room temperature, (aqueous) FA and the corresponding formate salts are of interest for hydrogen storage technologies.^[53,55]

1.4.1 Hydrogen Storage in Formic Acid

Among the possible hydrogen storage materials, FA has emerged as an attractive candidate, due to its inherent properties like low toxicity and kinetic stability at room temperature. It is a liquid hydrogen carrier with a hydrogen content of 4.4 wt%. This corresponds to 43.8 g of H₂ per kilogram of pure formic acid.^[56]

Besides, FA is an important (by)product and intermediate in the chemical industry.^[57] The market size volume was around 995000 tons in 2024.^[58] On an industrial scale, formic acid is produced from methanol and carbon monoxide, emitting around 3100 tons of CO₂ for one ton of FA. The production of formic acid from CO₂ has gained increased attention, as it could reduce product-related greenhouse gas emissions by a factor of 10, especially when green hydrogen is applied.^[59] The production of FA utilizing cheap and abundant carbon dioxide is particularly interesting, as it opens a carbon-neutral cycle. The pathway of storing hydrogen in formic acid *via* CO₂ reduction was first suggested in 1978 by the group of Williams.^[60] Hydrogen stored in FA is 100 % available for conversion, making it very atom-efficient. This contrasts with other CO₂-hydrogenation products such as methanol (66 %) and methane (50 %), in which H₂ is lost as water. Thermodynamically, the hydrogenation of CO₂ is unfavorable when the reaction takes place in the gas phase (Eq. 5). The use of a suitable solvent like water or DMSO and the addition of a base, e.g. amines or formates, reverses this trend (Eq. 6).



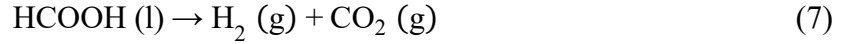
$$\Delta_f H^0 = -31.2 \frac{\text{kJ}}{\text{mol}}; \Delta_f S^0 = -215 \frac{\text{J}}{\text{mol}\cdot\text{K}}; \Delta_f G^0 = 32.9 \frac{\text{kJ}}{\text{mol}} [61]$$



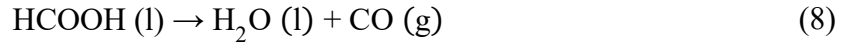
$$\text{NH}_3; \Delta_f H^0 = -59.8 \frac{\text{kJ}}{\text{mol}}; \Delta_f S^0 = -81 \frac{\text{J}}{\text{mol}\cdot\text{K}}; \Delta_f G^0 = -35.4 \frac{\text{kJ}}{\text{mol}} [61]$$

The dehydrogenation of FA (FAD) is exergonic and endothermic (Eq. 7), enabling hydrogen release at low temperatures (> 80 °C) and high pressures (> 600 bar). FAD can be promoted by the addition of a base, which forms the corresponding formate that undergoes faster

decomposition. In addition to the desired FAD to H₂ and CO₂, dehydration is also thermodynamically possible (Eq. 8). The formation of toxic CO should be prevented, as it can shorten the lifetime of catalysts and fuel cells.^[62] By developing a suitable catalyst, this side reaction can be avoided.



$$\Delta_f H^0 = 31.2 \frac{\text{kJ}}{\text{mol}}; \Delta_f S^0 = 215 \frac{\text{J}}{\text{mol} \cdot \text{K}}; \Delta_f G^0 = -32.9 \frac{\text{kJ}}{\text{mol}}; K_{\text{eq}}(298 \text{ K}) = 58 \cdot 10^5 \frac{\text{kJ}}{\text{mol}}^{[36]}$$

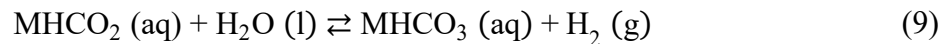


$$\Delta_f H^0 = 28.7 \frac{\text{kJ}}{\text{mol}}; \Delta_f S^0 = 138 \frac{\text{J}}{\text{mol} \cdot \text{K}}; \Delta_f G^0 = -12.4 \frac{\text{kJ}}{\text{mol}}^{[61]}$$

FA-based hydrogen storage is being researched and commercialized for various applications, including portable power systems and stationary energy storage. The Dutch company DENS for example produces FA-based generators for mobile applications like construction sites. Here hydrogen is released from FA and converted in a fuel cell^[63] Team FAST, a spin-off from the University Eindhoven designs busses powered by FA-based fuel cells.^[64]

1.4.2 Hydrogen Storage in Formate Salts

Formic acid is a promising energy carrier, but the decomposition requires careful manipulation of the reaction conditions to avoid CO formation and subsequent catalyst intoxication.^[53] Moreover, the endothermic FAD and the gas purification add to the loss cascade in the H₂ storage and release process. By moving from FA to its salts, the formates, this issue can be avoided: hydrogen storage in formates is a reversible process (Eq. 9) with the free energy close to zero (e.g. $\Delta_f G^0 = 0$ for potassium at 47 °C), meaning slight changes in temperature or pressure can easily shift the equilibrium into the desired direction. No side reactions occur, and bicarbonate remains in solution after H₂ release - simplifying gas purification and rendering the formate/bicarbonate cycle carbon-neutral.^[65] Unlike CO₂ hydrogenation to formic acid, bicarbonate hydrogenation is thermodynamically favored at low temperatures.^[65] They can either be used as a solid hydrogen storage material or liquid as an aqueous solution.



$$\text{M} = \text{K}:^{[35]} \Delta_f H^0 = 19.43 \frac{\text{kJ}}{\text{mol}}; \Delta_f S^0 = 62.43 \frac{\text{J}}{\text{mol} \cdot \text{K}}; \Delta_f G^0 = 1.34 \frac{\text{kJ}}{\text{mol}}; K_{\text{eq}}(298 \text{ K}) = 0.58 \frac{\text{kJ}}{\text{mol}}$$

Although formate salts only have half of the hydrogen storage capacity of FA, they are non-corrosive, non-irritating and inherently safe,^[34] which is why both the loaded and the unloaded carrier are being used in the food industry (Formate: E237, E238; bicarbonate: E500-504).

There are multiple industrial processes to generate metal and ammonium formates and bicarbonates. On an industrial scale, formates are synthesized *via* direct carbonylation of a base or by neutralization of formic acid with the corresponding metal-hydroxide.^[49,66] Overall, around one million tons of formate are produced per year.^[67,68] Bicarbonate is generally produced from CO₂ and carbonate, e.g., utilizing the Solvay process (sodium bicarbonate), aqueous or dry carbonation.^[49,69,70]

Table 3. Physical properties of various formate species.

Counterion	Solubility _{mass} [g/100 mL] ^[a]	Solubility _{molar} [mol/100 mL] ^[a]	Energy density [gH ₂ /L] ^[b]	Price [€/kg] ^[c]
Li ⁺	39	0.8	11.6	600
Na ⁺	81	1.2	16.9	60
K ⁺	337	4.0	29.2	80
Rb ⁺	554	4.3	22.7	> 5000
Cs ⁺	450	2.5	17.3	250
NH ₄ ⁺	143	2.3	21.4	80

[a] Values at 20 °C for aqueous solutions.^[71,72] [b] Energy density was calculated for maximum solubility in water at 20 °C, taking the volume of water into account. [c] Prices were calculated for 1 kg and rounded. They can vary in-between different suppliers.^[73,74]

VEG of formates depends on the counterion, and only alkali metals and ammonium are considered appropriate cations due to their weight.^[44] Table 3 compares solubility, hydrogen content per liter, and cost. While potassium, rubidium, and cesium formate exhibit high maximum mass and molar solubility, lithium dissolves poorly, making it less suitable for H₂ storage technologies. The maximum hydrogen amount in one liter of aqueous solution suggests potassium as an ideal candidate. Additionally, sodium, potassium, and ammonium offer reasonable prices for a hydrogen carrier.

Selecting an optimal cation requires balancing storage capacity, availability, toxicity, energy demand, and catalytic activity. The companies Hydro X^[75] and Akros^[76] are currently developing sustainable hydrogen storage technologies based on the potassium formate/bicarbonate cycle.

1.5 Catalysts for Hydrogen Storage and Release

Homogeneous as well as heterogeneous catalysts can be used for chemical hydrogen storage and release, each with distinct advantages (Table 4). Homogeneous catalysts tend to exhibit higher activity, selectivity, and repeatability, as well as a well-defined structure. However, they are difficult to separate from the reaction solution, often require non-aqueous solvents (higher price and toxicity), have higher costs, and exhibit lower resistance to thermal stress and oxidation. Heterogeneous catalysts, on the other hand, are often easier to synthesize and more

temperature- and oxygen-stable. Furthermore, they are simple to recover and reactivate and are applicable in water. On the downside, they tend to lack selectivity, activity, and repeatability.^[35]

Table 4. Opportunities and challenges for homogeneous and heterogeneous catalysis.^[35]

Category	Homogeneous Catalyst	Heterogeneous Catalyst
Price	High	Low
Synthesis	Multiple steps	Straight forward
Repeatability	High	Low
Activity and selectivity	High	Low
Stability	Low	High
Recyclability	Possible	Easy
Structure and mechanism	Defined	Complex

The following chapters provide an overview of existing heterogeneous and homogeneous catalyst systems for the charge–discharge reactions in the formic acid/CO₂ and formate/bicarbonate cycles, with a particular emphasis on the underlying catalytic cycles and catalyst recyclability.

1.5.1. Catalyst Systems for the Formic Acid/CO₂ Cycle

Heterogeneous Catalyst Systems: Formic Acid/CO₂ Cycle

FAD in the presence of a heterogeneous catalyst in the form of metal oxides was first reported by Sabatier in 1912.^[77] In 1935, Farlow and Adkins demonstrated the first synthesis of amine/formic acid adducts from CO₂, utilizing heterogeneous Raney[®] Ni.^[78] Mainly, dispersed palladium, gold, ruthenium, and iridium on supports like activated carbon and metal oxide are being used for both half-cycles.^[79]

A lot of attention has been focused on nitrogen-modified carbon supports. The group of Yoon applied palladium on graphitic carbon nitride (g-C₃N₄) for both reactions: the hydrogenation of CO₂ to formic acid (CH) and the reverse reaction. They suggested that the basic sites of the carbon support activate the substrate carbon dioxide (Scheme 1).^[80] Utilizing a similar Pd/g-C₃N₄ catalyst, Lee and co-workers studied the mechanism of CH. According to their work, dihydrogen is activated on Pd, while the support sites are necessary for the activation of CO₂; meanwhile, the reaction takes place at the interface.^[81]

Cao and his co-workers applied palladium nanoparticles (NP) on flexible pyridinic-N-doped carbon hybrids as support materials for CH (Scheme 1). With the catalyst Pd/CN_{0.25}, an outstanding turnover number (TON) of 18370 (60 bar H₂/CO₂ 1:1; H₂O, NEt₃, 100 °C) was achieved. High yields in FAD were also reported (turnover frequency (TOF) = 5530 h⁻¹, 25 °C). The authors addressed the increased activity to the electronic modification of the support.^[82]

Highly dispersed palladium nanoclusters immobilized on a nitrogen-functionalized porous carbon support from Xu's group exhibited high catalytic activity ($\text{TOF} = 8414 \text{ h}^{-1}$) and recyclability for FAD (15 times). According to the authors, the stability of the catalyst systems arises from the confinement of Pd within the pores of the support (Scheme 1).^[83]

The group of Zhang obtained very high activity in the hydrogenation of CO_2 with a Schiff-base-modified Au catalyst supported on SiO_2 . Here, Au was present in two different forms, clusters and single atoms. Again, a mechanism was proposed, including support substrate interaction.^[84] The reversible hydrogenation of captured CO_2 with Pd/AC was published by the Lin group in 2018. The hydrogenation of piperidine-captured CO_2 in isopropanol/water yielded a TON of 5540 (27.6 bar H_2 , 30 °C, 1 h). Full conversion for FAD was reached within 40 min (100 °C). Combining both steps, five consecutive charge/discharge cycles were performed without a significant loss in activity (Scheme 1).^[85]

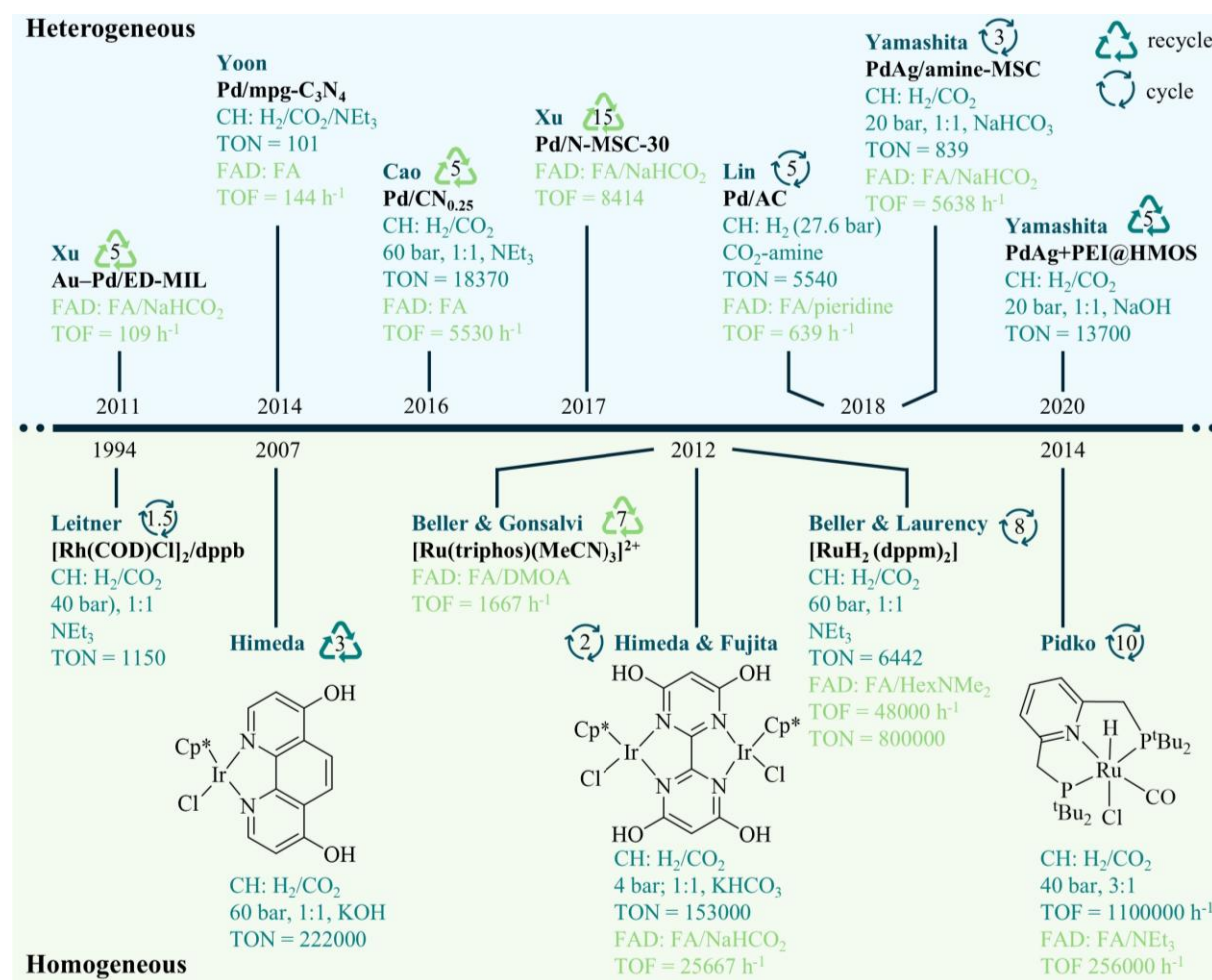
Bimetallic systems also garnered considerable interest for both half-cycles. In 2011, Xu's group introduced bimetallic Au-Pd catalysts immobilized on MOFs for FAD. Moderate yields, recyclability, and high resilience to CO intoxication were reported (Scheme 1).^[86]

Yamashita and colleagues presented highly dispersed PdAg NPs supported on phenylamine-functionalized mesoporous carbon (MSC) in 2018. This catalyst exhibits good activity in CH (TON = 839) and FAD ($\text{TOF} = 5638 \text{ h}^{-1}$), and can perform at least three cycles (Scheme 1). Experimental and theoretical studies have shown that the cooperative action of the basic phenylamine groups near the active PdAg NPs is essential for their catalytic activities.^[87] The same group further developed their catalyst system. In 2020, they published a catalyst based on PdAg NPs and polyethyleneimine (PEI), confined in hollow mesoporous organosilica spheres (HMOSs) for CO_2 hydrogenation. High formate yields were detected (TON = 2700 for 22 h, TON = 13700 for 110 h) under mild reaction conditions (20 bar, 100 °C). Thanks to its robust design, the catalyst was reusable over five cycles, maintaining high activity due to the protective effect and alkali-tolerant properties of HMOSs (Scheme 1).^[88]

Homogeneous Catalyst Systems: Formic Acid/ CO_2 Cycle

Several complexes of the noble metals ruthenium, iridium, and rhodium have shown excellent catalytic activity for CH and FAD.^[54] The first report dates to the 1960s, when the group led by Coffey investigated various precious metal complexes bearing mono- and chelating phosphine ligands for their capability of FAD. Initial gas release rates of up to $80 \text{ mol}(\text{H}_2 + \text{CO}_2)/\text{L} \cdot \text{h}$ ($\text{TOF} \approx 8900 \text{ h}^{-1}$) were attained with an $[\text{IrH}_3(\text{PPh}_3)_3]$ catalyst in refluxing acetic acid (118 °C).^[89] Inoue and co-workers continued with testing a series of precious metal complexes in the presence of alcohols and amines as co-catalysts for CH. The highest activity (TON = 87) was detected for $[\text{RuH}_2(\text{PPh}_3)_4]$ in benzene/water with NEt_3 (50 bar H_2/CO_2 1:1; rt).^[90]

Scheme 1. Timeline of heterogeneous (top) and homogeneous (bottom) catalysts for the formic acid/CO₂ cycle with a focus on (re)cyclability. CH stands for CO₂ hydrogenation to FA, and FAD for the dehydrogenation of FA.



Twenty years later, the group of Leitner achieved record activities for CH (TON = 1150) utilizing [Rh(COD)Cl]₂/dppb (1,1-bis(diphenylphosphino)butane) in DMSO/NEt₃ (40 bar H₂/CO₂ 1:1; 25 °C).^[91] In 1994, they successfully performed 1.5 cycles using the catalyst above (Scheme 1).^[92] CH results were improved with a screening of a series of phosphine ligands in combination with [Rh(COD)(μ-Cl)₂]. Applying 1,1-bis-(diphenylphosphino)methane (dppm), concentrations of FA of up to 2.58 M were achieved.^[93]

Starting from 2008, FAD as a liquid organic hydrogen carrier was intensively studied.^[94,95] Laurency and colleagues reported the selective decomposition of aqueous FA with [Ru(H₂O)₆](Tos)₂ (toluene-4-sulfonate). In a continuous setup, a TON of over 40000 was reached (sodium formate; 120 °C, 90 h, no CO).^[94,96]

Beller and co-workers have studied the dehydrogenation of FA-amine adducts. In general, amines have a beneficial effect as co-catalysts on the reaction rate. High catalytic activities were reported for [RuCl₂(PPh₃)₃] (TOF = 445 h⁻¹)^[95] and [RuCl₂(C₆H₆)₂]/dppe (1,1-bis(diphenylphosphino)ethane; TOF = 460 h⁻¹)^[97] in DMF (40 °C). Initially, FA/NEt₃ (5:2) mixtures were used.^[98] Replacing the volatile base with N,N-dimethylhexylamine improved performances (TOF = 900 h⁻¹, TON = 260000).^[99,100] Later, the groups of Laurency and Beller reported a

rechargeable H₂ battery based on [RuH₂(C₆H₆)₂]/dppe, which was stable for eight cycles (Scheme 1).^[101]

A base-free system was introduced by the group of Puddephatt using Ru₂(μCO)(CO)₄(μ-dppm)₂ (TOF = 500 h⁻¹; acetone, rt).^[102]

The group of Gonsalvi and Beller investigated ruthenium catalysts with the tripodal 1,1-tris(diphenylphosphinomethyl)ethane (triphos). Full conversion in FAD was observed for an 11:10 FA/DMOA (N,N-dimethyloctylamine) mixture with [Ru(κ³-triphos)(MeCN)₃](OTf)₂ (TON = 10000, 6 h). The stability of the catalysts was assessed through recycling, resulting in over eight consecutive runs (TTON = 8000, Scheme 1).^[103]

The Himeda group investigated CH in basic aqueous media using catalysts featuring proton-responsive ligands, allowing for activity tuning and recycling through pH-controlled solubility of the complexes (Scheme 1). The highest activity (TOF = 42000 h⁻¹, TON = 222000) was reported for [Cp*Ir(dhphen)Cl]Cl (60 bar, H₂/CO₂ 1:1; 120 °C; dhphen: 4,7-dihydroxy-1,10-phenanthroline). Recycling of the compound was possible by simple filtration, due to pH-induced precipitation.^[104] Analogue systems were applied for FAD, e.g. [Cp*Ir(dhbp)(H₂O)]SO₄ (TOF = 14000 h⁻¹, 2 M FA, 90 °C; 4,4'-dhbp: dihydroxy-2,2'-bipyridine).^[105] Another modified 2,2'-bipyridine (bpy) Cp*Ir complex generated pressures up to 1750 bar in a closed vessel.^[106] A binuclear iridium complex based on a tetradentate, bridging bipyrimidine ligand with four pH-responsive hydroxyl moieties reached a TOF of 228000 h⁻¹ (90 °C) for FAD.^[107]

Nozaki and co-workers achieved outstanding yields by applying an iridium trihydride PNP pincer catalyst for CH in a 1 M aqueous KOH solution in the presence of THF. The TOF (150000 h⁻¹; 50 bar H₂/CO₂ 1:1; 200 °C) and TON (3500000; 60 bar H₂/CO₂ 1:1; 120 °C) values, respectively represent 1.5-fold and 15-fold improvements to previously reported systems. The coordination of the pincer ligand enhances the stability of the metal center.^[108]

Building on pincer chemistry, the group of Pidko reported a highly efficient ruthenium PNP complex in 2014 for CH. The base influences the acid-to-amine ratio, but not the rate of formate formation. The highest TOF (1100000 h⁻¹) and an AAR (Acid-to-amine ratio) of 1.1 were observed in a DMF/DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) solvent mixture (40 bar H₂/CO₂ 3:1; 120 °C).^[109] The pincer complex also exhibited high yields for CO₂ hydrogenation using FA/NEt₃ (TOF = 256000 h⁻¹, TON = 706500; DMF, 90 °C) without CO contamination. The rate-determining step depends on the nature of the basic additive: applying NEt₃, the cleavage of the C-H bond turn out to be the limiting step. At the same time, with less nucleophilic DBU, H₂ formation becomes rate-limiting.^[109] Using DBU, a total of ten (de)hydrogenation cycles were performed (Scheme 1).^[54,109]

1.5.2. Catalyst Systems for the Formate/Bicarbonate Cycle

Heterogeneous Catalyst Systems: Formate/Bicarbonate Cycle

The first report for the reduction of sodium bicarbonate using supported palladium dates back to the 80s.^[110] In 1986, Sasson suggested reversible hydrogen storage in the formate/bicarbonate system. Applying a catalyst with 10 wt% Pd, they reported potassium bicarbonate conversions up to 27 %. Furthermore, hydrogen release was also possible.^[111,112]

In literature, palladium, stabilized on activated carbon or metal oxides, is mainly used for the formate/bicarbonate cycle. The group of García-Fierro performed a comparative study for the hydrogenation of sodium bicarbonate with various metals (Pd, Ru, Ni, Co and Re) on activated carbon. They demonstrated that the corresponding palladium material not only showed the highest activity but also the best long-term stability.^[113]

A rechargeable hydrogen storage system, directed by palladium nanoparticles based on reduced graphite oxide (rGO), was established by Cao and colleagues (Scheme 2). This catalyst system showed outstanding stability and was used for six consecutive charge/discharge cycles without loss of efficiency ($M = K^+$; 1 wt % Pd/r-GO; charge: 40 bar H_2 , 100 °C; discharge: 80 °C).^[114]

The Lin group investigated the influence of reaction time and salt concentration for 5 wt% Pd/AC. Whilst bicarbonate hydrogenation (BH) was possible at rt ($M = NH_4^+$; 96 % yield; 27.5 bar), higher temperatures were necessary for formate dehydrogenation (FD), leading to nearly 100 % conversion. Increasing the salt concentration to 15 M had a positive effect, raising the TOF to 5061 h^{-1} (Scheme 2).^[115]

The group of Asefa reported in 2017 mesoporous carbon-supported palladium nanoparticles generated from polyaniline and colloidal silica composites (Scheme 2). After pyrolysis and silica removal, ultrasmall nanoparticles were deposited on mesoporous carbon (Pd/PDMC). Activities for FD of up to TOF = 2562 h^{-1} were reported for a 1 M sodium formate solution (80 °C). The reverse reaction was possible, too (TON = 1625).^[116]

Bimetallic catalyst systems have shown synergistic effects. The group of Kawanami investigated different Pd and Au ratios and found that a 1:1 mixture ($Pd_{0.5}Au_{0.5}/PDA-rGO$, Scheme 2) was the most efficient, with enhanced Pd^0 percentage (54 %) and BH yields up to 94 % ($M = K^+$; 50 °C, 16 h). FD reached a TOF of 1630 h^{-1} (80 °C).^[117]

Shishido and co-workers reported that Pd-Au alloys were active in both half-cycles, with $Au_{10}Pd_1/AC$ best for BH ($M = NH_4^+$; TOF = 5820 h^{-1}) and Au_1Pd_1/AC for FD (TOF = 4200 h^{-1}). Mechanistically, bicarbonate solely adsorbs on Au, while dihydrogen is adsorbed dissociatively on both metals. The nucleophilic hydrogen atom on Pd adds to the carbonyl group adsorbed on Au, releasing formate from the surface. The hydrogen on Au adds to the hydroxyl group to produce water. Au in the bimetallic alloy becomes more electron-deficient, resulting

in an increased Lewis acidity. This allows Au atoms to more strongly withdraw electrons from the carbonyl oxygen in adsorbed bicarbonate, facilitating nucleophilic addition of hydrogens from electron-rich Pd.^[118]

Building on the research above, Yamashita and co-workers investigated various Pd-M alloys on rutile TiO₂ (M: Cu, Ni, Fe, Au, Co, and Ag). Again, both charge and discharge reactions were tested, and different optimal catalysts were identified for the half-cycles. Alloying with Au, Ni, and Ag enhanced the activity in BH (TOF $\approx$ 2750 h⁻¹), while Pd-Ag improved the activity in CH (TON $\approx$ 700). Activity and stability were increased by a TiO_x shell (Ag@Pd@TiO_x/TiO₂). The optimized catalyst achieved a TON of 820 (M = Na⁺; 30 bar H₂, 2 h, 80 °C, [Scheme 2](#)) for CH aqueous solution. Additionally, dehydrogenation was possible, too (TOF = 6499 h⁻¹; 75 °C). The shell modification increased the Pd-TiO₂ interface area, enhancing catalytic activity and reducing CO adsorption. X-ray photoelectron spectroscopy (XPS) analysis revealed electron-rich Pd species – analogue to the Pd-Au alloys from above – generated by the TiO_x shell. The high activity of the catalyst was attributed to electronic effects from Pd-Ag and electronic/geometric effects from the Pd-TiO₂ interface.^[119]

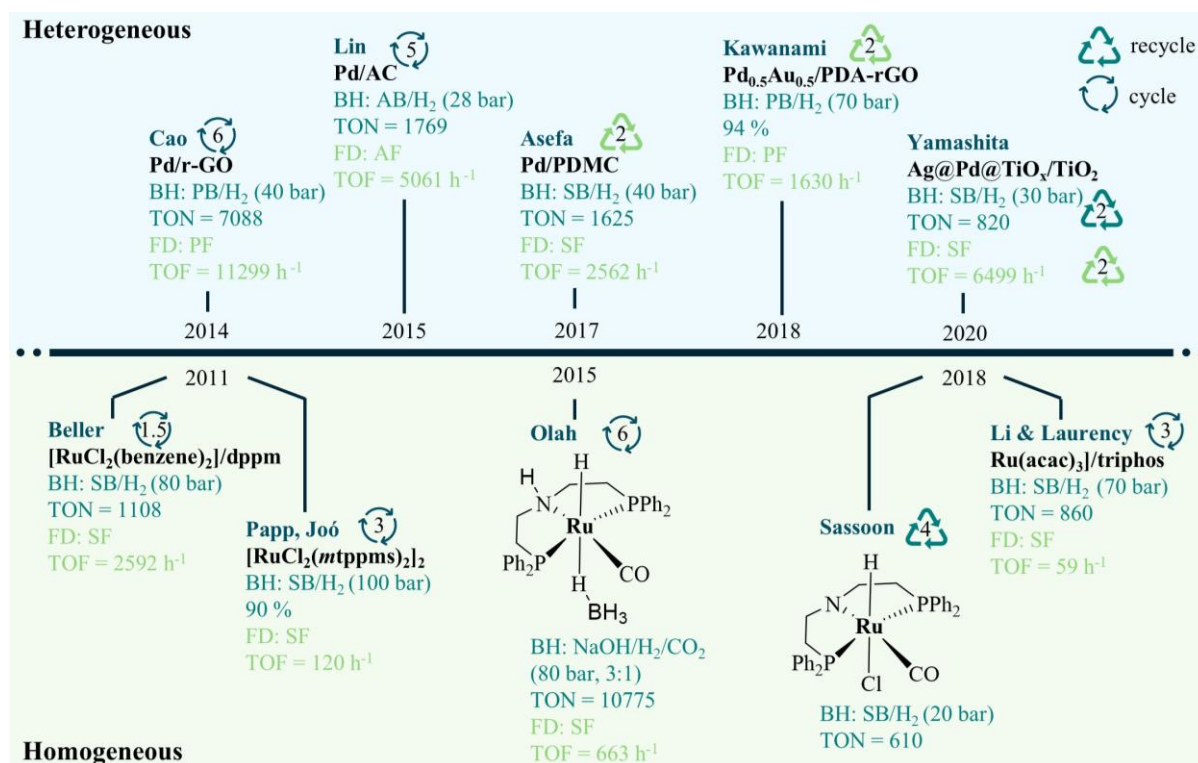
The group of Ji investigated co-doping of carbon materials with nitrogen and a second heteroatom (B, S, or P) and found that 4.7 wt% Pd/N,P-C have better efficiency (M = K⁺ (4 M), TOF = 3246 h⁻¹, 80 °C, 2 h) than single-doped carbon materials. They reasoned that the electronic characteristics and surface polarity changed due to the co-doping, and there could be a synergistic coupling effect between heteroatoms with different electronegativity.^[120]

Homogeneous Catalyst Systems: Formate/Bicarbonate Cycle

The first reports on homogeneous catalysis for BH can be found in patents from the 1980s.^[121] The earliest publications date back to the 2000s and applied ruthenium with mono- and bidentate phosphine ligands (Joó, Laurenczy and Beller),^[122,123] iron with tripodal phosphine ligands (Laurenczy and Beller),^[124] as well as iridium half-sandwich complexes (Himeda).^[125]

The first reversible system was published in 2011 by the Beller group ([Scheme 2](#)). Applying an *in situ* formed catalyst from [RuCl₂(benzene)₂] and dppm, 1.5 consecutive cycles were performed in water-THF/DMF either starting with the hydrogenation of sodium bicarbonate (single experiment: TON = 1108, 96 % yield, 70 °C, 20 h) or the dehydrogenation of set formate (single experiment: TOF = 2592 h⁻¹, TON = 2000, 60 °C, 3 h).^[126] In the same year, Papp, Joó and colleagues published the first reversible system (three consecutive cycles, [Scheme 2](#)) free of organic solvents using [RuCl₂(mtppps)₂]₂ (M = Na; BH: 90 % yield, 83 °C; FD: TOF = 120 h⁻¹, 80 °C; mtppps: monosulfonated triphenylphosphine).^[127]

Scheme 2. Timeline of heterogeneous (top) and homogeneous (bottom) catalysts for formate/bicarbonate interconversion with a focus on (re)cyclability. BH stands for bicarbonate hydrogenation and FD for formate dehydrogenation. B stands for bicarbonate and F for formate. The counterions are abbreviated as follows: A: ammonium, P: potassium, S: sodium.



Later, the group of Beller studied Ru-MACHO ({Bis[2-(diphenylphosphino)ethyl]amine}carbonylnchlorohydridoruthenium(II)) for the hydrogenation of sodium bicarbonate in methanol (10 bar H₂, 100 °C), achieving a TON of 1420 after 20 h.^[128] The group of Sasson used the same catalyst in an isopropanol/water mixture and presented four consecutive half-cycles for BH (Scheme 2).^[129] The group led by Olah explored the Ru-MACHO-BH complex for sodium formate dehydrogenation, reaching 100 % of hydrogen yield in dioxane-water (initial TOF = 430 h⁻¹, 70 °C). They also performed CO₂ hydrogenation and formate dehydrogenation with said catalyst for six consecutive cycles (Scheme 2).^[130]

Applying the *in situ* formed pincer catalyst from Ru(acac)₃ (acetylacetonate) and triphos yields > 90 % of potassium formate, as reported by the group of Li. This system was active in both reactions, hydrogenation and dehydrogenation. Three consecutive cycles (discharge, charge) were performed without a significant loss in activity Scheme 2).^[131]

Applying an Ir(I)-*N*-heterocyclic carbene complex as a catalyst, Horváth and Joó presented a hydrogen storage system capable of three cycles using a flow system.^[132,133]

These studies collectively highlight significant progress in the development of efficient and stable catalyst systems for reversible hydrogen storage with a focus on recyclability and reusability.

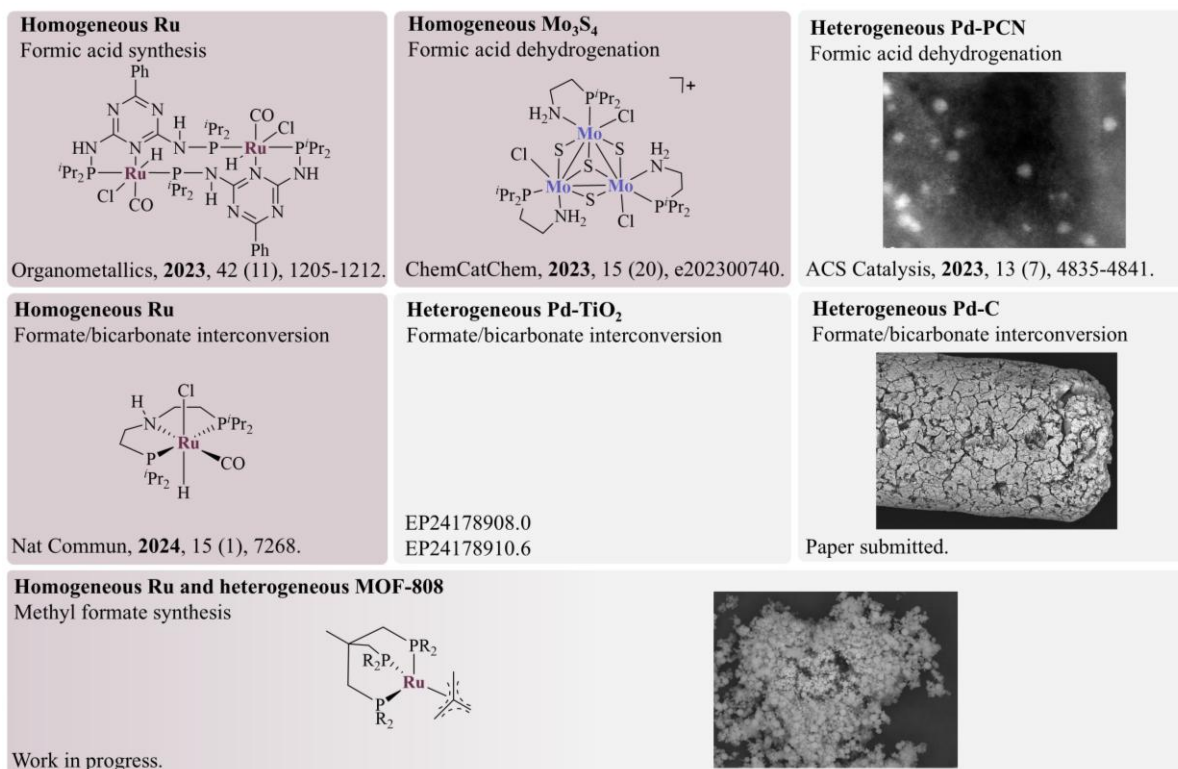
2. Objectives

The transition to a hydrogen-based energy economy requires safe, efficient, and reversible hydrogen storage technologies. Among various approaches, chemical storage using CO₂ and its derivatives as carrier molecules shows promising potential due to their abundance, low toxicity, and ability to achieve carbon neutrality.^[112]

This work aims to develop and evaluate catalytic systems for hydrogen storage and release using three carriers: formic acid, potassium formate, and methyl formate. A combination of homogeneous and heterogeneous catalysts was examined, with a focus on key performance factors such as activity, selectivity, catalyst recyclability, and suitability under industrially relevant conditions. The research spans from fundamental studies on the feasibility of methyl formate as a liquid hydrogen carrier, including direct CO₂ hydrogenation to methyl formate catalyzed by Ru triphos complexes, to the practical implementation of robust hydrogen storage systems. These studies involve long-term investigations using heterogeneous Pd-C pellet catalysts for reversible hydrogen storage in formate.

Beyond gaining mechanistic insights and screening catalysts, selected systems were tested in collaboration with an industrial partner under scalable and application-relevant conditions. This comprehensive approach bridges the gap between academic research and industrial feasibility. An overview of all investigated catalyst-carrier combinations is shown in Scheme 3.

Scheme 3. Investigated catalyst systems and their desired hydrogen storage material.



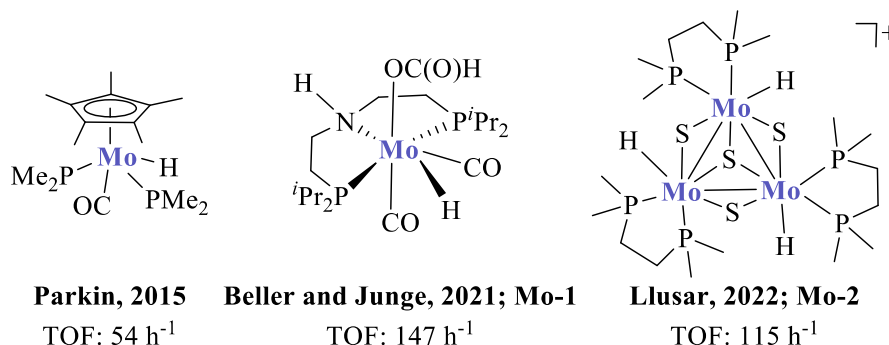
3. Summary of Research Projects

This section highlights the summary of new hydrogen storage systems based on selected catalysts for the carriers FA/CO₂, formate/bicarbonate, and methyl formate/CO₂. Different homogeneous and heterogeneous catalysts will be presented, capable of hydrogenating CO₂/bicarbonate and/or dehydrogenating formic acid/formate.

3.1 Formic Acid Dehydrogenation with Cuboidal PN Molybdenum Sulfide Clusters

Only a few Mo-based catalyst systems for hydrogen storage and release are known. Some heterogeneous systems based on carbides,^[134,135] nitrides,^[136,137] or sulfides^[138,139] have been reported for FAD, but generally lack selectivity. Homogeneous Mo catalysts for selective FAD were reported by Parkin,^[140] and later Beller and Junge (Scheme 4).^[141] However, these catalyze the disproportionation of FA to methanol, with both reaction pathways competing in the absence of a base. In contrast, a molybdenum sulfide cluster published by the group of Llusar^[142] showed high selectivity towards H₂ production under base-free conditions. Inspired by these findings, we set out to identify more Mo₃S₄ cluster complexes active in FAD.

Scheme 4. Literature known homogeneous catalyst systems based on molybdenum for FAD.^[143]

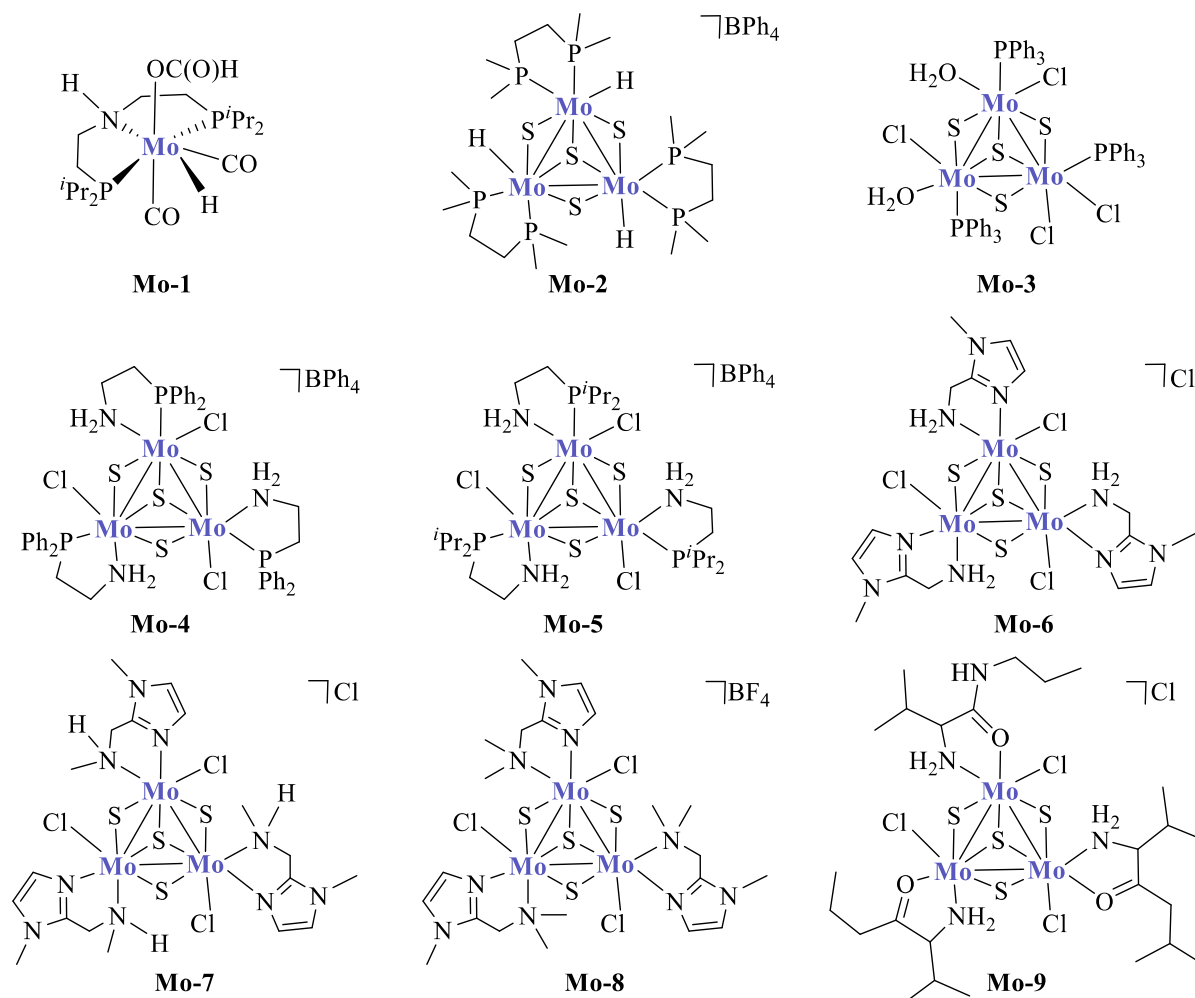


Evaluation of Reaction Conditions: Catalyst Screening for Formic Acid Dehydrogenation

We started our investigation with a broad catalyst screening, summarized in Table 5. The two literature-known molybdenum complexes displayed different behavior under basic conditions (entries 1 and 2). While the PNP complex **Mo-1** was barely active, the activity of the reported cluster hydride **Mo-2** (entry 3) was improved (TOF 116 h⁻¹^[142] vs. 411 h⁻¹). **Mo-3**, a typical cluster precursor, showed little activity in FAD, emphasizing the crucial role of the phosphine ligands. **Mo-4** and **Mo-5** (entries 4 and 5) resulted in similar TON values, **Mo-5** presented the highest TOF and full conversion within 7 min. Replacing the phenyl substituent in **Mo-4** with isopropyl (**Mo-5**) increased the catalytic activity. In general, alkyl-substituted phosphine ligands are better σ -donors and thereby increase the electron density at the molybdenum center. Moreover, they are less sterically demanding, which can simplify the coordination of a substrate

to the metal center. ESI-MS of the reaction solution with **Mo-5** detected only the presence of the cationic species. No decomposition was observed, emphasizing the stability of the cluster compound.

Table 5. Catalyst screening for formic acid dehydrogenation with homogeneous molybdenum complexes.^[143]



Entry	Catalyst	Yield [%]	TON	TOF _{10min}
1	Mo-1	2	2	18
2	Mo-2	99	98	411
3	Mo-3	25	25	55
4	Mo-4	98	96	272
5	Mo-5	>99	98	589
6	Mo-6	85	84	117
7	Mo-7	10	10	18
8	Mo-8	4	4	18
9	Mo-9	75	75	
10 ^[a]	Mo-5	0	-	-

Reaction conditions: 1.0 mmol FA, 0.40 mmol Et₃N, 10 μmol catalyst, 1.5 mL PC, 120 °C, 1 h. Gas evolution was monitored with manual burettes, corrected by the blank volume and purity was analyzed by gas chromatography (GC); No CO was detected (limit < 10 ppm). Experiments were performed at least twice (except entry 2). [a] No base.

In the absence of a base, zero conversion was observed, stressing the essential role of the base (entry 10). The proposed mechanism for FAD with bifunctional ligands proceeds *via* a formate intermediate. This is why the addition of a base is important for starting a catalytic cycle.^[144] Clusters **Mo-6**, **Mo-7** and **Mo-8** (entries 6-8) are imidazolyl amino clusters with gradually methylated NH₂-groups. Their catalytic activity decreased in the order of their degree of methylation, **Mo-6** (TON = 84) > **Mo-7** (TON = 10) > **Mo-8** (TON = 4). This trend reflects the loss of hydrogen bonding ability caused by methylation, which likely impairs substrate activation or intermediate stabilization.

Evaluation of Reaction Conditions: Optimization for Mo₃S₄ Cluster **Mo-5**

Having identified the most appropriate cluster, we proceeded to optimize the reaction conditions (Table 6). Varying the FA concentration from 1.0-10 mmol (entries 1-3) stepwise increased the TON from 98 to 834, while the TOF decreased. This is likely due to a pH increase during the reaction. Lowering FA concentration while keeping the absolute amount constant (entry 4) significantly improved the catalytic activity. Decreasing the catalyst loading by half (entry 5) increased the TON slightly, doubling (entry 6) caused only a two-fold increase of the TOF.

Testing various solvents (entries 7-9) confirmed PC as the most suitable one. Furthermore, decomposition of DMSO was observed under the chosen reaction conditions.

Table 6. Influence of substrate and catalyst amount, as well as different solvents on the catalytic activity of **Mo-5**.

Entry	FA [mmol]	NEt ₃ [mmol]	Catalyst [μmol]	Solvent [mL]	Yield [%]	TON	TOF _{10min} [h ⁻¹]
1	1.0	0.40	10	1.5	> 99	98	1472 ^[a]
2	5.0	2.0	10	1.5	> 99	574	791
3	10	4.0	10	1.5	84	834	288
4	10	4.0	10	5.0	> 99	921	546
5	10	4.0	5.0	5.0	79	1247	368
6	10	4.0	20	5.0	> 99	493	1251
7	10	4.0	10	5.0 ^[b]	0	-	-
8	10	4.0	10	5.0 ^[c]	62	622	168
9	10	4.0	10	5.0 ^[d]	75	751	1118

Reaction conditions: FA, NEt₃, **Mo-5**, PC, 120 °C, 4 h. Gas evolution was monitored with manual burettes, corrected by the blank volume and purity was analyzed by GC; CO content was below the detection limit. Experiments were performed at least twice. [a] TOF calculated after 4 min. [b] THF. [c] Toluene. [d] DMSO.

Following, we analyzed the influence of the temperature using the conditions from entry 4 (Table 6). As expected, lowering the temperature from 120 °C to 105 °C and 90 °C subsequently decreased the catalytic activity (Figure 6, left). Applying 120 °C we tested three different amine bases, NEt₃, DMOA and NMeBu₂ (Figure 6, middle). Replacing NEt₃ with DMOA more than tripled the TOF_{10min}. Finally, we varied the ratio of formic acid to DMOA

(Figure 6, right). Lowering the initial ratio to 5:1 decreased activity, while increasing it to 11:10 resulted in the highest TOF_{10min} (4254 h⁻¹) observed.

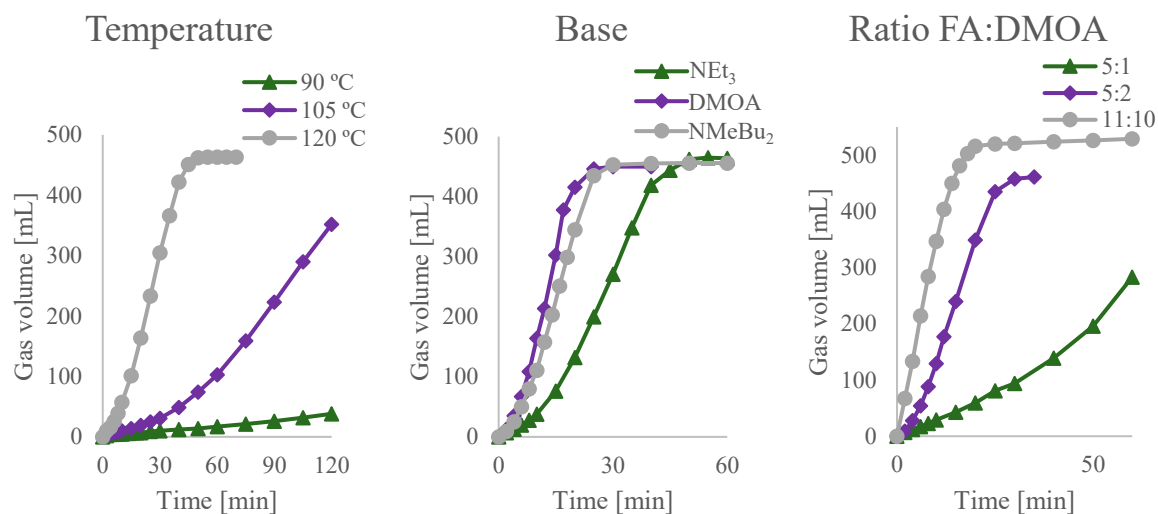


Figure 6. Variation of the temperature (left), base (middle) and ratio of FA to DMOA (right). Reaction conditions: 10 mmol FA, 4.0 mmol base, 10 μ mol **Mo-5**, 5.0 mL PC, 120 °C, 4 h. Gas evolution was monitored with manual burettes, corrected by the blank volume and purity was analyzed by GC; CO content was below the detection limit. Experiments were performed at least twice.^[143]

With the optimized reaction conditions established, we evaluated the catalyst's stability. Using 10 mmol formic acid and 4.0 mmol DMOA (11:10) in 5.0 mL PC, two consecutive restart of FAD were possible, resulting in an overall gas volume of 1.4 L (Figure 7). During a third restart, increased loss of activity was noticeable.

