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Chapter

Catalysis with Ruthenium for Sustainable Carbon Cycles

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Abstract

Nestled between the noble and non-noble metals in the periodic table, ruthenium, one of the transition metals, offers a combination of intriguing properties. Due to its variable oxidation states and its ability to form complexes with various Lewis base compounds, ruthenium, has been widely used in the field of catalysis. Its application has led to groundbreaking breakthroughs in a variety of chemical transformations and has attracted considerable attention in both academic research and industrial applications. Ruthenium catalysis is a dynamic and rapidly evolving field, with ongoing efforts to further advance the efficiency and selectivity of these catalysts. Importantly, in the context of sustainability, ruthenium-based catalysts play an important role in promoting green chemistry practices. Because ruthenium catalysts are highly efficient, only small amounts of the element need to be used. Recovery rates at the end of catalyst life are typically very high, minimizing the need to mine fresh ore. The use of ruthenium catalysts promotes the utilization of renewable resources in various chemical transformations, is at the heart of the realization of new energy-related processes, and by enabling efficient and highly selective chemical transformations reduces waste and harmful emissions. These aspects reinforce the metal's importance in the quest for a more sustainable future.

Keywords: ruthenium, catalysis, hydrogenation, sustainability, carbon cycles

1. Introduction

Sustainable chemistry is increasingly becoming an essential tool in the quest for greener processes and materials. It plays a critical role in conserving resources, reducing pollution, and ensuring the long-term health and survival of our planet. In this context, the element ruthenium is gaining prominence as a homogeneous or heterogeneous catalyst due to its intriguing combination of properties and versatile applications in sustainable chemistry. These include hydrogenation, reductive amination, hydroformylation, and other transformations in sustainable chemistry.

Ruthenium, which occupies a unique position between noble metals and nonnoble metals, possesses distinctive properties that will be discussed in terms of structure-property relationships in this chapter. A major focus will be on how ruthenium catalysts can be tuned for the creation of anthropogenic carbon cycles. One aspect we'll explore is the role of the interaction of metallic ruthenium particles with the support.

Another fascinating aspect is the influence of bimetallic catalysts, which can significantly alter the reaction pathways compared to their monometallic counterparts. In addition, this chapter will cover a variety of industrial applications of heterogeneous ruthenium catalysts. These include the reversible hydrogenation of liquid organic hydrogen carriers (LOHC) and ammonia synthesis in the context of hydrogen storage and lignin utilization, highlighting the importance of ruthenium in the broader context of sustainable chemistry.

1.1 Homogeneous and heterogeneous catalysis with ruthenium

The use of ruthenium catalysts has spanned numerous areas of catalysis, including, but not limited to, the following areas:

- **Hydrogenation Reactions**: The ability of ruthenium catalysts to facilitate hydrogenation reactions has been exploited in the synthesis of a wide range of compounds, with applications ranging from pharmaceuticals to agrochemicals. Ruthenium catalysts, thereby, accommodate a broad range of substrates:

  - Ruthenium catalysts can hydrogenate carbon-carbon double bonds in a variety of alkenes, facilitating the production of alkanes. Ruthenium catalysts can selectively hydrogenate carbon-carbon triple bonds in alkynes to alkenes (partial hydrogenation) or to alkanes (complete hydrogenation). Ruthenium catalysts can also facilitate the hydrogenation of aromatic rings, leading to the production of cycloalkanes.

  - Ruthenium catalysts can be used to hydrogenate carbonyl groups in aldehydes and ketones, forming alcohols. Ruthenium catalysts can hydrogenate carboxylic acids, esters, and amides, forming alcohols and amines.

  - Ruthenium catalysts can be used in the hydrogenation of nitro groups, nitriles, and other unsaturated nitrogen moieties forming amines.

    Ruthenium complexes can also act as catalysts in transfer hydrogenation reactions. The Noyori catalysts, which are complexes of ruthenium with chiral ligands, have been used in the asymmetric transfer of hydrogenation of ketones to alcohols. Ruthenium catalysts also effectively catalyze the hydrogenolytic breaking of chemical bonds, mostly oxygen-carbon bonds, in a molecule.

- **Amine Formation**: Ruthenium catalysts are used in the formation of amines in a number of ways. For instance, they facilitate the reductive amination of carbonyl compounds. In this reaction, an aldehyde or ketone is reacted with an amine in the presence of a hydrogen source. The ruthenium catalyst aids in the transfer of hydrogen from the source to the carbonyl group, forming a new amine. Ruthenium catalysts are also used in the borrowing hydrogen methodology (also known as hydrogen autotransfer) to synthesize amines. In this reaction, a ruthenium catalyst facilitates the removal of hydrogen from an alcohol, allowing it to react with an amine to form an imine intermediate. The catalyst then helps return the borrowed hydrogen to this intermediate to form the final amine product.

- **Olefin Metathesis**: Probably the best-known application of ruthenium catalysts is in olefin metathesis [1], a reaction that rearranges the alkene moieties of olefins while maintaining the number of double bonds. This reaction has undergone transformative advances with the introduction of ruthenium-based catalysts, such as the Grubbs catalysts. These catalysts exhibit high stability, are compatible with a wide range of substrates, and tolerate various functional groups. Ruthenium catalysts are also active for various C–C bond formation reactions [2], including cross-coupling reactions, cycloaddition reactions, and cyclization reactions.

- **Oxidation Reactions**: Ruthenium catalysts are also adept at facilitating oxidation reactions, such as alcohol oxidation, olefin epoxidation, and amine oxidation.

1.2 Electrocatalysis with ruthenium

Ruthenium is also widely used as an electrocatalyst. Well-known is the use of ruthenium in anodes for chloralkali electrolysis. The anodes are often constructed by electrochemically depositing a thin layer of ruthenium oxide and other mixed metal oxides on a conductive titanium substrate. This thin layer, typically only a few microns thick, is where the chlorine evolution reaction takes place. One of the primary factors contributing to the high performance of these ruthenium-based anodes is their ability to maintain a low chlorine overpotential. In addition, these anodes exhibit excellent resistance to the highly corrosive environment within the electrolytic cell, including a highly corrosive electrolyte and high current densities. Their high chemical stability and good electronic conductivity make ruthenium-based anodes suitable for long-term use in industrial-scale chloralkali electrolysis. Ruthenium is also a key anode component in water-splitting electrolyzers, which are central to the production of hydrogen as a clean and sustainable energy source. Ruthenium-based catalysts, often mixed with other metals such as iridium or titanium, have demonstrated high efficiency in the oxygen evolution reaction (OER), one of the half-reactions in water splitting. Similarly, ruthenium complexes are being explored for use used as electrocatalysts in organic electrosynthesis, where they allow the transformation of organic compounds under mild conditions with high selectivity. Ruthenium is used in the anode catalyst layer of proton exchange membrane fuel cells (PEMFC), where it catalyzes the oxidation of hydrogen or small organic molecules. It is also used as an electrocatalyst in metal-air batteries. Metal-air batteries combine a metal anode with an oxygen cathode that uses ambient oxygen from the air, separated by an electrolyte. They have attracted considerable interest due to their high theoretical energy densities, making them promising candidates for use in electric vehicles and large-scale grid storage. Ruthenium, with its unique electrochemical properties, has been shown to be an efficient electrocatalyst for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) that occur at the cathode in metal-air batteries. ORR occurs during the discharge phase of the battery, while OER occurs during the charge phase. Efficiently catalyzing these reactions is critical to improving the energy efficiency and cycle life of the battery.

1.3 Role of ruthenium in the context of sustainability

Ruthenium catalysts could play an important role in meeting the challenges associated with increased greenhouse gas emissions. An important contribution to

mitigating climate change will be the establishment of anthropogenic carbon cycles [3]. Below, we will discuss some of the potential contributions that ruthenium catalysis could make. The focus will be on exploiting the specific advantages that ruthenium catalysts can offer:

i. Ruthenium catalysts often operate at lower temperatures and pressures than other catalysts, thereby reducing energy consumption. In addition, these catalysts can be highly selective, resulting in fewer by-products and reducing the need for energy-intensive purification steps.

ii. Many ruthenium-catalyzed reactions, such as olefin metathesis or hydrogenation reactions, have high atom economy, meaning that a large fraction of the atoms from the starting materials end up in the final product. This reduces by-product formation and improves the overall sustainability of the process.

iii. Ruthenium catalysts can often be recovered and reused, reducing the need for new catalyst production and the need to mine ruthenium ores.

iv. With regard to energy applications, ruthenium complexes have been established for use in dye-sensitized solar cells, a type of thin-film solar cell. This could be an important contribution to more sustainable energy production.

v. Ruthenium catalysts have been investigated for their ability to make use of renewable feedstock from biological sources, such as lignin [4], and CO_2 [5], by reducing it to useful chemicals and fuels. Such applications could be an important component in establishing a circular carbon economy.

In the broader context of sustainability and climate change, the use of ruthenium catalysts in chemical processes could be part of the shift to cleaner and more efficient production methods that minimize the release of CO_2 and even effectively reuse it. It is important to note, however, that this would be only one piece of a much larger puzzle in mitigating human impacts [6] on carbon fluxes through geohabitats [3] and the climate [7].