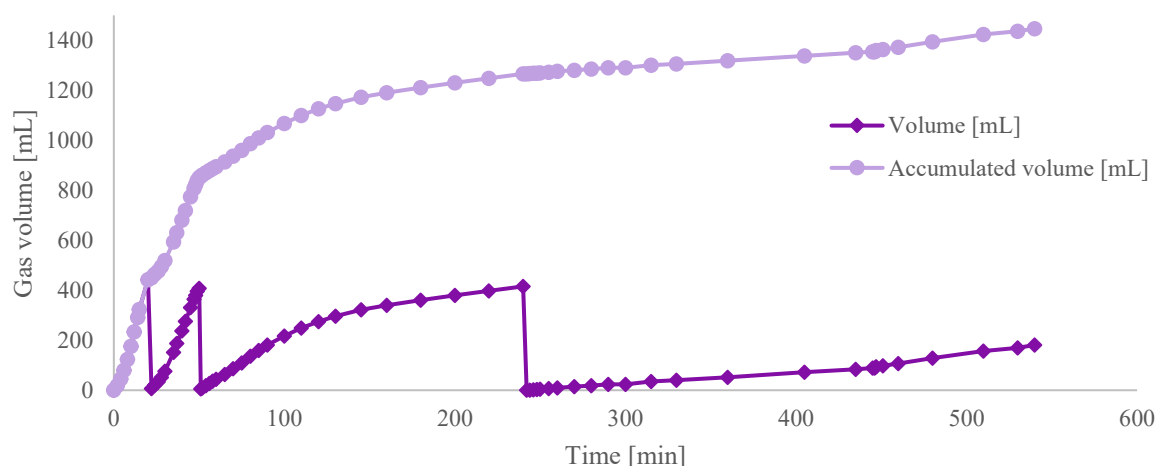


Figure 7. Restart experiment with **Mo-5**. Individual experiments and overall gas evolution. Reaction conditions: 10 mmol FA, 4.0 mmol DMOA, 10 μ mol **Mo-5**, 5.0 mL PC, 120 °C. Gas evolution was monitored with manual burettes, corrected by the blank volume. Purity was analyzed by GC. The CO content was below the detection limit.^[143]

Mechanistic Investigation: Formation of the Active Species and Hydrogen Release

The catalytic cycle starts with the activation of the pre-catalyst **Mo-5**. NMR studies (Figure 8) indicate that the chloride ligands are subsequently replaced with formate ligands, forming active

species $[\text{Mo}_3\text{S}_4\text{Cl}_{3-x}(\text{OCOH})_x(\text{ed}^i\text{PrP})_3]^+$ (with $x = 1-3$; see Figure 8). From these intermediates, β -hydride elimination occurs generates a hydridic cluster and releases CO_2 . The resulting metal hydride is protonated by a molecule of formic acid, leading to the release of molecular hydrogen. At the same time, the formate-substituted cluster is regenerated, thereby completing the catalytic cycle. In this mechanism, formic acid acts both as a hydrogen donor and as a proton source. The mechanism was further investigated with computational and ESI-MS methods.^[143]

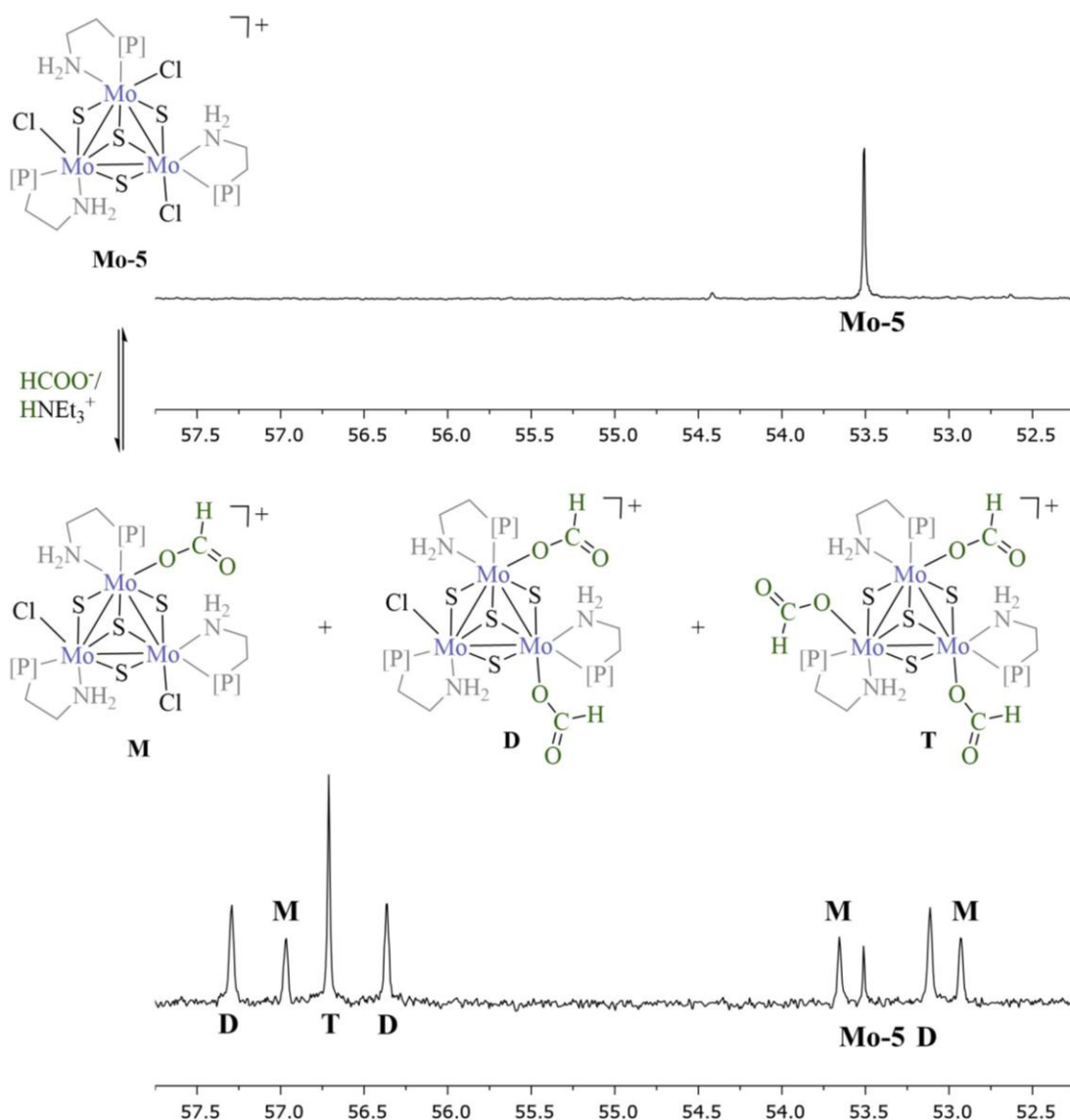


Figure 8. NMR study of **Mo-5** $[\text{Mo}_3\text{S}_4\text{Cl}_{3-x}(\text{OCOH})_x(\text{ed}^i\text{PrP})_3]^+$ before (top) and after the addition of FA (bottom). Formate-substituted complexes are represented by **M** (mono: $x = 1$), **D** (di: $x = 2$) and **T** (tri: $x = 3$).^[143]

3.2 Formic Acid Dehydrogenation with Palladium on Polymeric Carbon Nitrides

Heterogeneous catalysts are particularly attractive for industrial applications, due to their easy separation and recyclability. Palladium supported on carbon is widely used for FAD. Modified supports like nitrogen-doped carbon can be used for modulating the electronic properties, e.g., altering the Pd particle size or tuning the chemical environment.^[145–147] Polymeric carbon nitride (PCN) with its high nitrogen content ($\leq 60\%$), stabilizes metal nanoparticles and single centers and enhances the reactivity of the metal sites through Mott-Schottky heterojunctions that facilitate charge transfer. Additionally, the basic nitrogen sites are believed to promote hydrogen production from FA, rendering the addition of a base unnecessary.^[148,149] This study explores the synthesis of novel PCN-supported palladium nanoparticles for additive-free FAD.

Synthesis of Heterogeneous Catalyst: PCN-Supported Palladium Nanoparticles

The PCN support was prepared by calcining a preformed complex between melanin and cyanuric acid. Wet impregnation with PdCl₂ in 0.5 M HCl was followed by 1 h of sonication and 6 h stirring at rt. After solvent evaporation, and drying at 85 °C, the material was annealed (**Pd-PCN-1**; 7.56 wt% Pd) and subsequently reduced at different temperatures (350 °C: **Pd-PCN-2**, 7.92 wt% Pd; 500 °C: **Pd-PCN-3**, 8.42 wt% Pd).

Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) revealed the coexistence of single centers and particles in **Pd-PCN-1** and **Pd-PCN-2**, while **Pd-PCN-3** exclusively showed particles with an average size of 6 nm. Treatment at higher temperatures facilitates migration and agglomeration of Pd atoms leading to a higher number of Pd particles and the disappearance of single atoms in **Pd-PCN-3**.

XPS revealed the presence of C, N, O, and Pd in all samples, confirming a successful loading. While **Pd-PCN-1** only presents Pd²⁺ and Pd⁴⁺, **Pd-PCN-2** is still highly oxidized with little amount of Pd⁰. **Pd-PCN-3** mainly presents Pd⁰. The quantification of the average Pd charge follows the order of **Pd-PCN-1** (3.4) > **Pd-PCN-2** (2.6) > **Pd-PCN-3** (1.1), highlighting the stronger interaction of supported Pd with carbon nitride.

Catalytic Screening of Pd-PCN: Formic Acid Dehydrogenation

Table 7. Initial screening with Pd-PCN catalyst and a commercially available benchmark catalyst.

Entry	Catalyst	Pd [wt%]	H _{2(max)} [mL/g _{cath}]	H _{2(max)} [mL/g _{PdH}]
1	Pd/C	5.00	8.90	369
2	Pd-PCN-1	7.56	284	3775
3	Pd-PCN-2	7.92	766	9665
4	Pd-PCN-3	8.42	183	2175

Reaction conditions: 10 mmol FA, 10 mL PC and 40 μmol Pd, 110 °C.

Initial screening of the three catalysts was performed in PC at 110 °C (Table 7). All novel Pd-PCN catalysts outperform a benchmark catalyst from STREM (entry 1), with **Pd-PCN-2** showing the highest activity based on gas release.

The reaction conditions were optimized for **Pd-PCN-2** (Table 8). Among different solvents (entries 1-4), toluene has the highest gas release rate. Increasing the temperature from 90 °C to 120 °C (entries 5-8), resulted in a linear increase in the catalysts' performance (629 to 3844 mL/g_{cat}·h), while results for 130 °C were similar to 120 °C. Varying the acid amount showed an optimum for 10 mmol FA (entries 9-11). The influence of a basic additive was also investigated (entries 12-17). Sodium formate, unlike *p*-toluenesulfonic acid increased gas release rate, with the highest activity observed for 2.0 mmol sodium formate. No hydrogen evolution was observed for sodium formate without the presence of FA.

Table 8. Optimization of the reaction conditions based on **Pd-PCN-2**.

Entry	Solvent	FA [mmol]	Additive	T [°C]	H ₂ (max) [mL/g _{cat} ·h]	H ₂ (max) [mL/g _{pd} ·h]
1	Toluene	10	-	110	2068	26090
2	H ₂ O	10	-	110	1161	14655
3	Triglyme	10	-	110	1175	14830
4	<i>p</i> -Xylene	10	-	110	888	11200
5	Toluene	10	-	90	629	7940
6	Toluene	10	-	100	1398	17636
7	Toluene	10	-	120	3844	48485
8	Toluene	10	-	130	4103	51774
9	Toluene	2.5	-	120	3550	44799
10	Toluene	5.0	-	120	3557	44887
11	Toluene	20	-	120	1702	21473
12	Toluene	10	NaHCO ₂ (5 mol%)	120	7171	85463
13	Toluene	10	<i>p</i> -TsOH (5 mol%)	120	312	3935
14	Toluene	10	NaHCO ₂ (10 mol%)	120	8924	112609
15	Toluene	10	NaHCO ₂ (20 mol%)	120	14582	183996
16	Toluene	10	NaHCO ₂ (30 mol%)	120	9094	114757
17	Toluene	10	NaHCO ₂ (50 mol%)	120	8350	105362

Reaction conditions: 10 mmol FA and 50 mg **Pd-PCN-2** (corresponding to 40 μmol Pd), 10 mL solvent.

Combining all optimized parameters, we investigated the long-term stability of the catalyst in a continuous dosage mode, which proved a robust catalyst performance up to 350 h without noticeable deactivation. Finally, an overall TTON of 41395 was reached, which is significantly better than previously reported Pd-based heterogeneous systems. Analysis of the used catalyst with HAADF-STEM confirmed the preservation of the PCN morphology and the supported Pd nanoparticles, although a slight increase of the average particle size was observed (from ca. 2.5 to 3.0 nm).

3.3 Formate/Bicarbonate Interconversion with Ru Pincer Catalysts

The outstanding safety parameters of the formate/bicarbonate system motivated us to identify a unified hydrogen and energy storage using the same catalyst and solvent for both half-cycles - the hydrogenation of the unloaded carrier and the dehydrogenation of the loaded carrier. Homogeneous iridium and ruthenium complexes based on phosphine or pincer ligands have been proven to be efficient for this hydrogen storage system. To identify one optimal catalyst and solvent system, both half-cycles were investigated separately.

First, the dehydrogenation of different alkali formates was evaluated (Table 9). Based on our recent results,^[126] we utilized the *in situ* system $[\text{RuCl}_2(\text{benzene})]_2/\text{dppe}$. The formate salts of lithium (entry 1) and sodium (entry 2) presented the highest hydrogen yields. While rubidium (entry 4) and cesium (entry 5) performed well, they are cost-prohibitive. Considering molar solubility,^[72] H_2 purity, and price, potassium (entry 3) emerged as the ideal counterion.

Table 9. Effect of different cations on the dehydrogenation of formate.

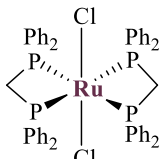
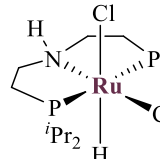
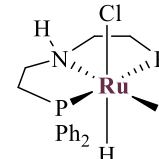
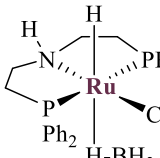
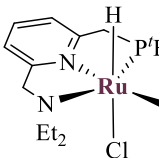
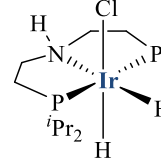
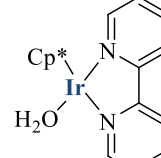
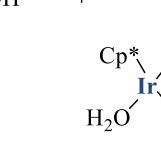
Entry	M ⁺	H ₂ [%]	CO ₂ [%]	Yield [%]	TON
1	Li ⁺	65	35	96	3820
2	Na ⁺	92	8	98	3920
3	K ⁺	99.5	0.5	45	1780
4	Rb ⁺	90	10	58	2320
5	Cs ⁺	97	3	53	2120

Reaction conditions: 20 mmol MHCO_2 , 5.0/30 μmol $[\text{RuCl}_2(\text{benzene})]_2/\text{dppe}$, DMF/ H_2O (20/5.0 mL), 60 °C, 6 h. Gas evolution was monitored with manual burettes, corrected by the blank volume and purity was analyzed by GC. No CO was detected (limit < 10 ppm). All experiments were performed at least twice; average values are shown (St. Dev. < 10 %).

Evaluation of the Half-Cycle: Dehydrogenation of Potassium Formate

We initiated the optimization of the reaction conditions for FD by conducting a catalyst screening (Table 10). *In situ* systems based on Ru (entries 1-3) showed low performance (yield < 15 %). Preformed catalysts performed better: **Ru-4** exhibited a TON of 2180 (entry 4), but ruthenium pincer complexes showed higher activity (entries 5-8). The catalysts Ru- $\text{P}^i\text{PrN}(\text{H})\text{P}^i\text{Pr}$ (**Ru-5**), Ru-MACHO (**Ru-6**), Ru-MACHO-BH (**Ru-7**) and Milstein's Ru-catalyst (**Ru-8**) reached TONs up to 7110 and H_2 yields up to 63 % with a negligible CO_2 release (≤ 0.5 %). Among iridium complexes, **Ir-1** showed promising results (entry 9, 69 % H_2 yield, TON 7790), the water-soluble Ir-Cp* complexes **Ir-2** and **Ir-3**, which are known to perform well in FAD, showed no activity under these basic conditions (entries 10-11).

Table 10. Dehydrogenation of potassium formate with various catalysts.^[150]

$[\text{RuCl}_2(\text{benzene})]_2/\text{dppe}$ Ru-1 $[\text{RuCl}_2(\text{benzene})]_2/\text{dppm}$ Ru-2 $\text{RuCl}_3 \cdot x\text{H}_2\text{O}/\text{tppts}$ Ru-3						
  						
    						
Entry	Catalyst	H ₂ [%]	CO ₂ [%]	Yield [%]	TON	H _{2(max)} [mL/h]
1	Ru-1	99	1	6	1150	30
2	Ru-2	99	1	14	1580	80
3	Ru-3	99	1	<1	70	4
4	Ru-4	99	1	19	2180	90
5	Ru-5	99.6	0.4	63	7110	330
6	Ru-6	99.5	0.5	51	5770	500
7	Ru-7	99.6	0.4	51	5760	420
8	Ru-8	99.5	0.5	3	350	18
9	Ir-1	99.5	0.5	69	7790	3600
10	Ir-2	-	-	0	-	-
11	Ir-3	-	-	0	-	-

Reaction conditions: 113 mmol KHCO₂, 10 μmol catalyst, DMF/H₂O (20/5.0 mL), 60 °C, 6 h. Gas evolution was monitored with manual burettes, corrected by the blank volume and purity was analyzed by GC. No CO was detected (limit < 10 ppm). All experiments were performed at least twice; average values are shown (St. Dev. < 10 %).

Ru-5 was chosen for further optimizations (Table 11). Increasing reaction time afforded almost full conversion (entry 1, TON 11260) without an observable rise in the CO₂ content. Increasing the substrate amount (entry 2) and temperature (entries 3 and 4) further improved the TONs, reaching up to 27470. The poor yield in pure water (entry 5) highlights the necessity of an organic co-solvent to solubilize the homogeneous catalyst. Among the co-solvents tested (entries 6-9), DMF gave the highest yields but was unstable under hydrogenation conditions. Sulfolane and triglyme exhibited acceptable activity, too. Continuing, we analyzed the optimal triglyme/H₂O ratio. Subsequent increase of the water amount (entries 9-14) revealed the highest TON for 10 mL triglyme/15 mL water (entry 13, TON 11761, 88 % H₂), but an optimal gas purity for 15 mL triglyme/10 mL water (entry 10, TON 8342, 92 % H₂). Extending reaction time achieved comparable results to DMF/H₂O (entry 11, TON 24475).

Table 11. Variation of the reaction conditions for the dehydrogenation of potassium formate with **Ru-5**.

Entry	Solvent/H ₂ O [x/y mL]	Formate [mmol]	T [°C]	Time [h]	H ₂ [%]	CO ₂ [%]	Yield [%]	TON	H _{2(max)} [mL/h]
1	DMF/H ₂ O (20/5.0)	113	60	13	99.7	0.3	99	11260	400
2	DMF/H ₂ O (20/5.0)	275	60	13	99.6	0.4	62	17390	600
3	DMF/H ₂ O (20/5.0)	113	90	6	98	2	> 99	11630	4650
4	DMF/H ₂ O (20/5.0)	275	90	6	96	4	99	27470	4800
5	H ₂ O (25)	275	90	6	87	13	12	1210	70
6	Dioxane/H ₂ O (20/5.0)	275	90	6	84	16	10	2710	600
7	2-MeTHF/H ₂ O (20/5.0)	275	90	6	78	22	4	1040	300
8	Sulfolane/H ₂ O (20/5.0)	275	90	6	94	6	89	24610	2100
9	Triglyme/H ₂ O (20/5.0)	275	90	6	91	9	21	5670	500
10	Triglyme/H ₂ O (15/10)	275	90	6	92	8	30	8342	500
11	Triglyme/H ₂ O (15/10)	275	90	50	86	14	89	24475	560
12	Triglyme/H ₂ O (12.5/12.5)	275	90	6	89	11	32	8827	500
13	Triglyme/H ₂ O (10/15)	275	90	6	88	12	43	11761	500
14	Triglyme/H ₂ O (5.0/20)	275	90	6	84	16	38	10341	600

Reaction conditions: 10.0 μ mol **Ru-5**. Gas evolution was monitored with manual burettes, corrected by the blank volume and purity was analyzed by GC. No CO was detected (limit < 10 ppm). All experiments were performed at least twice; average values are shown (St. Dev. < 10 %).

Long-term stability of the system was demonstrated for the dehydrogenation of potassium formate (PF) over 113 h on a 3.00 mol scale with only 3.3 ppm catalyst **Ru-5**, using triglyme/H₂O (150 mL/100 mL). Over 55.0 L of gas was released, corresponding to a TON of 210000 and a yield of 70 % (Figure 9). The catalyst remained active and full conversion can be achieved by elongation of the reaction time. The H₂ purity remained high (94 %) after the long reaction time and no CO was detected.

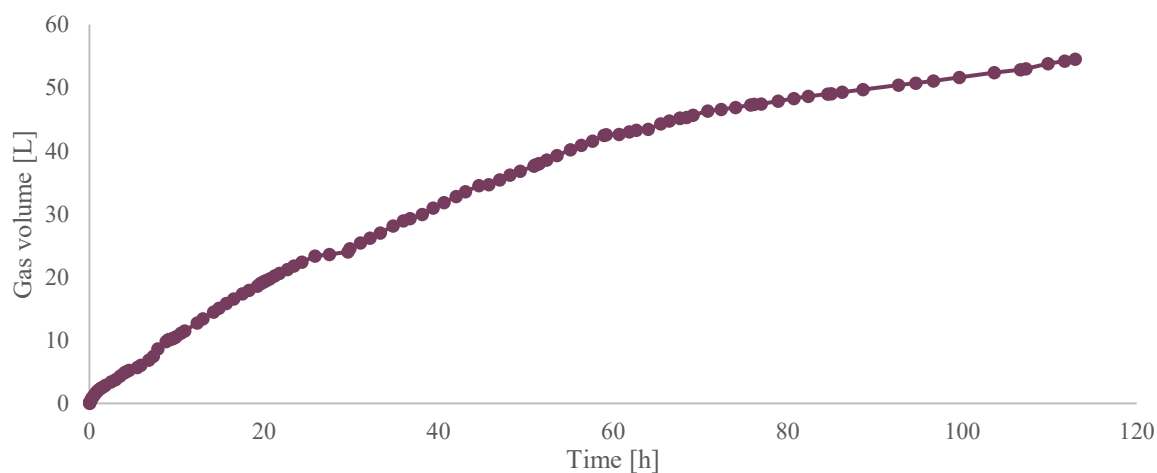


Figure 9. Long-term stability of the energy storage system. Reaction conditions: 3.00 mol KHCO₂, 10.0 μ mol **Ru-5**, 150 mL triglyme, 100 mL H₂O, 90 °C, 113 h. Gas evolution was monitored with manual burettes, corrected by the blank volume. Purity was analyzed by GC. No CO was detected (limit < 10 ppm).^[150]

Evaluation of the Half-Cycle: Hydrogenation of Potassium Bicarbonate

BH was investigated starting with a catalyst screening (Table 12) using selected catalysts from the previous FD screening. From the tested ruthenium and iridium pincer complexes (entry 1-4), Ru-PⁱPrN(H)PⁱPr (**Ru-5**) show the highest TON (990) in BH.

Partial decomposition *via* reductive cleavage of the amide^[151] was detected for DMF, so triglyme was selected as a more suitable co-solvent (entry 5). Optimizing the solvent ratio (entries 5-9) revealed a clear optimum for 15 mL/10 mL (triglyme/H₂O) with a yield of 74 % (entry 9, TON 9650). Finally, varying the reaction temperature (entries 10 and 11) confirmed 90 °C as the optimum.

Table 12. Hydrogenation of potassium bicarbonate under different reaction conditions.

Entry	Cat.	Solvent/H ₂ O [x/y mL]	T [°C]	Yield [%]	TON
1	Ru-5	DMF/H ₂ O (20/5.0)	90	7	990
2	Ru-6	DMF/H ₂ O (20/5.0)	90	6	810
3	Ru-7	DMF/H ₂ O (20/5.0)	90	7	910
4	Ir-1	DMF/H ₂ O (20/5.0)	90	4	488
5	Ru-5	Triglyme/H ₂ O (20/5.0)	90	4	590
6	Ru-5	Triglyme/H ₂ O (15/10)	90	74	9650
7	Ru-5	Triglyme/H ₂ O (12.5/12.5)	90	63	8040
8	Ru-5	Triglyme/H ₂ O (10/15)	90	66	8410
9	Ru-5	Triglyme/H ₂ O (5.0/20)	90	67	8580
10	Ru-5	Triglyme/H ₂ O (15/10)	75	50	6650
11	Ru-5	Triglyme/H ₂ O (15/10)	60	39	4540

Reaction conditions: 100 mL autoclave, 135 mmol KHCO₃, 10.0 μmol catalyst, 50 bar H₂, 18 h. Yields and TON values were determined by ¹H NMR using DMSO as an internal standard. All experiments were performed at least twice; average values are shown (St. Dev.<10%).

Combination of both Half-Cycles: Demonstration of Hydrogen Storage and Release

The overall storage capacity of a hydrogen battery relies on both performances: FD of the loaded carrier and BH of the unloaded carrier. With **Ru-5** identified as an efficient catalyst for both half-cycles and a stable solvent system at hand, we set out to demonstrate the cyclability of the energy storage system. The individually studied half-cycles were combined using a 100 mL autoclave in the presence of triglyme/H₂O (15 mL/10 mL), KHCO₃ (135 mmol), and **Ru-5** (10.0 μmol). The resulting 40 consecutive cycles are presented in Figure 10. Over six months, nearly 50 L of hydrogen with an average purity of 99.5 % was generated. Less than 10 ppm of carbon monoxide was detected. After a slight drop in activity following the first two cycles, high stability in activity and hydrogen yields was achieved (3rd cycle: 1195 mL; 37th cycle: 1116 mL). In general, the hydrogen yield can be increased by elongating the reaction time (as shown in Table 11). Nevertheless, for our proof of concept, we chose a shorter reaction

time to be able to showcase the long-term stability of the system, demonstrating its potential for practical applications.

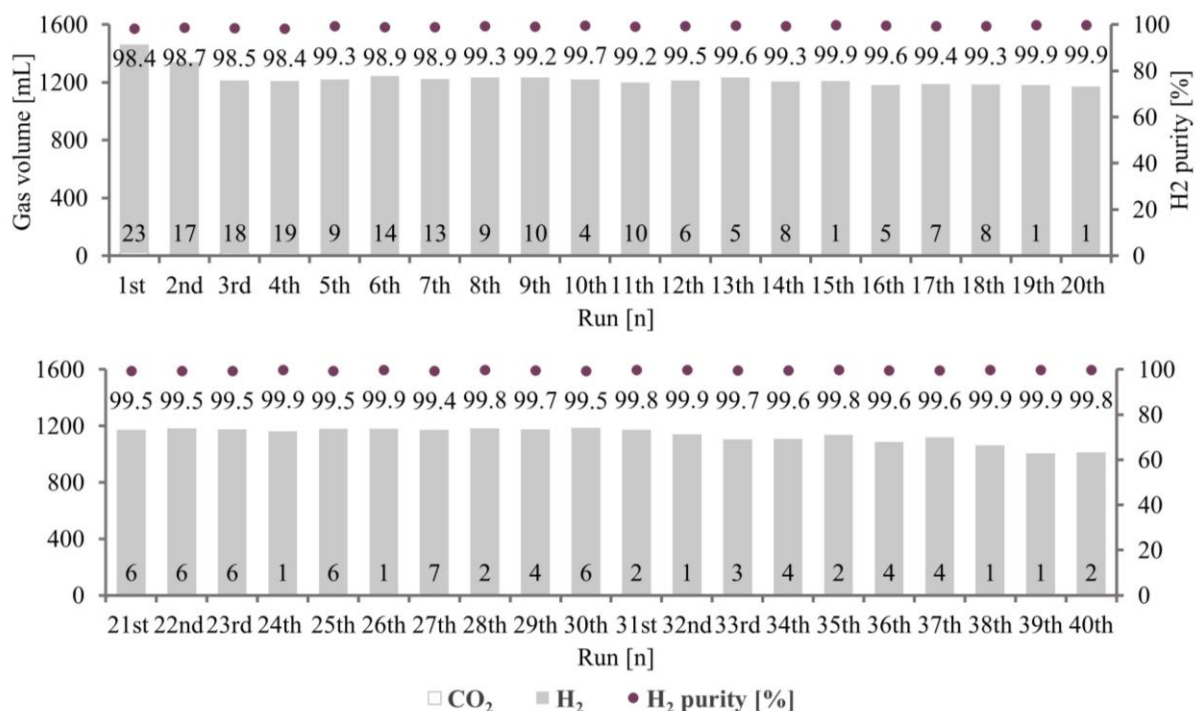


Figure 10. Consecutive hydrogenation and dehydrogenation cycles for the formate/bicarbonate energy storage system using Ru-5. Cycles were started with BH: 135 mmol KHCO₃, 10 μ mol Ru-5, triglyme/water (15 mL/10 mL), 60 bar, 90 $^{\circ}$ C, 18 h. After pressure release, FD was started: 90 $^{\circ}$ C, 12 h. Gas evolution was monitored with manual burettes, corrected by the blank volume. Purity was analyzed by GC. No CO was detected (limit < 10 ppm).^[150]

3.4 Formate/Bicarbonate Interconversion with Pd/C Eggshell Catalysts

Following Chapter 3.3, we sought to identify an even more robust hydrogen storage system applicable for both half-cycles: bicarbonate hydrogenation and formate dehydrogenation. Heterogeneous catalysts are generally less expensive, more stable, and easier to separate from the final product. As elaborated in the introduction, palladium on carbon is a highly active and stable catalyst for the interconversion of formates and bicarbonates. Focusing on industrial applicability, we set out to identify active pellet catalysts for aqueous hydrogen storage.

This chapter focuses on eggshell-type catalysts, in which the metal is concentrated primarily in a thin outer surface layer on the support. This design allows products to diffuse quickly away from active sites, enhancing reaction selectivity. We limited our investigation to palladium as the sole metal and carbon pellet supports and investigated the influence of different synthesis parameters.

Synthesis of Heterogeneous Catalysts: Variation of Carbon Pellets

The Jiang group deposited Pd from Na_2PdCl_4 on carbon powder and reduced it *in situ* in the presence of citric acid. We adapted this for carbon pellets by adding the aqueous precursor to commercial pellets at rt, stirring for 12 h, then filtering, washing, drying, and reduction (5 % H_2 , 200 °C, 2 h). The resulting catalysts and their mass activities for (de)hydrogenation based on the actual metal loading are presented in Table 13.

Table 13. Pd/C catalysts synthesized using different carbon pellet supports and their mass activity.

Entry	Catalyst	Carbon Support	Pd _{theo} [wt%]	Pd _{meas} [wt%]	Mass activity FD [mmol/mg _{Pd} ·h]	Mass activity BH [mmol/mg _{Pd} ·h]
1	Pd-C1	AKROS C1	5.00	3.33	1.04	0.15
2	Pd-C2	COC 4x8	5.00	2.78	1.11	0.10
3	Pd-C3	AFA-4-1050-S	5.00	1.74	0.99	0.09
4	Pd-C4	COL 4x8	5.00	3.94	0.65	0.09
5	Pd-C5	EcoSorb CK1	5.00	3.18	0.72	0.07
6	Pd-C6	WOS 4x8	5.00	3.65	0.72	0.06
7	Pd-C7	EcoSorb CE55	5.00	2.70	1.02	0.05
8	Pd-C8	EcoSorb CE70	5.00	4.91	1.32	0.04
9	Pd-C9	EcoSorb CK4	5.00	2.79	0.19	0.03
10	Pd-C10	COLPA 60	5.00	3.19	0.39	0
11	Pd-C11	AFA-4-dot-S	5.00	0.38	0	0
12	Pd-C12	Dopetac Sulfo 100	5.00	0.11	0	0

BH: 5.40 mmol KHCO_3 , 20.0 mg Pd/C, 1.5 mL H_2O , 30 bar H_2 , 60 °C, 18 h; FD: 250 mmol KHCO_2 , 7.50 mmol K_2CO_3 , 106 mg Pd/C, 25 mL H_2O , 60 °C, 3 h. No CO was detected (limit < 10 ppm). All experiments were performed at least twice; average values are shown (St. Dev. < 10 %).

Metal loading and catalytic activity varied widely, suggesting that some supports stabilize the Pd shell more effectively. Elementary analysis (EA) and X-ray fluorescence spectroscopy

(XRF) showed no clear correlation: carbon content ranged from 72-92 %, and poisons (S, Cl) or promoters (K, Ca) appeared in both high- and low-performance catalysts.

The chemical state of the catalysts was examined *via* XPS, indicating the presence of the Pd⁰ species at 335.2 eV and Pd²⁺ around 336.9 eV in different ratios depending on the carbon support.

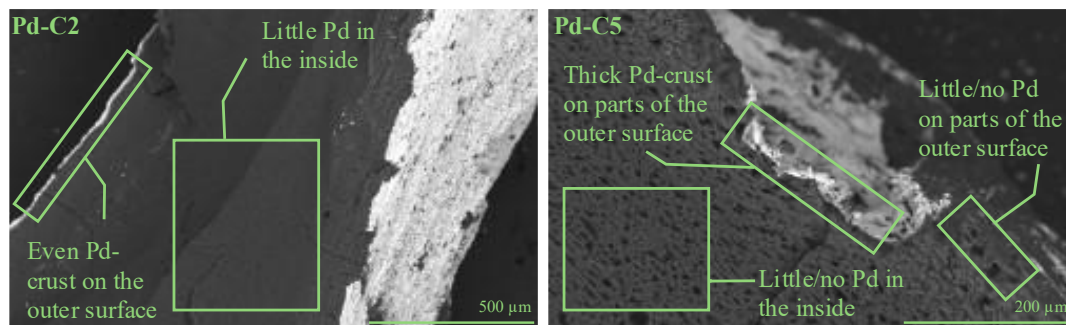


Figure 11. Backscattered electron (BSE) images of the cross-section of a well- (**Pd-C2**; left) and mediocre-performing catalyst (**Pd-C5**; right). Lighter regions on the outer surface correspond to Pd, while dark regions represent carbon.

Scanning electron microscopy (SEM) revealed key differences between well- and mediocre-performing catalysts. The well-performing catalyst **Pd-C2** (2.78 wt% Pd), shows a uniform surface Pd layer and little Pd in the cross-section (Figure 11, left), indicating an eggshell-type catalyst with consistent shell thickness. In contrast, **Pd-C5** (3.18 wt% Pd), a mediocre-performing catalyst, has large uncoated regions and inconsistent Pd thickness (Figure 11, right). These findings highlight the importance of a uniform surface distribution of palladium.

Synthesis of Heterogeneous Catalysts: Optimization for Pellet Support AKROS C1

The carbon support AKROS C1 was chosen for optimizations due to its affinity to Pd and the high performance of the resulting catalyst. Catalytic activities for selected optimization steps are shown in Figure 12. Heat pretreatment of the impregnated carbon support under argon or oxygen (Plot A) did not significantly affect the (de)hydrogenation activity, but it improved stability, as shown by ICP analysis of fresh and used catalysts. For the reduction temperature, 200 °C was optimal (Plot B) with reduction time having little effect (Plot C). Impregnation at elevated temperature results in lower mass activities normalized to Pd loading but an increased actual metal loading (3.23 wt% to 3.52 wt%, Plot D).

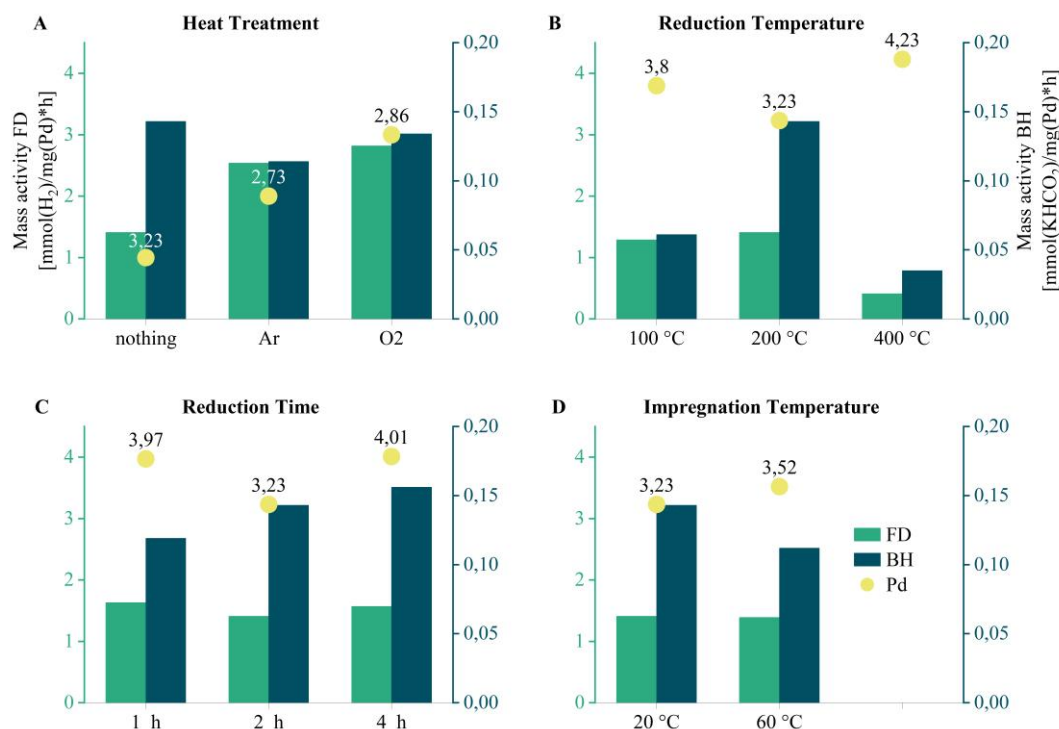


Figure 12. Optimization steps for catalysts with the carbon support AKROS C1. BH: 5.40 mmol KHCO₃, 20.0 mg Pd/C, 1.5 mL H₂O, 30 bar H₂, 60 °C, 18 h. FD: 250 mmol KHCO₂, 7.50 mmol K₂CO₃, 106 mg Pd/C, 25 mL H₂O, 60 °C, 3 h. Gas evolution was monitored with manual burettes, corrected by the blank volume. Purity was analyzed by GC. No CO was detected (limit < 10 ppm). All experiments were performed at least twice; average values are shown (St. Dev. < 10 %).

Following this, we performed wet impregnation at an elevated temperature and reduced the catalysts at 200 °C for 2 h, testing several chelators to increase the viscosity of the impregnation solution and prevent precursor crystallization, thereby enabling a homogeneous distribution of palladium on the surface. The results from Plot E (Figure 13, top) show that oxalic acid notably increased Pd loading. Adding 2.0 eq of oxalic acid enabled uniform distribution of palladium for loadings as low as 1.00 wt%, whereas 5.00 wt% were required without the additive (Plot F, Figure 13, bottom). This method reduced shell thickness by tenfold, minimized Pd loss, and produced a more homogeneous surface, even at low loadings, as confirmed by SEM. The observed increase in mass activity at lower loadings suggests that excess metal in thicker shells remains inaccessible to the reaction. **1.60Pd-C1-OA** (targeting 2.00 wt%) delivered the highest FD yields and an outstanding overall coating, so it was included in the analytical study shown below.

Combining the identified optimization steps, AKROS C1 carbon pellets were impregnated with 2.00 wt% Na₂PdCl₄ and 2.0 eq of oxalic acid at 60 °C, dried, calcined (200 °C, 2 h) and reduced with H₂ (200 °C, 2 h). The resulting catalyst **Pd-C1-OA-O₂** contained 1.81 wt% Pd.

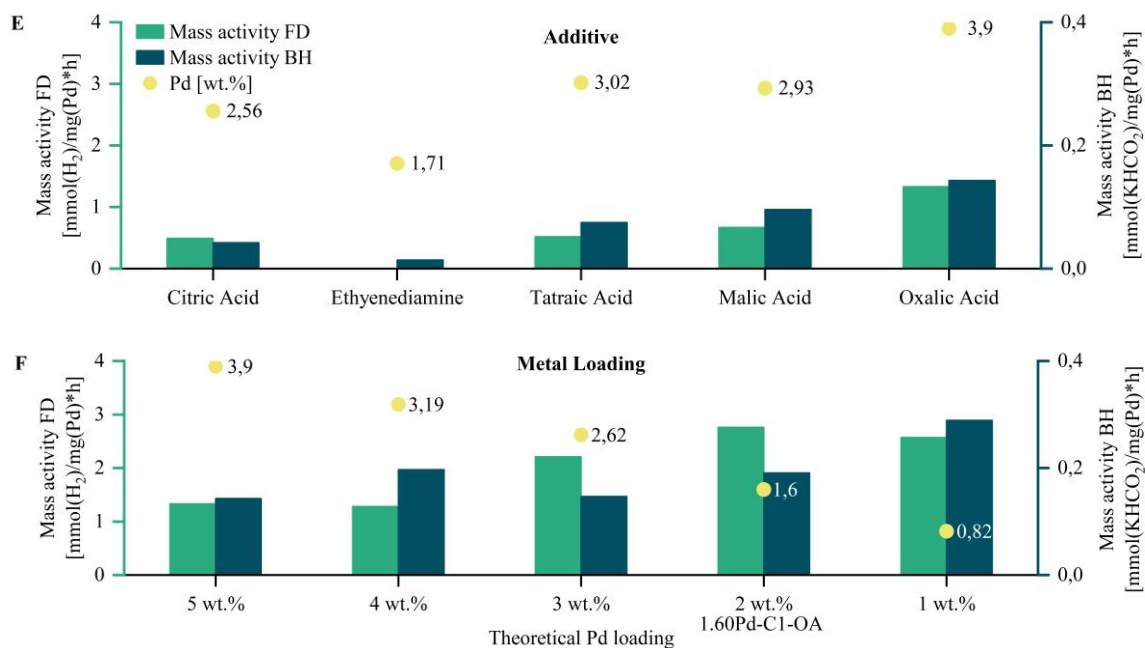


Figure 13. Influence of different additives (top) and metal loading on the catalytic activity in the (de)hydrogenation. BH: 5.40 mmol KHCO₃, 20.0 mg Pd/C, 1.5 mL H₂O, 30 bar H₂, 60 °C, 18 h; FD: 250 mmol KHCO₂, 7.50 mmol K₂CO₃, 106 mg Pd/C, 25 mL H₂O, 60 °C, 3 h. No CO was detected (limit < 10 ppm). All experiments were performed at least twice; average values are shown (St. Dev. < 10 %).

Characterization of Catalysts: Evolution of Catalysts based on AKROS C1

Using SEM, scanning transmission electron microscopy (STEM), and XPS, we tracked structural changes from the initial **Pd-C1** (5.00 wt % Pd *via* wet impregnation at rt, reduction with H₂ at 200 °C for 2 h) to the optimized **1.60Pd-C1-OA** (2.00 wt% Pd and 2.0 eq OA, impregnated at 60 °C, then reduced) and final **Pd-C1-OA-O₂** catalysts (same as **1.60Pd-C1-OA**, additional calcination step).

Pd-C1 already displayed an even metal shell on the support, though its thick Pd crust (3.33 wt%) showed some cracks (Figure 14, top, left). SEM of the cross-section confirmed an eggshell distribution with no Pd inside the pellet. STEM revealed Pd species ranging from single atoms to small clusters (Figure 14, bottom, left) and XPS showed a surface Pd⁰ to Pd²⁺ ratio of 10:1 (Figure 15, left). Depth measurements showed that the Pd signal peaked after 840 s of sputtering, confirming the shell thickness. The Pd⁰/Pd²⁺ ratio decreased with depth: Pd⁰ dominated the outermost layer (metal–metal bonds), while Pd²⁺ increased inward (possibly coordinated to linkers on the carbon support e.g. oxygen).

Adding 2.0 eq OA during impregnation allowed us to lower the Pd loading (2.00 wt% Pd_{theo}) while achieving a more uniform surface coating, resulting in **1.60Pd-C1-OA**. EDS/SEM confirmed Pd particles between 40.0 and 550 nm and STEM found Pd from single atoms to tens of nanometers. XPS indicated a lower Pd⁰/Pd²⁺ ratio than **Pd-C1**. The catalytic activity indicates that the ratio of Pd⁰/Pd²⁺ is important, and a specific amount of Pd²⁺ can be beneficial,

as published by the Bulusheva group^[57,152,153]. Their study on FAD identified Pd²⁺ species as the active site. Depth profiling showed an initial increase of Pd⁰/Pd²⁺, implying less metallic Pd on the surface, followed by a decrease after 2400 s as Pd²⁺ increased in the subsurface.

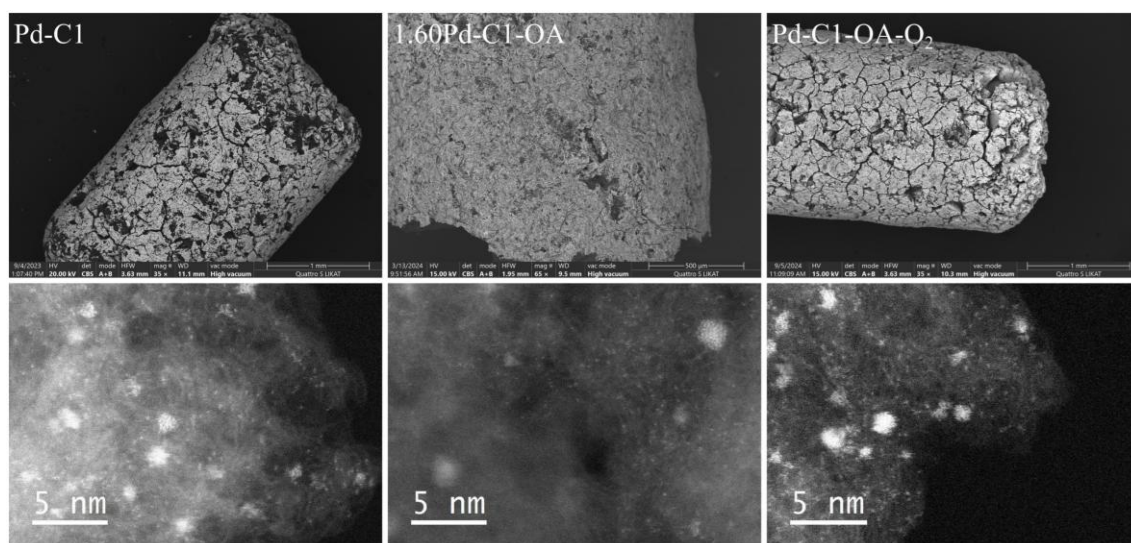


Figure 14. Selected BSE-SEM (whole particle; top) and HAADF-STEM (powder; active material scraped off from the pellet surface; bottom) images of the initial (left column, **Pd-C1**, 3.33 wt% Pd), the optimized (center column, **1.60Pd-C1-OA**, 1.60 wt%) and the final catalyst (right column, **Pd-C1-OA-O₂**, 1.81 wt%).

In **Pd-C1-OA-O₂** SEM/BSE revealed a fine distribution of the active material with minimal cracks, indicating that calcination enhances the stability of the palladium crust. STEM showed particle size ranging from large particles (ca. 200 nm) down to clusters and single centers with no sintering due to the mild heat treatment. Decreasing the ratio of Pd⁰/Pd²⁺ further, the microscopic structure of the material remained unaffected. Across the generations of the catalyst, activity and Pd²⁺ increased. By analogy to Masuda et al.^[87,119], Pd²⁺ and Pd⁰ may act as the electron-deficient and electron-rich partners needed for catalysis.

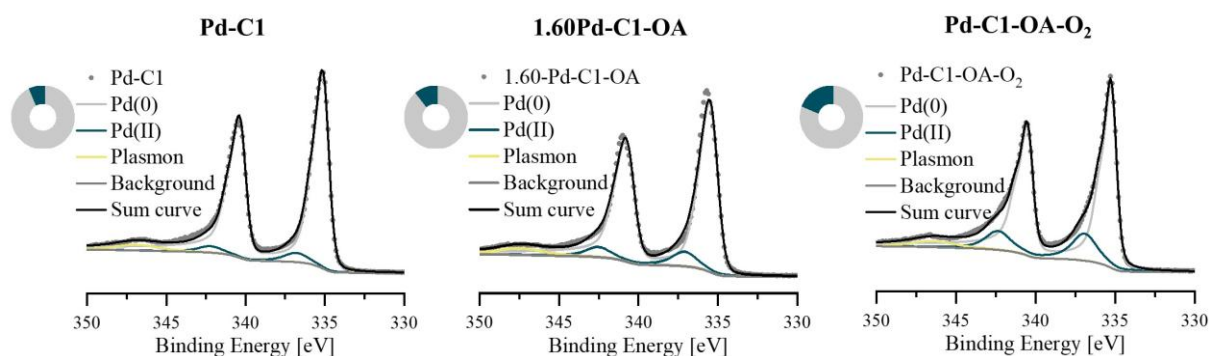


Figure 15. XPS (whole particle) analysis of the initial (left column, **Pd-C1**, 3.33 wt% Pd), the optimized (center column, **1.60Pd-C1-OA**, 1.60 wt%), and the final catalyst (right column, **Pd-C1-OA-O₂**, 1.81 wt%).

Catalytic Performance: (De)hydrogenation with Pd-C1-OA-O₂

With the optimized catalyst at hand, we wanted to demonstrate its industrial applicability. To test scalability, we ran both half-cycles with 106 mg **Pd-C1-OA-O₂**, 250 mmol of the corresponding (loaded) hydrogen carrier, and 25 mL of water. In BH, 23 % formate was generated, corresponding to a TON of 2550. FD gave rise to 1.14 L of gas (92 % H₂, 8 % CO₂, no CO detected) equivalent to TOF = 3261 h⁻¹. The conversions can be increased by elongation of the reaction time. CO₂ originates from partial decomposition of bicarbonate to carbonate and is expected at high formate concentrations.

The long-term stability and reusability of the catalyst are crucial for industrial applicability. In FD over 73 h, 200 mg of ground **Pd-C1-OA-O₂** and 200 mmol KHCO₂ yielded 1.36 L gas (90 % H₂, 10 % CO₂, 11 ppm CO) initially and 1.57 L gas (93 % H₂, 7 % CO₂, 18 ppm CO) on reuse. CO stems from the decomposition of formate *via* dehydration.

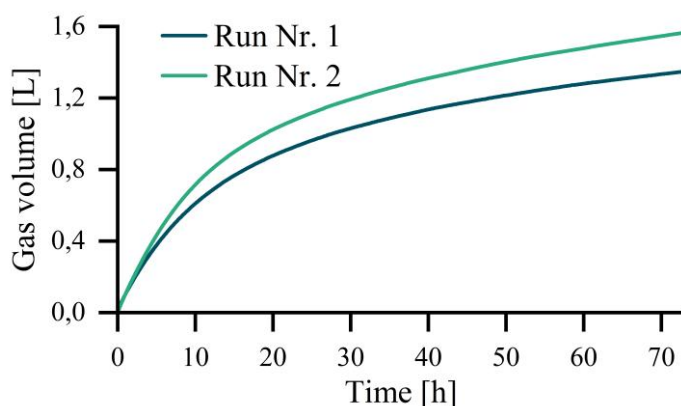


Figure 16. Recycling of the catalyst **Pd-C1-OA-O₂** in FD: Gas composition verified via GC every two hours. 200 mg **Pd-C1-OA-O₂**, 200 mmol KHCO₂, 60 °C, 72 h. No CO was detected (limit < 10 ppm). After the reaction, the catalyst was washed, dried, and used for a second run.

For BH, 200.00 mmol KHCO₃ were hydrogenated at 60 bars H₂ for 18 h using 200 mg of ground **Pd-C1-OA-O₂**, resulting in a TON of 1570. After reactivation (filtered, washed, calcined, reduced) the same catalysts achieved a similar TON of 1650. Without reactivation, activity dropped significantly, indicating that side products, such as CO, adsorb on the catalyst surface and must be removed.

In a fixed-bed reactor with 10 g of **Pd-C1-OA-O₂**, a total of 71 L gas was released (83 % H₂, 17 % CO₂) over 10 h. After washing and drying, a second run yielded 82 L gas (81 % H₂, 19 % CO₂) and a third run gave 53 L (84 % H₂, 16 % CO₂). The deactivation noticeable in the third run may arise from reversible blockage by the (intermediate) products like KHCO₃. Indeed, ICP-OES showed an increase of potassium salts on the used catalyst (fresh catalyst: no K detectable, catalyst after 1st run: 1.81 wt% K). Notably, no palladium leaching was detected (limit 0.006 wt%).