2. Catalytic transformations with ruthenium catalysts

2.1 Hydrogenation reactions

The strategic deployment of ruthenium catalysts to facilitate hydrogenation reactions holds substantial promise, particularly in energy-related applications. Hydrogenation is a chemical transformation involving the addition of hydrogen (H_2) to a substrate, and it requires catalysts to lower the activation energy and increase the reaction rate to a technically viable scale. Ruthenium catalysts have demonstrated superior efficacy in such roles. In the energy field, ruthenium is being considered for applications in hydrogen storage, where the reversible hydrogenation and dehydrogenation of specific compounds allow for compact and efficient storage of hydrogen. Ruthenium catalysts are also employed in the hydrogenation of carbon dioxide to

formic acid derivatives, a promising area for sustainable chemistry. Furthermore, in the production of synthetic fuels or synfuels, ruthenium catalysts are used to hydrogenate carbon dioxide to energy-rich liquid fuels. This conversion is a modified version of the Fischer-Tropsch process, which converts syngas, a mixture of carbon monoxide and hydrogen, into liquid hydrocarbons. These hydrocarbons serve as a potential renewable replacement for conventional petroleum-based fuels. Recent advances extend this concept to use a mixture of carbon dioxide and hydrogen to produce liquid hydrocarbons. With these diverse applications, ruthenium catalysts are paving the way for more sustainable and efficient energy solutions, underscoring their critical role in hydrogenation reactions in the energy sector.

2.1.1 Hydrogen storage

Renewable energy from many primary energy sources, such as wind and solar power, is inherently intermittent in nature. To balance the resulting mismatch between energy supply and demand, suitable energy storage is required. Electricity can be stored only in small quantities in physical form, e.g., in pump storage plants or batteries. An alternative is a storage of renewable energy in chemicals as secondary energy carriers. Hydrogen and other Power-to-X products [8] are considered as energy carrier.

Hydrogen has been recognized as a promising energy carrier due to its high energy density and potential for carbon-free energy conversion [9]. Establishing a hydrogen economy would involve the production of hydrogen by water splitting with electricity from renewable sources. Although hydrogen has a very high gravimetric energy density of 33.3 kWh kg^{-1}, its volumetric energy density is very low at 2.5 Wh dm^{-3} at ambient pressure [10].

One of the major challenges associated with hydrogen is its storage and transportation [11]. This poses a significant barrier to the wider use of hydrogen as an energy carrier, especially for nonstationary applications. Liquid Organic Hydrogen Carriers (LOHC) have been proposed as hydrogen transport and storage medium. This requires reversible charging and discharging of hydrogen from suitable storage molecules. In almost all cases, appropriate catalytic systems are required to overcome kinetic barriers and accelerate chemical conversion.

In this context, ruthenium catalysts are discussed for their capacity to enable chemical hydrogen storage systems. In chemical hydrogen storage, hydrogen is stored in the form of a stable molecule and released on demand. Common examples are hydrocarbons, formic acid, and ammonia-borane, which can store hydrogen in a relatively dense, nongaseous form. Ruthenium catalysts have been shown to be effective in both the hydrogenation (for storage of hydrogen) and dehydrogenation (for release of hydrogen) of these compounds. In particular, the high activity of ruthenium-based catalysts can improve the energy efficiency of these processes, their high selectivity, the formation of unwanted by-products, and, overall, increase the hydrogen storage capacity.

2.1.2 Hydrocarbons as liquid organic hydrogen carriers

For hydrogen storage in hydrocarbons various storage molecules are being discussed at LOHC (**Table 1**). The LOHC has to fulfill a number of boundary conditions. A suitable LOHC should be capable of storing a large amount of hydrogen per unit volume and weight. The LOHC should be thermally and chemically stable in both

its hydrogenated and dehydrogenated states. It should not degrade or react undesirably during the hydrogenation/dehydrogenation reaction or during storage and transportation. The LOHC system must be able to release the stored hydrogen on demand, and the spent carrier must be easily hydrogenated (**Table 2**). Therefore, the hydrogenation/dehydrogenation equilibrium should be in an appropriate temperature range, and the forward and backward reactions should be reasonably efficient. The LOHC should not be highly flammable, or toxic and should have a high flash point to ensure safe handling, storage, and transportation. Ideally, the LOHC should be environmentally benign, both in terms of its production and in its disposal or recycling. Lastly, the LOHC should be cost-effective to produce and recycle and ideally be derived from abundant or renewable sources.

Examples where ruthenium catalysts were explored for hydrogen storage include the use of benzyltoluene as LOHC (**Table 1**, Entry 1). The effect of the silica content in zirconia (ZrO_2) on the properties and hydrogenation activity of SiO_2-ZrO_2-supported ruthenium catalysts was investigated [14]. Catalysts were prepared with different Si/(Si + Zr) ratios from 0 to 30 mol%. Noteworthy, the textural properties, Ru particle size, and hydrogenation activity exhibit a volcano-shaped relationship with the Si content, with optimal results obtained at a ratio of 5 mol%. With a rising SiO_2 to ZrO_2 ratio, the thermal stability increased, and the particle size of tetragonal ZrO_2 decreased, which at a low ratio led to improved hydrogen storage efficiency. Further addition of SiO_2 led to decrease in the catalyst activity, along with increased surface heterogeneity and charge imbalance, which reduced the density of surface OH groups. Consequently, the addition of about 5 mol% SiO_2 to ZrO_2 appears to be optimal for enhancing the hydrogenation performance of Ru/ZrO_2 catalysts.

The selective hydrogenation of benzene to cyclohexene (**Table 1**, Entry 5) over supported ruthenium catalysts has been studied in a high-pressure slurry reactor [15], exploring suitable additives, supports, and reaction conditions to optimize cyclohexene yields. The addition of the organic base monoethanolamine (MEA) resulted in better selectivity than conventional inorganic salts such as zinc sulfate. Among different supports such as alumina, silica, titania, zirconia, and niobium oxide, alumina was found to be the best oxidic support. The presence of water was found to significantly improve the selectivity.

Entry	LOHC, parent form	m.p. [°C]	LOHC, reduced form	m.p. [°C]	n_{H2} [−]	w_{H2} [%]	H_2 storage [kWh dm^{-3}].
1	Benzyltoluene	−30	Perhydro-benzyltoluene	−70	3	3.21	1.66 [13]
2	*N*-Ethylcarbazole	68.43	Perhydro-*N*-ethylcarbazole	<20	6	5.84	1.8 [13]
3	Toluene	−95.05 ± 0.6	Methylcyclohexane	−126.6 ± 0.4	3	6.16	1.59 [13]
4	Dibenzyltoluene	−34	Perhydro-dibenzyltoluene	−45	9	6.24	1.94 [13]
5	Benzene	5.53 ± 0.08	Cyclohexane	6.45 ± 0.3	3	7.19	— —
6	Naphthalene	80.1 ± 0.7	Decalin (trans/cis)	−31.2 −43.2	5	7.29	2.1 [13]

Table 1.
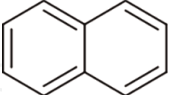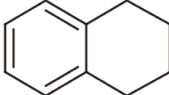*Selected liquid organic hydrogen carriers and their physical properties [12, 13].*
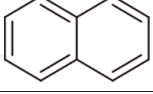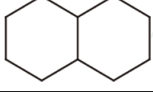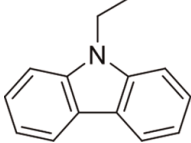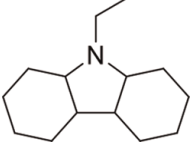
Entry	Reaction	$\Delta H_R°$ [kJ mol^{-1}]	Eq.
1 (5)	+ 3 H$_2$ ⇌	-205.3 ± 0.63 (6)	(1)
2	+ 2 H$_2$ ⇌	-120.5 ± 5.0 (6)	(2)
3	+ 2 H$_2$ ⇌	-318 (*cis* decalin) (6)	(3)
4 (2)	+ 6 H$_2$ ⇌	—	(4)

Table 2.
Reaction enthalpy for hydrogenation of selected LOHC. The entry number in brackets refers to **Table 1**.

2.1.3 Formic acid derivatives as liquid organic hydrogen carriers

Hydrogen can also be stored in formic acid by hydrogenating CO_2 to formic acid. CO_2-derived formic acid is a relevant candidate for hydrogen storage because it can carry 4.35 wt% hydrogen with excellent atomic efficiency [10]. The hydrogenation of CO_2 to formic acid is slightly exothermic and endergonic at standard conditions ($\Delta H_r° = -31{,}4$ kJ mol^{-1}, $\Delta G_r° = +31{,}8$ kJ mol^{-1}, [16]). This highlights the inherent thermodynamic instability of formic acid compared to the gaseous feedstocks. To overcome this thermodynamic hurdle, most reaction systems require the use of amines or other potent bases in stoichiometric amounts as co-reagents diminishing the weight percentage of hydrogen that is stored (**Figure 1**). The use of a stabilizing solvent such as dimethylsulfoxide (DMSO) was proposed as alternative [16].

Many molecular catalysts have been reported to highly efficiently convert CO_2 to formic acid, with turnover frequencies reaching several hundred thousand catalytic cycles per hour. The hydrogenation can be catalyzed by a number of ruthenium complexes, often in combination with specific ligands to improve performance. The
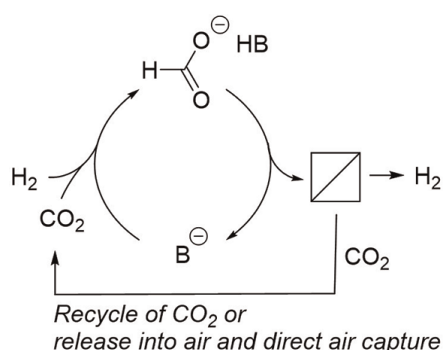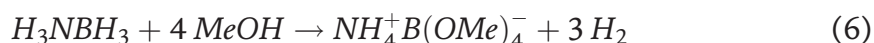
Base	Storage form	w$_{H2}$ [%]
None	Formic acid	4.35
NH$_3$	[HCO$_2$]$^-$ [NH$_4$]$^+$	3.17
Lysine, K-salt	[HCO$_2$]$^-$ K$^+$·Lysine	1.15
Na$_2$CO$_3$	2 [HCO$_2$]$^-$ Na$^+$·H$_2$O	2.60