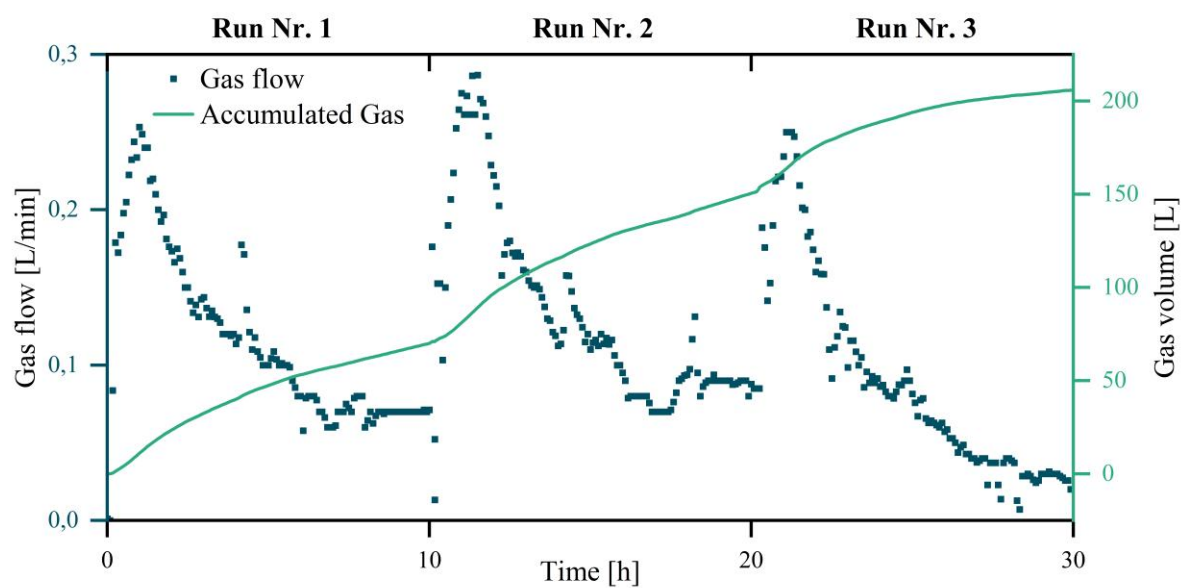
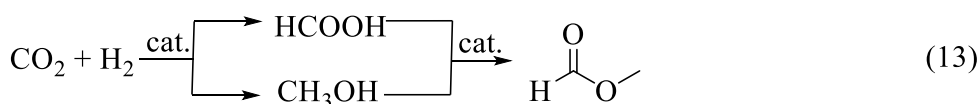
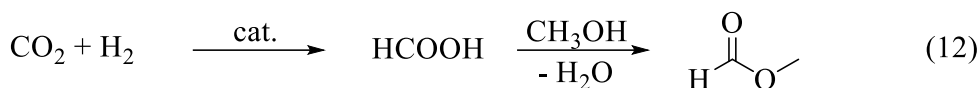
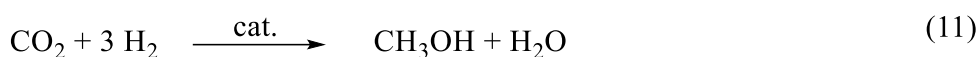


Figure 17. Gas flow for individual runs (left) and overall gas evolution (right) for FD. Reaction conditions: 10 g **Pd-C1-OA-O₂**, 4 M KHCO₂, 0.03 L/min volume flow, 60 °C, 10 h. Gas composition verified via GC every two hours. No CO was detected (limit < 10 ppm). After every run, the catalyst was washed and dried.

3.5 Direct CO₂ Conversion to Methyl Formate with Ru Triphos Complexes

Ruthenium triphos complexes of the type [Ru(Ar-triphos)(TMM)] (TMM = η^4 -trimethylenemethane) are active precatalysts for CO₂ hydrogenation. They have been reported to convert CO₂ to FA (Eq. 10),^[154] methanol (Eq. 11)^[155] and in methanol as (co)solvent, methyl format - *via* esterification of the solvent with *in situ* generated FA (Eq. 12).^[156] Like other C₁ products, methyl formate is an important bulk chemical, and a safe, non-corrosive liquid hydrogen storage (8.4 wt% H₂). The aqueous dehydrogenation of methyl formate was already shown by the groups of Beller (Ru-pincer complex)^[157] and Milstein (immobilized Mn-pincer complex).^[158] However, a direct route for CO₂ hydrogenation to methyl formate without the addition of methanol remains unknown.



The objective of this project was the direct conversion of CO₂ to methyl formate without the addition of methanol. Therefore, FA and methanol are synthesized *in situ* and subsequently esterified (Eq. 13). Different parameters were investigated for this one-pot reaction, results are being summarized in a separate manuscript. During the catalyst screening, we managed to crystallize and analyze a triphos complex. [(1,1,1-Tris(di(4-methoxyphenyl)phosphino)methyl)ethane)(η^4 -trimethylene-methane)ruthenium] was synthesized according to literature.^[155] [bis(2-methylallyl)(1,5-cyclooctadiene)ruthenium] was added to a solution of *p*-anisyl-triphos in toluene and refluxed for 18 h. After concentration of the solvent and precipitation, the solid was washed with acetone, (40 % yield). Crystals were obtained by diffusion of diethyl ether into a solution of the compound in dichloromethane.

At rt, the complex geometry is symmetric as shown by a singlet signal at δ 31.4 ppm in the ³¹P{¹H} NMR spectrum, indicating the spectroscopic equivalence of the phosphorus atoms in solution. The quaternary carbon of the η^4 -trimethylenemethane unit resonates at 107.0 ppm in the ¹³C{¹H} NMR spectrum - highly shifted - confirming its η^4 -coordination to the metal. The binding mode is further supported by the solid-state structure shown in Figure 18, where the Ru-C1 (2.0674(18) Å) distance is shorter than the other Ru-C bonds of the TMM ligand. This value is comparable to Ru-C1 bonds of previously reported [Ru(Ar-triphos)(TMM)] complexes, such as those with Ar = Ph,^[159,160] 4-methylphenyl,^[161] and 3,5-dimethylphenyl.^[161]

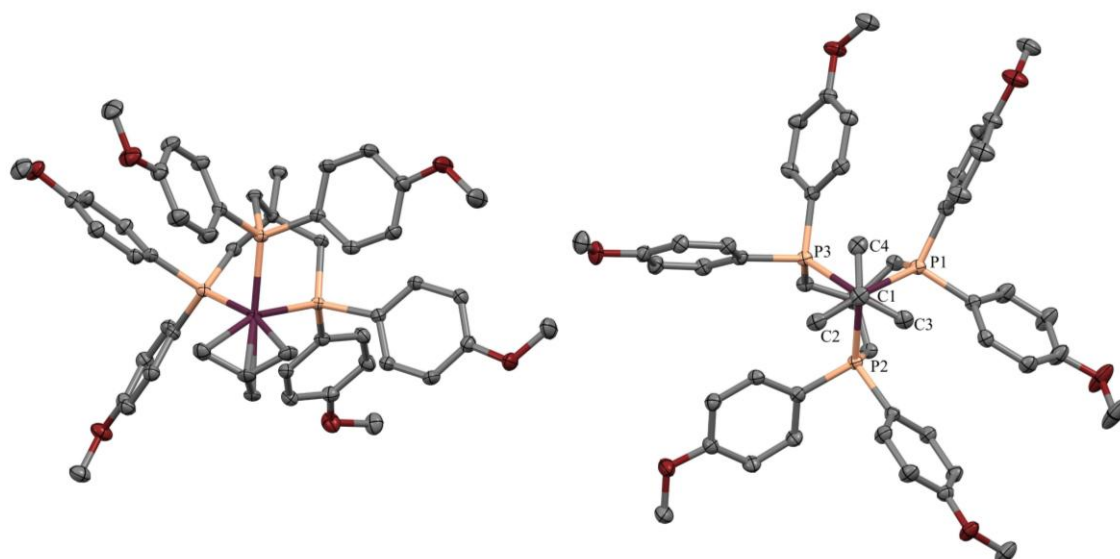


Figure 18. ORTEP plots of the solid-state molecular structure of [(1,1,1-Tris(di(4-methoxyphenyl)phosphino-methyl)ethane)(η^4 -trimethylene-methane)-ruthenium(II)] shown from two angles (left: front view; right: top view). Displacement ellipsoids are drawn at 50 % probability. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity.

The solid-state structure exhibits notable asymmetry in Ru-P bond lengths as well as in the corresponding P-Ru-P angles. Whilst the bond lengths between Ru-P1 (2.2787(6) Å) and Ru-P3 (2.2780(6) Å) are nearly identical, the length of Ru-P2 (2.2988(5) Å) is significantly elongated. This deviation suggests an uneven coordination of the *p*-anisyl-triphos ligand. Asymmetry for [Ru(II)(Ar-triphos)(TMM)] complexes is also evident in the P–Ru–P bond angles. Two angles are comparable (P1-Ru-P2 = 87.511(19)°, P2-Ru-P3 = 87.931(17)°), whereas the third one is enlarged (P3-Ru-P1 = 89.759(17)°). Similar observations have been reported for related [Ru(II)(Ar-triphos)(TMM)] complexes, for which selected data is presented in Table 14. The unsubstituted complex with Ar = Ph and the substituted one with Ar = 3,5-dimethylphenyl have one Ru-P bond with a significant length difference. In both examples, one bond deviates from the others; however, the deviating bond is shorter in those cases, whereas the *p*-anisyl complex displays an elongation. Likewise, the angles indicate an asymmetry. Notably, another literature known complex with Ar = 4-methylphenyl has a symmetric structure.

Table 14. Selected bond lengths and bond angles of [Ru(II)(Ar-triphos)(TMM)] complexes the solid-state structure of which is known. Schematic staggered conformation with relative numbering.

Bond Distances [Å]	4-OMe-Ph	Ph^[160]	Ph^[159]	4-Me-Ph^[161]	3,5-Me₂-Ph^[161]
<i>P1-Ru</i>	2.2787(6)	2.2679(15)	2.2893(5)	2.2757(6)	2.2907(7)
<i>P2-Ru</i>	2.2988(5)	2.2842(15)	2.2720(5)	2.2757(6)	2.2749(8)
<i>P3-Ru</i>	2.2780(6)	2.2861(15)	2.2885(5)	2.2757(6)	2.2812(8)
Bond Angles [°]					
<i>P1-Ru-P2</i>	87.511(19)	89.78(5)	89.606(17)	89.02(2)	90.95(3)
<i>P2-Ru-P3</i>	87.931(17)	88.03(5)	88.635(15)	89.02(2)	85.77(3)
<i>P3-Ru-P1</i>	89.759(17)	88.66(5)	87.907(16)	89.02(2)	89.52(3)

4. Conclusion and Outlook

In the context of mitigating climate change, we explored CO₂-derived (liquid) carriers for storing and transporting hydrogen safely and efficiently. Utilizing CO₂ or (bi)carbonates as unloaded hydrogen carriers serves two purposes: valorizing a greenhouse gas and creating a safe, energy-dense medium for hydrogen storage. In this context, we investigated three different hydrogen carriers – formic acid, potassium formate, and methyl formate.

Formic acid is an attractive liquid hydrogen carrier due to its significant hydrogen content (4.4 wt%) and ability to release H₂ under mild conditions. In this work, we investigated two catalyst systems: a homogeneous cuboidal PN Mo₃S₄ cluster **Mo-5** and a heterogeneous catalyst based on Pd nanoparticles supported on polymeric carbon nitride **Pd-PCN-2**. Both systems demonstrate efficient and selective H₂ evolution with minimal CO impurities, highlighting different trade-offs between activity, catalyst stability, and ease of separation. While the homogeneous system showed a higher activity (TOF_{10min} = 4254 h⁻¹), the heterogeneous system presented a better long-term stability (TTON = 41395, 350 h).

Formates are another promising hydrogen carrier because they release H₂ under mild conditions and are inherently safe. Here, we evaluated two catalyst systems: a homogeneous Ru pincer complex **Ru-5** and a heterogeneous pellet-based Pd/C catalyst **Pd-C1-OA-O₂**. Both systems enable reversible H₂ storage with high purity and low CO_x content. The homogeneous **Ru-5** achieved exceptionally high TONs (up to 210000 over 113 h) and fast FD kinetics (TOF ≈ 4800 h⁻¹). Notably, the system was stable over six months, resulting in 40 consecutive (de)hydrogenation cycles. In contrast, the Pd/C pellets **Pd-C1-OA-O₂** combine a cost-efficient, simple, and scalable synthesis route, easy separation, and compatibility in water – essential parameters for industrial applicability. These qualities were proven on a ten-gram scale in a fixed-bed reactor, yielding a total of 180 L H₂ gas (30 h).

Methyl formate, too, is considered a safe liquid hydrogen carrier with 8.4 wt% H₂. It can be synthesized in a one-pot manner from CO₂ with H₂ if formic acid and methanol intermediates undergo esterification. To enable this direct route, we crystallized and characterized the *p*-anisyl-substituted Ru triphos complex. Unlike the symmetric nature in solution at rt, detected *via* NMR, the solid-state structure exhibits slight asymmetry. Its detailed characterization lays the groundwork for efficient catalytic testing aimed at synthesizing methyl formate from CO₂ without the addition of methanol.

5. Literature

- [1] V. Smil, *Harvesting the Biosphere: What We Have Taken from Nature*, The MIT Press, **2012**.
- [2] J. S. Allen, *Transactions of the Newcomen Society* **1964**, 37, 57–84.
- [3] M.-B. Group, “Benz Patent-Motorwagen: Das erste Automobil (1885–1886),” can be found under <https://group.mercedes-benz.com/unternehmen/tradition/geschichte/1885-1886.html>, **2025**.
- [4] “Executive summary – Global EV Outlook 2022 – Analysis,” can be found under <https://www.iea.org/reports/global-ev-outlook-2022/executive-summary>, **2022**.
- [5] H. Ritchie, M. Roser, *Our World in Data* **2024**.
- [6] “About Earth Overshoot Day,” can be found under <https://overshoot.footprintnetwork.org/about-earth-overshoot-day/>, **2025**.
- [7] A. M. Oliveira, R. R. Beswick, Y. Yan, *Current Opinion in Chemical Engineering* **2021**, 33, 100701.
- [8] H. Ritchie, M. Roser, *Our World in Data* **2020**.
- [9] A. Züttel, A. Borgschulte, L. Schlapbach, *Hydrogen as a Future Energy Carrier*, John Wiley & Sons, **2011**.
- [10] R. Boyle, *Tracts Containing New Experiments, Touching the Relation Betwixt Flame and Air*, London, UK, **1673**.
- [11] *Phil. Trans. R. Soc.* **1766**, 56, 141–184.
- [12] H. Idriss, M. Scott, V. Subramani, in *Compendium of Hydrogen Energy*, Elsevier, **2015**, pp. 3–19.
- [13] P. Häussinger, R. Lohmüller, A. M. Watson, in *Ullmann’s Encyclopedia of Industrial Chemistry* (Ed.: Wiley-VCH Verlag GmbH & Co. KGaA), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2000**, p. a13_297.
- [14] G. Squadrito, G. Maggio, A. Nicita, *Renew. Energy* **2023**, 216, 119041.
- [15] G. Zang, E. J. Graham, D. Mallapragada, *Int. J. Hydrog. Energy* **2024**, 49, 1288–1303.
- [16] W. Ostwald, *Elektrochemie, Ihre Geschichte Und Lehre: Mit 260 Nachbildungen Geschichtlicher Originalfiguren*, Veit, **1896**.
- [17] “The European Green Deal - European Commission,” can be found under https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal_en, **2021**.
- [18] G. R. Timilsina, *Renew. Energy* **2021**, 180, 658–672.
- [19] United Nations Department of Economic and Social Affairs, *Energy Statistics Pocketbook 2025*, United Nations, **2025**.
- [20] P. Lewicki, “Erneuerbare Energien in Zahlen,” can be found under <https://www.umweltbundesamt.de/themen/klima-energie/erneuerbare-energien/erneuerbare-energien-in-zahlen>, **2013**.
- [21] “SMARD | Marktdaten visualisieren,” can be found under <https://www.smard.de/page/home/marktdaten/78?marketDataAttributes=%7B%22resolution%22:%22hour%22,%22from%22:1723972146479,%22to%22:1724576946478,%22moduleIds%22:%5B1004066,1004067,1004068,1001226,1001228,1001225,5000410%5D,%22selectedCategory%22:1,%22activeChart%22:true,%22style%22:%22color%22,%22categoriesModuleOrder%22:%7B%7D,%22region%22:%22DE%22,%22language%22:%22de%22,%22format%22:%22XLS%22%7D>, **2024**.
- [22] OpenAI, <https://chat.openai.com>, **2025**.
- [23] A. Hiesl, A. Ajanovic, R. Haas, *Greenhouse. Gas. Sci. Technol.* **2020**, 10, 1176–1192.
- [24] A. R. Dehghani-Sanij, E. Tharumalingam, M. B. Dusseault, R. Fraser, *Renew. Sustain. Energy Rev.* **2019**, 104, 192–208.
- [25] H. Becker, J. Murawski, D. V. Shinde, I. E. L. Stephens, G. Hinds, G. Smith, *Sustain.*

- Energy Fuels* **2023**, *7*, 1565–1603.
- [26] K. Bareiß, C. De La Rua, M. Möckl, T. Hamacher, *Appl. Energy* **2019**, *237*, 862–872.
 - [27] “H2data.de - Hydrogen fact sheet,” can be found under <http://www.h2data.de/>, **n.d.**
 - [28] G. Maggio, A. Nicita, G. Squadrito, *Int. J. Hydrog. Energy* **2019**, *44*, 11371–11384.
 - [29] A. Escamilla, D. Sánchez, L. García-Rodríguez, *Int. J. Hydrog. Energy* **2022**, *47*, 17505–17525.
 - [30] “12 Insights on Hydrogen,” can be found under https://www.agora-energiewende.de/fileadmin/Projekte/2021/2021_11_H2_Insights/A-EW_258_12_Thesen_zu_Wasserstoff_WEB.pdf, **2022**.
 - [31] Z. Myslikova, K. S. Gallagher, *Nat. Energy* **2020**, *5*, 732–734.
 - [32] S. Kharel, B. Shabani, *Energies* **2018**, *11*, 2825.
 - [33] J. Graetz, *Chem. Soc. Rev.* **2009**, *38*, 73–82.
 - [34] D. Russo, R. Andreozzi, M. Calabrese, R. Marotta, A. Di Benedetto, *Int. J. Hydrog. Energy* **2024**, *65*, 421–427.
 - [35] K. Grubel, H. Jeong, C. W. Yoon, T. Autrey, *J. Energy Chem.* **2020**, *41*, 216–224.
 - [36] J. Schuberth, “Wasserstoff – Schlüssel im künftigen Energiesystem,” can be found under <https://www.umweltbundesamt.de/themen/klima-energie/klimaschutz-energiepolitik-in-deutschland/wasserstoff-schluessel-im-kuenftigen-energiesystem>, **2021**.
 - [37] J. Andersson, S. Grönkvist, *Int. J. Hydrog. Energy* **2019**, *44*, 11901–11919.
 - [38] P. Jena, *J. Phys. Chem. Lett.* **2011**, *2*, 206–211.
 - [39] “Flaticon,” can be found under <https://www.flaticon.com/de/kostenlose-icons/chemie> title="chemie Icons">Chemie Icons erstellt von Maxim Basinski Premium - Flaticon, **2025**.
 - [40] J. Purewal, M. Veenstra, D. Tamburello, A. Ahmed, A. J. Matzger, A. G. Wong-Foy, S. Seth, Y. Liu, D. J. Siegel, *Int. J. Hydrog. Energy* **2019**, *44*, 15135–15145.
 - [41] M. Liu, Y. Peng, W. Chen, S. Cao, S. Chen, F. Lu Meng, Y. Jin, C.-C. Hou, R. Zou, Q. Xu, *Coord. Chem. Rev.* **2024**, *506*, 215726.
 - [42] N. Klopčič, I. Grimmer, F. Winkler, M. Sartory, A. Trattner, *J. Energy Storage* **2023**, *72*, 108456.
 - [43] L. Zhao, F. Xu, C. Zhang, Z. Wang, H. Ju, X. Gao, X. Zhang, L. Sun, Z. Liu, *Prog. Nat. Sci.: Mater. Int.* **2021**, *31*, 165–179.
 - [44] M. Calabrese, D. Russo, A. Di Benedetto, R. Marotta, R. Andreozzi, *Renew. Sustain. Energy Rev.* **2023**, *173*, 113102.
 - [45] M. Niermann, A. Beckendorff, M. Kaltschmitt, K. Bonhoff, *Int. J. Hydrog. Energy* **2019**, *44*, 6631–6654.
 - [46] P. Preuster, C. Papp, P. Wasserscheid, *Acc. Chem. Res.* **2017**, *50*, 74–85.
 - [47] “Hydrogen Storage,” can be found under <https://www.energy.gov/eere/fuelcells/hydrogen-storage>, **n.d.**
 - [48] “GESTIS Substance Database,” can be found under <https://gestis-database.dguv.de/data?name=007010#0600>, **2025**.
 - [49] S. S. Chadwick, *Ullmann’s Encyclopedia of Industrial Chemistry* (Ed.: Wiley-VCH Verlag GmbH & Co. KGaA), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **1988**, *16*, 31–34.
 - [50] Y. Jie Wu, J. Scarponi, A. Powell, J. Jayachandran, *Fuel* **2023**, *333*, 126232.
 - [51] M. Al-Breiki, Y. Bicer, *Int. J. Hydrog. Energy* **2020**, *45*, 34927–34937.
 - [52] D. Kaiser, L. Beckmann, J. Walter, M. Bertau, *Catalysts* **2021**, *11*, 869.
 - [53] I. Dutta, S. Chatterjee, H. Cheng, R. K. Parsapur, Z. Liu, Z. Li, E. Ye, H. Kawanami, J. S. C. Low, Z. Lai, X. J. Loh, K. Huang, *Adv. Energy Mater.* **2022**, *12*, 2103799.
 - [54] S. Kushwaha, J. Parthiban, S. K. Singh, *ACS Omega* **2023**, *8*, 38773–38793.
 - [55] K. Müller, K. Brooks, T. Autrey, *Energy & Fuels* **2017**, *31*, 12603–12611.

- [56] H. W. Gibson, *Chem. Rev.* **1969**, 69, 673–692.
- [57] D. A. Bulushev, J. R. H. Ross, *ChemSusChem* **2018**, 11, 821–836.
- [58] “CHEMANALYST,” can be found under https://www.chemanalyst.com/industry-report/formic-acid-market-688?utm_source=chatgpt.com, **2025**.
- [59] A. K. Singh, S. Singh, A. Kumar, *Catal. Sci. Technol.* **2016**, 6, 12–40.
- [60] R. Williams, R. S. Crandall, A. Bloom, *Appl. Phys. Lett.* **1978**, 33, 381–383.
- [61] K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy, *Chem. Rev.* **2018**, 118, 372–433.
- [62] T. Tingelöf, L. Hedström, N. Holmström, P. Alvfors, G. Lindbergh, *Int. J. Hydrog. Energy* **2008**, 33, 2064–2072.
- [63] “Sustainable Energy Solutions and Power Generators | DENS,” can be found under <https://www.dens.one/>, **2019**.
- [64] “Ant power: Take a ride on a bus that runs on formic acid,” can be found under <https://www.bbc.com/news/business-40403351>, **2017**.
- [65] A. Bahuguna, Y. Sasson, *ChemSusChem* **2021**, 14, 1258–1283.
- [66] R. D. Atwater, *Process for the Production of Sodium Formate*, **1942**, US2281715A.
- [67] Fact.MR, “Sodium Formate Sales to Revive as Manufacturers Emphasize on Non-Traditional Application Areas: Fact.MR Study,” can be found under <https://www.globenewswire.com/news-release/2019/06/17/1869629/0/en/Sodium-Formate-Sales-to-Revive-as-Manufacturers-Emphasize-on-Non-Traditional-Application-Areas-Fact-MR-Study.html>, **2019**.
- [68] “CHEMANALYST,” can be found under https://www.chemanalyst.com/industry-report/calcium-formate-market-2847?utm_source=chatgpt.com, **2025**.
- [69] I. M. le Baron, *Production of Potassium Bicarbonate*, **1964**, US3141730A.
- [70] A. E. Winston, *Process for the Production of Potassium Bicarbonate*, **1990**, US4919910A.
- [71] J. A. Dean, *Lange’s Handbook of Chemistry*, **1999**.
- [72] C. Balarew, T. P. Dirkse, O. A. Golubchikov, M. Salomon, C. Balarew, O. A. Golubchikov, T. P. Dirkse, S. Trendafilova, S. Tepavitcharova, T. Ageyeva, P. Baldini, G. D’Andrea, *J. Phys. Chem. Ref. Data* **2001**, 30, 1–163.
- [73] “Merck | Germany,” can be found under <https://www.sigmaaldrich.com/DE/de>, **2025**.
- [74] “Life Technologies - DE,” can be found under <https://www.thermofisher.com/de/de/home.html>, **2025**.
- [75] “Hydro X - Reinventing Hydrogen Storage,” can be found under <https://hydrox.earth/>, **2025**.
- [76] “H2APEX Chemische Wasserstoffspeicherung,” can be found under <https://h2apex.com/de/leistungen/h2apex-chemische-wasserstoffspeicherung/>, **2025**.
- [77] P. Sabatier, A. Mailhe, *Compt. Rend* **1912**, 152, 1212–1215.
- [78] M. W. Farlow, H. Adkins, *J. Am. Chem. Soc.* **1935**, 57, 2222–2223.
- [79] T. Asefa, K. Koh, C. W. Yoon, *Adv. Energy Mater.* **2019**, 9, 1901158.
- [80] J. H. Lee, J. Ryu, J. Y. Kim, S.-W. Nam, J. H. Han, T.-H. Lim, S. Gautam, K. H. Chae, C. W. Yoon, *J. Mater. Chem. A* **2014**, 2, 9490.
- [81] H. Park, J. H. Lee, E. H. Kim, K. Y. Kim, Y. H. Choi, D. H. Youn, J. S. Lee, *Chem. Commun.* **2016**, 52, 14302–14305.
- [82] Q. Bi, J. Lin, Y. Liu, H. He, F. Huang, Y. Cao, *Angew. Chem.-Int. Ed.* **2016**, 55, 11849–11853.
- [83] Z. Li, X. Yang, N. Tsumori, Z. Liu, Y. Himeda, T. Autrey, Q. Xu, *ACS Catal.* **2017**, 7, 2720–2724.
- [84] Q. Liu, X. Yang, L. Li, S. Miao, Y. Li, Y. Li, X. Wang, Y. Huang, T. Zhang, *Nat. Commun.* **2017**, 8, 1407.
- [85] M. Lu, J. Zhang, Y. Yao, J. Sun, Y. Wang, H. Lin, *Green Chem.* **2018**, 20, 4292–4298.

- [86] X. Gu, Z.-H. Lu, H.-L. Jiang, T. Akita, Q. Xu, *J. Am. Chem. Soc.* **2011**, *133*, 11822–11825.
- [87] S. Masuda, K. Mori, Y. Futamura, H. Yamashita, *ACS Catal.* **2018**, *8*, 2277–2285.
- [88] Y. Kuwahara, Y. Fujie, T. Mihogi, H. Yamashita, *ACS Catal.* **2020**, *10*, 6356–6366.
- [89] R. S. Coffey, *Chem. Commun. (London)* **1967**, 923b.
- [90] Y. Inoue, H. Izumida, Y. Sasaki, H. Hashimoto, *Chem. Lett.* **1976**, *5*, 863–864.
- [91] E. Graf, W. Leitner, *J. Chem. Soc., Chem. Commun.* **1992**, 623–624.
- [92] W. Leitner, E. Dinjus, F. Gaßner, *J. Organomet. Chem.* **1994**, *475*, 257–266.
- [93] E. Graf, W. Leitner, *Chem. Ber.* **1996**, *129*, 91–96.
- [94] C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem.-Int. Ed.* **2008**, *47*, 3966–3968.
- [95] B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem.-Int. Ed.* **2008**, *47*, 3962–3965.
- [96] C. Fellay, P. Dyson, G. Laurenczy, *International Patent WO2008047312 (A1)* **2006**.
- [97] A. Boddien, B. Loges, H. Junge, M. Beller, *ChemSusChem* **2008**, *1*, 751–758.
- [98] S. Gladiali, E. Alberico, *Chem. Soc. Rev.* **2006**, *35*, 226–236.
- [99] H. Junge, A. Boddien, F. Capitta, B. Loges, J. R. Noyes, S. Gladiali, M. Beller, *Tetrahedron Lett.* **2009**, *50*, 1603–1606.
- [100] A. Boddien, B. Loges, H. Junge, F. Gärtner, J. R. Noyes, M. Beller, *Adv. Synth. Catal.* **2009**, *351*, 2517–2520.
- [101] A. Boddien, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, G. Laurenczy, M. Beller, *Energy Environ. Sci.* **2012**, *5*, 8907.
- [102] Y. Gao, J. Kuncheria, R. J. Puddephatt, G. P. A. Yap, *Chem. Commun.* **1998**, 2365–2366.
- [103] I. Mellone, M. Peruzzini, L. Rosi, D. Mellmann, H. Junge, M. Beller, L. Gonsalvi, *Dalton Trans.* **2013**, *42*, 2495–2501.
- [104] Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, K. Kasuga, *Organometallics* **2007**, *26*, 702–712.
- [105] Y. Himeda, *Green Chem.* **2009**, *11*, 2018.
- [106] H. Kawanami, M. Iguchi, Y. Himeda, *Inorg. Chem.* **2020**, *59*, 4191–4199.
- [107] J. F. Hull, Y. Himeda, W.-H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman, E. Fujita, *Nat. Chem.* **2012**, *4*, 383–388.
- [108] R. Tanaka, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14168–14169.
- [109] G. A. Filonenko, R. van Putten, E. N. Schulpen, E. J. M. Hensen, E. A. Pidko, *ChemCatChem* **2014**, *6*, 1526–1530.
- [110] C. J. Stalder, S. Chao, D. P. Summers, M. S. Wrighton, *J. Am. Chem. Soc.* **1983**, *105*, 6318–6320.
- [111] H. Wiener, B. Zaidman, Y. Sasson, *J. Sol. Energy* **1989**, *43*, 291–296.
- [112] B. Zaidman, H. Wiener, Y. Sasson, *Int. J. Hydrog. Energy* **1986**, *11*, 341–347.
- [113] E. González, C. Marchant, C. Sepúlveda, R. García, I. T. Ghampson, N. Escalona, J. L. García-Fierro, *Appl. Catal. B: Environ.* **2018**, *224*, 368–375.
- [114] Q. Bi, J. Lin, Y. Liu, X. Du, J. Wang, H. He, Y. Cao, *Angew. Chem.-Int. Ed.* **2014**, *53*, 13583–13587.
- [115] J. Su, L. Yang, M. Lu, H. Lin, *ChemSusChem* **2015**, *8*, 813–816.
- [116] K. Koh, M. Jeon, D. M. Chevrier, P. Zhang, C. W. Yoon, T. Asefa, *Appl. Catal. B: Environ.* **2017**, *203*, 820–828.
- [117] H. Zhong, M. Iguchi, M. Chatterjee, T. Ishizaka, M. Kitta, Q. Xu, H. Kawanami, *ACS Catal.* **2018**, *8*, 5355–5362.
- [118] K. Nakajima, M. Tominaga, M. Waseda, H. Miura, T. Shishido, *ACS Sustainable Chem. Eng.* **2019**, *7*, 6522–6530.
- [119] S. Masuda, Y. Shimoji, K. Mori, Y. Kuwahara, H. Yamashita, *ACS Appl. Energy Mater.* **2020**, *3*, 5819–5829.

- [120] X. Shao, X. Miao, T. Zhang, W. Wang, J. Wang, X. Ji, *ACS Appl. Nano Mater.* **2020**, *3*, 9209–9217.
- [121] D. J. Drury, J. E. Hamlin, *Production of Formate Salts from Carbon Dioxide, Hydrogen and Amines*, **1984**, US4474959A.
- [122] C. Federsel, R. Jackstell, A. Boddien, G. Laurenczy, M. Beller, *ChemSusChem* **2010**, *3*, 1048–1050.
- [123] J. Elek, L. Nádasdi, G. Papp, G. Laurenczy, F. Joó, *Appl. Catal. A: Gen.* **2003**, *255*, 59–67.
- [124] C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem.-Int. Ed.* **2010**, *49*, 9777–9780.
- [125] Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, H. Arakawa, K. Kasuga, *Organometallics* **2004**, *23*, 1480–1483.
- [126] A. Boddien, F. Gärtner, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, M. Beller, *Angew. Chem. Int.-Ed.* **2011**, *50*, 6411–6414.
- [127] G. Papp, J. Csorba, G. Laurenczy, F. Joó, *Angew. Chem.* **2011**, *123*, 10617–10619.
- [128] Q. Liu, L. Wu, S. Gülak, N. Rockstroh, R. Jackstell, M. Beller, *Angew. Chem. Int.-Ed.* **2014**, *53*, 7085–7088.
- [129] Z. Treigerman, Y. Sasson, *ACS Omega* **2018**, *3*, 12797–12801.
- [130] J. Kothandaraman, M. Czaun, A. Goepfert, R. Haiges, J. Jones, R. B. May, G. K. S. Prakash, G. A. Olah, *ChemSusChem* **2015**, *8*, 1442–1451.
- [131] Z. Xin, J. Zhang, K. Sordakis, M. Beller, C. Du, G. Laurenczy, Y. Li, *ChemSusChem* **2018**, *11*, 2077–2082.
- [132] H. Horváth, G. Papp, R. Szabolcsi, Á. Kathó, F. Joó, *ChemSusChem* **2015**, *8*, 3036–3038.
- [133] H. Horváth, G. Papp, H. Kovács, Á. Kathó, F. Joó, *Int. J. Hydrog. Energy* **2019**, *44*, 28527–28532.
- [134] K. Agrawal, A. Roldan, N. Kishore, A. J. Logsdail, *Catal. Today* **2022**, *384–386*, 197–208.
- [135] D. W. Flaherty, S. P. Berglund, C. B. Mullins, *J. Catal.* **2010**, *269*, 33–43.
- [136] Z. Yu, X. An, I. Kurnia, A. Yoshida, Y. Yang, X. Hao, A. Abudula, Y. Fang, G. Guan, *ACS Catal.* **2020**, *10*, 5353–5361.
- [137] Z. Yu, Y. Yang, S. Yang, J. Zheng, X. Hao, G. Wei, H. Bai, A. Abudula, G. Guan, *Appl. Catal. B: Environ.* **2022**, *313*, 121445.
- [138] C. G. Morales-Guio, X. Hu, *Acc. Chem. Res.* **2014**, *47*, 2671–2681.
- [139] J. D. Benck, T. R. Hellstern, J. Kibsgaard, P. Chakthranont, T. F. Jaramillo, *ACS Catal.* **2014**, *4*, 3957–3971.
- [140] M. C. Neary, G. Parkin, *Chem. Sci.* **2015**, *6*, 1859–1865.
- [141] E. Alberico, T. Leischner, H. Junge, A. Kammer, R. Sang, J. Seifert, W. Baumann, A. Spannenberg, K. Junge, M. Beller, *Chem. Sci.* **2021**, *12*, 13101–13119.
- [142] E. Guillamón, I. Sorribes, V. S. Safont, A. G. Algarra, M. J. Fernández-Trujillo, E. Pedrajas, R. Llusar, M. G. Basallote, *Inorg. Chem.* **2022**, *61*, 16730–16739.
- [143] M. Gutiérrez-Blanco, C. A. M. Stein, C. Alfonso, E. Guillamón, V. S. Safont, I. Sorribes, H. Junge, M. Beller, R. Llusar, *ChemCatChem* **2023**, *15*, e202300740.
- [144] M. Iglesias, L. A. Oro, *Eur. J. Inorg. Chem.* **2018**, *2018*, 2125–2138.
- [145] J. J. Bravo-Suárez, R. V. Chaudhari, B. Subramaniam, in *ACS Symposium Series* (Eds.: J.J. Bravo-Suárez, M.K. Kidder, V. Schwartz), American Chemical Society, Washington, DC, **2013**, pp. 3–68.
- [146] J.-Y. Cho, H. Kim, J.-E. Oh, B. Y. Park, *Catalysts* **2021**, *11*, 1497.
- [147] M. Liu, Y. Xu, Y. Meng, L. Wang, H. Wang, Y. Huang, N. Onishi, L. Wang, Z. Fan, Y. Himeda, *Adv. Energy Mater.* **2022**, *12*, 2200817.
- [148] Y. Cai, X. Li, Y. Zhang, X. Wei, K. Wang, J. Chen, *Angew. Chem. Int.-Ed.* **2013**, *52*,

- 11822–11825.
- [149] Z. Chen, E. Vorobyeva, S. Mitchell, E. Fako, N. López, S. M. Collins, R. K. Leary, P. A. Midgley, R. Hauert, J. Pérez-Ramírez, *Natl. Sci. Rev.* **2018**, *5*, 642–652.
 - [150] R. Sang, C. A. M. Stein, T. Schareina, Y. Hu, A. Léval, J. Massa, V. Turan, P. Sponholz, D. Wei, R. Jackstell, H. Junge, M. Beller, *Nat. Commun.* **2024**, *15*, 7268.
 - [151] J. Muzart, *Tetrahedron* **2009**, *65*, 8313–8323.
 - [152] D. A. Bulushev, M. Zacharska, E. V. Shlyakhova, A. L. Chuvilin, Y. Guo, S. Beloshapkin, A. V. Okotrub, L. G. Bulusheva, *ACS Catal.* **2016**, *6*, 681–691.
 - [153] D. A. Bulushev, J. R. H. Ross, *Catalysis Reviews* **2018**, *60*, 566–593.
 - [154] D. P. Estes, M. Leutzsch, L. Schubert, A. Bordet, W. Leitner, *ACS Catal.* **2020**, *10*, 2990–2998.
 - [155] S. Wesselbaum, V. Moha, M. Meuresch, S. Brosinski, K. M. Thenert, J. Kothe, T. vom Stein, U. Englert, M. Hölscher, J. Klankermayer, W. Leitner, *Chem. Sci.* **2015**, *6*, 693–704.
 - [156] N. Westhues, M. Belleflamme, J. Klankermayer, *ChemCatChem* **2019**, *11*, 5269–5274.
 - [157] R. Sang, Z. Wei, Y. Hu, E. Alberico, D. Wei, X. Tian, P. Ryabchuk, A. Spannenberg, R. Razzaq, R. Jackstell, J. Massa, P. Sponholz, H. Jiao, H. Junge, M. Beller, *Nat. Catal.* **2023**, *6*, 543–550.
 - [158] L. Lu, C. You, M. Montag, A. Maity, M. Leskes, D. Milstein, *Angew. Chem.* **2025**, *137*, e202423074.
 - [159] S. Savourey, G. Lefèvre, J. Berthet, P. Thuéry, C. Genre, T. Cantat, *Angew. Chem.-Int. Ed.* **2014**, *53*, 10466–10470.
 - [160] T. vom Stein, T. Weigand, C. Merkens, J. Klankermayer, W. Leitner, *ChemCatChem* **2013**, *5*, 439–441.
 - [161] M. Meuresch, S. Westhues, W. Leitner, J. Klankermayer, *Angew. Chem. Int.-Ed.* **2016**, *55*, 1392–1395.

6. Selected Publications

The following chapter contains the original publications presented in Chapter 3. My contribution to each publication is outlined in the corresponding sub-chapter.

6.1 Selective Dehydrogenation of Formic Acid Catalyzed by Air-Stable Cuboidal PN Molybdenum Sulfide Clusters

María Gutiérrez-Blanco, Carolín A. M. Stein, Carmina Alfonso, Eva Guillamón, Vicent S. Safont, Iván Sorribes, Henrik Junge, Matthias Beller,* and Rosa Llusar*

ChemCatChem, **2023**, *15*, e202300740.

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Electronic supporting information is available online.

Contributions:

For this paper, I co-planned all experiments and performed parts of the catalytic screening and optimization of the reaction conditions. I executed all long-term and restart experiments. I conducted mechanistic NMR and MS studies to identify the deactivation path. In addition, I co-wrote the draft of the paper and the supporting information. My contribution to this paper accounts for 35 %.

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Signature of the student
Carolín A. M. Stein



Signature of the supervisor
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Selective Dehydrogenation of Formic Acid Catalyzed by Air-Stable Cuboidal PN Molybdenum Sulfide Clusters

María Gutiérrez-Blanco,^[a] Carolin A. M. Stein,^[b] Carmina Alfonso,^[a] Eva Guillaumon,^[a] Vicent S. Safont,^[a] Iván Sorribes,^[a, c] Henrik Junge,^[b] Matthias Beller,^{*,[b]} and Rosa Llusar^{*,[a]}

Formic acid is considered as a promising hydrogen storage material in the context of a green hydrogen economy. In this work, we present a series of aminophosphino and imidazolylamino Mo₃S₄ cuboidal clusters which are active and selective for formic acid dehydrogenation (FAD). Best results are obtained with the new [Mo₃S₄Cl₃(ed'p,p₃)(BPh₄) (4(BPh₄)) (ed'p,p = (2-diisopropylphosphino)ethylamine)) cluster, which is prepared through a simple ligand exchange process from the Mo₃S₄Cl₄(PPh₃)₃(H₂O)₂ precursor. Under the conditions investigated, complex 4⁺ showed significantly improved performance (TOF = 4048 h⁻¹ and 3743 h⁻¹ at 120 °C in propylene carbonate using N,N-dimethyloctylamine as base after 10 min and 15 min, respectively) compared to the other reported molybdenum

compounds. Mechanistic investigations based on stoichiometric and catalytic experiments show that cluster 4⁺ reacts with formic acid in the presence of a base to form formate substituted species [Mo₃S₄Cl_{3-x}(OCOH)_x(ed'p,p₃)₃]⁺ (x = 1–3) from which the catalytic cycle starts. Subsequently, formate decarboxylation of the partially substituted [Mo₃S₄Cl_{3-x}(OCOH)_x(ed'p,p₃)₃]⁺ (x = 1, 2, 3) catalyst through a β-hydride transfer to the metal generates the trinuclear Mo₃S₄ cluster hydride. Dehydrogenation takes place through protonation by HCOOH to form Mo–H...HCOOH dihydrogen adducts, with regeneration of the Mo₃S₄ formate cluster. This proposal has been validated by DFT calculations.

Introduction

Major worldwide transformations are required to achieve the United Nations sustainable development goals on affordable and clean energy.^[1–3] In this context, hydrogen has emerged as a promising option as a green energy carrier due to its straightforward availability from renewable energy and H₂O.^[4] However, specifically storage and transportation of hydrogen remain critical issues regarding safety and practicability. To overcome these limitations, a variety of physical and chemical

hydrogen storage materials are currently under investigation.^[5] Among them, formic acid (FA) is widely explored due to its chemical properties such as availability, low toxicity and its recyclability *via* CO₂ hydrogenation.^[6]

In general, FA decomposition can proceed *via* decarboxylation giving H₂ and CO₂ or by decarbonylation giving H₂O and CO. In addition, FA can disproportionate to afford CH₃OH, H₂O and CO₂. For practical applications, formation of CO should be avoided because it poisons the catalysts in potential follow up fuel cell applications.^[7] In the past decade, a variety of suitable homogeneous and heterogeneous catalysts for FA dehydrogenation have been developed.^[6,8] Many of the highly selective catalysts are homogeneous organometallic complexes based on precious metals such as Ru,^[9] Ir,^[10,11] or Rh.^[12] In recent years, many efforts have been devoted to develop their earth-abundant counterparts and remarkable advances have been achieved, e.g. using hydrido Fe-PN^HP pincer complexes^[13] while promising results were also obtained with Mn,^[14] Co,^[15] or Cu.^[16] In most cases, the structure of the ligand has a strong influence on the dehydrogenation activity due to metal-ligand cooperativity which causes stabilization of the active species or assists outer sphere interactions involved in key determining mechanism steps.^[17]

While molybdenum is one of the nature's favorite metals for many biological transformations, when it comes to CO₂ hydrogenation or FA dehydrogenation, the number of reported Mo-based catalysts for FA decomposition is still rare. In fact, only a few heterogeneous Mo-based catalysts (carbides, nitrides and/or sulfides) are known to catalyze the dehydrogenation of formic acid.^[18–23] However, in these cases the chemoselectivity remains a key issue due to the generation of CO. As an example, utilizing MoS₂ nanoclusters deposited on graphene surfaces

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allowed for quantitative conversion of FA at 250 °C.^[21] The major decomposition products are CO₂, H₂ and methyl formate (MF); therefore, in this case disproportionation competes with FA dehydrogenation. Simulation studies of the nanoclusters structure revealed the presence of Mo-edge atoms that the authors tentatively identified as the active sites of the reaction. In 2021, Li and coworkers reported a CO-free FA dehydrogenation protocol using MoS₂ on graphene decorated on Ni foam (Ni/G/MoS₂).^[23] Full conversion and 100% selectivity towards H₂ and CO₂ is achieved at 100 °C. Notably, this latter material has a sulfur terminated surface which has strong adsorption for the H sites and weak adsorption for the O sites of FA. According to the authors, this results in the high selectivity of their protocol.

Homogeneous catalytic systems for selective FA dehydrogenations using molybdenum are also limited to a few examples shown in Scheme 1.^[24–26] Interestingly, the pincer (PNⁱP)MoH(OCOH)(CO)₂ compound (Beller and Junge, Scheme 1), in addition to FA dehydrogenation, it also catalyzes its disproportionation to methanol while stoichiometric amounts of methanol are produced in the presence of the mononuclear Cp*Mo(PMe₃)₂(CO)H hydrido complex (Parkin, Scheme 1). In contrast, the hydrido [Mo₃S₄H₃(diphosphine)]₃⁺ (Llusar, Scheme 1) cluster catalyst is selective towards H₂ production.

The proposed dehydrogenation reaction mechanism for Cp*Mo(PMe₃)₂(CO)H and [Mo₃S₄H₃(diphosphine)]₃⁺ share common features. Both complexes interact with FA to form dihydride Mo(H)₂ species or dihydrogen Mo–H–HCOOH species, in the case of [Mo₃S₄H₃(diphosphine)]₃⁺, from which hydrogen is released with the concomitant formation of formate-substituted derivatives that regenerates the hydrido catalysts through a β-hydride elimination accompanied by CO₂ release. As to (PNⁱP)MoH(OCOH)(CO)₂, formate decarboxylation through a β-hydride transfer to the metal generates dihydride Mo(H)₂ species. Selectivity in favor of either dehydrogenation or decarboxylation is determined in the next step. More specifically, dehydrogenation takes place through dihydrogen reductive elimination or *via* protonation by HCOOH, with regeneration of the (PNⁱP)MoH(OCOH)(CO)₂ metal hydride. While not mandatory, N–H proton-assisted dehydrogenation may also be operative in this last case. Disproportionation in the presence of mononuclear complexes Cp*Mo(PMe₃)₂(CO)H and (PNⁱP)MoH(OCOH)(CO)₂ results from a hydride transfer from the metal dihydride Mo(H)₂ species to an activated/protonated

molecule of HCOOH. To date, the hydrido [Mo₃S₄H₃(diphosphine)]₃⁺ cluster is the most active and selective homogeneous Mo-based catalysts for FA dehydrogenation.

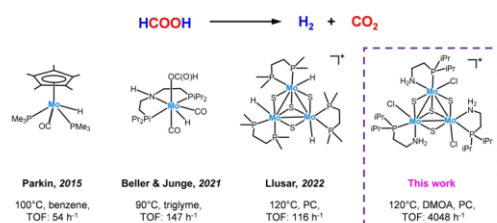
Herein, we report efficient and selective homogeneous molybdenum catalyst for FA dehydrogenation using a trinuclear non-hydride metal cluster sulfide decorated with aminophosphine ligands. The optimal [Mo₃S₄Cl₃(edⁱp,p)₃]⁺ (edⁱp,p = 2-(diisopropylphosphino)ethylamine)) pre-catalyst operates in the presence of a base without fragmentation of the cluster with an activity remarkably higher to that of known homogeneous molybdenum catalysts. The synthesis and crystal structure of this new complex is also presented. Finally, a tentative mechanism for this reaction is postulated based on stoichiometric and catalytic experiments, and validated by theoretical studies.

Results and Discussion

Synthesis and characterization of the catalyst

Motivated by the potential of molybdenum cluster sulfides as FA dehydrogenation catalysts, we undertook an exploratory study aimed to identify active cluster complexes. For that purpose, we tested several trinuclear Mo₃S₄ compounds, represented in Table 1. Except for 4⁺, the synthesis and crystal structures of the rest of the compounds have been previously reported.^[25,27–30] The catalytic tests were performed in a glass reactor connected to a manual burette (Figure S15). Initial experiments were performed under base-free reaction conditions (120 °C and propylene carbonate (PC) as solvent) employed for the catalytic hydrogen production from FA using the diphosphino [Mo₃S₄H₃(diphosphine)]₃⁺ (2⁺) cluster.^[26] As no gas evolution was observed using the Mo₃S₄ catalysts 3⁺ to 7⁺, catalytic tests were performed in the presence of Et₃N. In general, the proposed mechanism for FA dehydrogenation using bifunctional ligands proceeds *via* a formate intermediate, therefore, the base is important to start the catalytic cycle.^[31]

Two aminophosphino trinuclear complexes (3⁺ and 4⁺) differing in the nature of the group attached to the phosphorous atom and three imidazolyl amino cluster compounds (5⁺–7⁺) with the NH₂ moiety gradually substituted by methyl groups were investigated in our work.^[29,30] Complex 1, a typical precursor for the preparation of Mo₃S₄ complexes was also tested.^[27] For comparative purposes, we have also included in our studies the diphosphino Mo₃S₄ hydrido cluster (2⁺) and the pincer complex (PNⁱP)Mo(OCOH)(CO)₂ (8).^[25,28] The results of catalyst screening are summarized in Table 1. Gas evolution/time diagrams are represented in Figure S17. In the case of the already reported diphosphino [Mo₃S₄H₃(diphosphine)]₃⁺ (2⁺) catalyst, addition of Et₃N improved the catalytic activity (TOF 116 vs 411 h^{–1}).^[26] For the other Mo₃S₄ clusters (3⁺–7⁺), gas evolution started after addition of the HCOOH/Et₃N (5:2) mixture to the preheated solution of the catalysts. While similar TON were obtained for compounds 2⁺, 3⁺ and 4⁺ (Table 1, entries 2–4), the highest catalytic activity was achieved using compound 4⁺ (Table 1, entry 4). Therefore, replacing the phenyl



Scheme 1. Reported Mo-based catalysts active in the FA dehydrogenation.

Table 1. Catalyst screening for the FA dehydrogenation.^[a]

$\text{HCOOH} \xrightarrow[120^\circ\text{C, PC, 60 min, Et}_3\text{N}]{0.01 \text{ mmol catalyst}} \text{H}_2 + \text{CO}_2$				
Entry	Catalyst	Conversion(%) ^[c]	TON ^[d]	TOF ^[e]
1	1	25	25	55
2	2 ⁺	> 99	98	411
3	3 ⁺	97.5	96	272
4	4 ⁺	> 99	98	589
5	5 ⁺	85	84	117
6	6 ⁺	10	10	18
7	7 ⁺	4	4	18
8	8 ⁺	2	2	18
9 ^[h]	4 ⁺	–	–	–

[a] Reaction conditions: HCOOH (1 mmol), Et₃N (0.4 mmol), Mo₃S₄ catalyst (0.01 mmol), PC (1.5 mL), T(120 °C), 60 min. [b] Same conditions as [a] without addition of a base [c] Based on gas evolved. [d] TON values are calculated at the end of the reaction. [e] TOF is obtained for the most active 10 min period of the reaction. Gas evolution monitored with manual burettes, corrected by the blank volume and content of the gas phase analyzed by gas chromatography (GC). The CO content was below the detection limit (< 10 ppm) (Figure S16). Experiments were performed at least twice except entry 2.

group bound to the phosphorous atom of the aminophosphino ligand by isopropyl increased the catalytic activity of the Mo₃S₄ cluster complex. As expected, no catalytic activity was found for 4⁺ in the absence of a base (Table 1, entry 9). Little gas evolution was observed for the cluster precursor 1 corroborating the crucial role of the ligand.

The catalytic activity of the imidazolyl amino-containing clusters decreased in the order 5⁺ > 6⁺ > 7⁺ (Table 1, entries 5–7). Hence, we conclude that methylation of one hydrogen atom of the N–H moiety in 5⁺ leads to a significant decrease in the catalytic activity. In agreement with this observation, complete alkylation of the N–H moieties in 5⁺ drastically lowered the hydrogen yield. To obtain evidence about the cluster integrity during the catalytic protocol, ESI-MS was recorded after catalytic gas evolution in the presence of the 4⁺ cation. Notably, no decomposition products could be observed, and the only peak registered corresponds to the 4⁺ complex supporting a cluster catalysis mechanism (Figure S14). The catalytic activity of the mononuclear pincer Mo catalyst (8) reported as active by some of us for FA dehydrogenation and disproportionation was also tested under these conditions showing only a negligible activity. In all experiments, the

possibility of FA disproportionation was also investigated but neither methanol nor methyl formate were detected by gas chromatography.

For the synthesis of the new cluster cation [Mo₃S₄Cl₃(ed'p,p)]⁺ (4⁺), we followed the procedure developed by one of our groups for the synthesis of other Mo₃S₄ derivatives.^[30,32] The cluster precursor Mo₃S₄Cl₄(PPh₃)₃(H₂O)₂ was reacted with a slight excess of the aminophosphine ed'p,p ligand in EtOH at room temperature for 3 hours. The reaction proceeds with color changes from green to brown and back to green. The desired product was precipitated with pentane as the chloride salt, redissolved in methanol and precipitated with sodium tetraphenylborate as [Mo₃S₄Cl₃(ed'p,p)]⁺BPh₄[–] (4(BPh₄)). The product identity was confirmed by ESI-MS on the basis of its m/z value of 1005.9 and its characteristic isotopic pattern (Figure S14).

The structure of cation 4⁺ has been determined by single crystal X-ray diffraction as its chloride salt and solved in space group P-1. Figure 1 shows the ORTEP view of 4⁺ together with the most relevant bond distances. The crystal structure contains two crystallographically independent cluster units, two chloride atoms and one dichloromethane molecule. The trinuclear Mo₃S₄ unit possesses an incomplete cubane-type arrangement with the molybdenum and sulfur atoms occupying adjacent vertices leaving a vacant metal position. The three metal atoms define an approximately equilateral triangle and the Mo–Mo bond distance of 2.760(6) Å corresponds to a single metal-metal bond. Cluster 4⁺ shares main geometric features with other trinuclear cluster analogs.^[29]

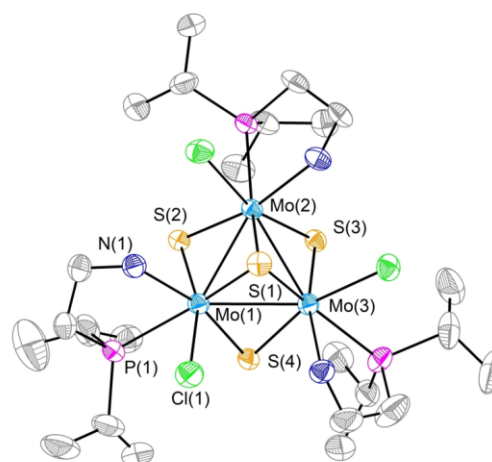


Figure 1. ORTEP representation of the [Mo₃S₄Cl₃(ed'p,p)]⁺ (4⁺) cation (ellipsoids at 50 % probability) with the atom-numbering scheme. Hydrogen atoms have been omitted for clarity. Main bond distances: Mo–Mo = 2.760(6) Å, Mo–S(1) = 2.346(4) Å, Mo–S_(trans-NH₂) = 2.300(5) Å, Mo–S_(trans-Cl) = 2.296(6) Å, Mo–Cl = 2.510(12) Å, Mo–N = 2.254(7) Å, Mo–P = 2.576(10) Å. Standard deviations for averaged values are given in square brackets. CCDC 2261460.

Each metal atom in 4^+ shows a pseudo-octahedral environment and its coordination sphere includes a phosphorous and a nitrogen atom from the ed'p,p ligand, a chlorine atom, one capping and two bridging sulfur atoms. A relevant feature for this compound is the specific coordination of the aminophosphino ligand in which the three phosphorous atoms are located *trans* to the capping sulfur atom as observed for other aminophosphino M_3S_4 ($M = Mo, W$) clusters.^[29,33]

The solid-state structure of complex 4^+ is preserved in solution as evidenced by the $^{31}P\{^1H\}$ NMR spectrum registered in CD_2Cl_2 , which showed a single signal at 53.55 ppm attributed to the three equivalent phosphorous atoms from the aminophosphine ligands which are located above the metal plane (Figure S11). The cluster C_3 symmetry is evidenced by 1H NMR spectroscopy where the aminophosphine signals demonstrate that all bidentate ligands are equivalent. In particular, the protons associated to the N–H moiety of the ligand appear at 2.80 and 3.29 ppm in agreement with two different hydrogen orientations. More details about 1H NMR and ^{13}C NMR spectra are given in the Supporting Information (Figures S12 and S13).

Catalytic performances

At this point, different important reaction variables were varied such as FA concentration and catalyst loading, solvent, base and FA to base ratio employing $[Mo_3S_4Cl_3(ed'p,p)_3]BPh_4$ ($4(BPh_4)$) as catalyst. The influence of the FA concentration was evaluated keeping the amount of catalyst 4^+ constant (Figure S18 and entries 1–3, Table 2). Increasing the amount of formic acid from 1 to 10 mmol (entries 1–3, Table 2) proportionally increased the TON. Interestingly, the diphosphino $[Mo_3S_4H_3(diposphine)_3]^+$ (2^+) losses efficiency at higher HCOOH loading that is at lower pH.^[26] However, the TOF_{10min} numbers using 4^+ decreased on going from 5 to 10 mmol of FA (entries 2–3, Table 2). This is likely due to pH changes over the course of the reaction. A

variation of the FA concentration by increasing the solvent volume (Figure S19 and entries 3–4, Table 2) resulted in a remarkable improvement of the catalytic activity. Next, the catalyst loading was investigated at constant FA concentration (entries 4–6, Figure S110). A decrease in the catalyst loading by half decreases the catalytic activity; however, doubling the amount of pre-catalyst caused only a ca. 2 fold increase of the TOF. Then, we decided to continue our studies using a catalyst concentration of 0.01%, that is, the conditions of entry 4 in Table 2.

Previous studies demonstrated that the solvent has a decisive influence in this transformation as it can shift FA decomposition from dehydrogenation to disproportionation.^[25] Hence, the effect of the solvent on the reaction was examined and the resulting gas evolution curves are represented in Figure 2a. Significant catalytic activity towards hydrogen evolution was observed in toluene although PC continues to be a better choice. In the case of THF, gas release was almost negligible. The reaction mixture was analysed to detect any potential products resulting from FA disproportionation but neither methyl formate nor methanol were detected. Then, the influence of the temperature was investigated using PC as solvent (Figure 2b). As expected, decreasing the temperature resulted in slower gas evolution. Both gas evolution/time curves in Figure 2a–2b show a slope change in the curve, that is an induction period, which is more visible for the systems with slower kinetics. In the early stage of the reaction, we also observed a color change from green to brown. These observations agree with $4(BPh_4)$ being the pre-catalyst from which active species are formed after HCOOH/ Et_3N addition. Incidentally, $4(BPh_4)$ does not react with HCOOH in the absence of a base (Figures S115–S116).

In the next step, we investigated the influence of the base as well as the FA to base ratio and the results are summarized in Figures 2c–2d. The corresponding gas evolution/time curves are given in the SI (Figures S111–S112). The use of N,N -dimethyloctylamine (DMOA) instead of Et_3N (Figure 2c) noticeably increased the performance achieving TOFs of ca. $2000\ h^{-1}$. Decrease of the FA to DMOA ratio (Figure 2d) to 11:10 resulted in a significant improvement of the catalytic activity reaching TOFs of $4048\ h^{-1}$ ($3743\ h^{-1}$ after 15 min). On the other hand, a significant drop in the catalytic activity was found upon increasing the FA to DMOA ratio from 5:2 to 5:1 (TOF: 1736 vs. $374\ h^{-1}$) which demonstrates the crucial role of the base during the reaction.

Finally, recycling experiments were performed. After each run, as the base is expected to be recovered, only neat formic acid was added to the solution. The catalyst system stayed active in the tested four runs; however, some loss of activity is observed after the second run as shown in Figure S113. We assume catalyst deactivation occurs through fragmentation of the trinuclear cluster catalyst, in agreement with the previously described diphosphino Mo_3S_4 cluster catalyst.^[26] Hence, to further improve this class of catalysts to a practically applicable level, it is important to increase the stability of the cluster by respective ligand design.

Table 2. Molybdenum-catalyzed dehydrogenation of formic acid: Influence of the formic acid concentration and catalyst loading.^[a]

Entry	FA (mmol)	Cat. (μ mol)	V_{PC} (mL)	$V_{H_2+CO_2}$ (mL) ^[d]	TON ^[d]	TOF _{10min} (h^{-1}) ^[f]
1	1	10	1.5	48	98	1472 ^[g]
2	5	10	1.5	281	574	791
3	10	10	1.5	408	834	288
4 ^[h]	10	10	5	450	921	546
5 ^[h]	10	5	5	305	1247 ^[e]	368
6 ^[h]	10	20	5	482	493	1251

[a] Reaction conditions: catalyst 4^+ (0.01 mmol), PC (1.5 mL), $T(120^\circ C)$. [b] HCOOH (10 mmol), Et_3N (4 mmol), catalyst 4^+ (0.01 mmol), PC (5 mL), $T(120^\circ C)$ [c] Gas evolution monitored with manual burettes, corrected by the blank volume and content of the gas phase analyzed by gas chromatography (GC). [d] TON values are calculated at the end of the reaction. [e] TON value is calculated after system saturation ($t = 240\ min$). [f] TOF values are calculated at the first 10 min of reaction [g] TOF value is calculated after 4 min. All the experiments were performed at least twice, and average values are used in the table. (St. Dev. < 10%)

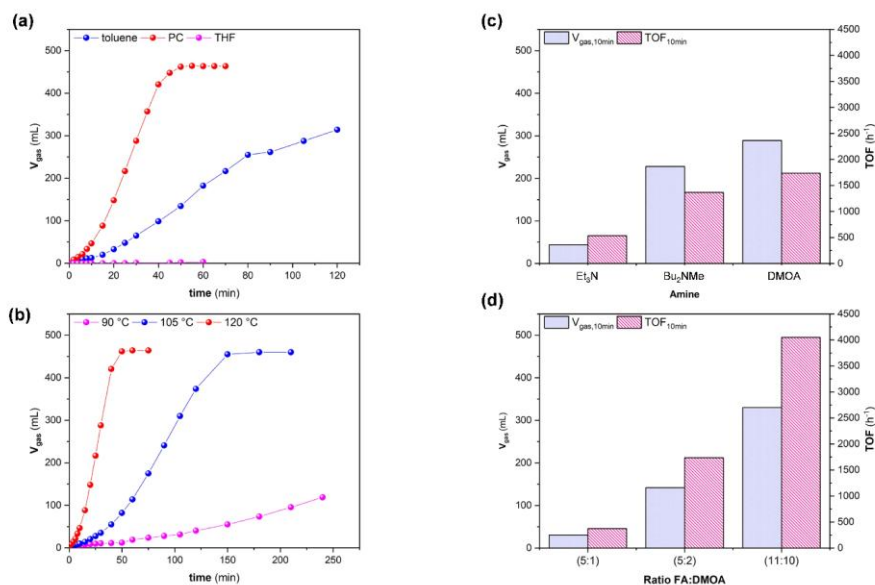


Figure 2. Molybdenum-catalyzed dehydrogenation of formic acid. Influence of (a) solvent (toluene, PC, THF), (b) temperature (90 °C, 105 °C, 120 °C), (c) base (Et₃N, Bu₄NMe, DMOA) and (d) ratio of FA:DMOA (5:1, 5:2, 11:10). TOF values are obtained for the first active 10 min period of the reaction. Standard conditions if not otherwise noted: **4**⁺ was used as the catalyst, 10 mmol of FA, 4 mmol Et₃N, T = 120 °C, 5 mL PC.

Mechanistic insights

Previous studies have shown that aminophosphino [M₃S₄X₃(aminophosphine)₃]⁺ (M=Mo, W) cluster complexes present distinctive features when compared to its diphosphine analogs such as the facile substitution of the halide ligands (X) by other halides or pseudohalides. Conversion occurs *via* the formation of two reaction intermediates associated to the mono and disubstituted trinuclear complexes.^[34] Kinetic studies showed that the mechanism of substitution is strongly dependent on the nature of the leaving group. On the other hand, Collision Induced Dissociation (CID) experiments combined with the calculated energy requirements for the partial decoordination of the ligand are contrary to the general idea regarding the hemilabile character of the aminophosphine ligand.^[29]

For FA dehydrogenation reactions it is generally accepted that the corresponding formate complex is the starting point or crucial intermediate of the catalytic cycle. Hence, the presence of base and pH are important factors for this transformation.^[17,24,26,31] From the formate species, β -hydride elimination produces the respective hydride complex. To gain insight on the ligand substitution process, halide by formate, we investigated the stoichiometric reaction between **4**⁺ and formic acid in presence of Et₃N using a FA:Et₃N (5:2) mixture. Milder reaction conditions (lower temperature) compared to those of the catalytic protocol were employed to prevent complications due to β -hydride elimination. The ³¹P{¹H} NMR spectrum of the mixture after 10 minutes of reaction in

acetonitrile-d₃ (CD₃CN) at 50 °C shows a series of signals with the typical pattern of a sequential substitution of the **4**⁺ chlorine atoms by formate ligands, represented in Figure 3a.^[26] It should be noted that the loss of symmetry of the two resulting intermediates the monosubstituted [Mo₃S₄Cl₂(OCOOH)(ed)₃]⁺ (**M**) and disubstituted [Mo₃S₄Cl(OCOOH)₂(ed)₃]⁺ (**D**) makes the three phosphorus atoms non-equivalent. For both cluster complexes, three signals of equal intensity are expected in the ³¹P{¹H} NMR spectrum. The singlet observed at δ = 56.70 ppm has been tentatively assigned to the triple substituted [Mo₃S₄(OCOOH)₃(ed)₃]⁺ product (**T**) which recovers the C₃ symmetry of its **4**⁺ cluster precursor.

To our delight, some crystals were formed overnight in the NMR tube by slow evaporation of the solvent. While the quality of most of these crystals was not suitable for single crystal X-ray diffraction experiments, finally we were able to select one crystal valid for that purpose. Figure 3b shows the ORTEP view of [Mo₃S₄Cl(OCOH)₂(ed)₃]⁺ (**D**) together with the most relevant bond distances. The crystal structure is solved in space group P-1 and it contains one crystallographically independent cluster unit of formula [Mo₃S₄Cl(OCOH)₂(ed)₃]⁺ resulting from the substitution of two of the chlorine atoms bound to molybdenum in **4**⁺ by two formate ligands. Incidentally, one of the ed ligand is disordered over two positions (see Experimental Section).

The [Mo₃S₄Cl(OCOH)₂(ed)₃]⁺ cation shares common structural features with its chloride cluster precursor **4**⁺. Inspection of the interatomic distances revealed the presence

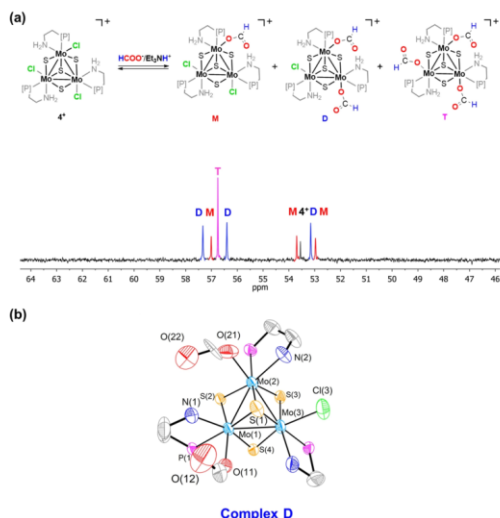


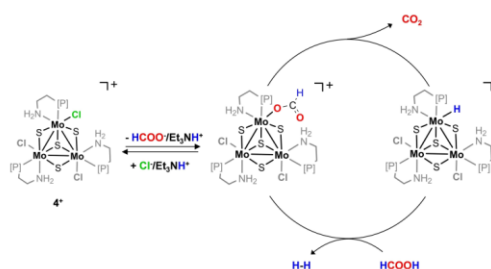
Figure 3. Reaction product between 4^+ and 7.5 equivalents of a FA/Et₃N(5:2) mixture at 50 °C in CD₃CN. (a) $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD₃CN) spectrum of the reaction mixture, recorded at room temperature. Signals have been tentatively assigned according to the shift in comparison with 4^+ and the trisubstituted complex (T). (b) ORTEP representation of the $[\text{Mo}_3\text{S}_4\text{Cl}(\text{ed}'\text{p},\text{p})_3]^+$ cation (ellipsoids at 50% probability) with the atom-numbering scheme. Hydrogen atoms, isopropyl substituents, and the minor component of the disordered ed'p,p ligand have been omitted for clarity. Main bond distances: Mo–Mo = 2.760(5) Å, Mo–S(1) = 2.357(13) Å, Mo–S_(trans-NH₂) = 2.295(12) Å, Mo–S_(trans-Cl) = 2.292 Å, Mo–S_(trans-O) = 2.288 [12] Å, Mo–N = 2.266(4) Å, Mo–P = 2.572(10) Å, Mo–O = 2.244(5) Å, Mo–Cl = 2.512(15) Å. Standard deviations for averaged values are given in square brackets. CCDC 2261461.

of (NH)–H···O(COH) hydrogen bonds with a N(1)–O(11) distance of 2.875 Å and a N(2)–O(21) distance of 2.787 Å. In addition, the terminal formate oxygen atoms O(12) and O(22) forms hydrogen contacts with the H(NH) moiety with a N(1)–O distance of 2.781 Å for O(12) and of 2.805 Å for O(22). In order to prove whether or not the measured crystal was representative of the crystalline sample, we recorded the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crystalline product after filtration (Figure SI17). The spectrum shows eight signals of similar intensity associated to 4^+ and to the mono- (M), di- (D) and tri-substituted (T) formate cluster complexes. Therefore, the crystal structure composition of $[\text{Mo}_3\text{S}_4\text{Cl}(\text{ed}'\text{p},\text{p})_3]^+$ is not representative of the whole crystalline sample. Next, we registered the ESI-MS spectra of the sample at 10 and 20 V (Figures SI18–SI19). The spectrum at 10 V showed one broad signal which can be tentatively assigned to 4^+ ($m/z = 1006$) and to the mono-substituted $[\text{Mo}_3\text{S}_4\text{Cl}_2(\text{ed}'\text{p},\text{p})_3]^+$ (M) ($m/z = 1016$) complex based on their m/z values and isotopic patterns. Therefore, the di- and tri-substituted species suffer a transformation at the mass spectrometer towards 4^+ (*vide infra*). At higher cone voltages (20 V), a new signal emerged identified as the hydrido $[\text{Mo}_3\text{S}_4\text{Cl}_2\text{H}(\text{ed}'\text{p},\text{p})_3]^+$ ($m/z = 972$) cluster cation, which suggests that $[\text{Mo}_3\text{S}_4\text{Cl}_2(\text{ed}'\text{p},\text{p})_3]^+$ (M) undergoes partially a β -

hydride elimination at the mass spectrometer to form the corresponding hydrido species.

Based on the above results, we propose a tentative catalytic cycle for FA dehydrogenation, represented in Scheme 2, simplified to a single metal center. In our proposal, the cluster 4^+ acts as pre-catalyst in agreement with the induction period observed in catalytic reaction monitoring (Figure 2a–2b), as mentioned above. First, the terminal chlorine atoms of the 4^+ cluster are substituted by HCOO^- ligands to form the formate complex. Next β -hydride elimination followed by CO_2 release leads to the hydrido cluster. In the final step, protonation of the hydride results in the formation of dihydrogen species from which hydrogen is released and the active formate species is regenerated. Protonation of the Mo–H group in cuboidal diphosphino Mo_3S_4 clusters by HCOOH to form dihydrogen $\text{Mo–H} \cdots \text{HCOOH}$ species is well established.^[26,35]

To obtain information about active species and reaction intermediates, the FA dehydrogenation reaction was monitored by ESI mass spectrometry and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, represented in Figure 4. For that purpose, milder reaction conditions (1 mmol of FA, 0.030 mmol of Et₃N and 0.010 mmol of the 4^+ catalyst) were employed to facilitate sampling. At first glance, the reaction monitoring results may seem contradictory. While ESI-MS only showed the presence of cluster $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{ed}'\text{p},\text{p})_3]^+$ (4^+) without any time evolution along the course of the reaction (Figure 4a); the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum evidenced the presence of several species in the reaction mixture (Figure 4b). Since aminophosphino Mo_3S_4 complexes can undergo transformations in the mass spectrometer, the utility of this technique for reaction monitoring is limited except to confirm the operation of a cluster catalysis mechanism. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra after 30 minutes of reaction (Figure 4b) within the 52 to 58 ppm range matches with the products obtained from the stoichiometric reaction between the 4^+ cluster catalyst and formic acid in presence of Et₃N (Figure 3a), that is the mono-, di- and tri-substituted $[\text{Mo}_3\text{S}_4\text{Cl}_{3-x}(\text{ed}'\text{p},\text{p})_3]^+$ ($x = 1, 2$ and 3) species (M, D and T) plus some unreacted 4^+ cluster. In addition, an extra singlet signal appeared at $\delta = 64.16$ ppm, marked with an H. Incidentally, this signal is also observed upon heating the reaction mixture formed by the mono-, di-, and tri-substituted $[\text{Mo}_3\text{S}_4\text{Cl}_{3-x}(\text{ed}'\text{p},\text{p})_3]^+$ ($x = 1, 2$ and 3) species (Figure SI20).



Scheme 2. Proposed catalytic cycle for the dehydrogenation of FA.

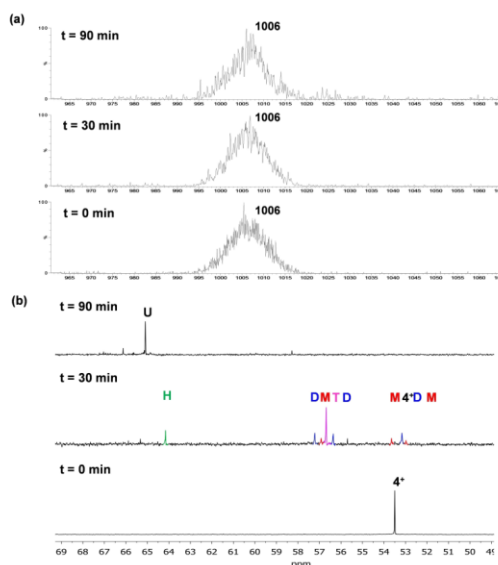


Figure 4. Monitoring of the catalytic reaction by (a) ESI-MS spectrometry and (b) $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_3CN) spectroscopy. Reaction conditions: HCOOH (1 mmol), Et_3N (0.03 mmol), catalyst 4^+ (0.01 mmol), PC (1.5 mL), T (120°C)

Because it is well known that formate complexes undergo β -hydride elimination to form hydrido species, we have tentatively assigned the singlet signal, labelled as **H**, to the hydrido $[\text{Mo}_3\text{S}_4\text{H}_3(\text{edpp})_3]^+$ cluster cation. Notably, we were unable to detect any signal of hydrido species by ^1H NMR spectroscopy. This is not surprising since previous NMR studies on the hydrido $[\text{W}_3\text{S}_4\text{H}_3(\text{edpp})_3]^+$ ($\text{edpp} = 2$ -aminoethyl)diphenylphosphine) cluster showed that one of the hydrogen atoms of the NH_2 aminophosphine group is rapidly exchanging with the hydride and as a consequence no hydride signal is seen by ^1H NMR spectroscopy.^[36] Unfortunately, all attempts to synthesize and isolate this last postulated species failed.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at the end of the reaction when no FA is left (Figure 4b, 90 min) showed a unique signal at $\delta = 65.09$ ppm labelled as **U**. This signal is also observed upon reacting the 4^+ complex catalyst with 40 equiv. of Et_3N at 50°C (Figure SI21). Previous spectroscopic studies combined with theoretical calculations on the reactivity of the aminophosphino $[\text{W}_3\text{S}_4\text{Br}_3(\text{edpp})_3]^+$ cluster towards Et_3N indicated that the amine acts as a base and abstracts one proton from the NH_2 group of the bidentate ligand while bromine dissociates.^[36] Also, Collision Induced Fragmentation (CID) of the $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{edpp})_3]^+$ (3^+) cluster catalyst occurred with HCl release to yield deprotonated $[\text{Mo}_3\text{S}_4(\text{edpp-H})_3]^+$ species.^[29] Based on these antecedents, we tentatively assigned the singlet signal at $\delta = 65.09$ ppm to the $[\text{Mo}_3\text{S}_4(\text{edp,p-H})_3]^+$ (**U**) unsaturated $\text{Mo}=\text{NH}$ amido cluster. It is of interest to remark that the ESI-MS of this reaction mixture, 4^+ and Et_3N , showed a sole peak (Figure SI22) attributed to the 4^+

cluster catalyst. This fact gives further support to the ability of these aminophosphine Mo_3S_4 clusters to react in the mass spectrometer and transform into the 4^+ cluster precursor.

Computational studies

Once direct or indirect experimental evidence were obtained to support our mechanism proposal depicted in Scheme 2, that is formation of the cluster formate and the hydrido complex, we undertook a theoretical DFT study to validate our proposal (see Computational Methods in the SI for details). The calculated free energy profile (Figure 5) has been restricted to a single metal center, a common simplification in this kind of cluster complexes where substitution reactions occur with statistically controlled kinetics.^[35] First, complex 4^+ exchanges a chlorine atom by a formate ligand generating the active species (**I**). The process is slightly exergonic ($-0.76 \text{ kcal}\cdot\text{mol}^{-1}$) in agreement with our experimental observation on the coexistence in the reaction mixture of the formate substituted $[\text{Mo}_3\text{S}_4\text{Cl}_{3-x}(\text{OCOH})_x(\text{edp,p})_3]^+$ ($x=1,2,3$) species and the 4^+ chloride precursor under stoichiometric conditions. The proposed catalytic cycle (Scheme 2) starts with the active formate complex (**I**). The initial step of the catalytic process entails the liberation of CO_2 from the formate complex (**I**) via a β -hydride elimination ($\text{TS}_{\text{H-H}}$). Notice that high temperatures are needed to overcome the barrier ($24.9 \text{ kcal}\cdot\text{mol}^{-1}$) towards the formation of the hydride species (**II**). This result supports our assignment of the $^{31}\text{P}\{^1\text{H}\}$ NMR signal registered at $\delta = 64.16$ ppm, labeled with an **H** in Figures 4b and SI20, only observed in the catalytic reaction mixture run at 120°C or upon heating at 90°C the $[\text{Mo}_3\text{S}_4\text{Cl}_{3-x}(\text{OCOH})_x(\text{edp,p})_3]^+$ ($x=0, 1, 2, \text{ and } 3$) reaction mixture prepared under stoichiometric conditions. In the second step, FA addition results in formation of a dihydrogen $\text{Mo}-\text{H}\cdots\text{HCOOH}$ (**III**) adduct with a variation in the free energy of $-3 \text{ kcal}\cdot\text{mol}^{-1}$. The opposite tendency is observed for the formation of the diposphino Mo_3S_4 dihydrogen adduct which is endergonic at 120°C by ca. $3 \text{ kcal}\cdot\text{mol}^{-1}$.^[26,35] We attribute the higher stabilization energy in the case of **III** to the hydrogen bond formation between the carbonyl group of the FA and the NH protons of the ligand in the adjacent metal, with a $\text{N}\cdots\text{O}$ optimized distance of $2.941 \text{ \AA}$. The beneficial role of ligands containing NH functionalities in stabilizing formic acid via hydrogen bond interactions has been well established in the literature.^[31,37]

In the final step, the dihydrogen adduct (**III**) releases hydrogen through $\text{TS}_{\text{H-H}}$ and regenerates the formate **I** active species. The calculated barrier for the H_2 release ($32.2 \text{ kcal}\cdot\text{mol}^{-1}$) indicates that dehydrogenation is the rate determining step. Hence, higher temperatures favor this last step of the catalytic cycle and we observe optimum TON upon increasing the reaction temperature to 120°C . Similar energy barriers were calculated for the FA dehydrogenation using the diposphino Mo_3S_4 cluster hydride.^[26] Overall, FA dehydrogenation is an exergonic process with a relative energy of $-11.8 \text{ kcal}\cdot\text{mol}^{-1}$ that leads to the regeneration of the catalytic active species.

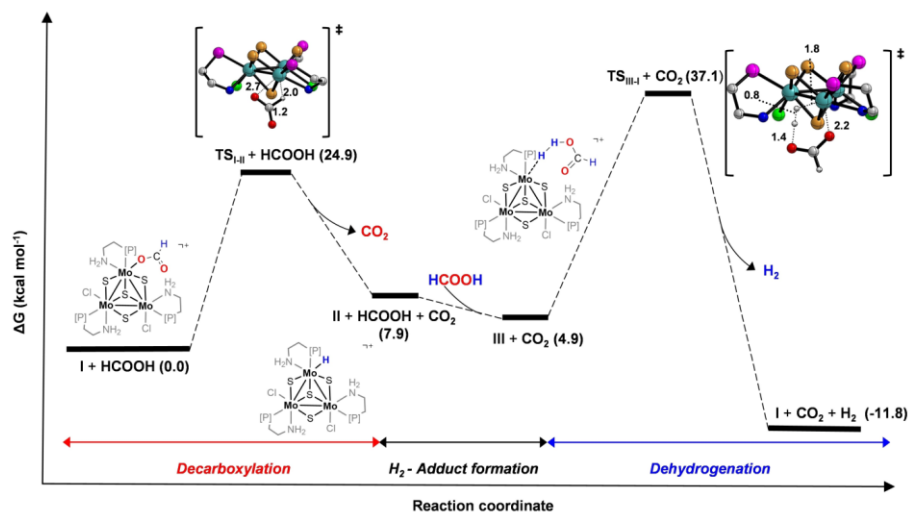


Figure 5. DFT calculated energy profile for FA dehydrogenation catalyzed by 4^+ . Free-energy values are given in kcal mol^{-1} , quoted relative to $\text{I} + \text{HCOOH}$ at 393.15 K and atmospheric pressure. For simplicity, only the skeleton of the ed,p ligands was drawn. Distances are given in Å. Color code: Mo (cyan), S (orange), P (pink), N (dark blue), O (red), C (grey), H (white).

Conclusions

In this work, we demonstrate that novel molybdenum catalysts are highly active and selective in formic acid dehydrogenation. Within a series of air-stable aminophosphino and imidazolylamino Mo_3S_4 cuboidal clusters, $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{ed},\text{p},\text{p})_3]^+$ (4^+ , ed,p = 2-(diisopropylphosphino)ethylamine) showed significantly improved performance ($\text{TOF} = 4048 \text{ h}^{-1}$) compared to all other molybdenum compounds reported for this transformation up to date. In the crystal structure of 4^+ , the three phosphorus atoms of the ligand are located *trans* to the capping sulfur atoms. Complex 4^+ acts as a pre-catalyst from which the active formate substituted species $[\text{Mo}_3\text{S}_4\text{Cl}_{3-x}(\text{OCOH})_x(\text{ed},\text{p},\text{p})_3]^+$ ($x = 1, 2, 3$) are generated.

These last species coexist with the 4^+ cluster precursor along the catalytic protocol. The crystal structure of one of the substitution products $[\text{Mo}_3\text{S}_4\text{Cl}(\text{OCOH})_2(\text{ed},\text{p},\text{p})_3]^+$ shows hydrogen bonding between the formate hydrogen atoms and the aminophosphine NH_2 protons. A cluster catalysis mechanism is proposed based on stoichiometric and catalytic experiments and our proposal has been validated by DFT calculations. The catalytic cycle entails as the first step elimination of CO_2 starting from the active Mo_3S_4 cluster formate through an intermolecular mechanism without the need of a vacant coordination site. The resulting hydrido cluster interacts with FA to form dihydrogen $\text{Mo}-\text{H}\cdots\text{HCOOH}$ species from which hydrogen is released with the concomitant regeneration of the active formate Mo_3S_4 cluster. The overall process is highly selective with a CO content in the generated gas phase below 10 ppm.

Experimental Section

General remarks

All reactions were carried out under inert atmosphere (nitrogen or argon) using standard Schlenk techniques. Reactants obtained from commercial sources were used as received. Solvents were degassed through three freeze-thaw cycles and stored under argon or nitrogen. Elemental analyses were carried out on a EuroEA3000 Eurovector Analyzer. ^1H NMR spectra were obtained at Bruker Avance III HD 400 MHz or 300 MHz. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained at 101 MHz. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 121 MHz or 162 MHz. NMR chemical shifts are reported in ppm and were referenced to the solvents. ^{31}P NMR chemical shifts are reported in ppm referenced to an external 85% solution of H_3PO_4 . Abbreviations used in the reported NMR experiments: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet. High resolution mass spectra were registered in a QTOF Premier instrument equipped with an orthogonal Z-spray-electrospray interface (Waters, Manchester, UK) operated in the V-mode at a resolution of ca. 10 000 (FWHM). The drying and cone gas was nitrogen set to flow rates of 300 and 30 L h^{-1} , respectively. A capillary voltage of 3.5 kV was used in the positive scan mode and the cone voltage was set to $U_c = 20 \text{ V}$. ESI-mass spectra were registered using a triple quadrupole mass spectrometer with an orthogonal Z-spray electrospray source (Waters, Manchester). The temperature of the source block was set to 100°C , and the solvation temperature was set to 120°C . A capillary voltage of 3.3 kV was used in the positive scan mode, and the cone voltage was set to $U_c = 20 \text{ V}$. Sample solutions in CH_3CN were injected with a syringe pump directly connected to the ESI source at a flow rate of $10 \mu\text{L min}^{-1}$. Chemical identification of the cluster species was carried out by comparing the experimental and theoretical isotopic pattern calculated from its elemental composition by using the MassLynx 4.1 program.^[38] Gas content was determined by gas-phase GC. Presence of methyl formate or methanol in the reaction mixture were performed in the liquid

phase(s) by GC using hexadecane as internal standard. GC measurements were carried out on an Agilent 6890A GC System equipped with a FID and a capillary column Agilent (HP-innowax, 30 m×250 μm×0.25 μm). Formic acid was quantified in the liquid phase by HPLC (Nucleodur C18 Pyramid 0.25 m, 5 μm, UV (210 nm)) applying propionic acid as internal standard.

Catalyst preparation

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. The trinuclear precursor $\text{Mo}_3\text{S}_4\text{Cl}_6(\text{PPh}_3)_3(\text{H}_2\text{O})_2$ (1) was prepared according to the literature procedure.^[27] Cluster salts $[\text{Mo}_3\text{S}_4\text{H}_3(\text{dmpe})_3](\text{BPh}_4)$ [2](BPh_4), $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{edpp})_3]\text{BPh}_4$ [3](BPh_4), $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{ImNH}_2)_3]\text{BF}_4$ [5](BF_4), $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{ImNHMe})_3]\text{BF}_4$ [6](BF_4) and $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{ImNMe}_2)_3]\text{BF}_4$ [7](BF_4) were obtained following previously reported synthetic methodologies.^[28–30] Mononuclear molybdenum catalyst was provided by the group “Catalysis for Energy Technologies” in LIKAT.

Synthesis of $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{edp,p})_3](\text{BPh}_4)$ [4](BPh_4): A small excess of the diisopropylaminophosphine ligand (0.076 g, 0.473 mmol) was added to a green suspension of the freshly prepared $[\text{Mo}_3\text{S}_4\text{Cl}_6(\text{PPh}_3)_3(\text{solvent})]$ cluster (0.200 g, 0.147 mmol) in 40 mL of nitrogen flushed ethanol. This addition was accompanied by color changes (green→brown→green) and caused the complete dissolution of the solid. The reaction mixture was reacted for 3 hours at room temperature and then, the volume is reduced to $\frac{1}{4}$ of the initial volume in the vacuum line. Following, pentane was added until a precipitate appeared and the mixture was kept in the fridge overnight to complete precipitation process. Next, the solid was separated by filtration, washed with hot hexane and counter anion exchange was carried out by redissolving the solid in the minimum amount of methanol and adding NaBPh_4 to the methanolic solution caused the precipitation of the desired green solid. Again, the solid was separated by filtration and washed with methanol and diethyl ether, affording the air-stable product characterized as $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{edp,p})_3](\text{BPh}_4)$ (0.110 g, 68% yield).

^1H NMR (CD_2Cl_2 , 400 MHz): δ =1.17 (dd, J = 15.1 Hz and 7.4 Hz, 9H, CH_3 , H_f), 1.26 (dd, J = 14.0 and 7.0 Hz, 9H, CH_3 , H_f), 1.59–1.67(m, 9H, CH_3 , H_f), 1.70 (dd, J = 15.5 and 7.0 Hz, 9H, CH_3 , H_f), 2.32–2.49(m, 6H, CH_2 -N, H_g), 2.56 (m, 3H, CH–P, H_c), 2.74 (b, 3H, NH, H_d), 3.16 (dp, J = 9.2 and 7.1 Hz, 3H, CH, H_e), 3.32 (d, J = 11.3 Hz, 3H, NH, H_d), 3.37–3.50 (m, 3H, CH–P, H_c), 3.71 (h, J = 7.4 Hz, 3H, CH, H_e), 6.87 (t, J = 6.6 Hz, 4H, CH, BPh_4^-), 7.03 (t, J = 7.4 Hz, 8H, CH, BPh_4^-), 7.29–7.34 (m, 8H, CH, BPh_4^-); ^{13}C { ^1H } NMR (CD_3CN , 101 MHz): δ =20.77 (s, CH_3 , C_f), 21.39 (s, CH_3 , C_f), 21.61 (s, CH_3 , C_f), 21.96 (s, CH_3 , C_f), 27.09 (d, CH_2 , C_g), 27.47 (d, CH, C_d), 29.65 (d, CH, C_d), 46.57 (d, CH_2 , C_e), 122.28 (s, CH, BPh_4^-), 126.19 (s, CH, BPh_4^-), 136.51 (s, CH, BPh_4^-); ^31P { ^1H } NMR (162 MHz, CD_2Cl_2) δ : 53.55 (s, 3P) ppm; HR-MS (ESI) m/z calcd for $\text{Mo}_3\text{S}_4\text{Cl}_3\text{C}_{24}\text{H}_{46}\text{N}_3\text{P}_3$: 1005.9100 [M] $^+$; found: 1005.8958 Elemental analysis (%) calcd for $\text{Mo}_3\text{S}_4\text{Cl}_3\text{P}_3\text{N}_3\text{C}_{24}\text{H}_{46}$: C: 43.50; H: 6.08; N: 3.17; S: 9.68; found C: 43.95; H: 6.18; N: 3.32; S: 9.79.

X-ray data collection and structure refinement

Single crystals of $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{edp,p})_3]\text{Cl}$ [4](Cl) cluster suitable for X ray analysis were obtained by slow diffusion of pentane over a dichloromethane solution containing the cluster. Crystals of $[\text{Mo}_3\text{S}_4\text{Cl}(\text{HCOO})_2(\text{edp,p})_3]\text{BPh}_4$ were grown by slow evaporation of a sample solution of the reaction mixture between 4^+ and excess of FA:Et₃N (5:2) in CD_3CN . Diffraction data collection was performed at $T=200(14)$ K on an Agilent Supernova diffractometer equipped with an Atlas CCD detector. Mo- K_α radiation ($\lambda=0.71073$ Å) was used for cluster 4^+ and Cu- K_α radiation ($\lambda=1.54184$ Å) in the case of $[\text{Mo}_3\text{S}_4\text{Cl}(\text{OCHO})_2(\text{edp,p})_3]^+$. No instrument

or crystal instabilities were observed during data collection. Absorption corrections based on the multiscan method were applied.^[39,40] The structures were solved by direct methods and refined by the full-matrix method based on F^2 with the program SHELXL-13 using the Olex2 software package.^[41–43]

The structures of the complex salts $[\text{4}]\text{Cl}\cdot\text{CH}_2\text{Cl}_2$ and $[\text{Mo}_3\text{S}_4\text{Cl}(\text{OCHO})_2(\text{edp,p})_3]\text{BPh}_4\cdot\text{CH}_3\text{CN}$ were refined in the triclinic $P\bar{1}$ space group. Graphics were performed with the Diamond visual crystal structure information system software.^[44] Hydrogen atoms were refined in their geometrically calculated positions using a riding model, whereas those bond to disordered C atoms were not included in the model. The non-hydrogen atoms of the clusters and the counterions were refined anisotropically. In both cases, a solvent molecule was found in the model. In the 4^+ complex one of the chloride counter anions was found disordered over two positions with relative occupancies of 0.58 and 0.42. Also, one C atom of the isopropyl ligand was disordered over two positions, C44 and C45, with relative occupancies of 0.5. For $[\text{Mo}_3\text{S}_4\text{Cl}(\text{OCHO})_2(\text{edp,p})_3]^+$, also one P atom of one of the edp ligands was disordered over two positions P28 A and P28 B with a chemical occupancy of 0.15 and 0.85. No restraints neither constraints were employed during the refinement. One disordered molecule of acetonitrile was modeled using the solvent mask tool (21 electrons detected, 22 electrons assigned to the disordered CH_3CN ; solvent $r=1.2$; truncation = 1.2)

General procedure for FA dehydrogenation

A 3-neck double wall reactor is attached to a condenser connected to a manual burettes system, illustrated in Figure S15. The apparatus is purged 3 times and flushed with argon for 15 minutes. Solvent and the catalyst are added under an argon overpressure. The setup is heated to the desired temperature while being flushed with argon. Once the temperature is reached, the burette is closed to the atmosphere and the argon/vacuum line is closed. After letting the system equilibrates for 30–60 min, the mixture formic acid: amine is added into the reactor and the timer turns on. When the reaction is finished, a 5 mL degassed syringe was used to obtain a gas sample analyzed by gas chromatography.

Computational details

DFT calculations were run with Gaussian 09 (Revision D.01).^[44] Geometry optimizations were carried out at the BP86/BS1 level,^[45,46] where Mo and S atoms were described using the SDD relativistic ECP and associated basis set,^[47] with added polarization functions for the latter ($\zeta=0.503$).^[48] and the remaining atoms were described with the 6-31G(d,p) basis set.^[49,50] Solvent effects (propylene carbonate, $\epsilon=64.0$) were included self-consistently in these optimizations through the PCM method.^[51,52] Temperature used was 120 °C and atmospheric pressure. All stationary points were characterized at this level of theory by analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue). Intrinsic reaction coordinate (IRC) calculations and subsequent geometry optimizations were used to confirm the minima linked by each transition state. In addition, single-point dispersion corrections were computed using Grimme's D3 parameter set and zero damping.^[53] Thus, the free energies shown herein were obtained by adding the dispersion correction to the Gibbs energies computed at the BP86/BS1(PCM) level.

CCDC

Deposition Number(s) CCDC 2261460 (4), CCDC 2261461 (D) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Supporting Information

Details on characterization spectra of $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{edp},\text{p})_3](\text{BPh}_4)$ cluster, crystallographic data, additional information on catalytic and mechanistic experiments and theoretical details including Cartesian coordinates for all optimized systems were provided in the Supporting Information.

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Conflict of Interests

There are no conflicts of interest to declare.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: dehydrogenation · formic acid · homogeneous catalysis · hydrogen · molybdenum sulfide

- [1] D. Mellmann, P. Sponholz, H. Junge, M. Beller, *Chem. Soc. Rev.* **2016**, *45*, 3954–3988.
- [2] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098.
- [3] United Nations, "Sustainable Development Goals," can be found under <https://sdgs.un.org/goals/goal7>, n.d.
- [4] S. J. Davis, N. S. Lewis, M. Shaner, S. Aggarwal, D. Arent, I. L. Azevedo, S. M. Benson, T. Bradley, J. Brouwer, Y.-M. Chiang, C. T. M. Clack, A. Cohen, S. Doig, J. Edmonds, P. Fennell, C. B. Field, B. Hannegan, B.-M. Hodge, M. I. Hoffert, E. Ingersoll, P. Jaramillo, K. S. Lackner, K. J. Mach, M. Mastrandrea, J. Ogden, P. F. Peterson, D. L. Sanchez, D. Sperling, J. Stagner, J. E. Trancik, C.-J. Yang, K. Caldeira, *Science* **2018**, *360*, DOI 10.1126/science.aas9793.
- [5] P. Preuster, C. Papp, P. Wasserscheid, *Acc. Chem. Res.* **2017**, *50*, 74–85.
- [6] K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy, *Chem. Rev.* **2018**, *118*, 372–433.
- [7] A. Kumar, S. Semwal, J. Choudhury, *ACS Catal.* **2019**, *9*, 2164–2168.
- [8] M. Younas, M. Rezakazemi, M. S. Arbab, J. Shah, W. U. Rehman, *Int. J. Hydrogen Energy* **2022**, *47*, 11694–11724.
- [9] S. Kar, M. Rauch, G. Leitner, Y. Ben-David, D. Milstein, *Nat. Catal.* **2021**, *4*, 193–201.
- [10] J. H. Barnard, C. Wang, N. G. Berry, J. Xiao, *Chem. Sci.* **2013**, *4*, 1234.
- [11] A. Iturmendi, M. Iglesias, J. Munarriz, V. Polo, V. Passarelli, J. J. Pérez-Torrente, L. A. Oro, *Green Chem.* **2018**, *20*, 4875–4879.
- [12] P. Hermosilla, A. Urriolabeitia, M. Iglesias, V. Polo, M. A. Casado, *Inorg. Chem. Front.* **2022**, *9*, 4538–4547.
- [13] E. A. Bielinski, P. O. Lagaditis, Y. Zhang, B. Q. Mercado, C. Würtele, W. H. Bernskoetter, N. Hazari, S. Schneider, *J. Am. Chem. Soc.* **2014**, *136*, 10234–10237.
- [14] I. Dutta, N. A. Alobaid, F. L. Menicucci, P. Chakraborty, C. Guan, D. Han, K.-W. Huang, *Int. J. Hydrogen Energy* **2023**, *48*, 26559–26567.
- [15] N. Lentz, A. Aloisi, P. Thury, E. Nicolas, T. Cantat, *Organometallics* **2021**, *40*, 565–569.
- [16] N. Scotti, R. Psaro, N. Ravasio, F. Zaccaria, *RSC Adv.* **2014**, *4*, 61514–61517.
- [17] M. Iglesias, F. J. Fernández-Alvarez, *Catalysts* **2021**, *11*, 1288.
- [18] J. Cao, J. Wang, Y. Ma, X. Li, P. Xiaokaiti, X. Hao, A. Abudula, G. Guan, *J. Alloys Compd.* **2018**, *735*, 1463–1471.
- [19] J. Wang, X. Li, J. Zheng, J. Cao, X. Hao, Z. Wang, A. Abudula, G. Guan, *Energy Convers. Manage.* **2018**, *164*, 122–131.
- [20] Z. Yu, Y. Yang, S. Yang, J. Zheng, X. Hao, G. Wei, H. Bai, A. Abudula, G. Guan, *Appl. Catal. B* **2022**, *313*, 121445.
- [21] V. O. Koroteev, D. A. Bulushev, A. L. Chuvilin, A. V. Okotrub, L. G. Bulusheva, *ACS Catal.* **2014**, *4*, 3950–3956.
- [22] I. Kurnia, A. Yoshida, Y. A. Situmorang, Y. Kasai, A. Abudula, G. Guan, *ACS Sustainable Chem. Eng.* **2019**, *7*, 8670–8677.
- [23] X. Bai, S. Li, Y. Zhang, S. Zhu, L. Gao, R. Cong, W. Yu, S. Wang, B. Liang, Y. Li, *Green Chem.* **2021**, *23*, 7630–7634.
- [24] M. C. Neary, G. Parkin, *Chem. Sci.* **2015**, *6*, 1859–1865.
- [25] E. Alberico, T. Leischner, H. Junge, A. Kammer, R. Sang, J. Seifert, W. Baumann, A. Spannenberg, K. Junge, M. Beller, *Chem. Sci.* **2021**, *12*, 13101–13119.
- [26] E. Guillaumon, I. Sorribes, V. S. Safont, A. G. Algarra, M. J. Fernández-Trujillo, E. Pedrajas, R. Llusar, M. G. Basallote, *Inorg. Chem.* **2022**, *61*, 16730–16739.
- [27] V. P. Fedin, M. N. Sokolov, Y. V. Mironov, B. A. Kolesov, S. V. Tkachev, V. Y. Fedorov, *Inorg. Chim. Acta* **1990**, *167*, 39–45.
- [28] A. G. Algarra, M. G. Basallote, M. J. Fernández-Trujillo, M. Feliz, E. Guillaumon, R. Llusar, I. Sorribes, C. Vicent, *Inorg. Chem.* **2010**, *49*, 5935–5942.
- [29] T. F. Beltrán, V. S. Safont, R. Llusar, *Eur. J. Inorg. Chem.* **2016**, *2016*, 5171–5179.
- [30] M. Gutiérrez-Blanco, E. Guillaumon, V. S. Safont, A. G. Algarra, M. J. Fernández-Trujillo, K. Junge, M. G. Basallote, R. Llusar, M. Beller, *Inorg. Chem. Front.* **2023**, *10*, 1786–1794.
- [31] M. Iglesias, L. A. Oro, *Eur. J. Inorg. Chem.* **2018**, 2125–2138.
- [32] E. Pedrajas, I. Sorribes, K. Junge, M. Beller, R. Llusar, *ChemCatChem* **2015**, *7*, 2675–2681.
- [33] T. F. Beltrán, R. Llusar, *Polyhedron* **2019**, *167*, 39–43.
- [34] T. F. Beltrán, J. A. Pino-Chamorro, M. J. Fernández-Trujillo, V. S. Safont, M. G. Basallote, R. Llusar, *Inorg. Chem.* **2015**, *54*, 607–618.
- [35] V. S. Safont, I. Sorribes, J. Andrés, R. Llusar, M. Oliva, M. R. Ryzhikov, *Phys. Chem. Chem. Phys.* **2019**, *21*, 17221–17231.
- [36] J. A. Pino-Chamorro, T. F. Beltrán, M. J. Fernández-Trujillo, M. G. Basallote, R. Llusar, A. G. Algarra, *Eur. J. Inorg. Chem.* **2017**, 5006–5014.
- [37] A. Luque, A. Iturmendi, L. Rubio-Pérez, J. Munarriz, V. Polo, V. Passarelli, M. Iglesias, L. A. Oro, *J. Organomet. Chem.* **2020**, *916*, 121259.
- [38] *MassLynx*, Waters Corporation, Milford, MA, **2005**.
- [39] *CrysAlis*, version 171.36.24, Agilent Technologies, Santa Clara, CA, **2012**.
- [40] R. C. Clark, J. S. Reid, *Acta Crystallogr. Sect. A* **1995**, *51*, 887–897.
- [41] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [42] L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Acta Cryst* **2015**, *71*, 59–75.
- [43] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
- [44] Gaussian 09, Revision D.01; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P.

- Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr. J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc.: Wallingford CT. 2013.
- [45] J. P. Perdew, *Phys. Rev. B* **1986**, 33, 8822–8824.
[46] A. D. Becke, *Phys. Rev. A* **1988**, 38, 3098.
[47] D. Andrae, U. Häussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, 77, 123–141.
- [48] A. Hollwarth, M. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, 208, 237–240.
[49] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, 56, 2257–2261.
[50] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, 28, 213–222.
[51] M. Cossi, G. Scalmani, N. Rega, V. Barone, *J. Chem. Phys.* **2002**, 117, 43–54.
[52] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, 105, 2999–3093.
[53] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, 132, 154104.

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6.2 Designing a Robust Palladium Catalyst for Formic Acid Dehydrogenation

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Contributions:

For this paper, I performed parts of the catalytic screening and optimization of the reaction conditions, as well as long-term experiment. I conducted analytical analysis *via* MS. Additionally, I co-authored the draft of the paper and its supporting information. My contribution to this paper accounts for 10 %.