Recycle of CO$_2$ or release into air and direct air capture

Figure 1.
Hydrogen storage cycle (left) based on formates as liquid organic hydrogen carrier (LOHC) and weight fraction w$_{H2}$ of usable hydrogen in formic acid and various formate salts (right) [13, 17].

reverse process, the dehydrogenation of formic acid to release hydrogen and CO_2, can also be catalyzed by ruthenium. Importantly, the CO_2 released in this process can be captured and reused, creating a closed carbon cycle.

2.1.4 The ammonia-borane system as liquid organic hydrogen carriers

Ammonia-borane (NH_3BH_3) is another potential hydrogen storage option, with a remarkable theoretical hydrogen content of 19.6 wt% [18, 19]. Hydrolysis (Eq. (5)) or methanolysis (Eq. (6), [20–22]) are two practical methods of producing hydrogen from ammonia-borane for use in hydrogen fuel cells. In the presence of suitable catalysts, these reactions take place at ambient temperature under mild conditions. Ruthenium catalysts have been shown to be especially effective in promoting the dehydrogenation of ammonia-borane to release hydrogen. Despite these advantages, employing ammonia-borane as a hydrogen storage medium is not without its challenges. The primary issue lies in the regeneration of the spent fuel, which is often converted to a mixture of polymeric aminoborane and borazine. Regeneration requires substantial energy input and stringent conditions:

$$H_3NBH_3(aq) + 2\,H_2O(l) \rightarrow NH_4^+BO_2^-(aq) + 3\,H_2(g) \qquad (5)$$

$$H_3NBH_3 + 4\,MeOH \rightarrow NH_4^+B(OMe)_4^- + 3\,H_2 \qquad (6)$$
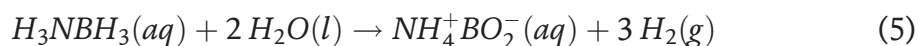
2.1.5 Role of ruthenium catalysts in hydrogen storage

Overall, the use of ruthenium catalysts in hydrogen storage can contribute to the development of sustainable hydrogen energy systems. By improving the efficiency and selectivity of chemical hydrogen storage processes, these catalysts can help to make hydrogen a more practical and sustainable energy carrier. However, challenges remain, including the development of more efficient catalysts, the improvement of fuel regeneration processes, and the integration of these systems with renewable energy sources and carbon capture technologies. With ongoing research in these areas, ruthenium catalysts will likely continue to play an important role in the future of hydrogen energy.

2.1.6 Hydrogenation of carbon dioxide

Carbon dioxide (CO_2) is an abundant, sustainable, and renewable feedstock [23] that holds great promise for the production of value-added products [24] spanning fuels, bulk and commodity chemicals, specialty products, and pharmaceuticals [25]. At the end of their life, when other recycling options are no longer feasible, carbon-based products are typically burnt to generate heat. Increased use of the released carbon dioxide as a feedstock could play a key role in closing anthropogenic carbon cycles [3].

CO_2, having a positively polarized carbon atom with two double bonds to electronegative oxygen atoms, is in the formal oxidation state of +IV. Therefore, except for the formation of carbonates [26] and carbonic acids [27], chemical transformations of CO_2 mostly involve the reduction of the carbon center [25]. The required reduction equivalents may be supplied by hydrogen or other reducing agents or may be provided electrochemically.

Considered a viable route for both CO_2 utilization and hydrogen storage, the hydrogenation of CO_2 to formic acid (Eq. (7)) has considerable potential [28]. Formic acid, a base chemical widely used in the chemical industry, can serve as a feedstock for fuel cells and as a medium for hydrogen storage. As of 2021, formic acid is a large-scale commodity with a production volume of 800 kt a^{-1} [29]. It has a theoretical hydrogen storage capacity of 53.4 g dm^{-3} [30]. A noteworthy aspect of using formic acid as an energy vector is that the CO_2 released during hydrogen production can be reused for formic acid production [30]. Thus, the hydrogenation of CO_2 to formic acid could contribute toward establishing a sustainable circular carbon economy.