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Signature of the student
Carolyn A. M. Stein



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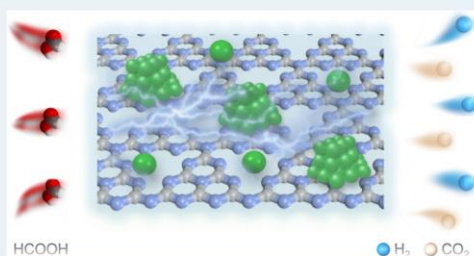
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ABSTRACT: The efficient production of hydrogen from biomass- or CO₂-derived formic acid (FA) is of considerable attention for a competitive hydrogen-powered economy. In this study, we report the synthesis of effective palladium catalysts with tunable metal-support interaction and electronic properties via a stepwise annealing and reduction strategy. Highly dispersed Pd nanoparticles on carbon nitride with a moderate average charge were identified as the optimal system. This material exhibits an increased rate of gas formation under standard conditions by two orders of magnitude compared to the commercially available benchmark catalyst (Pd/C). The activity was further improved by optimally adjusting the effects of solvent, temperature, amount of FA, and additive, reaching a maximum of 1.46 L g_{cat}^{−1} h^{−1}. The state-of-the-art catalyst shows superior long-term stability and is still active after 15 days of operation, achieving the highest total turnover number of 41,395 of any known palladium system.

KEYWORDS: formic acid dehydrogenation, palladium, carbon nitride, heterogeneous catalysis, energy storage



1. INTRODUCTION

Today's worldwide fuel supply is dominated by nonrenewable fossil fuels, which are the main reason for the significant increase of carbon dioxide in our atmosphere since preindustrial times.^{1,2} In this context, green hydrogen is an attractive and clean alternative with a high gravimetric energy density that produces H₂O as the only byproduct. It is therefore regarded as one of the promising solutions to the current dilemma of increased fuel demand and the resulting environmental issues.^{3,4} Compared to the traditional pressurization of H₂ in a cylinder, the development of safe and efficient techniques for reversible hydrogen storage and release at will is the key to ensuring the success of a competitive hydrogen-powered economy.^{5,6} Among the currently explored hydrogen carriers (e.g., NH₃BH₃, NaBH₄, N₂H₄, CH₃OH, cyclohexylmethane, and decalin), biomass- or carbon dioxide-derived formic acid (FA, HCOOH) has some specific features [e.g., low toxicity (LD₅₀: 1.8 g/kg), abundance, H₂-capacity (53 g/L or 4.4 wt %), and simple H₂ release], which makes it attractive for hydrogen storage.⁷ Meanwhile, FA could be directly synthesized from CO₂ and H₂, underlining the green character of hydrogen storage in the form of FA.⁸

A hydrogen economy based on FA includes hydrogenation of carbon dioxide and dehydrogenation of FA. Both steps have been widely studied and, more recently, also combinations thereof.^{4,9–11} Catalytic dehydrogenation of FA has been

performed mainly using different molecularly defined homogeneous catalysts based on Ru, Ir, Fe, Mn, and others.^{11–16} However, the addition of external additives such as a base, often organic amines, is the prerequisite for high hydrogen evolution rates. Meanwhile, the intrinsic drawbacks of homogeneous systems include difficult catalyst separation, recovery, and facile deactivation, which limit their practical applications. Therefore, the development of efficient and selective heterogeneous catalysts for additive-free FA dehydrogenation is of interest.^{4,17,18} Among the library of heterogeneous catalysts, supported palladium in combination with a second or third element forming alloys or core-shell nanostructures provides the most active and promising catalysts for this type of reaction.^{19–21} For example, core-shell Ag@Pd was reported to exhibit almost 10 times higher turnover frequency compared to the related single Pd catalyst, which is explained by the improved electron transfer from Ag to Pd.²² Other bimetallic or trimetallic alloys including PdAg, PdAu, PdCu, PdNi, PdAuCo, and PdAuNi have also

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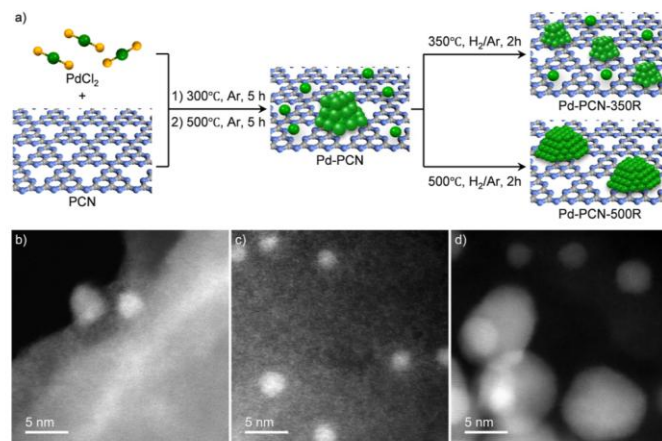


Figure 1. (a) Scheme of synthesis of Pd-PCN catalysts. Representative HAADF-STEM images of (b) Pd-PCN, (c) Pd-PCN-350R, and (d) Pd-PCN-500R are shown at the bottom.

demonstrated higher activity than monometallic Pd catalysts.^{19,23,24} However, the introduction of additional components increases the complexity of the catalytic system, complicates its preparation, and makes the structural control more difficult. Instead of including other metals, altering the particle size of Pd and changing the support to tune the chemical environment of the catalytic sites are other strategies to modulate the electronic properties of palladium catalysts.^{25–29} In this regard, carbon materials, for example, activated carbon, nitrogen/boron-doped carbon, and hierarchically porous carbon, are the most widely used supports.^{21,28,30,31} Notably, the utility of any catalyst depends on various performance indicators, and high activity is only one of them. In this respect, catalyst stability is crucial for most applications, and long-term stability (days or weeks) still exists as a challenge.

Polymeric carbon nitride (PCN) is a unique material that contains a relatively high amount of nitrogen (ca. 60 wt %) and hence is extensively used as a support for the stabilization of metal nanoparticles or even single metal sites.^{32–35} The formation of an effective Mott–Schottky heterojunction between the supported metals and PCN facilitates the charge transfer at the interface, which is known to improve the reactivity of the metal sites.^{36,37} Furthermore, the presence of numerous basic nitrogen sites is believed to promote H₂ production by FA dehydrogenation. For example, mesoporous carbon nitride-supported Pd nanoparticles (8–10 wt %) were reported independently by Chen³⁷ and Yoon,³⁸ showing enhanced catalytic FA dehydrogenation compared to monometallic Pd and multimetallic CoAuPd and AgPd on carbon materials.

Herein, we report the synthesis of PCN-supported Pd nanoparticles with distinct electronic properties *via* a stepwise annealing and reduction approach. The novel material exhibited significantly improved activity for FA dehydrogenation compared to the benchmark carbon-supported Pd nanoparticles. For the first time, long-term stability (>2 weeks) of such catalysts could be achieved, reaching a record-high total turnover number (TON > 40,000).

2. RESULTS AND DISCUSSION

At the start of this project, a PCN support was prepared *via* calcination of a preformed supramolecular complex between melamine and cyanuric acid. The Pd-supported materials with distinct metal species were synthesized according to a modified procedure with a stepwise annealing (Pd-PCN) approach, followed by further reduction at 350 °C (Pd-PCN-350R) or 500 °C (Pd-PCN-500R) (Figure 1a). The Pd content of these samples was determined by inductively coupled plasma-optical emission spectrometry to be 7.56, 7.92, and 8.42 wt % (Table S1). The dispersions of Pd over these samples were revealed by aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). As shown in Figures 1b,c and S1, S2, the coexistence of Pd single atoms (the bright spots on the lower atomic-number PCN support) and particles are observed in Pd-PCN and Pd-PCN-350R, although the average particle size in the former material (ca. 4–5 nm) is larger than that in the latter one (ca. 2–3 nm). Further increase of the reduction temperature to 500 °C (Pd-PCN-500R) resulted in the disappearance of single palladium atoms, with the exclusive formation of Pd nanoparticles with a size slightly below 6 nm (Figures 1d and S3). Moreover, a significantly higher number of particles is observed in the reduced samples (Pd-PCN-350R and Pd-PCN-500R) compared to Pd-PCN, which suggests the facile migration and agglomeration of Pd atoms during the reduction step.

The deposition of different Pd species does not alter the intrinsic structure of PCN, which is confirmed by two similar characteristic peaks at 2θ of 12.8 and 27.7° in their X-ray diffraction (XRD) patterns, corresponding to the periodic in-plane and interlayer stacking of heptazine units, respectively (Figure 2). The absence of diffractions from any Pd-related compounds in Pd-PCN suggests the high dispersion or poor crystallinity of Pd on PCN. On the contrary, a tiny peak of Pd (111) at 2θ of 40.1° emerged when the sample was reduced at 350 °C, which becomes more obvious if a higher reduction temperature is applied, consistent with the microscopic results. As evidenced by nitrogen sorption (Figure S4), the reduction step improved the specific surface area from 68 m² g^{−1} (Pd-

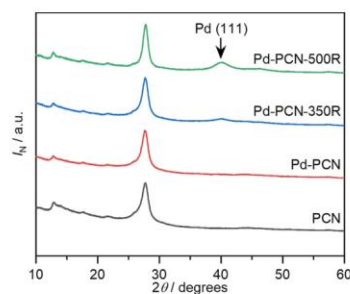


Figure 2. XRD patterns of Pd-PCN, Pd-PCN-350R, and Pd-PCN-500R.

PCN) to $95 \text{ m}^2 \text{ g}^{-1}$ (Pd-PCN-350R) and $136 \text{ m}^2 \text{ g}^{-1}$ (Pd-PCN-500R). Further analysis by hydrogen temperature-programmed reduction (H_2 -TPR) revealed negative peaks in the order of Pd-PCN-500R > Pd-PCN-350R > Pd-PCN (Figure S5), which could be attributed to the desorption of hydrogen adsorbed during the synthesis or before reduction.

Furthermore, the chemical state of the prepared materials was investigated by X-ray photoelectron spectroscopy (XPS). The survey XPS evidenced the presence of C, N, O, and Pd in all samples (Figure 3a), indicating the successful loading of palladium. As shown in Figure 3b, the main peak at 288.3 eV is observed in the C 1s XP spectra, which corresponds to the N-C=N sites in the heptazine rings. The minor peak at 284.8 eV arises from the concomitant C-C bonds. Three contributions can be deconvoluted from the N 1s XP spectra: ring nitrogen C-N=C (398.7 eV), tertiary nitrogen NC_3 (399.9 eV), and terminal $-\text{NH}_x$ groups (401.1 eV) (Figure 3c). Note that the area ratio of C-N=C/ NC_3 is close to 6, confirming the

heptazine building unit. The distinct electronic properties of the supported Pd species were examined by core-level Pd 3d XP spectra (Figure 3d). The Pd in Pd-PCN exhibits a strongly oxidized character with two peaks at 338.3 and 336.6 eV, which can be attributed to Pd^{4+} and Pd^{2+} , respectively, according to the formal assignments. The metallic Pd fingerprint at 335.3 eV appeared when the catalyst was reduced in an H_2 atmosphere, which became the main contribution at a higher reduction temperature (Pd-PCN-500R). As shown in the donut plots in the insets, significantly different contributions of Pd^0 (purple), Pd^{2+} (blue), and Pd^{4+} (green) are observed in these catalysts. Therefore, the quantification of the average charge of Pd (Q_{Pd} , defined by a weighted average of the fitted peak areas from the deconvoluted XP spectra) was calculated, which follows the order of Pd-PCN (3.4) > Pd-PCN-350R (2.6) > Pd-PCN-500R (1.1). Note that the assignment of formal charges is debatable, and these results are only used to highlight the different degrees of oxidation and the strength of interaction of the supported palladium with carbon nitride hosts.

The performance of the prepared catalysts was first evaluated in the FA dehydrogenation in propylene carbonate (PC) at 110°C based on previous studies using less active cobalt-based catalysts.^{39,40} The generated gas was measured using a manual gas burette (Figure S6), and its composition was analyzed by gas chromatography (GC) (exemplarily a typical chromatogram is shown in Figure S7). As shown in Figure 4a, all catalysts exhibited enhanced activity compared to the commercial benchmark catalyst 5 wt % Pd/C (STEM images in Figure S8). More specifically, the rate of gas formation reached $766 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$ in the case of Pd-PCN-350R, followed by Pd-PCN ($284 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$) and Pd-PCN-500R ($183 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$). A volcano type of relationship could be observed between Q_{Pd} and the catalytic activity of FA dehydrogenation (Figure S9). On the contrary, the respective

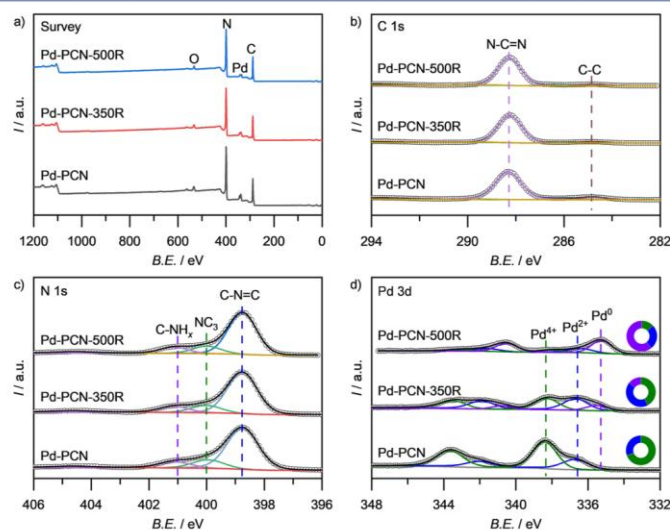


Figure 3. XPS of (a) survey, (b) C 1s, (c) N 1s, and (d) Pd 3d region of Pd-PCN, Pd-PCN-350R, and Pd-PCN-500R. The donut plots in (d) indicate the relative distribution of Pd^0 (purple), Pd^{2+} (blue), and Pd^{4+} (green).

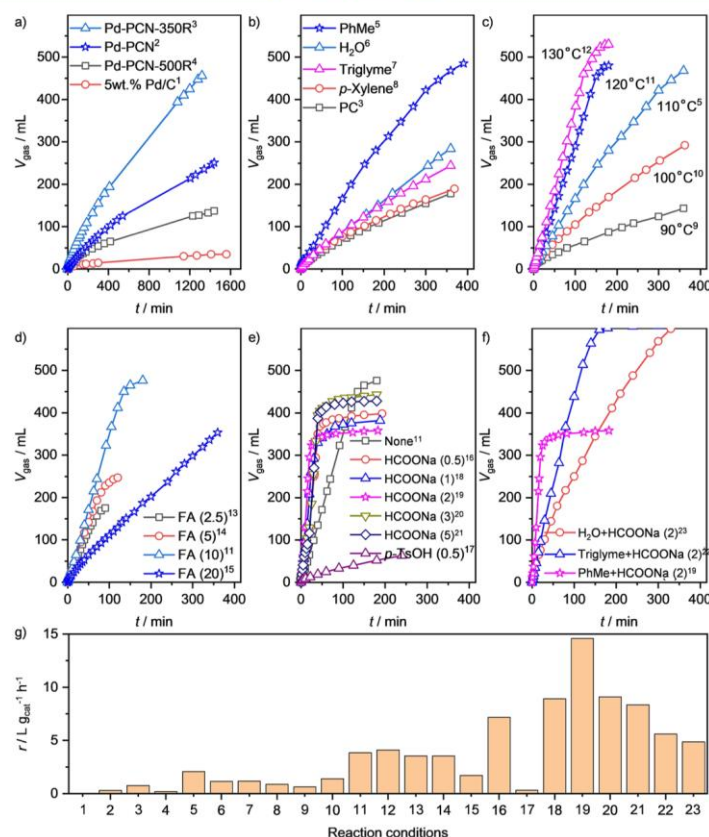


Figure 4. Dependency of the generated gas ($\text{H}_2 + \text{CO}_2$) upon different (a) catalysts (5 wt % Pd/C, Pd-PCN, Pd-PCN-350R, and Pd-PCN-500R) ($T_{\text{set}} = 110^\circ\text{C}$, 10 mL PC), (b) solvents (PhMe, H_2O , triglyme, *p*-xylene, and PC) ($T_{\text{set}} = 110^\circ\text{C}$), (c) set temperature (90–130 $^\circ\text{C}$), (d) amount of FA (2.5–20 mmol), (e) additives [HCOONa (0.5–5 mmol) or *p*-TsOH (0.5 mmol)], and (f) solvents in the presence of 2 mmol HCOONa . (g) Gas production rate ($\text{L g}_{\text{cat}}^{-1} \text{h}^{-1}$) under different reaction conditions. Standard conditions if not otherwise noted: Pd-PCN-350R was used as the catalyst, $T_{\text{set}} = 120^\circ\text{C}$, 10 mL PhMe; 40 μmol Pd, 10 mmol FA. The superscripts in (a–f) correspond to the reaction conditions in (g), which refer to the entries in Table S2.

gas evolution rate of the benchmark catalyst (5 wt % Pd/C) was as low as $8.9 \text{ mL g}_{\text{cat}}^{-1} \text{h}^{-1}$, which is nearly two orders of magnitude lower in comparison with the best catalyst Pd-PCN-350R. Therefore, Pd-PCN-350R was selected for further studies. Its performance could be significantly improved by applying water, triglyme, *p*-xylene, or toluene as solvents, where the latter stands out as the optimal reaction medium, achieving a gas formation rate of $>2000 \text{ mL g}_{\text{cat}}^{-1} \text{h}^{-1}$ (Figure 4b).

Thus, toluene was used as the solvent for further screening tests. Increasing the reaction temperature from 90 to 120 $^\circ\text{C}$ resulted in a linearly increased performance, with the rate increasing from 629 to $3844 \text{ mL g}_{\text{cat}}^{-1} \text{h}^{-1}$ (Figure 4c). Further increasing the temperature to 130 $^\circ\text{C}$ only slightly improved the rate to $4103 \text{ mL g}_{\text{cat}}^{-1} \text{h}^{-1}$; thus, 120 $^\circ\text{C}$ was applied as the reaction temperature. Next, the optimal amount of FA was examined (Figure 4d). The rate of gas formation increased with increased FA amounts from 2.5 to 10 mmol, while a

higher amount of FA (20 mmol) was found to be detrimental, thus affording a volcano-type performance. Also, the presence of additives was found to impose a significant impact on the activity. As shown in Figure 4e, the addition of basic sodium formate (HCOONa) significantly affected FA dehydrogenation performance. The gas formation rate reached $14,582 \text{ mL g}_{\text{cat}}^{-1} \text{h}^{-1}$ when 2 mmol HCOONa (20 mol % relative to FA) was added. This is clear evidence that the dehydrogenation reaction process occurred *via* a formate anion dehydrogenation pathway.⁴¹ However, further increasing the sodium formate amount exhibited a negative effect and decreased the rate to $8350 \text{ mL g}_{\text{cat}}^{-1} \text{h}^{-1}$ in the case of the addition of 5 mmol HCOONa (50 mol % relative to FA). Interestingly, no H_2 was generated if only HCOONa was used without the presence of FA. In contrast, the addition of a small amount of acid, for example, *p*-toluenesulfonic acid (*p*-TsOH) (0.5 mmol, 5 mol % relative to FA), suppressed the FA dehydrogenation reaction, resulting in a much lower gas evolution rate of $312 \text{ mL g}_{\text{cat}}^{-1}$

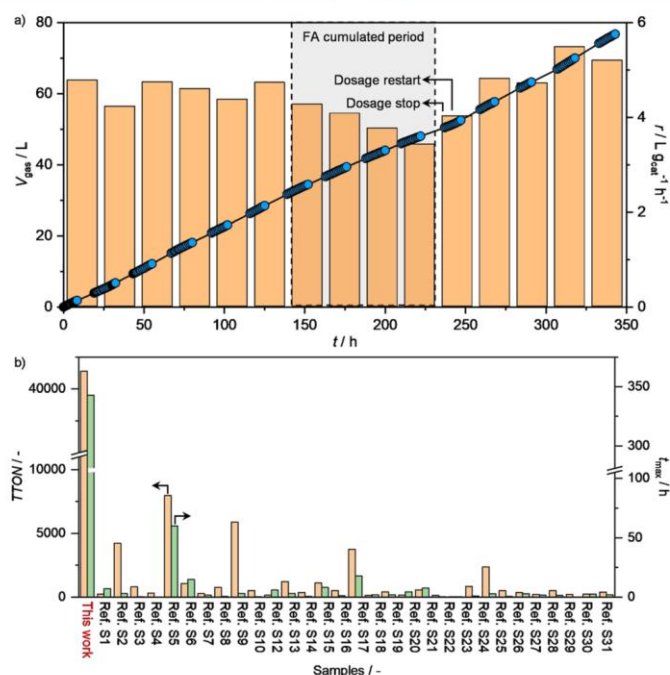


Figure 5. (a) Long-term stability test of Pd-PCN-350R up to ca. 350 h under continuous dosage of FA. Conditions: $T_{\text{set}} = 120\text{ }^{\circ}\text{C}$, 10 mL triglyme, 40 μmol Pd, 10 mmol FA, and 2 mmol NaFA. The blue circles and orange bars indicate the cumulated gas formation (L) during 15 days of operation and daily average gas production rate ($\text{L g}_{\text{cat}}^{-1} \text{h}^{-1}$). (b) Performance comparison of this work with previous Pd-based systems for FA dehydrogenation. Detailed information can be found in Table S3.

h^{-1} . Furthermore, variation of the solvent concentration (10–30 mL, 1 M) seems to have no effect on the catalyst performance, showing a similar rate of gas formation (Figure S10). The control experiment at optimized conditions (*i.e.*, PhMe: 10 mL; FA: 10 mmol; $T_{\text{set}} = 120\text{ }^{\circ}\text{C}$) without the catalyst exhibited negligible gas generation (Figure S11). Next, to gain insights into the adsorption of FA, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was carried out. As shown in Figure S12, FA was found to be adsorbed (2938 cm^{-1} , C–H; 1791 cm^{-1} , C=O; 1200 cm^{-1} , C–O) as formate²¹ on the surface of Pd-PCN-350R at $25\text{ }^{\circ}\text{C}$, which was desorbed from the catalyst when increasing the temperature to $120\text{ }^{\circ}\text{C}$. The associated relative mass intensities for fragments $m/z = 2$ (H_2) and $m/z = 44$ (CO_2) showed an increase in intensity at elevated temperatures which might indicate dehydrogenation of adsorbed FA (Figure S13). Unfortunately, the formation of the intermediates of HCOOH^* and CO_2^* species could not be observed. An overview of the obtained gas evolution rates under different reaction conditions is shown in Figure 4g and Table S2.

A potential advantage of using carbon nitride as the support for metal catalysts lies in its strong interaction between Pd and carbon nitride support which enhances the stability of the resultant catalysts. A preliminary investigation was performed by adding fresh FA when the initial first batch of FA was consumed (Figure S14). To our delight, the gas evolution was resumed after 2 days of interval, which followed a linear

increase of gas production by adding the specific amount of FA that was consumed for the given time (1:1 H_2/CO_2 analyzed by GC). After these encouraging results, the long-term stability of the optimized catalyst was evaluated in a continuous dosage mode, which proved a robust catalyst performance up to ca. 350 h without obvious deactivation (Figure 5a). It should be noted that the average gas evolution rate is found to be constant throughout the reaction. The decreased rate of gas formation between 142 and 230 h was due to the cumulation of FA, which is caused by the mismatching between the amounts of the consumed and added FA. Notably, the gas evolution rate is recovered to the original level after stopping dosage for a few hours. It is important to note that the catalyst productivity (TTON) reached 41,395 during the long-term stability test, which is significantly better compared to all previous Pd-based systems (Figure 5b).

Analysis of the used Pd-PCN-350R catalyst by HAADF-STEM showed the preservation of the morphology of the PCN support and the supported Pd nanoparticles, although their average size slightly increased from ca. 2.5 to 3.0 nm (Figure S15). The diffraction peaks of Pd can be clearly observed in the used catalyst (Figure S16), which was due to the highly reductive reaction conditions. The XPS analysis of the used catalyst was also performed, showing similar C 1s and N 1s spectra compared with the fresh Pd-PCN-350R (Figure S17). Moreover, the core-level Pd 3d XPS signal confirmed the slightly reduced Pd species after FA dehydrogenation, with a

smaller Q_{Pd} value of 2.5, showing the increased contribution of metallic Pd from 14.4 to 18.4% (Table S1). Furthermore, leaching of Pd was excluded by analyzing the metal content in the recovered solvent.

3. CONCLUSIONS

In summary, we present a novel active and stable palladium catalyst for FA dehydrogenation. Although Pd-based catalysts have demonstrated impressive activity, their long-term stability (days or weeks) remained a grand challenge, specifically under acidic conditions. Crucial for the significantly improved performance of this material compared to a commercial benchmark system is the support of Pd nanoparticles on PCN. The dispersion and electronic properties of the catalyst can be easily tuned by a stepwise annealing and reduction strategy. The optimal material with an ultrafine Pd nanoparticle size (2.4 nm) and a moderate average charge (2.6) exhibits nearly two orders of magnitude higher rate of gas formation from FA in comparison to Pd nanoparticles on carbon. The excellent stability of the optimized catalyst is shown by a long-term experiment (>2 weeks) with only negligible loss of activity. Thus, high productivity (TTON >41,000) was achieved too, which is more than 5 times higher compared to the best Pd system on nitrogen-doped carbon material. The findings highlight the potential of designing an efficient Pd-based catalyst for continuous hydrogen generation from the biomass-derived liquid hydrogen carrier FA.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.3c00009>.

Additional experimental details, additional characterization results of HAADF-STEM, nitrogen isotherms, H_2 -TPR, *in situ* DRIFTS, XRD, XPS, and a summary of the literature on the representative Pd-based catalysts for liquid-phase FA dehydrogenation (PDF)

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Author Contributions

H.J. and M.B. conceived and coordinated all stages of this research. Z.C. prepared and conducted the catalytic tests. C.A.M.S. contributed to the catalytic tests. R.Q. and K.J. contributed to the synthesis. N.R. conducted the STEM analysis. S.B. conducted the XPS analysis. J.W. and C.K. conducted the DRIFTS analysis. Z.C., H.J., and M.B. cowrote the manuscript in discussion with other coauthors.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Riahi, K., et al. *GEA Writing Team Global Energy Assessment: Toward a Sustainable Future* 1203–1306; Cambridge Univ. Press and IASA, 2012.
- (2) Fontecave, M. Energy for a sustainable world. from the oil age to a sun-powered future. by nicola armaroli and vincenzo balzani. *Angew. Chem., Int. Ed.* **2011**, *50*, 6704–6705.
- (3) Schlapbach, L.; Züttel, A. Hydrogen-storage materials for mobile applications. *Nature* **2001**, *414*, 353–358.
- (4) Wei, D.; Shi, X.; Qu, R.; Junge, K.; Junge, H.; Beller, M. Toward a hydrogen economy: development of heterogeneous catalysts for chemical hydrogen storage and release reactions. *ACS Energy Lett.* **2022**, *7*, 3734–3752.
- (5) Graetz, J. New approaches to hydrogen storage. *Chem. Soc. Rev.* **2009**, *38*, 73–82.
- (6) Dalebrook, A. F.; Gan, W.; Grasmann, M.; Moret, S.; Laurency, G. Hydrogen storage: beyond conventional methods. *Chem. Commun.* **2013**, *49*, 8735–8751.
- (7) Dutta, I.; Chatterjee, S.; Cheng, H.; Parsapur, R. K.; Liu, Z.; Li, Z.; Ye, E.; Kawanami, H.; Low, J. S. C.; Lai, Z.; Loh, X. J.; Huang, K.-W. Formic acid to power towards low-carbon economy. *Adv. Energy Mater.* **2022**, *12*, 2103799.
- (8) Moret, S.; Dyson, P. J.; Laurency, G. Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media. *Nat. Commun.* **2014**, *5*, 4017.
- (9) Chatterjee, S.; Dutta, I.; Lum, Y.; Lai, Z.; Huang, K.-W. Enabling storage and utilization of low-carbon electricity: power to formic acid. *Energy Environ. Sci.* **2021**, *14*, 1194–1246.
- (10) Sun, R.; Liao, Y.; Bai, S.-T.; Zheng, M.; Zhou, C.; Zhang, T.; Sels, B. F. Heterogeneous catalysts for CO_2 hydrogenation to formic acid/formate: from nanoscale to single atom. *Energy Environ. Sci.* **2021**, *14*, 1247–1285.
- (11) Wei, D.; Sang, R.; Sponholz, P.; Junge, H.; Beller, M. Reversible hydrogenation of carbon dioxide to formic acid using a Mn-pincer complex in the presence of lysine. *Nat. Energy* **2022**, *7*, 438–447.

- (12) Loges, B.; Boddien, A.; Junge, H.; Beller, M. Controlled generation of hydrogen from formic acid amine adducts at room temperature and application in H_2/O_2 fuel cells. *Angew. Chem., Int. Ed.* **2008**, *47*, 3962–3965.
- (13) Boddien, A.; Mellmann, D.; Gärtner, F.; Jackstell, R.; Junge, H.; Dyson, P. J.; Laurenczy, G.; Ludwig, R.; Beller, M. Efficient dehydrogenation of formic acid using an iron catalyst. *Science* **2011**, *333*, 1733–1736.
- (14) Wei, D.; Junge, H.; Beller, M. An amino acid based system for CO_2 capture and catalytic utilization to produce formates. *Chem. Sci.* **2021**, *12*, 6020–6024.
- (15) Sordakis, K.; Tang, C.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M.; Laurenczy, G. Homogeneous catalysis for sustainable hydrogen storage in formic acid and alcohols. *Chem. Rev.* **2018**, *118*, 372–433.
- (16) Mellmann, D.; Sponholz, P.; Junge, H.; Beller, M. Formic acid as a hydrogen storage material—development of homogeneous catalysts for selective hydrogen release. *Chem. Soc. Rev.* **2016**, *45*, 3954–3988.
- (17) Li, Z.; Xu, Q. Metal-nanoparticle-catalyzed hydrogen generation from formic acid. *Acc. Chem. Res.* **2017**, *50*, 1449–1458.
- (18) Liu, M.; Xu, Y.; Meng, Y.; Wang, L.; Wang, H.; Huang, Y.; Onishi, N.; Wang, L.; Fan, Z.; Himeda, Y. Heterogeneous catalysis for carbon dioxide mediated hydrogen storage technology based on formic acid. *Adv. Energy Mater.* **2022**, *12*, 2200817.
- (19) Doustkhah, E.; Hasani, M.; Ide, Y.; Assadi, M. H. N. Pd Nanoparticles for H_2 generation from formic acid. *ACS Appl. Nano Mater.* **2020**, *3*, 22–43.
- (20) Wang, C.; Astruc, D. Recent developments of nanocatalyzed liquid-phase hydrogen generation. *Chem. Soc. Rev.* **2021**, *50*, 3437–3484.
- (21) Jiang, K.; Xu, K.; Zou, S.; Cai, W.-B. B-doped Pd catalyst: boosting room-temperature hydrogen production from formic acid—formate solutions. *J. Am. Chem. Soc.* **2014**, *136*, 4861–4864.
- (22) Tedsree, K.; Li, T.; Jones, S.; Chan, C. W. A.; Yu, K. M. K.; Bagot, P. A. J.; Marquis, E. A.; Smith, G. D. W.; Tsang, S. C. E. Hydrogen production from formic acid decomposition at room temperature using a Ag–Pd core–shell nanocatalyst. *Nat. Nanotechnol.* **2011**, *6*, 302–307.
- (23) Yan, J.-M.; Wang, Z.-L.; Gu, L.; Li, S.-J.; Wang, H.-L.; Zheng, W.-T.; Jiang, Q. AuPd– MnO_2 /MOF–graphene: an efficient catalyst for hydrogen production from formic acid at room temperature. *Adv. Energy Mater.* **2015**, *5*, 1500107.
- (24) Yan, J.-M.; Li, S.-J.; Yi, S.-S.; Wulan, B.-R.; Zheng, W.-T.; Jiang, Q. Anchoring and upgrading ultrafine NiPd on room-temperature-synthesized bifunctional NH_2 -N-rGO toward low-cost and highly efficient catalysts for selective formic acid dehydrogenation. *Adv. Mater.* **2018**, *30*, 1703038.
- (25) Wang, Z.-L.; Yan, J.-M.; Ping, Y.; Wang, H.-L.; Zheng, W.-T.; Jiang, Q. An efficient CoAuPd/C catalyst for hydrogen generation from formic acid at room temperature. *Angew. Chem., Int. Ed.* **2013**, *52*, 4406–4409.
- (26) Zhu, Q.-L.; Song, F.-Z.; Wang, Q.-J.; Tsumori, N.; Himeda, Y.; Autrey, T.; Xu, Q. A solvent-switched in situ confinement approach for immobilizing highly-active ultrafine palladium nanoparticles: boosting catalytic hydrogen evolution. *J. Mater. Chem. A* **2018**, *6*, 5544–5549.
- (27) Li, J.; Chen, W.; Zhao, H.; Zheng, X.; Wu, L.; Pan, H.; Zhu, J.; Chen, Y.; Lu, J. Size-dependent catalytic activity over carbon-supported palladium nanoparticles in dehydrogenation of formic acid. *J. Catal.* **2017**, *352*, 371–381.
- (28) Wang, Q.; Tsumori, N.; Kitta, M.; Xu, Q. Fast dehydrogenation of formic acid over palladium nanoparticles immobilized in nitrogen-doped hierarchically porous carbon. *ACS Catal.* **2018**, *8*, 12041–12045.
- (29) Podyacheva, O. Y.; Bulushev, D. A.; Suboch, A. N.; Svintsitskiy, D. A.; Lisitsyn, A. S.; Modin, E.; Chuvilin, A.; Gerasimov, E. Y.; Sobolev, V. I.; Parmon, V. N. Highly stable single-atom catalyst with ionic Pd active sites supported on N-doped carbon nanotubes for formic acid decomposition. *ChemSusChem* **2018**, *11*, 3724–3727.
- (30) Bi, Q.-Y.; Lin, J.-D.; Liu, Y.-M.; He, H.-Y.; Huang, F.-Q.; Cao, Y. Dehydrogenation of formic acid at room temperature: boosting palladium nanoparticle efficiency by coupling with pyridinic-nitrogen-doped carbon. *Angew. Chem., Int. Ed.* **2016**, *55*, 11849–11853.
- (31) Li, Z.; Yang, X.; Tsumori, N.; Liu, Z.; Himeda, Y.; Autrey, T.; Xu, Q. Tandem nitrogen functionalization of porous carbon: toward immobilizing highly active palladium nanoclusters for dehydrogenation of formic acid. *ACS Catal.* **2017**, *7*, 2720–2724.
- (32) Zhao, E.; Li, M.; Xu, B.; Wang, X.-L.; Jing, Y.; Ma, D.; Mitchell, S.; Pérez-Ramírez, J.; Chen, Z. Transfer hydrogenation with a carbon-nitride-supported palladium single-atom photocatalyst and water as a proton source. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202207410.
- (33) Chen, Z.; Vorobyeva, E.; Mitchell, S.; Fako, E.; López, N.; Collins, S. M.; Leary, R. K.; Midgley, P. A.; Hauert, R.; Pérez-Ramírez, J. Single-atom heterogeneous catalysts based on distinct carbon nitride scaffolds. *Nat. Sci. Rev.* **2018**, *5*, 642–652.
- (34) Shi, H.; Wang, H.; Zhou, Y.; Li, J.; Zhai, P.; Li, X.; Gursadyan, G. G.; Hou, J.; Yang, H.; Guo, X. Atomically dispersed indium-copper dual-metal active sites promoting C–C coupling for CO_2 photo-reduction to ethanol. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202208904.
- (35) Chen, Z.; Vorobyeva, E.; Mitchell, S.; Fako, E.; Ortuño, M. A.; López, N.; Collins, S. M.; Midgley, P. A.; Richard, S.; Vilé, G.; Pérez-Ramírez, J. A heterogeneous single-atom palladium catalyst surpassing homogeneous systems for Suzuki coupling. *Nat. Nanotechnol.* **2018**, *13*, 702–707.
- (36) Wu, Y.; Wen, M.; Navlani-García, M.; Kuwahara, Y.; Mori, K.; Yamashita, H. Palladium nanoparticles supported on titanium-doped graphitic carbon nitride for formic acid dehydrogenation. *Chem.-Asian J.* **2017**, *12*, 860–867.
- (37) Cai, Y.-Y.; Li, X.-H.; Zhang, Y.-N.; Wei, X.; Wang, K.-X.; Chen, J.-S. Highly efficient dehydrogenation of formic acid over a palladium nanoparticle-based mott–schottky photocatalyst. *Angew. Chem., Int. Ed.* **2013**, *52*, 11822–11825.
- (38) Lee, J. H.; Ryu, J.; Kim, J. Y.; Nam, S.-W.; Han, J. H.; Lim, T.-H.; Gautam, S.; Chae, K. H.; Yoon, C. W. Carbon dioxide mediated, reversible chemical hydrogen storage using a Pd nanocatalyst supported on mesoporous graphitic carbon nitride. *J. Mater. Chem. A* **2014**, *2*, 9490–9495.
- (39) Li, X.; Surkus, A.-E.; Rabeah, J.; Anwar, M.; Dastigir, S.; Junge, H.; Brückner, A.; Beller, M. Cobalt single-atom catalysts with high stability for selective dehydrogenation of formic acid. *Angew. Chem., Int. Ed.* **2020**, *59*, 15849–15854.
- (40) Tang, C.; Surkus, A.-E.; Chen, F.; Pohl, M.-M.; Agostini, G.; Schneider, M.; Junge, H.; Beller, M. A Stable nanocobalt catalyst with highly dispersed CoN_x active sites for the selective dehydrogenation of formic acid. *Angew. Chem., Int. Ed.* **2017**, *56*, 16616–16620.
- (41) Kim, Y.; Kim, S.-h.; Ham, H. C.; Kim, D. H. Mechanistic insights on aqueous formic acid dehydrogenation over Pd/C catalyst for efficient hydrogen production. *J. Catal.* **2020**, *389*, 506–516.

6.3 Development of a practical formate/bicarbonate energy system

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Contributions:

For this paper, I designed and executed parts of the catalytic experiments. I performed and analyzed parts of the long-term experiments for formate dehydrogenation. I conducted a mechanistic analysis *via* NMR studies. In addition, I wrote the draft of the paper and the supporting information. My contribution to this paper accounts for 40 %.

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Development of a practical formate/bicarbonate energy system

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Liquid (organic) hydrogen carriers ([18H]-dibenzyltoluene, MeOH, formic acid, etc.) form a toolbox for the storage and transport of green hydrogen, which is crucial for the implementation of renewable energy technologies. Simple organic salts have been scarcely investigated for this purpose, despite many advantages such as low cost and minor toxicity, as well as easy handling. Here, we present a potassium formate/potassium bicarbonate hydrogen storage and release energy system, that is applicable and shows high stability (6 months). Utilizing ppm amounts of the molecularly defined Ru-5 complex, hydrogen release rates of up to 9.3 L h^{-1} were achieved. The same catalyst system promoted the hydrogenation of KHCO_3 to HCOOK with a TON of 9650. In this way, combined hydrogen storage-release cycles can be performed for 40 times.

The widespread availability and use of low-cost energy has been one of the most important pillars of global economic development over the past century. It's also the foundation for the progress of mankind regarding health and aging, food production, mobility as well as most social activities. These positive advancements are based on an increasing use of all kinds of resources. In fact, the demand of the human population statistically exceeds the amount of biological resources regenerated on earth by more than a factor of two¹, mainly due to fossil-based energy generation. Since the industrial revolution, global energy consumption has increased dramatically and is expected to continue increasing². This means that a complete change in the way we generate and use energy will have to take place over the next two decades. Accordingly, the reduction of carbon dioxide emissions by using renewable energy sources is a crucial aspect. As most forms of renewable energy, such as wind and solar power, are dynamic and not constantly available, energy storage will be a vital part of this transformation. Alongside classical engineering concepts, chemical energy storage has recently attracted increased attention³. In this respect, (green) hydrogen is a very promising energy carrier due to its availability from water via electrolysis utilizing renewable electricity⁴. Later on, the stored energy can be released on demand via combustion or

with the aid of fuel cells providing water. Due to the physical properties and the poor volumetric energy density of hydrogen, several (organic) hydrogen carriers are considered for safe energy storage (Fig. 1)⁵. All these concepts share the use of an available hydrogen acceptor that can be reversibly hydrogenated and dehydrogenated using suitable catalysts. Ideally, the resulting hydrogen carrier would be liquid at ambient conditions, with the advantage that the current energy infrastructure could be used for distribution. Apart from so called liquid organic hydrogen carriers (LOHC), e.g. (hetero)arenes⁶, hydrogen can be converted with cheap and abandoned nitrogen or carbon dioxide to form carrier molecules like ammonia^{7,8}, methane⁹, methanol^{10,11}, or formic acid (FA)^{12,13}. Notably, a number of these processes are currently investigated on pilot or demonstration scale^{14,15}.

Formic acid is a particularly interesting hydrogen carrier with its volumetric energy density of 1.77 kWh L^{-1} (relating to a volumetric hydrogen content of $53 \text{ g H}_2 \text{ L}^{-1}$). Compared to other carriers it shows favorable thermodynamics for the individual hydrogenation and dehydrogenation process (Eq. (1)). Both steps can be performed under comparably mild conditions ($<100^\circ\text{C}$; $<50 \text{ bar}$) and FA as well as its derivatives are relatively non-toxic and can be easily handled¹⁶. In fact, after the original proposal of FA for such applications¹⁷, many research

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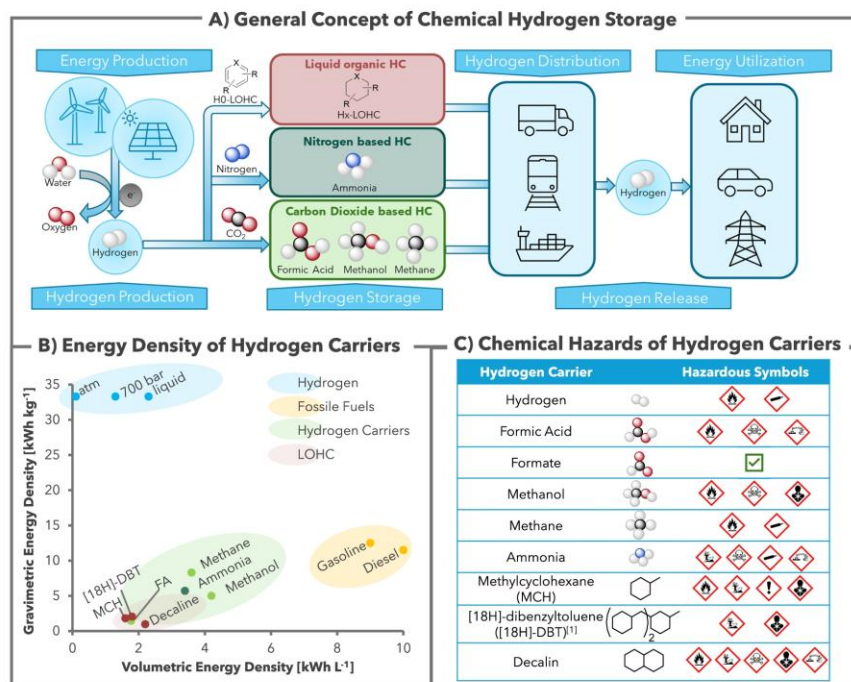
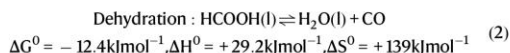
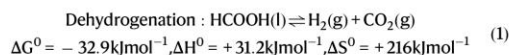


Fig. 1 | The principal concept of chemical hydrogen storage considering energy density and chemical hazards of hydrogen carriers. A Green hydrogen pathway from production to utilization. Excess energy from renewable sources can be used to electrolyze water. The hydrogen can then be chemically stored in so called

hydrogen carriers (HC) and released using suitable catalysts. Finally, energy can be recovered via combustion or fuel cell⁵. **B** Overview of volumetric and gravimetric energy densities for various energy carriers^{30,31}. **C** Chemical hazards of loaded HC compared to H₂. [1] Hazardous symbols are listed for DBT.

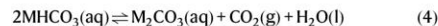
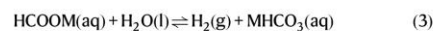
groups made important contributions to this research field^{18–20}. Interestingly, already in 2017, a comparative analysis of several process options applying formic acid as a hydrogen carrier, showed that the combination of aqueous, highly concentrated formate salts and their corresponding bicarbonates allows achieving the highest energy efficiency²¹.

A crucial issue for the use of carbon dioxide-based stationary hydrogen storage is the release of CO₂ in the dehydrogenation reaction (Eq. (1)). To reintroduce the carrier molecule CO₂ into the storage system, energy-intensive gas purification is required, or an excess of CO₂ must be available on site. In the case of FA, under acidic conditions, the dehydrogenation step competes with dehydration yielding CO (Eq. (2)), which is a well-known poison for fuel cells and precludes many potential applications²². Both reaction pathways show minor variations in free Gibbs enthalpy²³, making the selective dehydrogenation of FA difficult.



To recycle the hydrogen acceptor (CO₂) and avoid a net increase in carbon dioxide emissions, we recently reported an α -amino acid-promoted “chemical hydrogen battery” based on the reversible hydrogenation of carbon dioxide to formic acid. Here, the

corresponding ammonium formate is the crucial intermediate, which is formed by hydrogenation and can liberate the hydrogen. Even though a high stability and reusability of the applied manganese catalyst was achieved, a drawback of this system is the necessity to use stoichiometric amounts of the respective amino acid lysine²⁴. To solve this problem, we became interested in the dehydrogenation of more simple formate salts instead of FA/amino acid mixtures. Obviously, dehydrogenation of metal formates in basic aqueous solution gives the corresponding bicarbonates (Eq. (3)). The equilibrium of this formate/bicarbonate cycle can be shifted easily, as the free energy change of the cycle is nearly zero at near-ambient conditions, making it an attractive reversible storage system. Although the volumetric energy density is lower compared to FA (e.g. 29.1 g H₂ L⁻¹ for HCOOK (aq) at 25 °C)²⁵, its safety and toxicological aspects as well as sustainability make it an ideal hydrogen storage system. Formate salts are non-corrosive, non-irritating, non-toxic and compounded by earth-abundant elements, making them cheap and easy to handle²⁶.



In general, the storage capacity of a formate/bicarbonate system is limited by the solubility²⁷ of the respective salts. Figure 2 shows both, the mass, and the molar solubility of various formates. Although lithium presents the highest hydrogen content per weight (1.92 wt%) among the alkali salts, the low solubility of lithium formate makes it

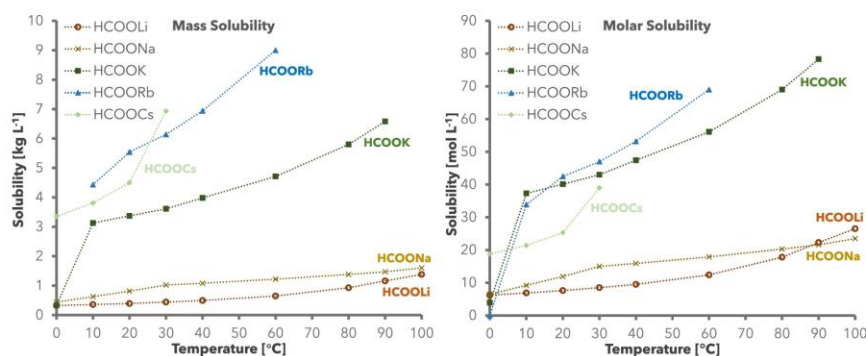


Fig. 2 | Mass and molar solubility curves for different alkali formates depending on the counter ion and the temperature^{32,33}. In the past decade, there have been plenty of examples, both homogeneous as well as heterogeneous, for either the hydrogenation of CO₂/bicarbonate^{34,35} or the dehydrogenation of FA/formate^{36–38}. To realize a chemical hydrogen battery, it is necessary for both, the hydrogenation and the dehydrogenation steps to be performed reversibly in the same device. This requires the catalysts to be applicable to both steps. Ideally the whole catalytic system (catalysts, additive, solvent) is applicable for both reactions. Another challenge of such a system is to avoid carbon dioxide loss through bicarbonate decomposition (Eq. 4), which would reduce the capacity of the hydrogen storage-release system after each cycle. In fact, to the best of our knowledge, no stable operating formate/bicarbonate storage system has yet been reported. Some of us

have shown that an in situ formed Ru complexes enables a reversible hydrogen storage system for one cycle starting from sodium formate or sodium bicarbonate³⁹. In the same year, Joó and Papp^{39,40} reported a homogeneous Ru system for formate/bicarbonate interconversion which was stable for 3 cycles in total. Soon after this work, the groups of Olah and Prakash⁴¹, as well as Laurenczy⁴² described improved homogeneous systems. Applying heterogeneous Pd catalysts Cao⁴³ and Lin⁴⁴ performed up to 6 cycles based on various bicarbonate salts. However, in no case more than 10 bicarbonate hydrogenation/formate dehydrogenation cycles were achieved without recharging carbon dioxide or reactivation of the catalysts⁴⁵. A detailed overview of state of the art systems for reversible hydrogen storage and release based on carbon dioxide/bicarbonate and formic acid/formate is provided in Supplementary Table 3.

unattractive for usage. Both rubidium (0.77 wt%) and potassium (1.19 wt%) show high molar solubility at room temperature as well as at elevated temperatures. Considering the availability and price of the metals, potassium seems to be a good candidate for a hydrogen battery.

Here, we report an important step towards the development and practical implementation of a carbon-neutral hydrogen storage system. In this respect, the interconversion of metal bicarbonates and formates via (de)hydrogenation has been systematically studied. The presented optimal reaction system enables CO-free hydrogen generation in the presence of Ru-P^{Ph}N(H)P^{Ph} (**Ru-5**). Notable features of the concept are the excellent catalyst stability (>40 cycles within 6 months) and good productivity for both reaction steps at low temperature (90 °C).

Results

Evaluation of hydrogen generation step: dehydrogenation of alkali formates (FD)

In an ideal hydrogen storage system, the same catalyst and solvent system should be applied for both hydrogenation and dehydrogenation steps. Nevertheless, to identify most suitable conditions for a combined process, initially the hydrogenation of bicarbonate (BH) and formate dehydrogenation (FD) were investigated separately. In general, the nature of the formate/bicarbonate cation has a decisive influence on the volumetric and gravimetric energy content of the reaction system. Consequently, FD was studied utilizing Li, Na, K, Rb, and Cs formates under identical conditions (Table 1 and Supplementary Table 4). In previous works, it has been shown that the latter reaction proceeds well in aqueous DMF using [RuCl₂(benzene)₂]₂ and biphosphine ligands as in situ catalysts²⁸.

Following this protocol, HCOOLi provided H₂ in 96% yield with a TON of 3820 at 60 °C after 6 h (Table 1, entry 1). Notably, the obtained gas contained a mixture of H₂/CO₂ in a ratio of 65/35, demonstrating the loss of a significant amount of carbon dioxide in this system. In contrast, simple HCOONa showed high H₂ productivity (98% yield;

TON = 3920) and improved gas purity (H₂/CO₂ = 92/8) (Table 1, entry 2). Applying HCOOK as the starting material led to decreased dehydrogenation activity (45% yield and TON = 1780), but at the same time almost all carbon dioxide remained in the reaction solution (H₂/CO₂ = 99.5/0.5; Table 1, entry 3). HCOORb (58% yield and TON = 2320) and HCOOCs (53% yield and TON = 2120) showed comparable reactivity with a gas proportion of H₂/CO₂ = 90/10 and H₂/CO₂ = 97/3, respectively. Based on these results and considering substrate costs, molar solubility, and the composition of produced gas, HCOOK was chosen for further investigations.

Next, the impacts of different catalysts, co-solvent, and the amount of water as well as reaction temperature were studied at increased substrate concentration in more detail (Table 2, and Supplementary Tables 5–8). First, different catalysts were tested. The combinations of [RuCl₂(benzene)₂]₂/dppe (**Ru-1**), [RuCl₂(benzene)₂]/dppm (**Ru-2**) and RuCl₂/TPPTS (**Ru-3**) showed low productivity with H₂ yields <15% and TONs <1600. In all cases, the ratio of H₂/CO₂ was around 99/1 (Table 2, entries 1–3). The activity of the defined complex **Ru-4** was slightly improved compared to the in situ generated system (Table 2, entry 4). Higher productivity was achieved with ruthenium pincer complexes. Using Ru-P^{Ph}N(H)P^{Ph} (**Ru-5**), Ru-MACHO (**Ru-6**), Ru-MACHO-BH (**Ru-7**) and Milstein's Ru-catalyst (**Ru-8**) H₂ yields up to 63%, and TONs up to 7110 were obtained (Table 2, entries 5–8). Again, the CO₂ release was negligible (≤0.5%). Besides ruthenium, different Ir-pincer catalysts were tested. **Ir-1** showed good results (69% H₂ yield, TON 7790), but the reactivity decreased with the reaction time (Table 2, entry 9). Notably, the water-soluble Ir-Cp' complexes **Ir-2** and **Ir-3**, which work well in formic acid dehydrogenation, showed no activity under these basic conditions (Table 2, entries 10–11). Overall, **Ru-5** was selected as the catalyst for further investigations. Almost full conversion of HCOOK was obtained by increasing the reaction time from 6 h to 13 h (TON 11,260, Table 2, entry 13). Further increasing the substrate amount to 275 mmol, a TON of 17,390 and 62% H₂ yield were observed (Table 2, entry 14). Additionally, increasing the reaction temperature and/or decreasing the catalyst amount (3.6 ppm) gave

Table 1 | Comparison of the dehydrogenation of alkali formates (FD) in the presence of Ru-1

$\text{HCOOM} + \text{H}_2\text{O} \xrightarrow[\text{DMF/H}_2\text{O} (20/5 \text{ mL}), 60^\circ\text{C}, 6 \text{ h}]{[\text{RuCl}_2(\text{benzene})]_2/\text{dppe} (\text{Ru-1}) (5/30 \text{ } \mu\text{mol})} \text{H}_2 \uparrow + \text{MHCO}_2$						
Entry	Formate	Gas volume [mL]	H ₂ /CO ₂ [%]	H ₂ [mmol]	H ₂ yield [%]	H ₂ [TON]
1	HCOOLi	720	65/35	19.1	96	3820
2	HCOONa	522	92/8	19.6	98	3920
3	HCOOK	220	99.5/0.5	8.9	45	1780
4	HCOORb	315	90/10	11.6	58	2320
5	HCOOCs	268	97/3	10.6	53	2120

General conditions: Formate (20 mmol), [RuCl₂(benzene)]₂/dppe (0.025/0.15 mol%), 5/30 μmol, DMF/H₂O (20/5 mL), 60 °C, 6 h. Volume and content of the gas phase were analyzed by manual burettes and gas chromatography (GC), respectively, after correction by the blank volume. CO is undetectable in all cases (CO quantitation limit of the applied GC is <10 ppm). Yield of H₂ is calculated by (mmol H₂)/(mmol HCOOM)100%. TON of H₂ is calculated by (mmol H₂)/(mmol catalyst). All experiments were performed at least twice; average values are shown (St. Dev. <10%). dppe: 1,2-bis(diphenylphosphino)ethane.

excellent H₂ yields up to 99% and TONs up to 263,200 (Table 2, entries 15–17). Noteworthy, utilizing **Ru-5** for HCOONa dehydrogenation instead of HCOOK gave significantly lower H₂ yield and purity (Table 2, entry 12). Among the different co-solvents tested, sulfolane, *t*-amylol, and triglyme allowed for significant hydrogen production rate; however, DMF performed best in FD (Supplementary Table 8). Then, the ratio of DMF and water was varied. Optimal results with respect to catalyst activity and CO₂ release were obtained in DMF/water (15/10) (Table 2, entry 18 and Supplementary Table 8, entries 15–19). With regards to the activity of **Ru-5** in the BH (see next chapter, Table 4), different ratios of triglyme were investigated for FD, too (Table 2, entries 18–20 and Supplementary Table 8). Using the solvent ratio of 15 mL triglyme and 10 mL water, the highest gas purity within the triglyme experiments was reached. Under the standard conditions 32% H₂ yield were observed with a gas ratio of 94/6 H₂/CO₂ (Table 2, entry 19; for 275 mmol HCOOK: 30% H₂ yield, 92/8 H₂/CO₂; Table 2, entry 20). Elongation of the reaction time from 6 h to 46 h increased the yield to 91% (Table 2, entry 21). Thus, FD productivity in triglyme/H₂O is comparable to DMF/water (although activity is lower), and full conversion of formate in triglyme/H₂O is possible.

To showcase the catalytic efficiency, the dehydrogenation of HCOOK was performed on >250 g-scale (3 mol) with only 3.3 ppm catalyst **Ru-5**, using DMF/H₂O (150/100). Full conversion was observed with a remarkable gas release of >72 L in 25 h. This corresponds to a practically relevant catalyst turnover number (TON = 290,000), frequency (TOF_{max} = 38,400 h⁻¹), maximum space-time yield (0.76 mol h⁻¹ L⁻¹), and rate of hydrogen release_{max} (9.3 L h⁻¹) (Table 3 and Supplementary Table 10; for reaction in triglyme/H₂O see Supplementary Table 11). The purity of the produced hydrogen was 97% and no CO was detected (detection limit <10 ppm) under these reaction conditions.

Evaluation of the hydrogen storage step: hydrogenation of potassium bicarbonate (BH)

Similar to the dehydrogenation experiments, different catalysts, solvent mixtures, and temperatures were examined for the hydrogenation step (Table 4 and Supplementary Table 12). In an ideal hydrogen storage device both H₂ loading and release should be performed in the presence of the same catalyst system (catalyst, solvent). Consequently, selected well-performing catalysts in FD were investigated for their capability of BH in DMF/H₂O (20/5 mL) at 90 °C (Table 4, entries 1–7). Since **Ru-1**, **Ru-5** and **Ru-7** exhibited similar activities (≤7% yield) in BH, **Ru-5** was selected for further studies due to its superior performance in the dehydrogenation. Unfortunately, DMF was partially decomposed under hydrogen pressure due to catalytic reductive cleavage of the amide²⁹. To avoid this issue, further catalytic experiments were conducted using triglyme as co-solvent. Triglyme was chosen for its anticipated stability, thermal resistance (boiling point 216 °C) and previous performance in the formate dehydrogenation *vide supra*. Noteworthy, applying triglyme water mixture as solvent in FD, hydrogen yields >91% were achieved (Table 2, entries 18–20; Supplementary Table 8).

Interestingly, the concentration of this co-solvent has a significant effect on the hydrogenation reaction. While a low yield (4%; Table 4, entry 8) was observed at a triglyme/H₂O ratio of 20/5 mL, increasing the water concentration led to a significant increase in the formate yield up to 74% (Table 4, entries 9–12). As expected, decreasing the reaction temperature from 90 °C to 50 °C resulted in reduced formate yields (Table 4, entries 13–14 and Fig. 2).

Combination of hydrogenation and dehydrogenation steps: demonstration of H₂ storage and release cycles

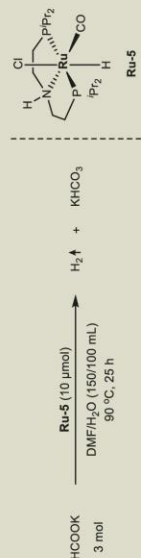
To demonstrate the stability of the catalysts system, we investigated the cyclability of the (de)hydrogenation over a long period with an appropriate number of cycles. Principally, the storage capacity of a

Table 2 | Dehydrogenation of HCOOK: Variation of catalysts and solvent

$\text{HCOOK} + \text{H}_2\text{O} \xrightarrow[\text{solvent/H}_2\text{O (x/y mL)}]{\text{Catalyst (10 } \mu\text{mol)}} \text{H}_2 \uparrow + \text{KCH}_2\text{O}_3$ 113 mmol, 60 °C, 6 h									
Entry	Cat.	Solvent/H ₂ O (x/y mL)	Gas volume [mL]	H ₂ /CO ₂ [%]	H ₂ yield [%]	TON H ₂	Rate H ₂ release [mL h ⁻¹] _{max}		
1	Ru-1	DMF/H ₂ O (20/5)	285	99/1	6	1150	30		
2	Ru-2	DMF/H ₂ O (20/5)	390	99/1	14	1580	80		
3	Ru-3	DMF/H ₂ O (20/5)	18	99/1	<1	70	4		
4	Ru-4	DMF/H ₂ O (20/5)	540	99/1	19	2180	90		
5	Ru-5	DMF/H ₂ O (20/5)	1765	99.6/0.4	63	7110	330		
6	Ru-6	DMF/H ₂ O (20/5)	1420	99.5/0.5	51	5770	500		
7	Ru-7	DMF/H ₂ O (20/5)	1415	99.6/0.4	51	5760	420		
8	Ru-8	DMF/H ₂ O (20/5)	87	99.5/0.5	3	350	18		
9	Ir-1	DMF/H ₂ O (20/5)	1915	99.5/0.5	69	7790	3600		
10	Ir-2	DMF/H ₂ O (20/5)	0	–	–	–	–		
11	Ir-3	DMF/H ₂ O (20/5)	0	–	–	–	–		
12 ^[a]	Ru-5	DMF/H ₂ O (20/5)	1100	85/15	34	3820	165		
13 ^[a]	Ru-5	DMF/H ₂ O (20/5)	2765	99.7/0.3	99	11,260	400		
14 ^[b,d]	Ru-5	DMF/H ₂ O (20/5)	4275	99.6/0.4	62	17,390	600		
15 ^[d]	Ru-5	DMF/H ₂ O (20/5)	2920	98/2	99	11,630	4650		
16 ^[c,d]	Ru-5	DMF/H ₂ O (20/5)	7005	96/4	99	27,470	4800		
17 ^[c,d]	Ru-5	DMF/H ₂ O (20/5)	6575	98/2	94	263,200	2700		
18	Ru-5	DMF/H ₂ O (15/10)	6700	98/2	98	26,820	5100		
19	Ru-5	Triglyme/H ₂ O (15/10)	764	94/6	32	3181	360		
20 ^[c,d]	Ru-5	Triglyme/H ₂ O (15/10)	2210	92/8	30	8342	500		
21 ^[f]	Ru-5	Triglyme/H ₂ O (15/10)	2799	90/10	91	10,283	360		

General conditions: 113 mmol HCOOK, 0.009 mol% metal-catalyst (10 μmol, 88 ppm). Solvent/H₂O (25 mL total), 60 °C, 6 h. [a] HCOONa. [b] 13 h. [c] 275 mmol HCOOK. [d] 90 °C. [e] 0.0004 mol% Ru-5 (1 μmol, 3.6 ppm). [f] 46 h. Volume and content of the gas phase were analyzed by manual burettes and gas chromatography (GC), respectively, after correction by the blank volume. CO is not detectable in all cases (CO quantitation limit of applied GC is <10 ppm). Yield of H₂ is calculated by (mmol H₂)/(mmol HCOOK)·100%. TON of H₂ is calculated by (mmol H₂)/(mmol catalyst). All experiments were performed at least twice; average values are shown (St. Dev. <10%). dppe: 1,2-bis(diphenylphosphino)ethane; dppm: bis(diphenylphosphino)methane; TPPTS: triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt.

Table 3 | Scaled up dehydrogenation of HCOOK



General conditions: 3 mol HCOOK (292.4 g), 0 μ mol **1** (0.3 ppm), 150 mL DMF, 100 mL H₂O, 500 mL glass reactor, 80 °C, 25 h. Volume and content of the gas phase were analyzed by manual burettes and gas chromatography (GC), respectively. Values after GC correction by the blank volume, CO is undetectable in all cases (CO quantitation limitation of GC is $\sim$ 10 ppm). Yield of H₂ is calculated by (mol H₂)/(mol HCOOK $\times$ 100%). TON of H₂ is calculated by (mol H₂)/(mol catalyst). Space-time-yield is calculated by (TON of H₂ in a certain time interval)/(V_{reactor}). TOF of H₂ is calculated by (TON of H₂ in a certain time interval)/(V_{reactor} $\times$ time). Gas release rate is calculated by (L V_{gas})/(mol H₂).

Table 4 | Catalytic hydrogenation of KHCO₃ to HCOOK in aqueous DMF and triglyme

$\text{KHCO}_3 + \text{H}_2 \xrightarrow[\text{solvent/H}_2\text{O (x/y mL)}]{\text{Catalyst (10 } \mu\text{mol), T } ^\circ\text{C, 18 h}} \text{HCOOK} + \text{H}_2\text{O}$					
		135 mmol	50 bar		
Entry	Cat.	Solvent/H ₂ O [x/y mL]	T [°C]	HCOOK yield [%]	TON
1	Ru-1	DMF/H ₂ O (20/5)	90	7	910
2	Ru-3	DMF/H ₂ O (20/5)	90	2	300
3	Ru-5	DMF/H ₂ O (20/5)	90	7	990
4	Ru-6	DMF/H ₂ O (20/5)	90	6	810
5	Ru-7	DMF/H ₂ O (20/5)	90	7	910
6	Ir-1	DMF/H ₂ O (20/5)	90	4	488
7	Ir-3	DMF/H ₂ O (20/5)	90	<1	120
8	Ru-5	triglyme/H ₂ O (20/5)	90	4	590
9	Ru-5	triglyme/H ₂ O (15/10)	90	74	9650
10	Ru-5	triglyme/H ₂ O (12.5/12.5)	90	63	8040
11	Ru-5	triglyme/H ₂ O (10/15)	90	66	8410
12	Ru-5	triglyme/H ₂ O (5/20)	90	67	8580
13	Ru-5	triglyme/H ₂ O (15/10)	75	50	6650
14	Ru-5	triglyme/H ₂ O (15/10)	60	39	4540

General conditions: 100 mL autoclave, 135 mmol KHCO₃, 10 μmol catalyst, x mL co-solvent, y mL H₂O, 50 bar H₂, T °C, 18 h. Yields and TON values were determined by ¹H NMR using DMSO as an internal standard. All experiments were performed at least twice; average values are shown (St. Dev. <10%).

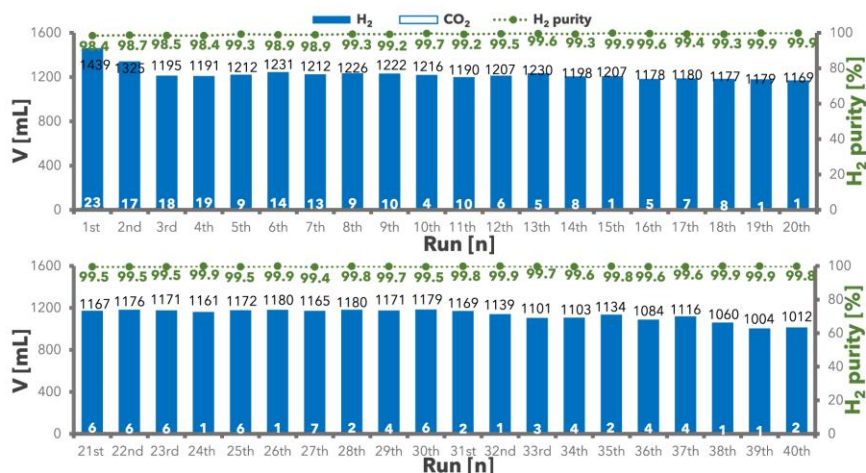


Fig. 3 | H₂ storage and release cycles of the KHCO₃/HCOOK system using Ru-5. H₂ storage and release cycles were started with BH: 135 mmol KHCO₃ (13.5 g), 10 μmol Ru-5 (4.7 mg), triglyme/water (15 mL/10 mL), 60 bar H₂, 90 °C, 18 h. After

pressure release, FD was started: 90 °C, 12 h. The generated gas was measured with manual burettes. The gas was analyzed by GC. CO is undetectable in all cases (CO quantitation limit of the applied GC is <10 ppm).

hydrogen battery relies on both, FD and BH performance. Thus, a compromise of productivities achieved in FD and BH has to be made. Taken all results from the (de)hydrogenation into account, triglyme/H₂O (15/10 mL) was chosen as the appropriate solvent due to its high stability and activity in BH (up to 74%) and almost full conversion for FD (up to 91%). The individual formate dehydrogenation and bicarbonate hydrogenation steps were combined using a 100 mL autoclave in the presence of KHCO₃ (135 mmol), Ru-5 (10 μmol, 74 ppm). As shown in Fig. 3, 40 consecutive cycles of hydrogen storage and release were performed over a period of 6 months. While in the first two experiments, a slight decrease of the hydrogen yield was observed,

from the third run onwards, highly stable activity and hydrogen yields were obtained (3rd cycle: 1195 mL; 37th cycle: 1116 mL). In 40 hydrogen storage and release cycles, nearly 50 L of hydrogen with an average purity of 99.5% were generated utilizing ppm amounts of Ru-5. In addition, the produced gas contained <0.5% carbon dioxide and less than 10 ppm carbon monoxide. As shown above, the hydrogen yield can even be increased by the elongating the reaction time. By shortening the FD reaction time, we were able to show that the optimal molecularly defined Ru complex allows for a stable operation of the hydrogen generation for 6 months, demonstrating its potential for practical applications.

Discussion

The present work describes a robust carbon neutral formate-based hydrogen storage and release system consisting only of HCOOK, KHCO_3 , water, an organic solvent and ppm amounts of the commercially available ruthenium complex **Ru-5**. Under comparably mild conditions, without the addition of a base or a Lewis acid, a noteworthy efficiency for HCOOK dehydrogenation was achieved. Performing the dehydrogenation reaction in DMF/ H_2O (150/100) led to a maximum hydrogen release rate of 9.3 L/h (>72 L gas in 25 h with space-time-yield_{max} of 0.76 mol h⁻¹ L⁻¹). On the other hand, the same catalyst promoted H_2 storage in HCOOK from KHCO_3 using triglyme/ H_2O (15/10) with a TON of 9,650. The combination of the individual storage and release processes, based on the optimal reaction conditions for BH, led to a very stable system, which was tested for 6 months with 40 cycles. The average H_2 purity obtained in triglyme/ H_2O (15/10) was 99.5% with <10 ppm CO detected in the produced gas (GC quantification limitation <10 ppm). The overall efficiency of the 40 cycles is 22%. However, elongating the reaction time for FD increases the H_2 yield and consequently the potential storage efficiency. Based on the separate (de)hydrogenation reactions, a storage efficiency of up to 67% is possible. The results demonstrate the technological readiness of this methodology and pave the way for the construction of a carbon-neutral chemical hydrogen battery set-up employing HCOOK/ KHCO_3 salts.

Methods

General procedure for FD

Under an Ar atmosphere, 113 mmol HCOOK (9.5 g), H_2O and the co-solvent (25 mL in total) were added to a 50 mL three-neck glass reactor equipped with a magnetic stir bar. The reaction solution was heated to 60 °C if not stated otherwise. Following, the reaction was started by addition of 10 μmol metal catalyst and performed for 6 h. Passed through a cooling condenser, the generated gas was collected by a manual burette and the volume was corrected by the blank volume. The gas was analyzed by GC.

General procedure for BH

Under an Ar atmosphere, 135 mmol KHCO_3 (13.5 g), 10 μmol catalyst and the respective solvent mixture (25 mL in total) were added to a 100 mL autoclave. The autoclave was pressurized with 50 bar H_2 . The reaction solution was heated to the desired temperature and stirred for 18 h. Water (50 mL) was added, washing along the inner wall of the glass inlet and dissolving the bicarbonate as well as formate. DMSO (1 mL, 14.08 mmol) was added as an internal standard to the solution. A mixture of 0.4 mL of the reaction solution with 0.1 mL of D_2O was then analyzed by ¹H NMR.

Data availability

The experimental and analytical data generated in this study are provided in the Supplementary Information. All data are available from the corresponding author upon request.

References

- About Earth Overshoot Day. *Earth Overshoot Day* <https://overshoot.footprintnetwork.org/about-earth-overshoot-day/> (2024).
- Ritchie, H., Rosado, P. & Roser, M. *Energy Production and Consumption* (Our World Data, 2024).
- Khan, N., Dilshad, S., Khalid, R., Kalair, A. R. & Abas, N. Review of energy storage and transportation of energy. *Energy Storage* **1**, e49 (2019).
- Oliveira, A. M., Beswick, R. R. & Yan, Y. A green hydrogen economy for a renewable energy society. *Curr. Opin. Chem. Eng.* **33**, 100701 (2021).
- Andersson, J. & Grönkvist, S. Large-scale storage of hydrogen. *Int. J. Hydrog. Energy* **44**, 11901–11919 (2019).
- Preuster, P., Papp, C. & Wasserscheid, P. Liquid Organic Hydrogen Carriers (LOHCs): Toward a Hydrogen-free Hydrogen Economy. *Acc. Chem. Res.* **50**, 74–85 (2017).
- Aziz, M., Wijayanta, A. T. & Nandiyanto, A. B. D. Ammonia as Effective Hydrogen Storage: A Review on Production, Storage Utilization. *Energ.* **13**, 3062 (2020).
- Klerke, A., Christensen, C. H., Nørskov, J. K. & Vegge, T. Ammonia for hydrogen storage: challenges and opportunities. *J. Mater. Chem.* **18**, 2304 (2008).
- Saxena, S., Kumar, S. & Drozd, V. A modified steam-methane-reformation reaction for hydrogen production. *Int. J. Hydrog. Energy* **36**, 4366–4369 (2011).
- Onishi, N., Laurency, G., Beller, M. & Himeda, Y. Recent progress for reversible homogeneous catalytic hydrogen storage in formic acid and in methanol. *Coord. Chem. Rev.* **373**, 317–332 (2018).
- Saeidi, S., Amin, N. A. S. & Rahimpour, M. R. Hydrogenation of CO_2 to value-added products—A review and potential future developments. *J. CO₂ Util.* **5**, 66–81 (2014).
- Chen, Z. et al. Designing a Robust Palladium Catalyst for Formic Acid Dehydrogenation. *ACS Catal.* **13**, 4835–4841 (2023).
- Mellmann, D., Sponholz, P., Junge, H. & Beller, M. Formic acid as a hydrogen storage material – development of homogeneous catalysts for selective hydrogen release. *Chem. Soc. Rev.* **45**, 3954–3988 (2016).
- Grasemann, M. & Laurency, G. Formic acid as a hydrogen source – recent developments and future trends. *Energy Environ. Sci.* **5**, 8171 (2012).
- Olah, G. A. Towards Oil Independence Through Renewable Methanol Chemistry. *Angew. Chem. Int. Ed.* **52**, 104–107 (2013).
- Dutta, I. et al. Formic Acid to Power towards Low-Carbon Economy. *Adv. Energy Mater.* **12**, 2103799 (2022).
- Williams, R., Crandall, R. S. & Bloom, A. Use of carbon dioxide in energy storage. *Appl. Phys. Lett.* **33**, 381–383 (1978).
- Kushwaha, S., Parthiban, J. & Singh, S. K. Recent Developments in Reversible CO_2 Hydrogenation and Formic Acid Dehydrogenation over Molecular Catalysts. *ACS Omega* **8**, 38773–38793 (2023).
- Onishi, N. et al. Development of Effective Catalysts for Hydrogen Storage Technology Using Formic Acid. *Adv. Energy Mater.* **9**, 1801275 (2019).
- Sordakis, K. et al. Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols. *Chem. Rev.* **118**, 372–433 (2018).
- Müller, K., Brooks, K. & Autrey, T. Hydrogen Storage in Formic Acid: A Comparison of Process Options. *Energy Fuels* **31**, 12603–12611 (2017).
- Baschuk, J. J. & Li, X. Carbon monoxide poisoning of proton exchange membrane fuel cells. *Int. J. Energy Res.* **25**, 695–713 (2001).
- Eppinger, J. & Huang, K.-W. Formic Acid as a Hydrogen Energy Carrier. *ACS Energy Lett.* **2**, 188–195 (2017).
- Wei, D., Sang, R., Sponholz, P., Junge, H. & Beller, M. Reversible hydrogenation of carbon dioxide to formic acid using a Mn-pincer complex in the presence of lysine. *Nat. Energy* **7**, 438–447 (2022).
- Asefa, T., Koh, K. & Yoon, C. W. CO_2 -Mediated H_2 Storage-Release with Nanostructured Catalysts: Recent Progresses, Challenges, and Perspectives. *Adv. Energy Mater.* **9**, 1901158 (2019).
- Calabrese, M. & Russo, D. Di Benedetto, A., Marotta, R. & Andreozzi, R. Formate/bicarbonate interconversion for safe hydrogen storage: A review. *Renew. Sustain. Energy Rev.* **173**, 113102 (2023).
- Marion, G. M. Carbonate mineral solubility at low temperatures in the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system. *Geochim. Cosmochim. Acta* **65**, 1883–1896 (2001).
- Boddien, A. et al. CO_2 “Neutral” Hydrogen Storage Based on Bicarbonates and Formates. *Angew. Chem. Int. Ed.* **50**, 6411–6414 (2011).
- Muzart, J. N,N-Dimethylformamide: much more than a solvent. *Tetrahedron* **65**, 8313–8323 (2009).

30. Graetz, J. New approaches to hydrogen storage. *Chem. Soc. Rev.* **38**, 73–82 (2009).
31. Niemann, M., Beckendorff, A., Kaltschmitt, M. & Bonhoff, K. Liquid Organic Hydrogen Carrier (LOHC) – Assessment based on chemical and economic properties. *Int. J. Hydrog. Energy* **44**, 6631–6654 (2019).
32. *CRC Handbook of Chemistry and Physics* (CRC Press, 2016). <https://doi.org/10.1201/9781315380476>.
33. Balarew, C. et al. IUPAC-NIST Solubility Data Series. 73. Metal and Ammonium Formate Systems. *J. Phys. Chem. Ref. Data* **30**, 1–163 (2001).
34. Ziebart, C. et al. Well-Defined Iron Catalyst for Improved Hydrogenation of Carbon Dioxide and Bicarbonate. *J. Am. Chem. Soc.* **134**, 20701–20704 (2012).
35. Gunasekar, G. H., Park, K., Jung, K.-D. & Yoon, S. Recent developments in the catalytic hydrogenation of CO₂ to formic acid/formate using heterogeneous catalysts. *Inorg. Chem. Front.* **3**, 882–895 (2016).
36. Marcos, R. et al. Mechanistic Studies on NaHCO₃ Hydrogenation and HCOOH Dehydrogenation Reactions Catalysed by a Fe^{II} Linear Tetraphosphine Complex. *Chem. Eur. J.* **24**, 5366–5372 (2018).
37. Wang, A. et al. Reviews on Homogeneous and Heterogeneous Catalysts for Dehydrogenation and Recycling of Formic Acid: Progress and Perspectives. *Energy Fuels* **37**, 17075–17093 (2023).
38. Kushwaha, S., Parthiban, J. & Singh, S. K. Ruthenium-Catalyzed Formic Acid/Formate Dehydrogenation and Carbon Dioxide/(bi)carbonate Hydrogenation in Water. *Organometallics* **42**, 3066–3076 (2023).
39. Horváth, H., Papp, G., Szabolcsi, R., Kathó, Á. & Joó, F. Water-Soluble Iridium-NHC-Phosphine Complexes as Catalysts for Chemical Hydrogen Batteries Based on Formate. *ChemSusChem* **8**, 3036–3038 (2015).
40. Papp, G., Csorba, J., Laurenczy, G. & Joó, F. A Charge/Discharge Device for Chemical Hydrogen Storage and Generation. *Angew. Chem.* **123**, 10617–10619 (2011).
41. Kothandaraman, J. et al. Amine-Free Reversible Hydrogen Storage in Formate Salts Catalyzed by Ruthenium Pincer Complex without pH Control or Solvent Change. *ChemSusChem* **8**, 1442–1451 (2015).
42. Sordakis, K., Dalebrook, A. F. & Laurenczy, G. A Viable Hydrogen Storage and Release System Based on Cesium Formate and Bicarbonate Salts: Mechanistic Insights into the Hydrogen Release Step. *ChemCatChem* **7**, 2332–2339 (2015).
43. Bi, Q. et al. An Aqueous Rechargeable Formate-Based Hydrogen Battery Driven by Heterogeneous Pd Catalysis. *Angew. Chem. Int. Ed.* **53**, 13583–13587 (2014).
44. Su, J., Yang, L., Lu, M. & Lin, H. Highly Efficient Hydrogen Storage System Based on Ammonium Bicarbonate/Formate Redox Equilibrium over Palladium Nanocatalysts. *ChemSusChem* **8**, 813–816 (2015).
45. Wei, D., Sang, R., Moazezbarabadi, A., Junge, H. & Beller, M. Homogeneous Carbon Capture and Catalytic Hydrogenation: Toward a Chemical Hydrogen Battery System. *JACS Au* **2**, 1020–1031 (2022).

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Author contributions

Conceptualization: R.S., D.W., P.R., R.J., H.J. and M.B.; catalytic experiments and results analysis: R.S., C.A.M.S., T.S., D.W., and Y.H.; discussion and experiment design: R.S., C.A.M.S., T.S., Y.H., A.L., J.M., V.T., P.S., D.W., R.J., H.J. and M.B.; funding acquisition: P.S., R.J., H.J. and M.B.; writing (original draft): C.A.M.S., R.S. and Y.H.; supervision and writing (review and editing): M.B., H.J., C.A.M.S. and R.S. All authors have read and agreed to the published version of this work. These authors contributed equally: R.S. and C.A.M.S.

Competing interests

The authors declare no competing interests.

Additional information

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6.4 Synthesis of Industrial-Relevant Pd/C Egg-Shell Catalysts for Reversible Hydrogen Storage in Formate/Bicarbonate

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Submitted manuscript

Contributions:

For this paper, I synthesized the catalysts, planned all experiments and performed parts of the catalytic screening and optimization of the reaction conditions. I executed long-term, upscale, and restart experiments. I conducted mechanistic NMR and IR studies. In addition, I wrote the draft of the paper and the supporting information. My contribution to this paper accounts for 70 %.

Signature of the student
Carolin A. M. Stein



Signature of the supervisor
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Synthesis of Industrial-Relevant Pd/C Egg-Shell Catalysts for Reversible Hydrogen Storage in Formate/Bicarbonate

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ABSTRACT: The catalytic interconversion of the formate/bicarbonate redox system has emerged as a promising method of chemical hydrogen storage. This energy system is inherently safe and hydrogen storage and release can be easily controlled by pressure or temperature. The presented study focuses on the synthesis of industrial-relevant palladium on carbon egg-shell catalysts for reversible hydrogen storage, employing novel methods that maximize material efficiency and a relatively simple process. The form of the catalyst material and its stability enable its use in industry, as demonstrated in a fixed bed reactor. The presented Pd/C catalyst is active in both the storage of hydrogen *via* hydrogenation of bicarbonate and the release of the gas *via* formate dehydrogenation. Applying the optimized catalyst, hydrogen release rates of up to 17.4 Lh⁻¹ were achieved corresponding to 180 L of CO-free hydrogen gas produced in three consecutive half-cycles.

1. INTRODUCTION

In 2024, fossil fuels such as coal, oil, and natural gas accounted for 37.4 billion tons of the global CO₂ emissions. This is approximately 90 % of the total global release marking an increase of 0.8 % from the previous year.¹ Achieving carbon neutrality and mitigating climate change necessitates the decarbonization of the energy sector. Green hydrogen, produced *via* water electrolysis using renewable energy, offers high energy density and CO₂ neutrality. However, its volatility and low volumetric energy density pose challenges for

storage, transport, and utilization. To overcome this inherent problem, a variety of concepts have been proposed.² Besides traditional storage methods (compression or liquefaction), chemical storage of hydrogen has been proposed using liquid organic hydrogen carriers (LOHC),^{3,4} metal hydrides,^{5,6} as well as bulk chemicals such as ammonia,^{7,8} formic acid^{9,10} and methanol.^{11,12} From a toxicity perspective, hydrogen storage systems based on the bicarbonate/formate redox equilibrium offer

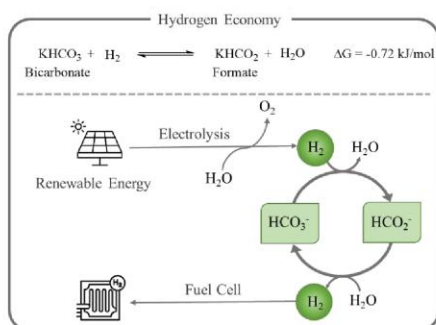
Table 1. Properties of different chemical hydrogen carriers versus compressed hydrogen.^{11,13,14,15,16}

Hydrogen Carrier	Toxicity	Storage Conditions	H ₂ content [wt.%]	Volumetric Energy Density [g/L]	Gravimetric Energy Density [MJ/L]
H ₂	-	700 bar	100	41.4	4.97
MgH ₂	Toxic	Ambient	7.6	110	13.2
Perhydro-benzyltoluene/benzyltoluene	Toxic	Ambient	6.2	56.0	6.72
Ammonia	Toxic	-33.5 °C, 1 bar	17.6	136	11.5
Methanol	Toxic	Ambient	12.6	150	17.8
Formic Acid	Toxic	Ambient	4.4	53.4	5.9
Formate ^[a] /Bicarbonate	-	Ambient	2.2	45.7	2.0 ^[b]

[a] Solid potassium formate. [b] 10 M solution of potassium formate.

advantages over previously mentioned systems (see Table 1). Here, bicarbonate (HCO_3^-) can be hydrogenated to form the corresponding formate (HCO_2^-) salt (hydrogenation of bicarbonate, BH). This half-cycle can be completed by the dehydrogenation of formate (FD), which releases the gas (see Scheme 1). The reversible (de)hydrogenation reactions only require (dehydrogenation) or yield (hydrogenation) an additional molecule of water. Formates are non-corrosive, non-irritating and show low toxicity.¹⁵

Scheme 1. Hydrogen storage based on the formate/bicarbonate redox equilibrium.



Excess electricity is converted into green hydrogen *via* electrolysis. Hydrogen can be safely stored in formate by hydrogenolysis of bicarbonate. After release, hydrogen can be converted into electricity in a fuel cell.

Numerous catalysts, including both homogeneous and heterogeneous ones, have been reported to catalyze one of the two distinct reactions (SI, Table S1).^{17–20} The most active heterogeneous catalysts for bicarbonate hydrogenation are based on palladium with supports like activated carbon (AC), carbon nitrides (CN) and metal oxides as well as mixed metal catalysts. The hydrogenation of sodium bicarbonate dates back to the work of the groups of Bredig and Carter in 1914, who used simple Pd black as a catalyst.²¹ More recently, Su et al. utilized Pd/AC at 5 wt.% to achieve formate yields of 43 % and a TON of 782 (NH_4COOH) while working at $T = 20^\circ\text{C}$, $p(\text{H}_2) = 27.5$ bar and $t = 1$ h.²² Using mesoporous graphitic CN (2.0 wt.% Pd/mpg- C_3N_4) Shao et al. demonstrated yields up to 85 %.²³ Mixtures of metals enhanced the catalyst activity further. Masuda et al. designed a TiO_x shell-coated Pd/Ag catalyst (1.0 wt.% Pd, 0.5 wt.% Ag)

supported on TiO_2 that achieves TON up to 820 for hydrogenation of sodium bicarbonate.²⁴

The catalytic concepts that proved highly efficient in the hydrogenation, also exhibit good performance in the catalysis of formate dehydrogenation. Hwang and coworkers demonstrated that activated carbon is also a good support for this type of reaction, yielding 92 % H_2 and a TOF of 6190 h^{-1} using ammonium formate in the presence of 3 wt.% Pd/AC. Furthermore, palladium nanoparticles supported on TiO_2 , as used by Wang, showed TOF of up to 2184 h^{-1} after 10 min at 25°C . In addition, bimetallic catalysts supported in activated carbon were employed for the dehydrogenation process. Nakajima et al. showed that Pd-Au/AC (molar ratio 1:4.91 wt.% Ag + Pd) yields up to $5136\text{ mmol/g}^*\text{h}$ of hydrogen leading to a TOF of 4200 h^{-1} for ammonium formate.

The cyclability of the reaction was first reported for homogeneous catalyst systems. Some of us demonstrated that an *in situ* formed Ru complex enables a reversible hydrogen storage system based on bicarbonate and formate.²⁵ Recently, our group also demonstrated a homogeneous Ru catalyst capable of 40 hydrogenation-dehydrogenation cycles for this energy storage system.²⁶ Interconversion between formate and bicarbonate is easily adjustable *via* pressure or temperature. The first heterogeneous catalyst systems for reversible dehydrogenation of aqueous formate to bicarbonate have been published by Sasson²⁷ and Cao.²⁸

While these studies demonstrate high catalytic activity at the laboratory scale, further challenges are faced when attempting to implement them on an industrial scale. Catalysts for industrial processes should be easy to separate from the reaction products to facilitate efficient recovery and recycling without the need for complex separation procedures, a factor that often renders homogeneous catalysts disadvantageous. Catalysts must be mechanically robust to withstand long-term operation without particle fragmentation, which can lead to pressure drops and clogging.²⁹ Economic viability is also a crucial consideration. The high cost of precious metals necessitates optimized metal loading and dispersion. Carbon-based supports offer high surface area, aid in metal recovery and recycling, and align with sustainable industrial practices.³⁰ Moreover, catalyst synthesis must be simple, reproducible, and scalable to ensure industrial viability.³¹

To address these challenges, structured catalyst supports are employed, such as pellets or extrudates, which have been shown to offer enhanced flow properties while preserving catalytic efficiency.²⁹ Impregnation yields egg-shell type catalysts, where the active phase is concentrated on a thin outer layer, ensuring uniform macroscopic distribution of active sites.³² This design allows rapid product migration away from the active sites, thereby preventing unwanted consecutive reactions, such as overreduction in hydrogenation reactions.²⁹ Consequently, such materials are frequently used in industry e.g. for selective hydrogenation reactions like Fischer-Tropsch.³³

In this study, we focus on the design and optimization of Pd/C egg-shell catalysts for reversible hydrogen storage in the formate/bicarbonate redox system. The objective is to identify a suitable commercially available carbon support and to explore key synthesis parameters that influence uniform shell-impregnation, catalytic performance, and industrial applicability while ensuring that the synthesis remains economically viable, scalable, and technically straightforward for large-scale production.

2. MATERIALS AND METHODS

2.1 Catalyst Preparation. General procedure for the carbon support screening: A solution of Na_2PdCl_4 (0.40 mmol, 20.0 mL H_2O) was added dropwise to 808 mg carbon support in 40.0 mL H_2O . The reaction was stirred for 12 h at room temperature, filtered and washed. The dry sample was reduced with 5 % H_2 for 2 h at 200 °C (heating 5 °C/min).

General procedure for the synthesis based on AKROS C1: A solution of Na_2PdCl_4 (0.08-0.40 mmol, 10.0 mL H_2O ; if noted: chelating additive) was added dropwise to 808 mg carbon pellet support AKROS C1 in 50.0 mL H_2O at room temperature or 60 °C. The reaction solution was stirred until it cleared up. The solvent was removed *via* filtration (for room temperature) or *via* evaporated at 60 °C. If noted, the catalyst was calcinated for 2 h at 200 °C. Then the catalyst was reduced with 5 % H_2 for 1-4 h at 100-400 °C (heating 5 °C/min).

Synthesis of the final catalyst Pd-C1-OA- O_2 : A solution of Na_2PdCl_4 (1.00 mmol) and 2.0 eq oxalic acid (1.98 mmol) in 30.0 mL H_2O was added dropwise to 5 g carbon pellet support AKROS C1 in 95.0 mL H_2O at 60 °C. The reaction solution was

stirred until it cleared up. The solvent was evaporated at 60 °C. The washed and dried catalysts were calcinated for 2 h at 200 °C, then reduced with 5 % H_2 (50.0 mL/min) at 200 °C for 2 h (heating rate 5 °C/min).

2.2 Catalyst Performance Test. Bicarbonate hydrogenation (BH) and formate dehydrogenation (FD) was performed to evaluate the catalysts performance. In a typical hydrogenation (BH) 5.40 mmol potassium bicarbonate and 20 mg catalyst were placed in 12.0 mL vial, evacuated, flushed with Ar and dissolved in 1.5 mL degassed H_2O . The vials were positioned in a 300 mL autoclave, flushed with H_2 for three times and pressurized with 30 bar H_2 . The reaction was heated at 60 °C for 18 h. The formate yield was determined by ^1H NMR based on the internal standard DMSO.

Formate dehydrogenation (FD) was performed in a double walled glass reactor connected to a manual burette at ambient pressure. The reaction vessel was loaded with 250.00 mmol potassium formate, 7.50 mmol potassium carbonate and 106 mg catalyst. The vessel was evacuated, flushed with Ar and filled with 25.0 mL degassed H_2O . The reaction was heated to 60 °C and dehydrogenation was performed for 3 h. Yield is based on the evolution of H_2 (Gas constitution verified *via* GC. CO quantification limit <10 ppm).

2.3 Catalyst Characterization. Elementary analysis (EA) was performed with a Leco TruSpec Micro CHNS Elemental analyzer for the quantification of C, H, N and S. Other elements were quantified *via* Atomic emission spectroscopy (ICP-OES) using Varian/Agilent 715-ES. Pellets have been analyzed as powders.

Scanning Electron Microscope (SEM) analysis was performed on a Thermo Fisher Scientific (Hillsboro, USA) Quattro S equipped with a Thermo Fisher Scientific UltraDry 60M Energy Dispersive X-ray Spectrometer (EDXS) for elemental identification. A secondary electron (SE) detector (Everhart-Thornley type) and a backscatter electron (BSE) detector (solid-state detector, segmented) have been used for image acquisition. The microscope was operated at 15 kV acceleration voltage. Pellet samples have been analyzed as presented.

Scanning transmission electron microscopy (STEM) measurements were performed at 200 kV with a probe aberration-corrected JEM-ARM200F (microscope: JEOL, Japan; corrector: CEOS,

Germany) using annular bright field (ABF) and high angle annular dark field (HAADF) detectors. The microscope is equipped with a DRY SD60GV (JEOL) energy-dispersive X-ray-spectrometer (EDXS) for chemical analysis. The outer pellet surface has been scraped off the pellet and was deposited on a holey carbon supported Cu-grid (mesh 300) without any further pretreatment and transferred to the microscope.

The XPS measurements were performed on an ESCALAB 220iXL (Thermo Fischer Scientific) with monochromated Al K α radiation ($E = 1486.6$ eV). Samples are prepared as complete pellet on a stainless-steel holder with conductive double-sided adhesive carbon tape. The electron binding energies were obtained without charge compensation leading to a main C 1s peak at around 284.5 eV. For quantitative analysis the peaks were deconvoluted with Gaussian-Lorentzian curves using the software Unifit 2023. The peak areas were divided by the transmission function of the spectrometer and the element specific sensitivity factor of Scofield. The depth profiling is performed in the same machine using EX-05 sputter source (Thermo Fischer Scientific) with an Argon pressure of $2 \cdot 10^{-7}$ mbar with an acceleration voltage of 2 kV, resulting in a sputter current of approximately $2.0 \mu\text{A}$.

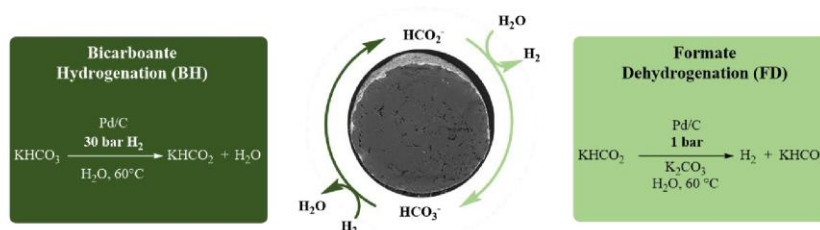
3. RESULTS AND DISCUSSION

Based on our recent results applying homogeneous catalysts, we sought to optimize the formate/bicarbonate hydrogen storage system with a focus on industrial applicability. In our previous work a triglyme/water solvent mixture and the homogeneous catalyst Ru-Macho-Pr were used for bicarbonate hydrogenation yielding up to 74 % of formate (TON = 9650).²⁶ In the present study, we have selected water exclusively as a green solvent. Although organic solvents like triglyme are

commonly used to enhance the catalyst activity, their utilization comes with significant drawbacks in comparison to water. Organic solvents exhibit higher levels of toxicity and flammability, raising safety concerns that could hinder social acceptance of the respective technology.³⁴ Furthermore, it is important to consider the financial implications, as organic solvents generally cause higher costs compared to potassium bicarbonate itself, rendering them less economical for industrial applications. Therefore, choosing water ensures both safety and economic concerns.

Eliminating the organic phase resulted in a substantial decline in activity for bicarbonate hydrogenation with Ru-Macho-Pr (20 % yield in BH; SI, Table S2, entry 8). Although homogeneous catalyst systems are generally quite active and selective towards both the hydrogenation and dehydrogenation reaction, they pose significant challenges in terms of separation from the final product in industrial settings. Therefore, the performance of commercially available heterogeneous catalysts was tested next. Investigating various metals, we found that Pd demonstrated the highest activities in BH (SI, Table S2, entries 15-24) with yields up to 49 % in BH (SI, Table S2, entry 15). Considering industrial applicability, we started to investigate heterogeneous pellet catalysts. Despite their utmost importance in industry, such catalysts have rarely been employed in the presented hydrogen storage system.¹⁸ The utilization of these materials facilitates efficient separation of the product. Furthermore, pellet catalysts exhibit enhanced stability and generate reduced levels of solid particles within the reaction setup. Unfortunately, it turned out that commercially available pellet systems leak in activity during operation (0-2 % yield in BH, SI, Table S2, entries 20-24).

Scheme 2. Reaction conditions for the testing of different catalysts



BH: 5.40 mmol KHCO_3 , 20 mg catalyst, 1.5 mL H_2O , 30 bar H_2 , 60 °C, 18 h. Yield is determined by ^1H NMR with DMSO as internal standard; FD: 250.00 mmol KHCO_2 , 7.50 mmol K_2CO_3 , 106 mg catalyst, 25.0 mL H_2O , 60 °C, 3 h. Yield is based on the evolution of H_2 (Gas composition verified *via* GC).

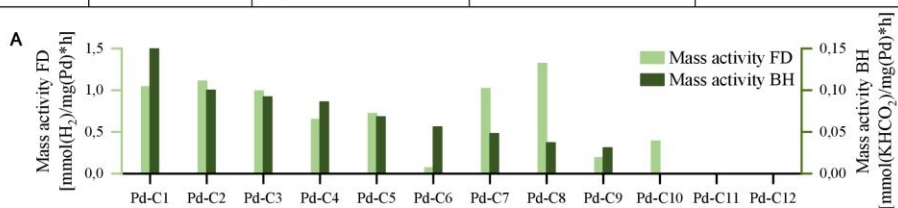
In this study, we sought to design innovative shell-impregnated pellet catalysts for reversible hydrogen storage and release within the formate/bicarbonate energy system. Initially, we defined the chemical reaction parameters in line with the goals of the investigation. Considering the multitude of parameters that must be adjusted for the synthesis of pellet-based catalysts, our investigation focused on carbon pellet supports and palladium as the sole metal. To achieve optimal activity, metal loading as well as stability, the reduction, calcination and impregnation conditions were systematically varied. Different pretreatments of the commercially available supports and additives were performed to generate a homogeneous surface. The effectiveness of all catalysts was assessed by their activity in both half-cycle reactions, namely the hydrogenation of bicarbonate (BH) and the dehydrogenation of formate (FD), based on their mass activity. The general reaction conditions are shown in Scheme 2.

As a starting point, we modified the approach outlined in the publication by the Jiang group.³⁵ In the original paper, palladium is deposited from a Na_2PdCl_4 precursor and reduced on carbon powder in the presence of citric acid. We adapted this approach and performed the deposition of Pd on several carbon supports in a few optimization steps. To this end, water was added to various commercially available pellets. Under stirring a solution of the palladium precursor was added dropwise to the support at room temperature and stirred for 12 h. The pellets were filtered, washed, dried and reduced with H_2 at 200 °C. The palladium loadings and performances in (de)hydrogenation reactions of different carbon pellet supports are shown in Table 2. Due to deviations in the theoretical and measured metal loading, we chose the mass activity based on the maximum available amount of active material (measured metal content) to evaluate the catalytic performance. The results are shown in Plot A.

3.1 Investigation of different carbon supports

Table 2: Pd/C catalysts synthesized using different carbon pellet supports and their mass activity.

Entry	Catalyst name	Carbon Support	Pd _{theoretical} [wt.%]	Pd _{measured} [wt.%]
1	Pd-C1	AKROS C1	5.00	3.33
2	Pd-C2	COC 4x8	5.00	2.78
3	Pd-C3	AFA-4-1050-S	5.00	1.74
4	Pd-C4	COL 4x8	5.00	3.94
5	Pd-C5	EcoSorb CK1	5.00	3.18
6	Pd-C6	WOS 4x8	5.00	3.65
7	Pd-C7	EcoSorb CE55	5.00	2.70
8	Pd-C8	EcoSorb CE70	5.00	4.91
9	Pd-C9	EcoSorb CK4	5.00	2.79
10	Pd-C10	COLPA 60	5.00	3.19
11	Pd-C11	AFA-4-dot-S	5.00	0.38
12	Pd-C12	Dopetac Sulfo 100	5.00	0.11



Plot A: mass activities based on the measured metal loading. Catalyst synthesis: Na_2PdCl_4 (400 μmol , corresponding to 5.00 wt.%, 20.0 mL H_2O), carbon support (808 mg, 40.0 mL H_2O), rt, 12 h, filtered, washed and dried. The samples were reduced with H_2 (2 h at 200 °C); Catalytic screening: BH: 5.40 mmol KHCO_3 , 20 mg Pd/C, 1.5 mL H_2O , 30 bar H_2 , 60 °C, 18 h; FD: 250.00 mmol KHCO_2 , 7.50 mmol potassium carbonate, 106 mg catalyst, 25.0 mL H_2O , 60 °C, 3 h.

The objective of the catalyst synthesis was to achieve a Pd loading of 5.00 wt.%. However, significant variations in the actual metal loading were observed among the different carbon supports. No detected activity of the catalysts with

Pd loadings below 1.00 wt.% can be attributed to the low metal content and the detection limit at our measuring system. More importantly, no correlation was observed between varying metal loadings above 1.00 wt.% and the activity of the catalysts in (de)hydrogenation. To understand this variation, analytical studies were conducted on specific supports and their corresponding palladium catalysts. First, the elementary composition of the carbon supports was analyzed using elementary analysis (EA) and X-ray fluorescence spectroscopy (CHN analysis and XRF; see SI, Table S19-21). The observed deviation between the targeted and measured metal loading indicated a higher Pd loading capacity for some of the carbon supports. This finding suggests that different functional groups on the carbon surface exhibit varying adsorption affinities for the Pd species being formed during the impregnation step. The carbon content in the samples exhibited significant variation, ranging

from 92-72 %. Although catalyst poisons, promoters, and catalytically active metals like iron, copper and nickel were detected in certain samples, no clear correlation was observed. Sulfur and chlorine, both predominantly found in mediocre and poorly performing supports (1-2 %), often act as catalyst poisons by binding to active metal sites.^{36,37} In addition, promoters such as potassium and calcium³⁸ were mainly present in high quantities in poorly performing supports, suggesting that excessive amounts of these elements reverse their positive effect.

As there is no parallel between the measured palladium loading and the activity, we investigated the metal distribution further. The uniformity and thickness of the Pd layer in the Pd/C egg-shell catalysts were estimated using scanning electron microscopy (SEM; SI, Figure S18-S26). Figure 1 shows backscattered electron images of the surface (top) and cross-section (bottom) of a well- (Pd-C2, Figure 1, left, 2.78 wt.% Pd) and a mediocre-performing catalyst (Pd-C5, Figure 1, right, 3.18 wt.% Pd). Highly active catalysts like Pd-C2 exhibit a

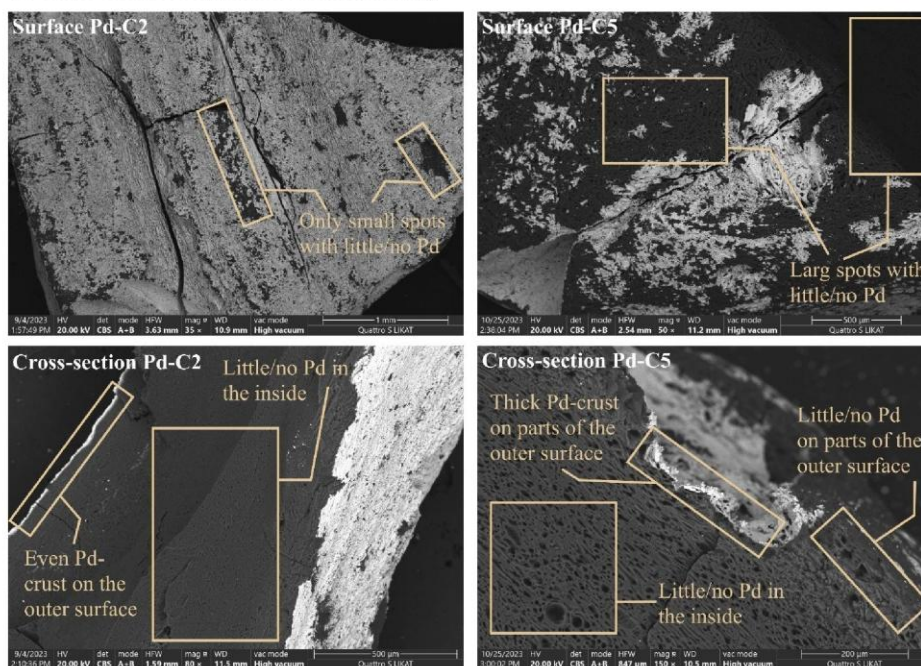


Figure 1. Backscattered electron (BSE) images of well- (Pd-C2; left) and mediocre-performing catalysts (Pd-C5; right). Top: surface, bottom: cross-section. Lighter regions on the outer surface correspond to Pd, while dark regions represent carbon. Further enlargements can be seen in the SI (Figure S19 and S22).