The hydrogenation of carbon dioxide to formic acid (**Table 3**) is slightly exothermic but endergonic (Eq. (7)), [10, 31]). Also in the liquid phase, the reaction has a very low driving force (Eq. (8)). Consequently, basic co-reagents or solvents, such as ammonia or DMSO [16], respectively, are necessary to shift the chemical equilibrium toward the products either through salt formation (Eq. (9)) or stabilization of the formic acid. Ruthenium-based catalysts have shown great potential in the hydrogenation of CO_2 to formic acid, owing to their high activity and selectivity, coupled with high stability. Among them, supported ruthenium catalysts, especially those with ruthenium-hydroxide moieties, have shown superior performance. Nonetheless, the synthesis of these catalysts and the role of the hydroxyl groups in the catalytic reaction mechanism remain subjects of ongoing research.

For CO_2 hydrogenation with homogeneous catalysts, very high reaction rates have been reported including ruthenium [32, 33] and iridium [34] pincer complexes. In contrast, heterogeneous catalysts have recently received increased attention as many supported metal nanoparticles initially tested lacked substantial activity for the hydrogenation of CO_2 to formic acid.

A study of the synthesis of ruthenium-based catalysts for the hydrogenation of CO_2 to formic acid highlights the critical role of Ru-OH species in the reaction [22]. Detailed characterization of the catalysts using various spectroscopic and microscopic techniques revealed that hydroxyl groups strongly interact with the ruthenium moieties in the catalyst and influence its performance. Highly dispersed ruthenium-hydroxide species were beneficial for the CO_2 hydrogenation process, while the formation of crystalline RuO_2 species, which formed at high ruthenium content or high pH during catalyst preparation, hindered formic acid production. The study proposed an optimal set of conditions for catalyst preparation, including 2.0 wt% ruthenium loading, pH 12.8, and the use of aqueous ammonia as the stabilizing solvent.

For the efficient synthesis of liquid fuels (C5+ hydrocarbons) by CO_2 hydrogenation, homogeneous and heterogeneous catalysis have been combined [35] to overcome the challenges associated with heterogeneous catalysts for reverse water-gas shift (RWGS) and Fischer-Tropsch synthesis (FTS), which typically suffer from high operating temperatures and low selectivity. The system with combined homogeneous

Reaction	$\Delta H_R^0 \left[\frac{kJ}{mol}\right]$	$\Delta G_R^0 \left[\frac{kJ}{mol}\right]$	Eq.
$CO_2(g) + H_2(g) \rightleftharpoons HC(O)OH\ (l)$	−31.2	32.9	(7)
$CO_2(l) + H_2(l) \rightleftharpoons HC(O)OH\ (l)$	−31.2	−4	(8)
$CO_2(l) + H_2(l) + NH_3 \rightleftharpoons [HC(O)O^-][NH_4^+]\ (l)$	−84	−9.5	(9)

Table 3.
Enthalpy of reaction and change in free energy of CO_2 hydrogenation to formic acid derivatives. H2 (l) refers to hydrogen dissolved in the aqueous solution.

RuCl3 and heterogeneous Ru0 catalysts achieved excellent C5+ selectivity (71.1%) at a low temperature of 180°C.

The publication reviews progress in the catalytic hydrogenation of CO_2 to C2+ hydrocarbons and oxygenates using both solid and molecular catalysts [36]. The study recognizes the value of these products due to their high energy density and compatibility with existing fuel infrastructure. However, the selective production of these compounds remains a challenge compared to C1 hydrogenation products such as methane and methanol. The work highlights the need for optimal catalytic functionalities integration for reductive and chain growth steps. The review also considers the thermodynamic and kinetic limitations of the process, in particular, the reverse water-gas shift reaction. It is suggested that future research should focus on metal carbide catalysts and liquid phase molecular catalysts to decouple the chain growth kinetics from the gas phase CO concentration.

Merging the fields of homogeneous and heterogeneous catalysis could be a way to improve the efficiency of CO_2 hydrogenation. These two fields of catalysis have developed separately, although they share common challenges and mechanisms. A "catalytic ensemble" of a dual ruthenium catalyst, in which a homogeneous and a heterogeneous catalyst work in tandem, works well for the conversion of CO_2 to hydrocarbons of different chain lengths [37]. A high hydrocarbon yield of more than 70% is obtained under mild conditions. The key questions concern the mechanism of this improved performance, the role of lithium in the reaction, and the feasibility of replacing rare metals with sustainable alternatives.

The performance of two ruthenium-based catalysts, Ru/SiO_2 and Ru/MCM-41, for the selective hydrogenation of CO_2 to formic acid, is compared [38]. The researchers used well-established protocols for the synthesis of these catalysts and analyzed their physicochemical properties using a variety of analytical techniques. The Ru/MCM-41 system was found to be more efficient than the Ru/SiO_2 system in terms of turnover number (TON) and turnover frequency (TOF). Functional ionic liquids were used as both reaction medium and absorbent for CO_2 solubilization and formic acid anchoring. This allowed the reaction to proceed in a more optimized manner, improving the selectivity and recyclability of the catalyst. The ionic liquid di(N,N-dimethylaminoethyl)-2-methylimidazolium (DAMI) sulfonate [DAMI] $[CF_3(CF_2)_3SO_3]$ proved to be particularly effective due to its high CO_2 absorption capacity. The use of diamine-functionalized ionic liquids also improved the coordination with formic acid. The Ru/MCM-41 catalyst in the ionic liquid [DAMI] $[CF_3(CF_2)_3SO_3]$ provided the highest TON of formic acid.