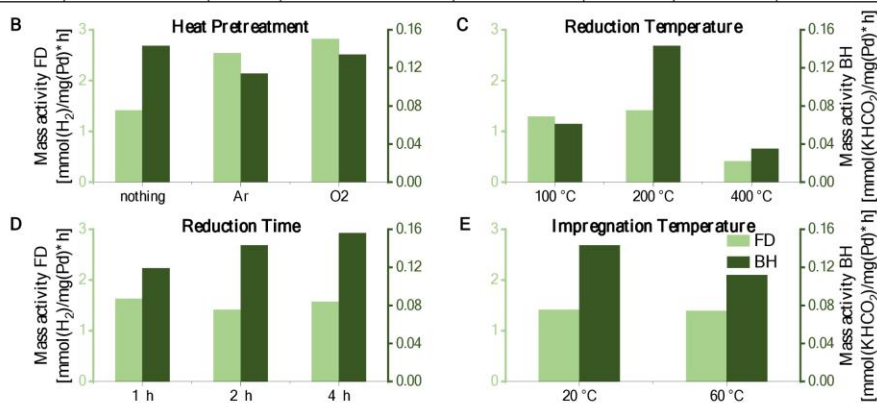
relatively uniform metal distribution on the surface (Figure 1, left, top). The presence of black spots on the surface of the catalyst was attributed to crust chipping. Little to no palladium was found on the inside of the pellet, indicating egg-shell type catalysts (Figure 1, left, bottom). The cross-section of the materials revealed an even thickness of the palladium crust on the outer surface of the support. Conversely, mediocre-working catalysts like Pd-C5 show a different distribution of the metal. Although Pd-C5 has a higher metal loading than Pd-C2, the surface (Figure 1, right, top) is unevenly impregnated with palladium and large parts of the pellet remain uncoated. This disparity is more pronounced upon examination of the cross-section (Figure 1, right, bottom), which reveals a

variable thickness of the metal layer from little/no palladium to thicker parts. These findings indicate that not only the overall metal loading, but also the distribution of palladium on the surface plays a crucial role in the activity of the catalysts.

Next, we analyzed the chemical state of the freshly prepared catalysts *via* X-ray photoelectron spectroscopy (XPS). The obtained results indicate the presence of the Pd(0) species at 335.2 eV as well as Pd(II) around 336.9 eV.³⁹ Among the different supports, the ratio of Pd(0) to Pd(II) varies. Nitrogen sorption using the Brunauer–Emmett–Teller (BET) method was used to investigate the external surface area of the catalysts (SI, Tables S25). All analyzed catalysts exhibit large

Table 3. Optimization steps in the synthesis of shell-impregnated Pd/C catalysts based on AKROS C1 and their mass activity in the (de)hydrogenation.

Entry	Catalyst name	T _{Imp} [°C]	Pretreatment atmosphere	T _{Pre} [°C]	T _{Red} [°C]	Time _{Red} [h]	Pd _{measured} [wt.%]
1	Pd-C1	rt		-	200	2	3.23±0.1
2	Pd-C1-Ar	rt	argon	200	200	2	2.73
3	Pd-C1-O ₂	rt	oxygen	200	200	2	2.86
4	Pd-C1-100	rt		-	100	2	3.80
5	Pd-C1-400	rt		-	400	2	4.23
6	Pd-C1-1	rt		-	200	1	3.97
7	Pd-C1-4	rt		-	200	4	4.01
8	Pd-C1-60	60		-	200	2	3.52



The mass activity for BH and FD are presented in plot B-E. Plot B: entries 1-3; Plot C: entries 1, 3, 4; Plot D: entries 1, 6, 7; Plot E: entries 1 and 8. Catalyst synthesis: Na₂PdCl₄ (400 μ mol, 10.0 mL H₂O) was added dropwise to the carbon pellet AKROS C1 (808 mg, 50.0 mL H₂O) at rt or 60 °C. For reactions at rt, the solvent was removed by filtration, for reactions at 60 °C the solvent was evaporated. The catalyst was washed, dried and reduced with H₂ at the mentioned temperature. Catalytic screening: BH: 5.40 mmol KHCO₃, 20 mg Pd/C, 1.5 mL H₂O, 30 bar H₂, 60 °C, 18 h. FD: 250.00 mmol KHCO₂, 7.50 mmol K₂CO₃, 106 mg catalyst, 25.0 mL H₂O, 60 °C, 3 h.

external surface areas. Overall, no direct correlation between catalyst properties and catalytic performance was observed.

3.2 Further optimization of the catalyst synthesis based on AKROS C1 carbon support

The carbon support AKROS C1 was chosen for further catalyst optimizations due to its high affinity to palladium and its effective catalytic activity in the (de)hydrogenation reactions. A selection of these optimizations is shown in Table 3, while the mass activity based on the actual metal loading can be observed in Plot B-E.

First, we verified the reproducibility of the catalyst Pd-C1 synthesis multiple times. The results are presented in Table 3, entry 1. Initially, different Pd precursors were tested in the impregnation process. The palladium salt Na_2PdCl_4 yielded the highest loading (SI, Table S3, entries 5-7) for the selected carbon support and it was used for all further optimizations. Heat treatment procedures play an important role in controlling the catalysts morphology, activity and stability. It is known from literature that the combination of a calcination step prior to the reduction can be beneficial.⁴⁰ As shown in Plot B, the heat pretreatment of the impregnated carbon support under argon Pd-C1-Ar or oxygen Pd-C1-O₂ (Table 3, entries 2 and 3) did not significantly affect the overall activity in (de)hydrogenation. The mass activity for BH is lower and the one for FD is higher compared to the initial catalysts. Nevertheless, ICP analysis of the catalysts before and after the hydrogenation reaction (SI, Table S6) shows that calcination enhances the stability of the metal on the surface of the catalysts.

The reduction parameters were investigated regarding time and temperature. These adjustments can affect the degree of reduction and the Pd dispersion.⁴¹ Variation of the reduction temperature (Table 3, entries 4 and 5; Plot C) clearly showed an optimum for 200 °C (Pd-C1, Table 2, entry 1). The catalyst reduced at a higher temperature - Pd-C1-400 shows a drastic decrease of activity. Köhler *et al.* observed a decrease in dispersion of the metal with an increase of the reduction temperature.⁴¹ The reduction time (Table 2, entries 6-7) did not demonstrate a distinct optimum as evident from Plot D. Shorter reduction (Pd-C1-1, Table 2, entry 6) led to a decline in activity regarding BH, while similar outcomes were observed for FD. A longer reduction (Table 3, entry 7) exhibited a modest enhancement for BH and FD.

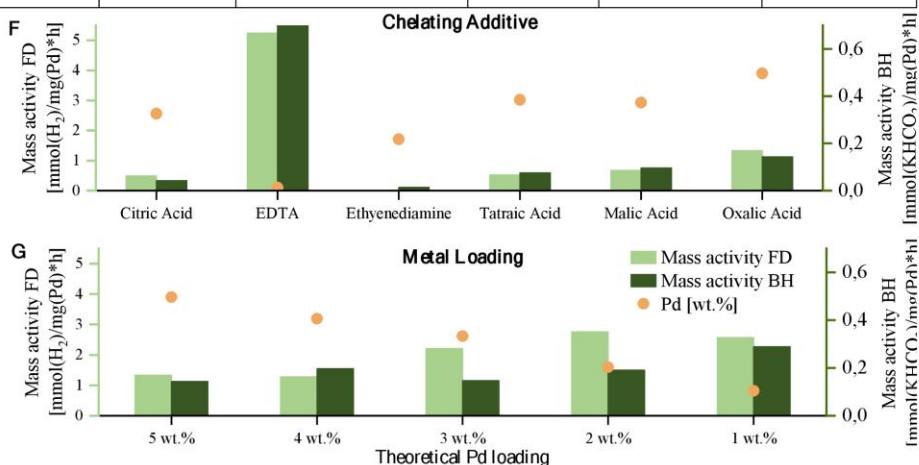
Wet impregnation at elevated temperatures was tested to streamline the synthesis method and mitigate Pd loss (Table 3, entry 8; Plot E). Although the mass activity based on the metal amount remained constant for Pd-C1-60, this impregnation method enhanced the overall yield and metal loading.

Using wet impregnation at elevated temperatures, the addition of chelating agents to the precursor during the impregnation was investigated (see Table 4, entries 1-6). Inspired by the positive effect of adding citric acid to the support as published by Jiang's group,³⁵ we tested the addition of several multidentate ligands. The addition of a chelating agent should increase the viscosity of the impregnation solution, thereby preventing crystallization of the precursor and enabling a more homogeneous spread of palladium over the carbon surface.⁴² The equivalents of additives were chosen based on their denticity to ensure optimal complexation of the palladium precursor. The mass activity of the resulting catalyst materials in (de)hydrogenation reaction can be seen in Plot F (Table 4). Indeed, one of the additives, oxalic acid (Table 4, entry 6), helped increase the metal loading of the catalysts and allowed a complete coating of the pellet's surface, which was demonstrated by scanning electron microscopy (SEM; SI, Figure S40). In our screening for carbon supports we recognized that uniform distribution over the entire surface is a key component for a well-functioning and economically feasible catalyst. Consequently, we worked with a metal loading of 5.00 wt.%, even though this is not economically optimal, because a lower metal content would have resulted in a more irregular coverage of the pellet's surface. The addition of oxalic acid in the impregnation step makes even egg-shell coating possible.

Utilizing this knowledge, we varied the theoretical palladium loading from 5.00 to 1.00 wt.% while maintaining high metal dispersion (see Table 4, entries 6-10; Plot G). Therefore, the wet impregnation process was done at elevated temperatures and 2.0 eq oxalic acid were used. It was observed that analogous tests lacking the presence of an additive resulted in pellets that exhibited significantly uneven coating. The incorporation of oxalic acid yielded several advantageous outcomes. The shell thickness was found to be reduced by a factor of 10 (SI, Table S23). Additionally, the loss of palladium in the catalyst synthesis was found to be reduced, which in turn decreases the price of the catalyst (see theoretical and measured Pd loading in Table 4). Moreover, the

Table 4. Influence of different additives in the impregnation step of the catalyst synthesis on the metal loading and catalytic activity in the (de)hydrogenation reactions.

Entry	Catalyst name	Additive	Amount [eq]	Pd _{theoretical} [wt.%]	Pd _{measured} [wt.%]
1	Pd-C1-CA	Citric acid	2.0	5.00	2.56
2	Pd-C1-EDTA	EDTA	1.1	5.00	0.10
3	Pd-C1-EN	Ethylenediamine	2.0	5.00	1.71
4	Pd-C1-TA	Tartaric acid	1.1	5.00	3.02
5	Pd-C1-MA	Malic acid	1.1	5.00	2.93
6	3.90Pd-C1-OA	Oxalic acid	2.0	5.00	3.90
7	3.19Pd-C1-OA	Oxalic acid	2.0	4.00	3.19
8	2.62Pd-C1-OA	Oxalic acid	2.0	3.00	2.62
9	1.60Pd-C1-OA	Oxalic acid	2.0	2.00	1.60
10	0.82Pd-C1-OA	Oxalic acid	2.0	1.00	0.82



The mass activity for BH and FD are presented in Plot F and G. Plot F: entries 1-6; Plot G: entries 6-10; Catalyst synthesis: An aqueous mixture of Na₂PdCl₄ and the additive (10.0 mL H₂O) was added dropwise to the carbon pellet AKROS C1 (808 mg, 50.0 mL H₂O) at 60 °C. The solution was stirred until it cleared up. The solvent was evaporated. The catalyst was washed, dried and reduced with H₂ (2 h, 200 °C). Catalytic screening: BH: 5.40 mmol KHCO₃, 20 mg Pd/C, 1.5 mL H₂O, 30 bar H₂, 60 °C, 18 h; FD: 250.00 mmol KHCO₂, 7.50 mmol K₂CO₃, 106 mg catalyst, 25.0 mL H₂O, 60 °C, 3 h.

surface is more homogeneously coated, even with low metal loadings, as evidenced by SEM (SI, Figure S27-S31). The increase of the mass activity from 5.00 wt.% to 4.00 wt.% indicates that a substantial amount of metal is distributed ineffectively, hindering its participation in the reaction process. It is noteworthy that these outcomes were only attainable through the incorporation of the additive. The metal loading data demonstrate that 2.0 eq of additive are optimal for the synthesis (SI, Table S13).

Combining all identified optimization steps, we synthesized a catalyst on a larger scale. The main objective was to attain an optimal activity-to-price.

ratio for the catalyst. Concerning industrial applications, it is imperative to maximize the activity per unit volume, given the inherent limitations of reactors in terms of size.³² Therefore, AKROS C1 carbon pellets were impregnated with a solution of 2.00 wt.% Na₂PdCl₄ and 2.0 eq of oxalic acid at 60 °C. The solvent was then evaporated, and the resultant dry pellets were calcinated at 200 °C for 2 h. Finally, the sample was reduced with 5 % H₂ for 2 h at 200 °C. The obtained catalyst Pd-C1-OA-O₂ showed a palladium loading of 1.81 wt.%.

3.3 Characterization of the catalysts based on AKROS C1

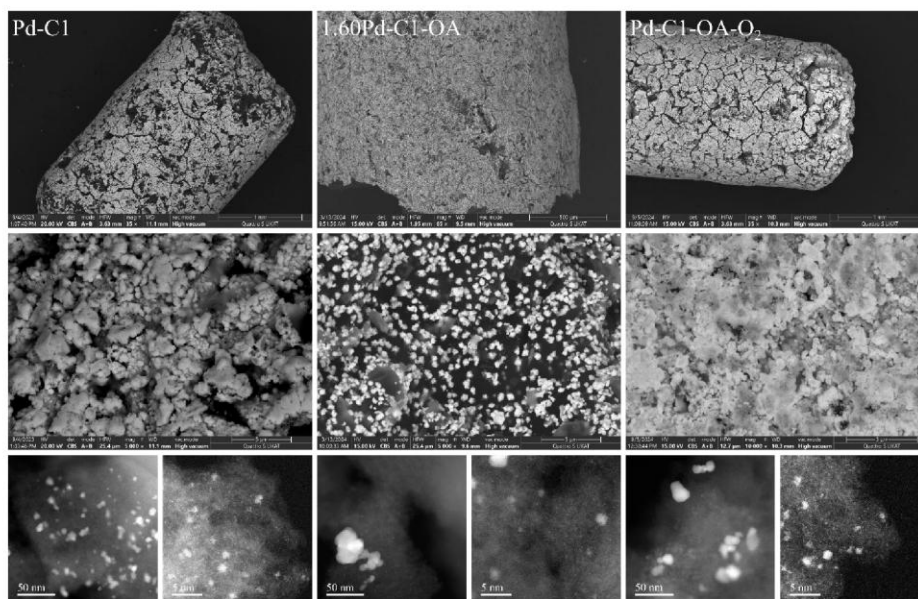


Figure 2. Selected BSE-SEM (whole particle) and HAADF-STEM (powder; active material scraped off from the pellet surface) images of the initial (left column, Pd-C1, 3.33 wt.% Pd), an optimized (center column, 1.60Pd-C1-OA, 1.60 wt.%) and the final catalyst (right column, Pd-C1-OA-O₂, 1.81 wt.%).

Utilizing a combination of scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and X-ray photoelectron spectroscopy (XPS) (see SI, 4.4, 4.6 and 4.7), comprehensive analyses of the macroscopic and microscopic structure of the catalysts were conducted along the way of the optimization. The initial catalyst Pd-C1, an optimized one, 1.60Pd-C1-OA and the final catalyst Pd-C1-OA-O₂ are depicted in Figure 2.

Pd-C1 was synthesized utilizing wet impregnation at room temperature and targeting 5.00 wt.% Pd (Table 1, entry 1). The catalyst 1.60Pd-C1-OA was impregnated at 60 °C with a mixture of Na₂PdCl₄ and oxalic acid (Pd_{theoretical}: 2.00 wt.%, 2.0 eq oxalic acid) and reduced with 5 % H₂ for 2 h at 200 °C. The final catalyst Pd-C1-OA-O₂ was prepared analog to 1.60Pd-C1-OA, but an additional calcination step

was added prior to reduction. SEM and XPS were performed on the entire pellet, while STEM analysis required the removal of the metal crust and its subsequent analysis as a powder.

The initial catalyst Pd-C1 (Figure 2, left) already showed a homogeneous shell coating of the carbon support. Nevertheless, black patches are visible, possibly due to cracking of the thick metal crust

(loading 3.33 wt.% Pd). The cross-section does not show any metal on the inside of the pellet, suggesting an egg-shell catalyst (see SI, Figure S18). In addition to the larger Pd particle fraction investigated by SEM, STEM provided evidence of the wide range of Pd morphology sizes present in the catalyst scaling down to single atoms, clusters and small particles not forming crystallites. According to XPS (Figure 3, left, top), the amount of Pd(0) is about ten times the amount of Pd(II). A depth profiling experiment of Pd-C1 using a sputter source was performed to understand the distribution of Pd better. As expected in Figure 3 (left, bottom), there was an initial increase of the overall palladium amount and a decrease of carbon, indicating the removal of a thin adventitious carbon layer in the first step. After a sputter period of 840 s, the amount of Pd started to decrease, thereby confirming the thickness of the outer crust. Over the time of the experiment, the ratio of Pd(0)/Pd(II) decreased, indicating a higher concentration of Pd(0) on the outer surface, while Pd(II) was more abundant within the crust. It is plausible that the palladium on the carbon surface is bound e.g. *via* oxygen bridges, resulting in an oxidation state of two, whilst the palladium on the outer crust is connected mainly *via* metal-metal bonds, explaining the presence of palladium (0).

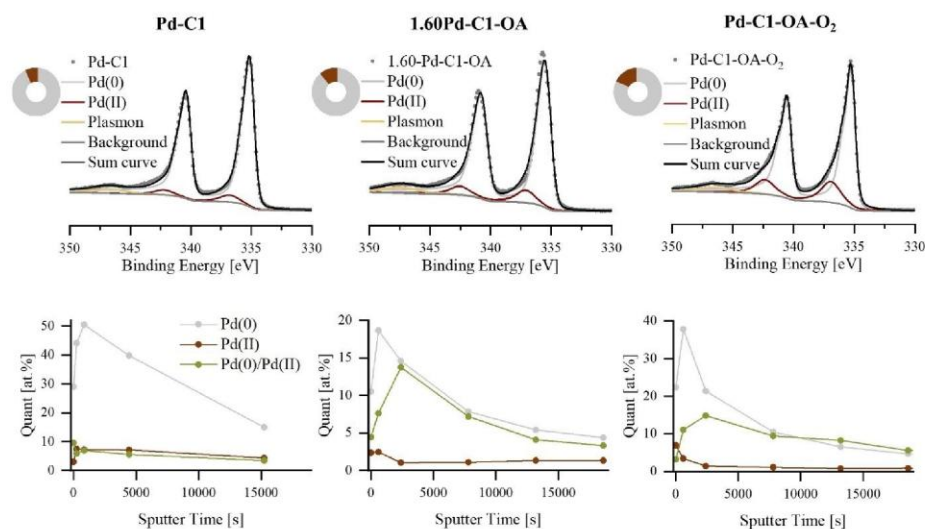


Figure 3. XPS (whole particle) analysis (top) as well as depth profiling experiments using a sputter source (bottom) of the initial (left column, Pd-C1, 3.33 wt.% Pd), an optimized (center column, 1.60Pd-C1-OA, 1.60 wt.%) and the final catalyst (right column, Pd-C1-OA-O₂, 1.81 wt.%).

Thanks to the addition of 2.0 eq of oxalic acid in the impregnation step, we were able to reduce the palladium loading while achieving an even better metal distribution on the surface (Figure 2, 1.60Pd-C1-OA, center). Energy Dispersive X-ray Spectroscopy (EDS) analysis confirms the presence of palladium. The SEM images of the whole pellet show particles in the range of 40–550 nm. STEM of the outer pellet surface showed again Pd having sizes in the range of single atoms to tens of nm. Interestingly, XPS (Figure 3, center) shows a lower Pd(0)/Pd(II) ratio compared to the initial catalyst Pd-C1. The data indicates that the ratio of Pd(0)/Pd(II) is important and a specific amount of Pd(II) can be beneficial for the catalytic activity as published by the Bulusheva group for the dehydrogenation of formic acid. Their study on formic acid dehydrogenation identified Pd(II) species as the active site.⁴³ The depth profiling shows an initial increase of the ratio Pd(0)/Pd(II) indicating less metallic palladium on the surface. Nevertheless, after 2400 s sputter time the ratio decreased again due to a higher amount of Pd(II) on the carbon. While the macroscopic structure is clearly affected by the cheating additive oxalic acid, the microscopic environment appears similar to the original catalyst.

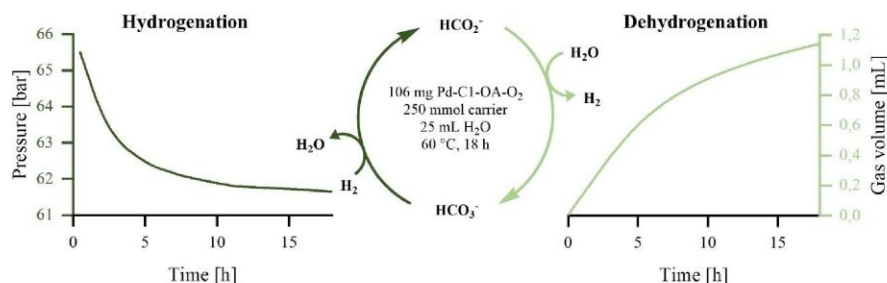
The SEM (back scattered electron detector) of the final catalyst Pd-C1-OA-O₂ shows a fine distribution of the active material. The presence of black spots is

minimal, suggesting that the calcination process enhances the stability of the palladium crust. According to STEM, the particle size ranges from large particles (ca. 200 nm) down to clusters and even single palladium atoms. The absence of sintering is attributed to the mild heat treatment. Decreasing the ratio of Pd(0)/Pd(II) further, the microscopic structure of the material remained unaffected. The depth profiling (Figure 3, right) shows a similar behavior of the metal. These results underscore the significance of ensuring a homogeneous distribution of the active metal on the surface. This objective was achieved by the addition of an additive in the impregnation step. Interestingly, an increase of Pd(II) can be seen over the different generations of catalysts which could correspond to a rise in activity. Masuda et al. indicated in their publication that an interplay between an electron-deficient and an electron-rich species is necessary for a catalytic reaction. In their case, they identified TiO₂ or Ag as electron-deficient species and Pd(0) as electron-rich species.²⁴ In the present study, these partners could be Pd(II) and Pd(0).

3.4 Up Scaling for Industrial Application

With an optimized catalyst for practical applications in hand, we were interested in demonstrating its activity and stability for the energy storage system

Scheme 3. Performance of the final catalyst in both half-cycles



Reaction conditions: BH: 250.00 mmol KHCO_3 , 106 mg Pd/C Pd-C1-OA-O₂, 25.0 mL degassed water, 60 °C, 18 h. Yield was determined with ¹H NMR using DMSO as internal standard. FD: 250.00 mmol KHCO_2 , 7.50 mmol K_2CO_3 , 106 mg Pd/C Pd-C1-OA-O₂, 25.0 mL degassed water, 60 °C, 18 h. Gas volume was measured with an automatic burette and Gas composition verified *via* GC.

formate/bicarbonate (see Scheme 3). More specifically, utilizing the optimal catalyst system Pd-C1-OA-O₂, 250.00 mmol of the corresponding (loaded) hydrogen carrier and 25.0 mL of water we performed both BH and FD at 60 °C for 18 h. BH was monitored by the pressure drop and yielded 23 % formate which corresponds to a TON of 2550. FD was performed in an automatic burette and gave rise to 1.14 L of gas (92 % H₂, 8 % CO₂, no CO detected) corresponding to a TOF of 3261 h⁻¹. CO₂ derived from the partial decomposition of bicarbonate to carbonate and is expected at high formate concentrations.²⁸ These half-cycles demonstrate the efficacy of the catalysts in facilitating both the loading and unloading of the carrier molecule, contingent on the availability of excess electricity from renewable energies (and green hydrogen). The activities exhibited by our pellet system are analogous to those previously reported for heterogeneous powder catalysts, including Pd/AC (BH: TON = 1672, 55 bar, 2 h, 20 °C; FD: 5061 h⁻¹, 80 °C)²² and Pd/NMC-8 (BH: TON = 1598; 60 bar, 2 h, 80 °C; FD: 2416 h⁻¹, 80 °C).⁴⁴ The conversion of both hydrogenation and dehydrogenation processes can be easily increased by elongation of the reaction time, as we have shown in our recent paper.²⁶

The long-term stability of the catalyst is a critical factor in determining its industrial applicability. To this end, we have demonstrated the recyclability of the catalyst on a lab scale (see Figure 4). To facilitate the separation of the catalysts from the used reaction solution, we slightly adjusted the reaction conditions. Although the pellet shape is ideal for large-scale applications, on a batch scale the stirring bar continuously grinds the catalyst. To ensure

constant reaction conditions over the whole experiment we grinded the catalyst for the following batch reactions. Figure 4 shows the results for the recycling of the catalysts in the dehydrogenation. Applying 200 mg of ground Pd-C1-OA-O₂, the dehydrogenation was performed for 73 h. Then, the catalyst was filtered, washed, dried and reused for a second dehydrogenation step. A total of 2.93 L gas was released (first run: 1.36 L, 90 % H₂, 10 % CO₂, 11 ppm CO; second run: 1.57 L, 93 % H₂, 7 % CO₂, 18 ppm CO). Interestingly, the catalyst showed a higher activity in the second run demonstrating the positive effect of process conditions for the catalyst activity. A small amount of formed CO can be explained by the decomposition of formate *via* dehydration.²² This pathway should be avoided in an industrial plant because CO is toxic to fuel cells.⁴⁵

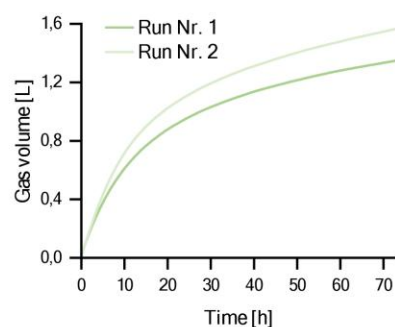


Figure 4. Recycling of the catalysts for FD. Reaction conditions: 200.00 mmol KHCO_2 , 15.00 mmol K_2CO_3 , 50.0 mL H₂O, 60 °C, 73 h. The catalyst was filtered, washed, dried and reused for a second dehydrogenation step. Gas volume was measured with an automatic burette and gas composition verified *via* GC.

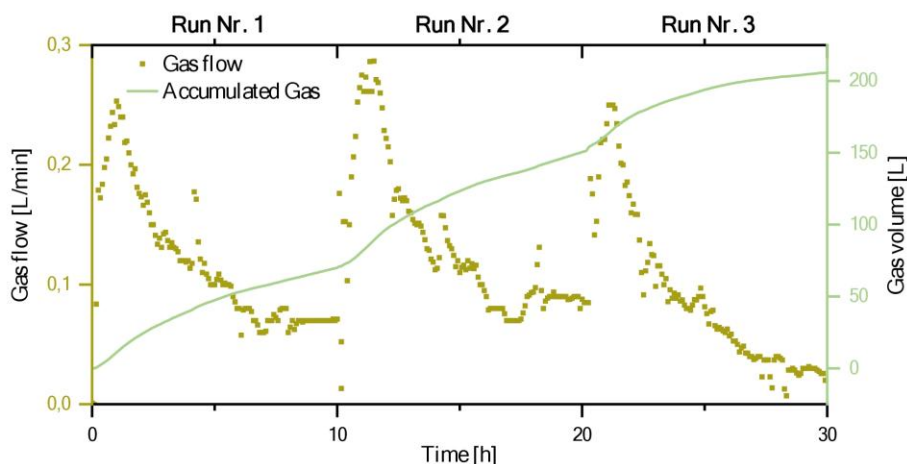


Figure 5. Gas evolution rate (left) and overall gas evolution (right) for the dehydrogenation reaction. All runs were performed for 10 h. Afterward, the catalyst was washed and dried on air. Reaction conditions: 10 g Pd/C, 4 M KHCO_2 in H_2O , 0.03 L/min volume flow, 60 °C, 10 h. Gas composition was verified *via* GC every two hours. No CO was detected (GC quantification limit <10 ppm).

Recycling was also demonstrated for BH. Here, 200.00 mmol bicarbonate was hydrogenated with 60 bars of H_2 for 18 h, applying 200 mg of ground Pd-C1-OA- O_2 . The first run resulted in a TON of 1570. Afterward, the catalyst was filtered, washed, calcinated (2 h, 200 °C) and reduced again (2 h, 200 °C). The second BH step achieved a similar TON of 1650. Without reactivation after the hydrogenation, only little activity was observed. This indicates the adsorption of (side) products like CO on the catalyst surface.

Finally, the catalyst was tested on a larger scale in a fixed bed reactor (see Figure 5). Here, the dehydrogenation process was performed in the presence of 10 g of catalyst. Over 10 h, a total of 71 L gas was released (Run Nr. 1: 83 % H_2 , 17 % CO_2) and no CO was detected. After the reaction, the catalyst

was washed and dried under air. No palladium was found in the reaction solution after filtration (SI, Table S18) demonstrating that there is no leaching. Then, a second and third consecutive FD step was performed with the used catalyst. Again, the activity of the catalyst was higher in the second run (Run Nr. 2: 82 L gas, 81 % H_2 , 19 % CO_2 , no CO was detected). In the third run a slight deactivation was noticeable (Run Nr. 3: 53 L 84 % H_2 , 16 % CO_2 , no CO was detected). Despite some breaking of the particles, no metal leaching was detected.

We presume a reversible blockage by the (intermediate) products like KHCO_3 as the cause for

the decreasing activity, which is in line with previous reports.^{46,44} Indeed, ICP-OES showed an increase of potassium salts on the used catalyst (fresh catalyst: no K detectable, catalyst after 1st run: 1.81 wt% K; SI, Table S19). Overall, a total of 180 L H_2 gas was released applying 10 g of Pd-C1-OA- O_2 which corresponds to a power-specific price (PSP) of 341 €/kW_{H₂,th} (see SI Eq. 12). The PSP is a purposed indicator for economic analysis. Herein the cost of palladium is associated with the hydrogen release performance of the catalyst.

4. Conclusion

In this work, the focus was placed on common issues associated with heterogeneous catalyst development for industrial applications in the domain of reversible hydrogen storage systems.²⁶ The presented optimal heterogeneous catalyst is recyclable, applicable in both half cycles of the hydrogen storage system formate/bicarbonate, and easily separable from the products. The usage of water as the sole solvent and formate as the hydrogen carrier ensures a safe process. In our study, we identified a novel palladium-based catalyst system on activated carbon pellets as support. The effect of different pretreatments, impregnations and reduction parameters on the activity of palladium on carbon pellet catalysts was investigated in detail. Following a series of straightforward optimization steps, a cost-effective shell-impregnated pellet catalyst was developed. It

was demonstrated that the synthesis protocol is simple, reproducible and scalable. The catalyst demonstrated stability under the selected reaction conditions, releasing 180 L of hydrogen from the carrier molecule formate in a medium-scale reactor. The estimated PSP for the catalysts presented was reduced by a factor of ten. While the first-generation catalyst Pd-C1 had a PSP of approximately

4175 €/kW_{H₂,th}, the final catalyst Pd-C1-OA-O₂ costs around 341 €/kW_{H₂,th}. The cost estimate is notable for its reasonable cost-benefit ratio, which is further enhanced by the increased activity per used palladium. Based on this catalyst system, we are currently working on the design of a 100 kW hydrogen battery device.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

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Conceptualization: C. S., J. M., V. T., H. J. and M. B.; Catalytic experiments: C. S., R. S., L. D. and J. M.; Analysis of the results: C. S., H. J. and S. W.; Discussion and experiment design: C. S., J. M., V. T., P. S., S. W., H. J. and M. B.; Analytical investigations: C.S., K. N., S. B. and C. K.; Funding acquisition: P. S., H. J. and M. B.; Writing (original draft): C. S.; Supervision and writing (review and editing) M. B., H. J., C. S., J. M., K. N. and S. W. All authors have read and agreed to the published version of this work.

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Notes

The authors declare no competing interests.

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REFERENCES

- (1) JV. *Fossil fuel CO₂ emissions increase again in 2024*. Global Carbon Budget. <https://globalcarbonbudget.org> (accessed 2025-01-29).
- (2) Ajanovic, A.; Sayer, M.; Haas, R. The Economics and the Environmental Benignity of Different Colors of Hydrogen. *Int. J. Hydrog. Energy* **2022**, *47* (57), 24136–24154. <https://doi.org/10.1016/j.ijhydene.2022.02.094>.
- (3) Preuster, P.; Papp, C.; Wasserscheid, P. Liquid Organic Hydrogen Carriers (LOHCs): Toward a Hydrogen-Free Hydrogen Economy. *Acc. Chem. Res.* **2017**, *50* (1), 74–85. <https://doi.org/10.1021/acs.accounts.6b00474>.
- (4) Niermann, M.; Beckendorff, A.; Kaltschmitt, M.; Bonhoff, K. Liquid Organic Hydrogen Carrier (LOHC) – Assessment Based on Chemical and Economic Properties. *Int. J. Hydrog. Energy* **2019**, *44* (13), 6631–6654. <https://doi.org/10.1016/j.ijhydene.2019.01.199>.
- (5) Klopčič, N.; Grimmer, I.; Winkler, F.; Sartory, M.; Trattner, A. A Review on Metal Hydride Materials for Hydrogen Storage. *Journal of Energy Storage* **2023**, *72*, 108456. <https://doi.org/10.1016/j.est.2023.108456>.
- (6) Sakintuna, B.; Lamaridarkrim, F.; Hirscher, M. Metal Hydride Materials for Solid Hydrogen Storage: A Review. *Int. J. Hydrog. Energy* **2007**, *32* (9), 1121–1140. <https://doi.org/10.1016/j.ijhydene.2006.11.022>.
- (7) Negro, V.; Noussan, M.; Chiaramonti, D. The Potential Role of Ammonia for Hydrogen Storage and Transport: A Critical Review of Challenges and Opportunities. *Energies* **2023**, *16* (17), 6192. <https://doi.org/10.3390/en16176192>.
- (8) Aziz, M.; Wijayanta, A. T.; Nandiyanto, A. B. D. Ammonia as Effective Hydrogen Storage: A Review on Production, Storage and Utilization. *Energies* **2020**, *13* (12), 3062. <https://doi.org/10.3390/en13123062>.
- (9) Eppinger, J.; Huang, K.-W. Formic Acid as a Hydrogen Energy Carrier. *ACS Energy Lett.* **2017**, *2* (1), 188–195. <https://doi.org/10.1021/acsenenergylett.6b00574>.
- (10) Chen, Z.; Stein, C. A. M.; Qu, R.; Rockstroh, N.; Bartling, S.; Weiß, J.; Kubis, C.; Junge, K.; Junge, H.; Beller, M. Designing a Robust Palladium Catalyst for Formic Acid Dehydrogenation. *ACS Catal.* **2023**, *13* (7), 4835–4841. <https://doi.org/10.1021/acscatal.3c00009>.
- (11) Onishi, N.; Laurenczy, G.; Beller, M.; Himeda, Y. Recent Progress for Reversible Homogeneous Catalytic Hydrogen Storage in Formic Acid and in Methanol. *Coord. Chem. Rev.* **2018**, *373*, 317–332. <https://doi.org/10.1016/j.ccr.2017.11.021>.
- (12) Schaub, T. CO₂-Based Hydrogen Storage: CO₂ Hydrogenation to Formic Acid, Formaldehyde and Methanol. *Phys. Sci. Rev.* **2018**, *3* (3), 20170015. <https://doi.org/10.1515/psr-2017-0015>.
- (13) Zaidman, B.; Wiener, H.; Sasson, Y. Formate Salts as Chemical Carriers in Hydrogen Storage and Transportation. *Int. J. Hydrog. Energy* **1986**, *11* (5), 341–347. [https://doi.org/10.1016/0360-3199\(86\)90154-0](https://doi.org/10.1016/0360-3199(86)90154-0).
- (14) Rivard, E.; Trudeau, M.; Zaghib, K. Hydrogen Storage for Mobility: A Review. *Materials* **2019**, *12* (12), 1973. <https://doi.org/10.3390/ma12121973>.
- (15) Müller, K.; Brooks, K.; Autrey, T. Hydrogen Storage in Formic Acid: A Comparison of Process Options. *Energy Fuels* **2017**, *31* (11), 12603–12611. <https://doi.org/10.1021/acs.energyfuels.7b02997>.
- (16) Léonard, G.; Giulini, D.; Villarreal-Singer, D. Design and Evaluation of a High-Density Energy Storage Route with CO₂ Re-Use, Water Electrolysis and Methanol Synthesis. In *Comput. Aided Chem. Eng.*; Elsevier, 2016; Vol. 38, pp 1797–1802. <https://doi.org/10.1016/B978-0-444-63428-3.50304-0>.
- (17) Bulushev, D. A.; Ross, J. R. H. Heterogeneous Catalysts for Hydrogenation of CO₂ and Bicarbonates to Formic Acid and Formates. *Catalysis Reviews* **2018**, *60* (4), 566–593. <https://doi.org/10.1080/01614940.2018.1476806>.
- (18) Kramer, H. Hydrogen Storage by the Bicarbonate/Formate Reaction. Studies on the Activity of Pd Catalysts. *Int. J. Hydrog. Energy* **1995**, *20* (3), 229–233. [https://doi.org/10.1016/0360-3199\(94\)E0025-T](https://doi.org/10.1016/0360-3199(94)E0025-T).
- (19) Mandal, T.; Kumar, R.; Kumar, S.; Choudhury, J. Single-Site Heterogenized Molecular Catalysts towards CO₂ Hydrogenation to Formates, Formamides and Methanol. *ChemCatChem* **2024**, e202400272. <https://doi.org/10.1002/cctc.202400272>.
- (20) Singh, T.; Chakraborty, S. Molybdenum-Catalyzed Hydrogenation of Carbon Dioxide, Bicarbonate, and Inorganic Carbonates to Formates. *Dalton Trans.* **2024**, 53 (24), 10244–10249.

<https://doi.org/10.1039/D4DT00916A>.

(21) Bredig, G.; Carter, S. R. Katalytische Synthese Der Ameisensäure Unter Druck. *Ber. Dtsch. Chem. Ges.* **1914**, 47 (1), 541–545. <https://doi.org/10.1002/cber.19140470188>.

(22) Su, J.; Yang, L.; Lu, M.; Lin, H. Highly Efficient Hydrogen Storage System Based on Ammonium Bicarbonate/Formate Redox Equilibrium over Palladium Nanocatalysts. *ChemSusChem* **2015**, 8 (5), 813–816. <https://doi.org/10.1002/cssc.201403251>.

(23) Shao, X.; Xu, J.; Huang, Y.; Su, X.; Duan, H.; Wang, X.; Zhang, T. Pd@C₃N₄ Nanocatalyst for Highly Efficient Hydrogen Storage System Based on Potassium Bicarbonate/Formate. *AIChE Journal* **2016**, 62 (7), 2410–2418. <https://doi.org/10.1002/aic.15218>.

(24) Masuda, S.; Shimoji, Y.; Mori, K.; Kuwahara, Y.; Yamashita, H. Interconversion of Formate/Bicarbonate for Hydrogen Storage/Release: Improved Activity Following Sacrificial Surface Modification of a Ag@Pd/TiO₂ Catalyst with a TiO_x Shell. *ACS Appl. Energy Mater.* **2020**, 3 (6), 5819–5829. <https://doi.org/10.1021/acsam.0c00744>.

(25) Boddien, A.; Gärtner, F.; Federsel, C.; Sponholz, P.; Mellmann, D.; Jackstell, R.; Junge, H.; Beller, M. CO₂ “Neutral” Hydrogen Storage Based on Bicarbonates and Formates. *Angew Chem Int Ed* **2011**, 50 (28), 6411–6414. <https://doi.org/10.1002/anie.201101995>.

(26) Sang, R.; Stein, C. A. M.; Schareina, T.; Hu, Y.; Léval, A.; Massa, J.; Turan, V.; Sponholz, P.; Wei, D.; Jackstell, R.; Junge, H.; Beller, M. Development of a Practical Formate/Bicarbonate Energy System. *Nat Commun* **2024**, 15 (1), 7268. <https://doi.org/10.1038/s41467-024-51658-2>.

(27) Sasson, A. METHOD FOR STORAGE AND RELEASE OF HYDROGEN. EP 3 065 865 B1, 2022.

(28) Bi, Q.; Lin, J.; Liu, Y.; Du, X.; Wang, J.; He, H.; Cao, Y. An Aqueous Rechargeable Formate-Based Hydrogen Battery Driven by Heterogeneous Pd Catalysis. *Angew Chem Int Ed* **2014**, 53 (49), 13583–13587. <https://doi.org/10.1002/anie.201409500>.

(29) Badano, J. M.; Betti, C.; Rintoul, I.; Vich-Berlanga, J.; Cagnola, E.; Torres, G.; Vera, C.; Yori, J.; Quiroga, M. New Composite Materials as Support for Selective Hydrogenation: Egg-Shell Catalysts. *Applied Catalysis A: General* **2010**, 390 (1–2), 166–174. <https://doi.org/10.1016/j.apcata.2010.10.008>.

(30) Auer, E.; Freund, A.; Pietsch, J.; Tacke, T. Carbons as Supports for Industrial Precious Metal Catalysts. *Applied Catalysis A: General* **1998**, 173 (2), 259–271. [https://doi.org/10.1016/S0926-860X\(98\)00184-7](https://doi.org/10.1016/S0926-860X(98)00184-7).

(31) Heveling, J. Heterogeneous Catalytic Chemistry by Example of Industrial Applications. *J. Chem. Educ.* **2012**, 89 (12), 1530–1536. <https://doi.org/10.1021/ed200816g>.

(32) Munnik, P.; De Jongh, P. E.; De Jong, K. P. Recent Developments in the Synthesis of Supported Catalysts. *Chem. Rev.* **2015**, 115 (14), 6687–6718. <https://doi.org/10.1021/cr500486u>.

(33) Carrara, N.; Badano, J. M.; Betti, C.; Lederhos, C.; Rintoul, I.; Coloma-Pascual, F.; Vera, C.; Quiroga, M. Selective Hydrogenation by Novel Composite Supported Pd Egg-Shell Catalysts. *Catal. Commun.* **2015**, 61, 72–77. <https://doi.org/10.1016/j.catcom.2014.12.012>.

(34) Russo, D.; Andreozzi, R.; Calabrese, M.; Marotta, R.; Di Benedetto, A. Quantitative Risk Assessment of Aqueous Formate for Hydrogen Storage. *Int. J. Hydrog. Energy* **2024**, 65, 421–427. <https://doi.org/10.1016/j.ijhydene.2024.04.069>.

(35) Wang, Z.-L.; Yan, J.-M.; Wang, H.-L.; Ping, Y.; Jiang, Q. Pd/C Synthesized with Citric Acid: An Efficient Catalyst for Hydrogen Generation from Formic Acid/Sodium Formate. *Sci Rep* **2012**, 2 (1), 598. <https://doi.org/10.1038/srep00598>.

(36) Wise, H. Mechanisms of Catalyst Poisoning by Sulfur Species. In *Stud. Surf. Sci. Catal.*; Elsevier, 1991; Vol. 68, pp 497–504. [https://doi.org/10.1016/S0167-2991\(08\)62676-2](https://doi.org/10.1016/S0167-2991(08)62676-2).

(37) Arabczyk, W.; Narkiewicz, U.; Moszyński, D. Chlorine as a Poison of the Fused Iron Catalyst for Ammonia Synthesis. *Applied Catalysis A: General* **1996**, 134 (2), 331–338. [https://doi.org/10.1016/0926-860X\(95\)00211-1](https://doi.org/10.1016/0926-860X(95)00211-1).

(38) Luo, M. Fischer–Tropsch Synthesis: Group II Alkali-Earth Metal Promoted Catalysts. *Applied Catalysis A: General* **2003**, 246 (1), 171–181. [https://doi.org/10.1016/S0926-860X\(03\)00024-3](https://doi.org/10.1016/S0926-860X(03)00024-3).

(39) Kibis, L. S.; Titkov, A. I.; Stadnichenko, A. I.; Koscheev, S. V.; Boronin, A. I. X-Ray Photoelectron Spectroscopy Study of Pd Oxidation by RF Discharge in Oxygen. *Appl Surf. Sci.* **2009**, 255 (22), 9248–9254. <https://doi.org/10.1016/j.apsusc.2009.07.011>.

(40) Macino, M.; Barnes, A. J.; Althahban, S. M.; Qu, R.; Gibson, E. K.; Morgan, D. J.; Freakley, S. J.; Dimitratos, N.; Kiely, C. J.; Gao, X.; Beale, A. M.; Bethell, D.; He, Q.; Sankar, M.; Hutchings, G. J. Tuning of Catalytic Sites in Pt/TiO₂ Catalysts for the Chemoselective Hydrogenation of 3-Nitrostyrene. *Nat Catal* **2019**, 2

- (10), 873–881. <https://doi.org/10.1038/s41929-019-0334-3>.
- (41) Köhler, K.; Heidenreich, R. G.; Krauter, J. G. E.; Pietsch, J. Highly Active Palladium/Activated Carbon Catalysts for Heck Reactions: Correlation of Activity, Catalyst Properties, and Pd Leaching. *Chem. Eur. J.* **2002**, *8* (3), 622–631. [https://doi.org/10.1002/1521-3765\(20020201\)8:3<622::AID-CHEM622>3.0.CO;2-0](https://doi.org/10.1002/1521-3765(20020201)8:3<622::AID-CHEM622>3.0.CO;2-0).
- (42) Van Den Brink, P. J.; Scholten, A.; Van Wageningen, A.; Lamers, M. D. A.; Van Dillen, A. J.; Geus, J. W. The Use of Chelating Agents for the Preparation of Iron Oxide Catalysts for the Selective Oxidation of Hydrogen Sulfide. In *Stud. Surf. Sci. Catal.*; Elsevier, 1991; Vol. 63, pp 527–536. [https://doi.org/10.1016/S0167-2991\(08\)64615-7](https://doi.org/10.1016/S0167-2991(08)64615-7).
- (43) Bulushev, D. A.; Zacharska, M.; Shlyakhova, E. V.; Chuvilin, A. L.; Guo, Y.; Beloshapkin, S.; Okotrub, A. V.; Bulusheva, L. G. Single Isolated Pd²⁺ Cations Supported on N-Doped Carbon as Active Sites for Hydrogen Production from Formic Acid Decomposition. *ACS Catal.* **2016**, *6* (2), 681–691. <https://doi.org/10.1021/acscatal.5b02381>.
- (44) Wang, F.; Xu, J.; Shao, X.; Su, X.; Huang, Y.; Zhang, T. Palladium on Nitrogen-Doped Mesoporous Carbon: A Bifunctional Catalyst for Formate-Based, Carbon-Neutral Hydrogen Storage. *ChemSusChem* **2016**, *9* (3), 246–251. <https://doi.org/10.1002/cssc.201501376>.
- (45) Baschuk, J. J.; Li, X. Carbon Monoxide Poisoning of Proton Exchange Membrane Fuel Cells. *Int. J. Energy Res.* **2001**, *25* (8), 695–713. <https://doi.org/10.1002/er.713>.
- (46) Hu, C.; Pulleri, J. K.; Ting, S.-W.; Chan, K.-Y. Activity of Pd/C for Hydrogen Generation in Aqueous Formic Acid Solution. *Int. J. Hydrog. Energy* **2014**, *39* (1), 381–390. <https://doi.org/10.1016/j.ijhydene.2013.10.067>.

6.5 $(\eta^4\text{-Trimethylenemethane})(1,1,1\text{-tris}\{[\text{bis}(4\text{-methoxyphenyl})\text{phosphanyl}]\text{methyl}\}\text{ethane})\text{-ruthenium(II) diethyl ether hemisolvate}$

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Contributions:

For this paper, I conducted literature research to identify optimal catalysts and performed parts of the catalyst synthesis and characterization. In addition, I co-wrote the draft of the paper and the supporting information. My contribution to this paper accounts for 50 %.

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Signature of the student
Carolyn A. M. Stein



Signature of the supervisor
Prof. Matthias Beller



$(\eta^4$ -Trimethylenemethane)(1,1,1-tris{[bis(4-methoxyphenyl)phosphanyl]methyl}ethane)-ruthenium(II) diethyl ether hemisolvate

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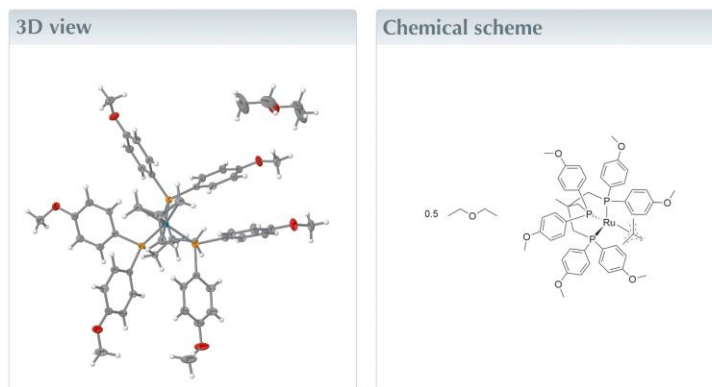
Edited by W. T. A. Harrison, University of Aberdeen, United Kingdom

Keywords: crystal structure; ruthenium; trimethylenemethane ligand; *p*-anisyl-triphos ligand.

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Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $[\text{Ru}(\text{C}_{47}\text{H}_{51}\text{O}_6\text{P}_3)(\text{C}_4\text{H}_6)] \cdot 0.5\text{C}_4\text{H}_{10}\text{O}$, consists of an Ru^{II} atom coordinated by 1,1,1-tris{[bis(4-methoxyphenyl)phosphanyl]methyl}ethane in κ^3 -coordination mode and an η^4 -coordinating trimethylenemethane ligand. The complex molecule is co-crystallized with a diethyl ether solvent molecule. A half diethyl ether molecule was considered, whereas additional disordered solvent molecules were removed from the diffraction data with the SQUEEZE procedure in *PLATON* [Spek (2015). *Acta Cryst.* **C71**, 9–18].



Structure description

Ruthenium complexes of the general formula $[\text{Ru}^{\text{II}}(\text{Ar-triphos})(\text{TMM})]$ (Ar-triphos = 1,1,1-tris(di(aryl)phosphino-methyl)ethane with aryl = *e.g.* phenyl, 4-methylphenyl, 3,5-dimethylphenyl; TMM = η^4 -trimethylenemethane) have been successfully applied as catalyst precursors in the hydrogenation of challenging substrates such as carboxylic esters, amides, carboxylic acids, carbonates and urea derivatives (vom Stein *et al.*, 2014) as well as in the hydrogenation of CO_2 (Wesselbaum *et al.*, 2012, 2015). The performance of the title compound, $[\text{Ru}^{\text{II}}(p\text{-anisyl-triphos})(\text{TMM})]$, either as pre-formed complex or formed *in situ*, in these transformations is not reported (Maeda *et al.*, 2010; the synthesis of the ligand *p*-anisyl-triphos is reported in the patent describing the ruthenium homogeneously catalysed hydrogenation of lactones and carboxylic acid esters in the liquid phase). On the other hand, as part of our interest in the design of efficient homogeneous catalytic processes based on non-noble metals, some of us have explored the application of cobalt complexes of Ar-triphos ligands, including *p*-anisyl-triphos, in the hydrogenation of CO_2 (Scharnagl *et al.*, 2019) and carbonates (Ferretti *et al.*, 2019) to methanol as well as in the reductive alkylation of anilines with carboxylic acids (Liu *et al.*, 2018) and the deoxygenative hydrogenation of amides to amines (Papa *et al.*, 2020). Xu, Wang, Shi



data reports

and coworkers have used Co/Ar-triphos complexes as catalysts for the transformation of levulinic acid and amines into pyrrolidines and pyrrolidinones using hydrogen (Pan *et al.*, 2022). In the latter three synthetic applications (Liu *et al.*, 2018; Papa *et al.*, 2020; Pan *et al.*, 2022), among those tested, the use of the *p*-anisyl-triphos ligand afforded the best results.