An industrially viable approach to the synthesis of *N,N*-dimethylformamide (DMF) *via* CO_2 hydrogenation involves the use of a ruthenium-grafted bisphosphine-based porous organic polymer (Ru/PP-POP) catalyst [39]. Historically, CO_2 conversion methods have been difficult to scale up for industrial use. The grafted Ru catalyst was shown to be highly efficient and recyclable. The catalyst developed in this work exhibits remarkable activity, achieving an unprecedented turnover number of 160,000 and an initial turnover frequency of 29,000 h^{-1} in a batch process. Furthermore, the catalyst shows excellent stability and selectivity in both batch and continuous flow processes. The continuous flow process was carried out in a trickle bed reactor which achieved a high productivity of 915 mmol $g_{Ru}^{-1} h^{-1}$. The breakthrough presented in this research may pave the way for the large-scale production of DMF, a commonly used industrial solvent, directly from CO_2.

The hydrogenation of CO_2 can be performed in a variety of solvents, including CO_2-rich scrubbing solvents from carbon capture units. Such solvents are capable of

capturing CO_2 from flue gas streams, making this process potentially useful for carbon capture and utilization (CCU) strategies. However, the direct hydrogenation of CO_2-rich scrubbing solvents remains challenging due to other components in the gas stream that can act as catalyst poisons. Furthermore, the hydrogenation of CO_2 to formic acid is reversible, which limits the net production of formic acid.

The research focuses on the synthesis and evaluation of alumina-supported Ru nanoparticles as catalysts for the selective hydrogenation of CO_2 to formic acid [40]. The Ru/Al_2O_3 (2–10 wt% Ru) catalysts were prepared by the ethylene glycol reduction method, and their physicochemical properties were thoroughly investigated using techniques such as XRD, transmission electron microscopy (TEM), EDX, H_2 chemisorption, XPS and H_2-TPD analysis. The catalysts showed promising activity and selectivity for CO_2 hydrogenation, with the performance closely related to their physicochemical properties, especially the Ru metal dispersion. In particular, the Ru/Al_2O_3 catalyst outperformed others when used in conjunction with the ionic liquid [DAMI] $[CF_3(CF_2)_4SO_3]$. This medium not only increased catalyst activity but also acted as a stabilizer, preventing catalyst deactivation and promoting formic acid formation via intermediate carbonate species. The multifunctional ionic liquid also facilitated the recovery and recycling of the heterogeneous catalyst. The Ru/Al_2O_3 catalyst showed remarkable stability and could be recycled up to eight times without significant catalyst leaching. This study therefore provides an effective, recyclable catalytic system for the conversion of CO_2 to formic acid, which has potential implications for CO_2 utilization and sustainable chemistry.

The synthesis and successful implementation of a heterogenized molecular Ru catalyst on bpyTN-30-CTF support the continuous hydrogenation of CO_2 to formic acid [10]. The support provides increased porosity and metal anchoring sites, enabling remarkable catalytic performance for commercialization. In an integrated trickle bed reactor system, the catalyst achieved a high productivity of 669.0 g g_{cat}^{-1} d^{-1} and a CO_2 conversion of 44.8%. Notably, the catalyst showed excellent stability over 30 days of operation, reaching a total turnover number of 524,000 without significant deactivation. The impressive performance and stability of the catalyst in a fixed-bed multiphase reactor system demonstrate the high industrial feasibility of this approach. The integrated pilot scale system for the production of pure formic acid, including a separation unit for the formate adduct, could provide a platform for an industrially viable CO_2 hydrogenation process.

2.2 Ruthenium catalysts in amine synthesis

A ruthenium-tungsten bimetallic catalyst was introduced for the hydrogenation of aliphatic, acyclic primary amides to primary amines, a key transformation for potential bio-based amine production [41]. The partial pressure of ammonia was identified as a key parameter in achieving high yields of primary amines, with up to 83% yield of hexylamine from hexanamide. The study examines the effects of catalyst support, platinum group metal to Lewis-acid ratio, hydrogen pressure, temperature, solvent tolerance, and product stability. The results show the ruthenium-tungsten catalyst is suitable for hydrogenating a wide range of primary amides.

2.3 Hydroformylation reactions

Hydroformylation, also known as the oxo process, is an important industrial process for the synthesis of aldehydes from alkenes, carbon monoxide, and hydrogen.