We therefore deemed it of interest to synthesize the title ruthenium complex to test it as a catalyst precursor. Structural analysis of the isolated complex provided further insights into its coordination chemistry. In the crystal, the three phosphorus atoms of the neutral $C_{47}H_{51}O_6P_3$ ligand coordinate to ruthenium generating a facially capped κ^3 complex. The metal coordination sphere is completed by an η^4 -trimethylene-methane $C_4H_6^{2-}$ dianion acting as a 6 e^- donor (Fig. 1). The title complex exhibits clear asymmetry in both the different Ru—P bond lengths and the corresponding P—Ru—P angles. Whilst the Ru—P1 [2.2787 (6) Å] and Ru—P3 [2.2780 (6) Å] bond lengths are nearly identical, the Ru—P2 bond [2.2988 (5) Å] is significantly elongated. Some asymmetry was also observed in related $Ru^{II}(\text{Ar-triphos})(\text{TMM})$ complexes: for Ar = Ph [2.2861 (15), 2.2842 (15), 2.2679 (15) Å (vom Stein *et al.*, 2013); 2.2893 (5), 2.2720 (5), 2.2885 (5) Å (Savourey *et al.*, 2014)]; Ar = 3,5-dimethylphenyl [2.2812 (8), 2.2907 (7), 2.2749 (8) Å (Meuresch *et al.*, 2016)]. Notably, another complex known in the literature with Ar = 4-methylphenyl has a highly symmetric structure: this complex crystallizes in the trigonal space group $R\bar{3}$ with only one third of the molecule in the asymmetric unit with Ru—P1 = 2.2757 (6) Å (Meuresch *et al.*, 2016). The uneven coordination of the 4-methoxy-triphos ligand in the title complex is also evident in the bond angles

about the metal atom: P1—Ru—P2 = 87.511 (19); P2—Ru—P3 = 87.931 (17); P3—Ru—P1 89.759 (17)°.

The TMM ligand adopts a pyramidal shape with a shorter bond length of the central carbon atom to ruthenium [Ru—C1 = 2.0674 (18) Å] than the terminal carbon atoms [Ru—C2 = 2.245 (2), Ru—C3 = 2.2249 (18), Ru—C4 = 2.263 (2) Å]. The three C—C bonds in the TMM unit are indistinguishable: 1.431 (3), 1.433 (3) and 1.435 (3) Å, which confirms the delocalization of the electrons within this ligand. This is also observed in the related $[Ru^{II}(\text{Ar-triphos})(\text{TMM})]$ complexes mentioned above. In solution, at room temperature, the complex exhibits a higher degree of symmetry: in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, a singlet at $\delta = 31.4$ ppm is observed, indicating the spectroscopic equivalence of the three phosphorus atoms, low field shifted compared to the free ligand, which resonates at $\delta = -30.4$ ppm. For the TMM anion, a singlet is present in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum at $\delta = 1.55$ ppm for the six equivalent methylene protons, while the corresponding three methylene carbon atoms all resonate at 42.5 ppm in the $^{13}\text{C}\{^1\text{H},^{31}\text{P}\}$ NMR spectrum. The connecting quaternary carbon atom resonates at 107.0 ppm.

The title Ru complex is co-crystallized with diethyl ether solvent molecules. A half diethyl ether molecule per complex molecule was considered, whereas the contribution of additional disordered solvent molecules to the intensity data was removed from the diffraction data with the SQUEEZE procedure in PLATON (Spek, 2015).

Synthesis and crystallization

The synthesis and isolation of the title complex were performed under an inert atmosphere (argon) with exclusion of air. Toluene, *n*-pentane, diethyl ether and dichloromethane were supplied by a solvent purification system and stored over 3 Å molecular sieves. Acetone, 99.8%, Extra Dry, AcroSeal[®], was purchased from Thermo Scientific Chemicals. [Bis(2-methylallyl)(1,5-cyclooctadiene)ruthenium(II)] was purchased from Strem and used as received. 1,1,1-Tris[[bis(4-methoxyphenyl)phosphanyl]methyl]ethane, *p*-anisyl-triphos, was prepared following a published procedure (Wesselbaum *et al.*, 2015).

^1H NMR spectra were obtained at 300 MHz (Bruker AV-300), $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained at 75 MHz and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained at 121 MHz. NMR chemical shifts are reported in ppm downfield from TMS and were referenced to the residual proton resonance and the natural abundance ^{13}C resonance of the solvents. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of H_3PO_4 .

To a clear colorless solution of *p*-anisyl-triphos (316 mg, 0.39 mmol, 1.1 eq.) in toluene (15 ml), [bis(2-methylallyl)(1,5-cyclooctadiene)ruthenium(II)] (226 mg, 0.36 mmol, 1.0 eq.) was added in one portion. The resulting clear green solution was refluxed for 18 h (overnight). Upon heating the solution became dark. At the end of the specified reaction time, the solution was clear and dark red. It was concentrated *in vacuo* to about 5 ml and *n*-pentane was added to induce precipita-

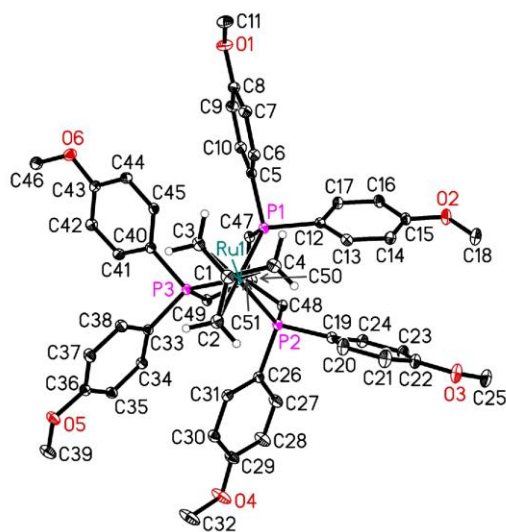


Figure 1
The molecular structure of the title compound without the solvent. Displacement ellipsoids correspond to 50% probability. Hydrogen atoms except those attached to C2, C3 and C4 are omitted for clarity.

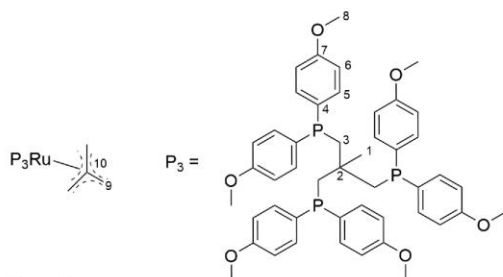


Figure 2
Chemical formula of the title compound with numbering for assignment for the NMR spectra.

tion. The dark brownish solid was collected and further washed with acetone thus leaving a gray-greenish solid (140 mg, 40% yield). Crystals suitable for X-ray diffraction were obtained by diffusion of diethyl ether into a solution of the title compound in dichloromethane.

^1H [^{31}P]-NMR (300 MHz, $[\text{CD}_2\text{Cl}_2]$): δ (ppm) = 6.99 (d , J_{HH} = 9 Hz, H5, 12H), 6.49 (d , J_{HH} = 9 Hz, H6, 12H), 3.70 (s , H8, 18H), 2.14 (s , H3, 6H), 1.55 (s , H9, 6H), 1.34 (s , H1, 3H) (Fig. 2). ^{31}P [^1H]-NMR (121 MHz, $[\text{CD}_2\text{Cl}_2]$): δ (ppm) = 31.4 (s). ^{13}C [^1H]-NMR (121 MHz, $[\text{CD}_2\text{Cl}_2]$): δ (ppm) = 159.5 (C7), 134.2 (C4), 133.9 (C5), 113.0 (C6), 106.8 (C10), 55.4 (C8), 42.5 (C9), 39.2 (C1), 38.5 (C2), 36.1 (C3) (see Fig. 2 for atom numbering).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Atoms H2A, H2B, H3A, H3B, H4A and H4B could be found from the difference-Fourier map and were refined freely. SADI and DFIX commands in *SHELXL* were used to optimize the shape of the half occupied diethyl ether molecule. Additionally, SIMU and EADP instructions were included to equalize the displacement parameters of the carbon atoms of the solvent (C53, C54 and C52, C55, respectively). For the final refinement, the contributions of further disordered solvent molecules were removed from the diffraction data with the SQUEEZE procedure in *PLATON* (Spek, 2015). SQUEEZE estimated the electron counts in the void volume of 328 Å³ to be 83.

Acknowledgements

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References

- Bruker (2013). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2014). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Ferretti, F., Scharnagl, F. K., Dall'Anese, A., Jackstell, R., Dastgir, S. & Beller, M. (2019). *Catal. Sci. Technol.* **9**, 3548–3553.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[\text{Ru}(\text{C}_{47}\text{H}_{51}\text{O}_6\text{P}_3)(\text{C}_4\text{H}_6)] \cdot 0.5\text{C}_4\text{H}_{10}\text{O}$
M_r	997.00
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	130
a, b, c (Å)	9.1504 (13), 11.6521 (16), 24.868 (4)
α, β, γ (°)	95.453 (3), 98.296 (3), 90.372 (3)
V (Å ³)	2611.3 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.44
Crystal size (mm)	0.36 × 0.21 × 0.08
Data collection	
Diffractionmeter	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.86, 0.97
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	111738, 13249, 12183
R_{int} ($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.033
	0.671
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.034, 0.084, 1.10
No. of reflections	13249
No. of parameters	620
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.33, -0.71

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *XP* in *SHELXTL* (Sheldrick, 2008) and *ChemDraw* (Mills, 2006).

- Liu, W., Sahoo, B., Spannenberg, A., Junge, K. & Beller, M. (2018). *Angew. Chem. Int. Ed.* **57**, 11673–11677.
Maeda, H., Inone, K., Matsumoto, T., Nagasaki, I., Noyori, R. & Saito, S. (2010). EP 2141142A1.
Meuresch, M., Westhues, S., Leitner, W. & Klankermayer, J. (2016). *Angew. Chem. Int. Ed.* **55**, 1392–1395.
Mills, N. (2006). *J. Am. Chem. Soc.* **128**, 13649–13650.
Pan, Y., Luo, Z., Yang, J., Han, J., Yang, J., Yao, Z., Xu, L., Wang, P. & Shi, Q. (2022). *Adv. Synth. Catal.* **364**, 2830–2836.
Papa, V., Cabrero-Antonino, J. R., Spannenberg, A., Junge, K. & Beller, M. (2020). *Catal. Sci. Technol.* **10**, 6125–6137.
Savourey, S., Lefèvre, G., Berthet, J.-C., Thuéry, P., Genre, C. & Cantat, T. (2014). *Angew. Chem. Int. Ed.* **53**, 10466–10470.
Scharnagl, F. K., Hertrich, M. F., Neitzel, G., Jackstell, R. & Beller, M. (2019). *Adv. Synth. Catal.* **361**, 374–379.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
Spek, A. L. (2015). *Acta Cryst.* **C71**, 9–18.
vom Stein, T., Meuresch, M., Limper, D., Schmitz, M., Hölscher, M., Coetzee, J., Cole-Hamilton, D. J., Klankermayer, J. & Leitner, W. (2014). *J. Am. Chem. Soc.* **136**, 13217–13225.
vom Stein, T., Weigand, T., Merckens, C., Klankermayer, J. & Leitner, W. (2013). *ChemCatChem* **5**, 439–441.
Wesselbaum, S., Moha, V., Meuresch, M., Brosinski, S., Thenert, K. M., Kothe, J., Stein, T. V., Englert, U., Hölscher, M., Klankermayer, J. & Leitner, W. (2015). *Chem. Sci.* **6**, 693–704.
Wesselbaum, S., vom Stein, T., Klankermayer, J. & Leitner, W. (2012). *Angew. Chem. Int. Ed.* **51**, 7499–7502.

full crystallographic data

IUCrData (2025). **10**, x250524 [<https://doi.org/10.1107/S2414314625005243>]

(η^4 -Trimethylenemethane)(1,1,1-tris[[bis(4-methoxyphenyl)phosphanyl]methyl]-ethane)ruthenium(II) diethyl ether hemisolvate

Carolyn A. M. Stein, Elisabetta Alberico, Anke Spannenberg, Matthias Beller and Henrik Junge

(η^4 -2-Methylidenepropane-1,3-diyl)(1,1,1-tris[[bis(4-methoxyphenyl)phosphanyl]methyl]ethane)ruthenium(II) diethyl ether hemisolvate

Crystal data

[Ru(C₄₇H₅₁O₆P₃)(C₄H₆)]·0.5C₄H₁₀O

M_r = 997.00

Triclinic, *P* $\bar{1}$

a = 9.1504 (13) Å

b = 11.6521 (16) Å

c = 24.868 (4) Å

α = 95.453 (3)°

β = 98.296 (3)°

γ = 90.372 (3)°

V = 2611.3 (6) Å³

Z = 2

F(000) = 1042

D_x = 1.268 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 9069 reflections

θ = 2.3–29.1°

μ = 0.44 mm⁻¹

T = 130 K

Needle, pale yellow

0.36 × 0.21 × 0.08 mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Detector resolution: 8.3333 pixels mm⁻¹

ϕ and ω scans

Absorption correction: multi-scan

(SADABS; Krause *et al.*, 2015)

T_{min} = 0.86, *T_{max}* = 0.97

111738 measured reflections

13249 independent reflections

12183 reflections with *I* > 2σ(*I*)

R_{int} = 0.033

θ_{max} = 28.5°, θ_{min} = 1.7°

h = −12→12

k = −15→15

l = −33→33

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.034

wR (*F*²) = 0.084

S = 1.10

13249 reflections

620 parameters

3 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.031*P*)² + 2.8623*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δσ)_{max} = 0.002

Δρ_{max} = 1.33 e Å⁻³

Δρ_{min} = −0.71 e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C52	0.2204 (13)	0.0943 (7)	0.0211 (6)	0.100 (3)	0.5
H52A	0.321347	0.080457	0.038154	0.150*	0.5
H52B	0.221119	0.108782	−0.017045	0.150*	0.5
H52C	0.181610	0.161598	0.040767	0.150*	0.5
C53	0.1226 (9)	−0.0114 (6)	0.0233 (3)	0.0644 (19)	0.5
H53A	0.161494	−0.079895	0.003776	0.077*	0.5
H53B	0.121860	−0.026913	0.061771	0.077*	0.5
O7	−0.0243 (8)	0.0106 (11)	−0.0018 (11)	0.062 (3)	0.5
C54	−0.1170 (8)	−0.0891 (6)	−0.0001 (3)	0.067 (2)	0.5
H54A	−0.117247	−0.107862	0.037923	0.080*	0.5
H54B	−0.084139	−0.157061	−0.021871	0.080*	0.5
C55	−0.2705 (12)	−0.0508 (8)	−0.0253 (6)	0.100 (3)	0.5
H55A	−0.342776	−0.113620	−0.026021	0.150*	0.5
H55B	−0.299640	0.017133	−0.003268	0.150*	0.5
H55C	−0.266792	−0.031680	−0.062593	0.150*	0.5
C1	0.5470 (2)	0.61076 (18)	0.28588 (8)	0.0242 (4)	
C2	0.4926 (2)	0.65582 (19)	0.33462 (9)	0.0252 (4)	
C3	0.5827 (2)	0.69415 (18)	0.25073 (9)	0.0246 (4)	
C4	0.4727 (2)	0.50839 (18)	0.25813 (9)	0.0263 (4)	
C5	0.3395 (2)	0.66565 (16)	0.11064 (8)	0.0195 (3)	
C6	0.4690 (2)	0.60314 (17)	0.11157 (8)	0.0224 (4)	
H6	0.498324	0.558938	0.141349	0.027*	
C7	0.5568 (2)	0.60328 (17)	0.07037 (8)	0.0238 (4)	
H7	0.644723	0.559989	0.072050	0.029*	
C8	0.5142 (2)	0.66761 (17)	0.02672 (8)	0.0237 (4)	
C9	0.3839 (2)	0.72973 (18)	0.02440 (8)	0.0254 (4)	
H9	0.353865	0.772831	−0.005717	0.030*	
C10	0.2984 (2)	0.72854 (17)	0.06592 (8)	0.0231 (4)	
H10	0.210109	0.771308	0.063997	0.028*	
C11	0.7246 (2)	0.6149 (2)	−0.01589 (9)	0.0327 (5)	
H11A	0.794129	0.643373	0.016441	0.049*	
H11B	0.767124	0.627435	−0.048888	0.049*	
H11C	0.705291	0.532286	−0.015106	0.049*	
C12	0.12986 (19)	0.52183 (16)	0.14134 (7)	0.0190 (3)	
C13	0.1551 (2)	0.42421 (16)	0.16889 (8)	0.0216 (4)	
H13	0.228118	0.427726	0.200326	0.026*	
C14	0.0769 (2)	0.32137 (17)	0.15196 (8)	0.0236 (4)	
H14	0.097120	0.255517	0.171361	0.028*	
C15	−0.0308 (2)	0.31589 (16)	0.10658 (8)	0.0231 (4)	

C16	−0.0551 (2)	0.41133 (17)	0.07690 (8)	0.0246 (4)
H16	−0.126566	0.406881	0.044977	0.029*
C17	0.0248 (2)	0.51225 (17)	0.09400 (8)	0.0228 (4)
H17	0.008361	0.576605	0.073294	0.027*
C18	−0.1004 (3)	0.12417 (19)	0.11811 (11)	0.0367 (5)
H18A	−0.000369	0.094808	0.117849	0.055*
H18B	−0.172719	0.063790	0.101735	0.055*
H18C	−0.115746	0.146852	0.155818	0.055*
C19	0.0495 (2)	0.48835 (16)	0.28390 (8)	0.0199 (3)
C20	0.1490 (2)	0.41319 (18)	0.30955 (10)	0.0291 (4)
H20	0.247118	0.439675	0.322893	0.035*
C21	0.1088 (2)	0.30162 (19)	0.31603 (10)	0.0340 (5)
H21	0.178997	0.252011	0.333241	0.041*
C22	−0.0350 (2)	0.26201 (17)	0.29728 (9)	0.0274 (4)
C23	−0.1365 (2)	0.33463 (18)	0.27237 (9)	0.0276 (4)
H23	−0.234924	0.308154	0.259661	0.033*
C24	−0.0937 (2)	0.44721 (17)	0.26592 (8)	0.0243 (4)
H24	−0.164210	0.496784	0.248836	0.029*
C25	−0.2109 (3)	0.1078 (2)	0.29005 (12)	0.0400 (6)
H25A	−0.277746	0.155715	0.309584	0.060*
H25B	−0.217844	0.028018	0.299041	0.060*
H25C	−0.238896	0.110321	0.250629	0.060*
C26	0.07060 (19)	0.70110 (16)	0.34557 (8)	0.0197 (3)
C27	−0.0748 (2)	0.7017 (2)	0.35736 (9)	0.0302 (5)
H27	−0.152348	0.669662	0.330462	0.036*
C28	−0.1071 (2)	0.7478 (2)	0.40708 (10)	0.0387 (6)
H28	−0.206612	0.748902	0.413908	0.046*
C29	0.0051 (2)	0.7930 (2)	0.44753 (9)	0.0319 (5)
C30	0.1493 (2)	0.79189 (18)	0.43740 (8)	0.0247 (4)
H30	0.226816	0.821753	0.464874	0.030*
C31	0.1803 (2)	0.74652 (16)	0.38648 (8)	0.0213 (4)
H31	0.279759	0.746755	0.379609	0.026*
C32	0.0767 (3)	0.8793 (3)	0.53848 (11)	0.0580 (9)
H32A	0.145836	0.817560	0.547211	0.087*
H32B	0.033439	0.906693	0.571062	0.087*
H32C	0.129588	0.943218	0.526316	0.087*
C33	0.3431 (2)	0.95068 (15)	0.32834 (7)	0.0189 (3)
C34	0.2506 (2)	1.00783 (17)	0.36094 (8)	0.0218 (4)
H34	0.147043	1.004400	0.349247	0.026*
C35	0.3056 (2)	1.07035 (17)	0.41053 (8)	0.0237 (4)
H35	0.239932	1.108747	0.432187	0.028*
C36	0.4563 (2)	1.07605 (17)	0.42795 (8)	0.0234 (4)
C37	0.5518 (2)	1.02067 (19)	0.39530 (9)	0.0279 (4)
H37	0.655551	1.025500	0.406651	0.034*
C38	0.4954 (2)	0.95914 (18)	0.34668 (8)	0.0256 (4)
H38	0.561361	0.921372	0.324953	0.031*
C39	0.4289 (3)	1.1922 (2)	0.50943 (9)	0.0389 (5)
H39A	0.375867	1.251689	0.489557	0.058*

H39B	0.488466	1.228405	0.542708	0.058*
H39C	0.357675	1.137463	0.519187	0.058*
C40	0.37004 (19)	0.96025 (16)	0.22014 (8)	0.0199 (3)
C41	0.3493 (2)	1.07899 (17)	0.22652 (8)	0.0239 (4)
H41	0.290308	1.109434	0.252756	0.029*
C42	0.4119 (2)	1.15405 (17)	0.19579 (8)	0.0250 (4)
H42	0.396987	1.234686	0.201235	0.030*
C43	0.4971 (2)	1.10942 (17)	0.15678 (8)	0.0233 (4)
C44	0.5182 (2)	0.99107 (17)	0.14955 (8)	0.0240 (4)
H44	0.575041	0.960299	0.122691	0.029*
C45	0.4567 (2)	0.91808 (16)	0.18132 (8)	0.0204 (4)
H45	0.474000	0.837695	0.176565	0.025*
C46	0.5586 (3)	1.29621 (18)	0.13423 (9)	0.0310 (4)
H46A	0.455742	1.320628	0.128510	0.047*
H46B	0.614246	1.332507	0.109294	0.047*
H46C	0.602619	1.319536	0.172036	0.047*
C47	0.0911 (2)	0.76620 (16)	0.15491 (8)	0.0194 (3)
H47A	0.139073	0.836920	0.145940	0.023*
H47B	0.019320	0.737444	0.122684	0.023*
C48	−0.03391 (19)	0.69010 (16)	0.23091 (8)	0.0189 (3)
H48A	−0.065966	0.627272	0.201836	0.023*
H48B	−0.119203	0.708473	0.250353	0.023*
C49	0.08936 (19)	0.89055 (16)	0.24598 (8)	0.0197 (3)
H49A	0.043689	0.893617	0.279826	0.024*
H49B	0.077100	0.966839	0.231636	0.024*
C50	0.00576 (19)	0.79829 (15)	0.20347 (7)	0.0181 (3)
C51	−0.1412 (2)	0.84997 (17)	0.18005 (8)	0.0230 (4)
H51A	−0.194292	0.878298	0.210030	0.034*
H51B	−0.201531	0.790550	0.156104	0.034*
H51C	−0.121562	0.914016	0.159085	0.034*
O1	0.58996 (17)	0.67523 (14)	−0.01606 (6)	0.0308 (3)
O2	−0.11837 (17)	0.22147 (13)	0.08752 (7)	0.0313 (3)
O3	−0.06470 (18)	0.14986 (13)	0.30570 (8)	0.0381 (4)
O4	−0.03867 (18)	0.8359 (2)	0.49571 (7)	0.0530 (6)
O5	0.52291 (16)	1.13276 (14)	0.47578 (6)	0.0309 (3)
O6	0.56350 (18)	1.17425 (13)	0.12387 (6)	0.0309 (3)
P1	0.23330 (5)	0.65646 (4)	0.16726 (2)	0.01707 (9)
P2	0.11526 (5)	0.63599 (4)	0.27960 (2)	0.01704 (9)
P3	0.28904 (5)	0.86405 (4)	0.26319 (2)	0.01700 (9)
Ru1	0.34344 (2)	0.67321 (2)	0.25595 (2)	0.01663 (4)
H2A	0.462 (3)	0.604 (2)	0.3568 (9)	0.022 (6)*
H2B	0.537 (3)	0.728 (2)	0.3517 (10)	0.025 (6)*
H3A	0.626 (3)	0.763 (2)	0.2679 (10)	0.030 (6)*
H3B	0.615 (3)	0.669 (2)	0.2170 (11)	0.033 (7)*
H4A	0.499 (3)	0.480 (2)	0.2226 (10)	0.025 (6)*
H4B	0.444 (3)	0.455 (2)	0.2785 (10)	0.025 (6)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C52	0.125 (8)	0.045 (5)	0.112 (5)	−0.021 (4)	−0.050 (5)	0.019 (5)
C53	0.081 (5)	0.057 (4)	0.053 (4)	0.026 (4)	−0.002 (4)	0.005 (3)
O7	0.073 (7)	0.040 (5)	0.072 (4)	−0.004 (5)	0.011 (8)	−0.001 (5)
C54	0.069 (4)	0.056 (4)	0.073 (5)	−0.024 (3)	0.026 (4)	−0.033 (3)
C55	0.125 (8)	0.045 (5)	0.112 (5)	−0.021 (4)	−0.050 (5)	0.019 (5)
C1	0.0125 (8)	0.0307 (10)	0.0281 (10)	0.0060 (7)	−0.0010 (7)	0.0009 (8)
C2	0.0166 (8)	0.0313 (10)	0.0261 (10)	−0.0004 (7)	−0.0026 (7)	0.0035 (8)
C3	0.0104 (8)	0.0298 (10)	0.0317 (10)	0.0018 (7)	0.0025 (7)	−0.0053 (8)
C4	0.0235 (9)	0.0264 (10)	0.0286 (10)	0.0086 (8)	0.0021 (8)	0.0029 (8)
C5	0.0175 (8)	0.0197 (8)	0.0206 (8)	−0.0004 (7)	0.0023 (7)	−0.0014 (7)
C6	0.0207 (9)	0.0234 (9)	0.0229 (9)	0.0016 (7)	0.0025 (7)	0.0018 (7)
C7	0.0200 (9)	0.0256 (9)	0.0261 (9)	0.0044 (7)	0.0042 (7)	0.0020 (7)
C8	0.0231 (9)	0.0263 (9)	0.0215 (9)	−0.0011 (7)	0.0046 (7)	−0.0003 (7)
C9	0.0270 (10)	0.0266 (10)	0.0225 (9)	0.0035 (8)	0.0027 (7)	0.0039 (8)
C10	0.0200 (9)	0.0240 (9)	0.0247 (9)	0.0033 (7)	0.0017 (7)	0.0013 (7)
C11	0.0255 (10)	0.0430 (13)	0.0318 (11)	0.0051 (9)	0.0106 (9)	0.0041 (9)
C12	0.0152 (8)	0.0205 (8)	0.0206 (8)	0.0006 (6)	0.0025 (6)	−0.0009 (7)
C13	0.0184 (8)	0.0231 (9)	0.0225 (9)	0.0038 (7)	0.0008 (7)	0.0007 (7)
C14	0.0235 (9)	0.0198 (9)	0.0274 (10)	0.0024 (7)	0.0019 (7)	0.0045 (7)
C15	0.0208 (9)	0.0198 (9)	0.0278 (10)	−0.0019 (7)	0.0033 (7)	−0.0014 (7)
C16	0.0229 (9)	0.0244 (9)	0.0242 (9)	−0.0017 (7)	−0.0031 (7)	0.0009 (7)
C17	0.0221 (9)	0.0206 (9)	0.0248 (9)	−0.0001 (7)	−0.0007 (7)	0.0037 (7)
C18	0.0373 (12)	0.0237 (10)	0.0479 (14)	−0.0070 (9)	0.0001 (10)	0.0077 (10)
C19	0.0169 (8)	0.0197 (8)	0.0227 (9)	0.0010 (7)	0.0027 (7)	0.0005 (7)
C20	0.0180 (9)	0.0237 (10)	0.0436 (12)	0.0001 (7)	−0.0035 (8)	0.0056 (9)
C21	0.0247 (10)	0.0254 (10)	0.0505 (14)	0.0037 (8)	−0.0027 (9)	0.0092 (9)
C22	0.0267 (10)	0.0195 (9)	0.0361 (11)	−0.0017 (7)	0.0046 (8)	0.0033 (8)
C23	0.0199 (9)	0.0284 (10)	0.0329 (11)	−0.0063 (8)	−0.0013 (8)	0.0033 (8)
C24	0.0179 (9)	0.0256 (9)	0.0287 (10)	0.0002 (7)	−0.0003 (7)	0.0049 (8)
C25	0.0351 (12)	0.0267 (11)	0.0588 (16)	−0.0100 (9)	0.0092 (11)	0.0044 (10)
C26	0.0150 (8)	0.0214 (8)	0.0224 (9)	0.0013 (6)	0.0031 (7)	−0.0001 (7)
C27	0.0140 (8)	0.0447 (12)	0.0291 (10)	−0.0012 (8)	0.0018 (7)	−0.0097 (9)
C28	0.0146 (9)	0.0615 (16)	0.0360 (12)	−0.0008 (9)	0.0049 (8)	−0.0173 (11)
C29	0.0217 (10)	0.0448 (13)	0.0266 (10)	0.0021 (9)	0.0033 (8)	−0.0097 (9)
C30	0.0181 (8)	0.0306 (10)	0.0234 (9)	−0.0009 (7)	−0.0012 (7)	−0.0011 (8)
C31	0.0150 (8)	0.0249 (9)	0.0243 (9)	0.0009 (7)	0.0027 (7)	0.0045 (7)
C32	0.0285 (12)	0.104 (3)	0.0331 (13)	−0.0007 (14)	0.0012 (10)	−0.0324 (15)
C33	0.0169 (8)	0.0187 (8)	0.0209 (8)	−0.0008 (6)	0.0033 (7)	0.0002 (7)
C34	0.0160 (8)	0.0253 (9)	0.0233 (9)	0.0013 (7)	0.0025 (7)	−0.0006 (7)
C35	0.0215 (9)	0.0264 (9)	0.0229 (9)	0.0022 (7)	0.0055 (7)	−0.0023 (7)
C36	0.0230 (9)	0.0252 (9)	0.0210 (9)	−0.0023 (7)	0.0018 (7)	−0.0008 (7)
C37	0.0158 (8)	0.0354 (11)	0.0304 (10)	−0.0026 (8)	0.0020 (7)	−0.0062 (8)
C38	0.0171 (8)	0.0315 (10)	0.0275 (10)	−0.0008 (7)	0.0061 (7)	−0.0051 (8)
C39	0.0349 (12)	0.0517 (15)	0.0265 (11)	0.0042 (10)	0.0027 (9)	−0.0128 (10)
C40	0.0155 (8)	0.0223 (9)	0.0216 (9)	0.0005 (6)	0.0023 (7)	0.0017 (7)

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C41	0.0231 (9)	0.0225 (9)	0.0268 (10)	0.0053 (7)	0.0071 (7)	0.0005 (7)
C42	0.0264 (9)	0.0204 (9)	0.0289 (10)	0.0050 (7)	0.0058 (8)	0.0029 (7)
C43	0.0209 (9)	0.0242 (9)	0.0253 (9)	−0.0007 (7)	0.0043 (7)	0.0037 (7)
C44	0.0219 (9)	0.0251 (9)	0.0257 (9)	0.0020 (7)	0.0075 (7)	−0.0002 (7)
C45	0.0165 (8)	0.0197 (8)	0.0246 (9)	0.0001 (6)	0.0033 (7)	−0.0009 (7)
C46	0.0396 (12)	0.0238 (10)	0.0308 (11)	0.0004 (9)	0.0071 (9)	0.0056 (8)
C47	0.0171 (8)	0.0190 (8)	0.0212 (9)	0.0025 (6)	−0.0005 (7)	0.0021 (7)
C48	0.0118 (7)	0.0200 (8)	0.0243 (9)	0.0008 (6)	0.0006 (6)	0.0026 (7)
C49	0.0137 (8)	0.0191 (8)	0.0256 (9)	0.0024 (6)	0.0024 (7)	−0.0009 (7)
C50	0.0138 (7)	0.0191 (8)	0.0214 (8)	0.0025 (6)	0.0013 (6)	0.0028 (7)
C51	0.0162 (8)	0.0221 (9)	0.0305 (10)	0.0031 (7)	0.0011 (7)	0.0048 (7)
O1	0.0283 (7)	0.0407 (9)	0.0265 (7)	0.0080 (6)	0.0109 (6)	0.0083 (6)
O2	0.0307 (8)	0.0221 (7)	0.0381 (9)	−0.0074 (6)	−0.0048 (6)	0.0027 (6)
O3	0.0315 (8)	0.0214 (7)	0.0608 (11)	−0.0036 (6)	0.0020 (8)	0.0082 (7)
O4	0.0213 (8)	0.0959 (16)	0.0343 (9)	−0.0015 (9)	0.0035 (7)	−0.0315 (10)
O5	0.0249 (7)	0.0406 (9)	0.0240 (7)	−0.0013 (6)	0.0011 (6)	−0.0096 (6)
O6	0.0388 (8)	0.0234 (7)	0.0341 (8)	0.0016 (6)	0.0155 (7)	0.0059 (6)
P1	0.01360 (19)	0.0177 (2)	0.0192 (2)	0.00138 (16)	0.00080 (16)	0.00047 (17)
P2	0.01133 (19)	0.0185 (2)	0.0206 (2)	0.00093 (16)	0.00078 (16)	0.00072 (17)
P3	0.01225 (19)	0.0183 (2)	0.0201 (2)	0.00043 (16)	0.00272 (16)	−0.00046 (17)
Ru1	0.01074 (7)	0.01885 (7)	0.01943 (7)	0.00181 (5)	0.00065 (5)	−0.00034 (5)

Geometric parameters (Å, °)

C52—C53	1.529 (8)	C25—O3	1.410 (3)
C52—H52A	0.9800	C25—H25A	0.9800
C52—H52B	0.9800	C25—H25B	0.9800
C52—H52C	0.9800	C25—H25C	0.9800
C53—O7	1.434 (11)	C26—C31	1.385 (3)
C53—H53A	0.9900	C26—C27	1.403 (3)
C53—H53B	0.9900	C26—P2	1.8425 (19)
O7—C54	1.441 (12)	C27—C28	1.373 (3)
C54—C55	1.540 (8)	C27—H27	0.9500
C54—H54A	0.9900	C28—C29	1.392 (3)
C54—H54B	0.9900	C28—H28	0.9500
C55—H55A	0.9800	C29—O4	1.369 (3)
C55—H55B	0.9800	C29—C30	1.378 (3)
C55—H55C	0.9800	C30—C31	1.393 (3)
C1—C2	1.431 (3)	C30—H30	0.9500
C1—C3	1.433 (3)	C31—H31	0.9500
C1—C4	1.435 (3)	C32—O4	1.438 (3)
C1—Ru1	2.0674 (18)	C32—H32A	0.9800
C2—Ru1	2.245 (2)	C32—H32B	0.9800
C2—H2A	0.92 (2)	C32—H32C	0.9800
C2—H2B	0.96 (2)	C33—C34	1.385 (2)
C3—Ru1	2.2249 (18)	C33—C38	1.402 (3)
C3—H3A	0.93 (3)	C33—P3	1.8275 (19)
C3—H3B	0.95 (3)	C34—C35	1.397 (3)

C4—Ru1	2.263 (2)	C34—H34	0.9500
C4—H4A	0.97 (2)	C35—C36	1.383 (3)
C4—H4B	0.90 (2)	C35—H35	0.9500
C5—C6	1.393 (3)	C36—O5	1.364 (2)
C5—C10	1.398 (3)	C36—C37	1.397 (3)
C5—P1	1.8335 (19)	C37—C38	1.376 (3)
C6—C7	1.390 (3)	C37—H37	0.9500
C6—H6	0.9500	C38—H38	0.9500
C7—C8	1.389 (3)	C39—O5	1.423 (3)
C7—H7	0.9500	C39—H39A	0.9800
C8—O1	1.360 (2)	C39—H39B	0.9800
C8—C9	1.396 (3)	C39—H39C	0.9800
C9—C10	1.383 (3)	C40—C45	1.392 (3)
C9—H9	0.9500	C40—C41	1.395 (3)
C10—H10	0.9500	C40—P3	1.8435 (19)
C11—O1	1.422 (3)	C41—C42	1.387 (3)
C11—H11A	0.9800	C41—H41	0.9500
C11—H11B	0.9800	C42—C43	1.395 (3)
C11—H11C	0.9800	C42—H42	0.9500
C12—C13	1.387 (3)	C43—O6	1.366 (2)
C12—C17	1.404 (3)	C43—C44	1.392 (3)
C12—P1	1.8398 (19)	C44—C45	1.383 (3)
C13—C14	1.390 (3)	C44—H44	0.9500
C13—H13	0.9500	C45—H45	0.9500
C14—C15	1.383 (3)	C46—O6	1.422 (3)
C14—H14	0.9500	C46—H46A	0.9800
C15—O2	1.363 (2)	C46—H46B	0.9800
C15—C16	1.394 (3)	C46—H46C	0.9800
C16—C17	1.379 (3)	C47—C50	1.548 (3)
C16—H16	0.9500	C47—P1	1.8448 (18)
C17—H17	0.9500	C47—H47A	0.9900
C18—O2	1.422 (3)	C47—H47B	0.9900
C18—H18A	0.9800	C48—C50	1.554 (3)
C18—H18B	0.9800	C48—P2	1.8456 (18)
C18—H18C	0.9800	C48—H48A	0.9900
C19—C24	1.389 (3)	C48—H48B	0.9900
C19—C20	1.397 (3)	C49—C50	1.549 (3)
C19—P2	1.8365 (19)	C49—P3	1.8504 (18)
C20—C21	1.379 (3)	C49—H49A	0.9900
C20—H20	0.9500	C49—H49B	0.9900
C21—C22	1.391 (3)	C50—C51	1.537 (2)
C21—H21	0.9500	C51—H51A	0.9800
C22—O3	1.374 (2)	C51—H51B	0.9800
C22—C23	1.381 (3)	C51—H51C	0.9800
C23—C24	1.397 (3)	P1—Ru1	2.2787 (6)
C23—H23	0.9500	P2—Ru1	2.2988 (5)
C24—H24	0.9500	P3—Ru1	2.2780 (6)

C53—C52—H52A	109.5	C29—C30—H30	120.3
C53—C52—H52B	109.5	C31—C30—H30	120.3
H52A—C52—H52B	109.5	C26—C31—C30	122.06 (17)
C53—C52—H52C	109.5	C26—C31—H31	119.0
H52A—C52—H52C	109.5	C30—C31—H31	119.0
H52B—C52—H52C	109.5	O4—C32—H32A	109.5
O7—C53—C52	108.6 (10)	O4—C32—H32B	109.5
O7—C53—H53A	110.0	H32A—C32—H32B	109.5
C52—C53—H53A	110.0	O4—C32—H32C	109.5
O7—C53—H53B	110.0	H32A—C32—H32C	109.5
C52—C53—H53B	110.0	H32B—C32—H32C	109.5
H53A—C53—H53B	108.3	C34—C33—C38	117.36 (17)
C53—O7—C54	108.9 (12)	C34—C33—P3	127.20 (14)
O7—C54—C55	103.0 (8)	C38—C33—P3	115.44 (14)
O7—C54—H54A	111.2	C33—C34—C35	121.78 (17)
C55—C54—H54A	111.2	C33—C34—H34	119.1
O7—C54—H54B	111.2	C35—C34—H34	119.1
C55—C54—H54B	111.2	C36—C35—C34	119.62 (18)
H54A—C54—H54B	109.1	C36—C35—H35	120.2
C54—C55—H55A	109.5	C34—C35—H35	120.2
C54—C55—H55B	109.5	O5—C36—C35	125.08 (18)
H55A—C55—H55B	109.5	O5—C36—C37	115.32 (17)
C54—C55—H55C	109.5	C35—C36—C37	119.61 (18)
H55A—C55—H55C	109.5	C38—C37—C36	119.85 (18)
H55B—C55—H55C	109.5	C38—C37—H37	120.1
C2—C1—C3	115.95 (18)	C36—C37—H37	120.1
C2—C1—C4	115.50 (18)	C37—C38—C33	121.77 (18)
C3—C1—C4	114.71 (18)	C37—C38—H38	119.1
C2—C1—Ru1	77.48 (11)	C33—C38—H38	119.1
C3—C1—Ru1	76.55 (11)	O5—C39—H39A	109.5
C4—C1—Ru1	78.20 (11)	O5—C39—H39B	109.5
C1—C2—Ru1	64.03 (10)	H39A—C39—H39B	109.5
C1—C2—H2A	117.9 (15)	O5—C39—H39C	109.5
Ru1—C2—H2A	116.4 (15)	H39A—C39—H39C	109.5
C1—C2—H2B	115.6 (14)	H39B—C39—H39C	109.5
Ru1—C2—H2B	113.6 (14)	C45—C40—C41	117.67 (17)
H2A—C2—H2B	118 (2)	C45—C40—P3	121.63 (14)
C1—C3—Ru1	64.65 (10)	C41—C40—P3	120.68 (14)
C1—C3—H3A	116.2 (16)	C42—C41—C40	122.12 (18)
Ru1—C3—H3A	115.1 (16)	C42—C41—H41	118.9
C1—C3—H3B	119.9 (16)	C40—C41—H41	118.9
Ru1—C3—H3B	117.6 (16)	C41—C42—C43	119.05 (18)
H3A—C3—H3B	114 (2)	C41—C42—H42	120.5
C1—C4—Ru1	63.42 (10)	C43—C42—H42	120.5
C1—C4—H4A	117.9 (14)	O6—C43—C44	115.84 (17)
Ru1—C4—H4A	112.8 (14)	O6—C43—C42	124.51 (18)
C1—C4—H4B	117.9 (16)	C44—C43—C42	119.65 (18)
Ru1—C4—H4B	117.1 (15)	C45—C44—C43	120.27 (18)

H4A—C4—H4B	117 (2)	C45—C44—H44	119.9
C6—C5—C10	117.52 (17)	C43—C44—H44	119.9
C6—C5—P1	117.64 (14)	C44—C45—C40	121.22 (18)
C10—C5—P1	124.82 (14)	C44—C45—H45	119.4
C7—C6—C5	122.20 (18)	C40—C45—H45	119.4
C7—C6—H6	118.9	O6—C46—H46A	109.5
C5—C6—H6	118.9	O6—C46—H46B	109.5
C8—C7—C6	119.06 (18)	H46A—C46—H46B	109.5
C8—C7—H7	120.5	O6—C46—H46C	109.5
C6—C7—H7	120.5	H46A—C46—H46C	109.5
O1—C8—C7	124.95 (18)	H46B—C46—H46C	109.5
O1—C8—C9	115.14 (18)	C50—C47—P1	114.60 (12)
C7—C8—C9	119.91 (18)	C50—C47—H47A	108.6
C10—C9—C8	120.04 (18)	P1—C47—H47A	108.6
C10—C9—H9	120.0	C50—C47—H47B	108.6
C8—C9—H9	120.0	P1—C47—H47B	108.6
C9—C10—C5	121.27 (18)	H47A—C47—H47B	107.6
C9—C10—H10	119.4	C50—C48—P2	115.84 (12)
C5—C10—H10	119.4	C50—C48—H48A	108.3
O1—C11—H11A	109.5	P2—C48—H48A	108.3
O1—C11—H11B	109.5	C50—C48—H48B	108.3
H11A—C11—H11B	109.5	P2—C48—H48B	108.3
O1—C11—H11C	109.5	H48A—C48—H48B	107.4
H11A—C11—H11C	109.5	C50—C49—P3	114.06 (12)
H11B—C11—H11C	109.5	C50—C49—H49A	108.7
C13—C12—C17	117.35 (17)	P3—C49—H49A	108.7
C13—C12—P1	119.79 (14)	C50—C49—H49B	108.7
C17—C12—P1	122.87 (14)	P3—C49—H49B	108.7
C12—C13—C14	122.08 (18)	H49A—C49—H49B	107.6
C12—C13—H13	119.0	C51—C50—C47	107.08 (15)
C14—C13—H13	119.0	C51—C50—C49	107.66 (15)
C15—C14—C13	119.33 (18)	C47—C50—C49	112.30 (15)
C15—C14—H14	120.3	C51—C50—C48	106.66 (14)
C13—C14—H14	120.3	C47—C50—C48	111.73 (15)
O2—C15—C14	124.54 (18)	C49—C50—C48	111.08 (15)
O2—C15—C16	115.53 (18)	C50—C51—H51A	109.5
C14—C15—C16	119.93 (18)	C50—C51—H51B	109.5
C17—C16—C15	119.84 (18)	H51A—C51—H51B	109.5
C17—C16—H16	120.1	C50—C51—H51C	109.5
C15—C16—H16	120.1	H51A—C51—H51C	109.5
C16—C17—C12	121.37 (18)	H51B—C51—H51C	109.5
C16—C17—H17	119.3	C8—O1—C11	117.95 (17)
C12—C17—H17	119.3	C15—O2—C18	116.94 (17)
O2—C18—H18A	109.5	C22—O3—C25	117.59 (18)
O2—C18—H18B	109.5	C29—O4—C32	116.31 (18)
H18A—C18—H18B	109.5	C36—O5—C39	116.73 (17)
O2—C18—H18C	109.5	C43—O6—C46	117.42 (16)
H18A—C18—H18C	109.5	C5—P1—C12	98.09 (8)

H18B—C18—H18C	109.5	C5—P1—C47	102.81 (8)
C24—C19—C20	117.37 (18)	C12—P1—C47	102.11 (8)
C24—C19—P2	124.96 (14)	C5—P1—Ru1	121.90 (6)
C20—C19—P2	117.60 (14)	C12—P1—Ru1	117.49 (6)
C21—C20—C19	121.86 (19)	C47—P1—Ru1	111.63 (6)
C21—C20—H20	119.1	C19—P2—C26	98.09 (9)
C19—C20—H20	119.1	C19—P2—C48	101.82 (8)
C20—C21—C22	119.74 (19)	C26—P2—C48	101.90 (8)
C20—C21—H21	120.1	C19—P2—Ru1	121.79 (6)
C22—C21—H21	120.1	C26—P2—Ru1	118.98 (6)
O3—C22—C23	124.68 (19)	C48—P2—Ru1	111.21 (6)
O3—C22—C21	115.52 (19)	C33—P3—C40	97.02 (9)
C23—C22—C21	119.80 (19)	C33—P3—C49	104.08 (8)
C22—C23—C24	119.71 (18)	C40—P3—C49	101.80 (9)
C22—C23—H23	120.1	C33—P3—Ru1	119.19 (6)
C24—C23—H23	120.1	C40—P3—Ru1	118.98 (6)
C19—C24—C23	121.51 (18)	C49—P3—Ru1	113.02 (6)
C19—C24—H24	119.2	C1—Ru1—C3	38.80 (8)
C23—C24—H24	119.2	C1—Ru1—C2	38.49 (8)
O3—C25—H25A	109.5	C3—Ru1—C2	65.82 (8)
O3—C25—H25B	109.5	C1—Ru1—C4	38.37 (8)
H25A—C25—H25B	109.5	C3—Ru1—C4	65.11 (8)
O3—C25—H25C	109.5	C2—Ru1—C4	65.06 (8)
H25A—C25—H25C	109.5	C1—Ru1—P3	123.22 (6)
H25B—C25—H25C	109.5	C3—Ru1—P3	97.30 (6)
C31—C26—C27	117.30 (17)	C2—Ru1—P3	102.46 (6)
C31—C26—P2	121.24 (14)	C4—Ru1—P3	161.15 (6)
C27—C26—P2	121.40 (14)	C1—Ru1—P1	126.73 (6)
C28—C27—C26	121.20 (19)	C3—Ru1—P1	104.12 (6)
C28—C27—H27	119.4	C2—Ru1—P1	164.85 (6)
C26—C27—H27	119.4	C4—Ru1—P1	100.79 (6)
C27—C28—C29	120.39 (19)	P3—Ru1—P1	89.759 (17)
C27—C28—H28	119.8	C1—Ru1—P2	129.19 (6)
C29—C28—H28	119.8	C3—Ru1—P2	167.20 (6)
O4—C29—C30	124.57 (19)	C2—Ru1—P2	101.69 (6)
O4—C29—C28	115.76 (19)	C4—Ru1—P2	107.93 (6)
C30—C29—C28	119.67 (19)	P3—Ru1—P2	87.931 (17)
C29—C30—C31	119.35 (18)	P1—Ru1—P2	87.511 (19)

7. Appendix

7.1 List of Abbreviations

AAR	Acid-to-amine ratio
AB	Ammonium bicarbonate
AC	Activated carbon
acac	acetylacetonate
AF	Ammonium formate
Ar	Aryle
BH	Bicarbonate hydrogenation
bpy	2,2'-Bipyridine
BSE	Backscattered electron images
Cat.	Catalyst
CCS	Carbon capture and storage
CH	CO ₂ hydrogenation
COD	Cyclo-1,5-octadiene
Cp*	1,2,3,4,5-Pentamethylcyclopentadienyl
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
dhbp	4,4'-Dihydroxy-2,2'-bipyridine
dhphen	4,7-Dihydroxy-1,10-phenanthroline
DMF	Dimethylformamide
DMOA	Dimethyloctylamine
DMSO	Dimethylesulfoxide
dppb	1,1-Bis(diphenylphosphino)butane
dppe	1,1Bis(diphenylphosphino)ethane
dppm	1,1Bis(diphenylphosphino)methane
EA	Elementary analysis
edⁱPrP	2-(diisopropylphosphino)ethylamine
e.g.	Example
ESI-MS	Electrospray ionization mass spectrometry
Eq	Equation
eq.	Equivalents
EU	European Union
FA	Formic acid
FAD	Formic acid dehydrogenation
FD	Formate dehydrogenation
GC	Gas chromatography
g-C₃N₄	Graphitic carbon nitride
GED	Gravimetric energy density
h	Hour

HAADF-STEM	Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy
HMOs	Hollow mesoporous organosilica sphere
ICP-OES	Inductively coupled plasma-optical emission spectrometry
LOHC	Liquid organic hydrogen carriers
MeCN	Acetonitrile
MOF	Metal-organic framework
MSC	Mesoporous carbon
<i>m</i>tppps	Monosulfonated triphenylphosphine
NEt₃	Triethylamine
NP	Nanoparticle
OA	Oxalic acid
OAc	Acetate
OTf	Trifluoromethanesulfonate
PB	Potassium bicarbonate
PC	Propylene carbonate
PCN	Polymeric carbon nitrides
PDA-rGO	Phenylenediamine-alkalized reduced graphene oxide
PEI	Polyethyleneimine
PPh₃	Triphenylphosphine
RES	Renewable energy sources
Ru-MACHO	({Bis[2-(diphenylphosphino)ethyl]amine} carbonyl chlorohydridoruthenium(II))
PF	Potassium formate
<i>p</i>-TsOH	<i>p</i> -toluenesulfonic acid
rGO	Reduced graphite oxide
rt	Room temperature
SB	Sodium bicarbonate
scCO₂	Supercritical carbon dioxide
SF	Sodium formate
SEM	Scanning electron microscopy
St. Dev.	Standard deviation
STEM	Scanning transmission electron microscopy
THF	Tetrahydrofuran
TMM	η^4 -Trimethylenemethane
TOF	Turnover frequency
TON	Turnover number
Tos	Toluene-4-sulfonate
TPPTS	Trisodium 3,3',3''-phosphanetriyltri(benzene-1-sulfonate)
triphos	1,1tris(diphenylphosphinomethyl)ethane
TTON	Total turnover number
VED	Volumetric energy density

WGS	Water-gas shift reaction
XPS	X-ray photoelectron spectroscopy
XRF	X-ray fluorescence spectroscopy

7.2 Preliminary Information

In the preparation of the presented work, the following programs were used, among others: ChemDraw Professional 23-1-2-7, ChatGPT (Version GPT-4), Grammarly (1.127.0.0), Mercury 2020.2.0, MestReNova 14.3.2-32681, Origin 10.0.5.157, and Zotero (6.0.37)

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