The reaction is typically catalyzed by transition metals, traditionally cobalt-based catalysts or, more recently, rhodium-based catalysts. However, ruthenium-based catalysts have also been investigated for this reaction. Ruthenium catalysts have some specific advantages in hydroformylation. They generally exhibit high activity and selectivity and are often resistant to sulfur and other impurities. This can make them particularly suitable for hydroformylation reactions involving difficult substrates or challenging reaction conditions. In addition, some ruthenium catalysts have been found to promote the isomerization of alkenes prior to hydroformylation, resulting in branched aldehydes, which may be desirable in certain applications. Despite these advantages, the use of ruthenium catalysts in industrial hydroformylation processes is less common than that of cobalt or rhodium catalysts. This is primarily due to the higher cost associated with ruthenium and its less explored nature in this specific application.

2.4 Metathesis reactions

Ruthenium catalysts have emerged as key agents in olefin metathesis, a widely used reaction in synthetic chemistry in which alkylidene groups are exchanged between different olefins to create a wide variety of complex molecular structures. Two examples shall be given below:

A highly active and reusable heterogeneous ruthenium catalyst specifically designed for olefin metathesis reactions involves ruthenium complexes [$L_2X_2Ru = CHR$], where L represents various ligands including triphenylphosphine, tricyclohexylphosphine, or *N*-heterocyclic carbenes, and X is a chlorine atom, all grafted onto the mesoporous silica material SBA-15 [42]. The unique approach is to anchor these ruthenium complexes within the pore channels of the SBA-15 material. This arrangement effectively prevents the decomposition of the catalytic species, a common problem with such catalysts. The result is a catalyst that not only exhibits impressive catalytic activity in olefin metathesis reactions but also shows significant durability. The activity of the catalyst does not decrease even after repeated use.

A promising avenue for the preparation of effective ruthenium-based metathesis catalysts is homogeneous and heterogeneous ruthenium-based metathesis catalysts that feature electron-withdrawing ligands. Such Grubbs–Hoveyda type metathesis catalysts can be prepared by chlorine exchange, replacing one or two chlorine ligands with trifluoroacetate and trifluoromethanesulfonate anions [43]. These catalysts exhibit higher reactivity in ring-closing metathesis (RCM) at 45°C compared to previous ruthenium-based catalysts, achieving turnover numbers (TONs) up to 1800 in RCM. They also showed superior performance in enyne metathesis and ring-opening cross-metathesis with norborn-5-ene and 7-oxanorborn-5-ene-derivatives. Notably, one of the catalysts exhibited significant RCM activity even at room temperature. In addition, heterogeneous catalysts were prepared by immobilization on polystyrene-divinylbenzene support. Especially, a variant with both chlorine ligands replaced showed high activity. Importantly, the leaching of ruthenium into the reaction mixture was exceptionally low, resulting in virtually Ru-free products.

Ruthenium-catalyzed olefin metathesis could play an important role in sustainable chemistry and the energy transition. For example, ruthenium metathesis catalysts can be used in reactions involving renewable feedstocks such as plant-derived oils and fats. This enables the production of bio-based chemicals and fuels, contributing to the transition to renewable energy sources. Olefin metathesis can also play a role in

recycling recovered gases such as lower olefins into valuable chemicals, creating carbon-neutral cycles.

2.5 Use of ruthenium catalysts in oxidation reactions

Due to their unique reactivity profiles, ruthenium catalysts can play a versatile role in oxidation reactions, enabling diverse applications in sustainable chemical synthesis. In particular, the oxidized form RuO_2 has a wide range of potential applications in oxidation reactions, ranging from zero energy air purification, low-temperature fuel cells, electrochemical water splitting, to the oxidative dehydrogenation of simple alcohols [44]. The low-temperature oxidation of hydrochloric acid (HCl) to chlorine and of ammonia (NH_3) to nitrogen monoxide (NO) is also catalyzed. Oxidation of carbon monoxide over supported Ru and single crystal ultrathin RuO_2 films [44] revealed that the most active and stable state is an ultrathin RuO_2 shell coating with a metallic Ru core. Catalytic conversions tend to cause structural deactivation of Ru-based catalysts.

There are different strategies for immobilizing redox-active elements in solid matrices for application in oxidation reactions including framework substitution, grafting or sol–gel methods, and ion exchange in layered double hydroxides [45]. In oxidations with O_2, H_2O_2, and RO_2H as primary oxidants, ruthenium catalysts are a good choice among other metal catalysts such as titanium, chromium, cobalt, manganese, iron, tungsten, molybdenum, vanadium, and tantalum. Many of these catalyst systems, particularly those involving oxometal species, are prone to leaching. Elements present as oxometal species are more susceptible to leaching due to their less stable coordination environments. Variable valence metals appear to be more resistant to solvolysis, but this is only true for low-conversion oxidations. In addition, secondary oxidation products can cause leaching of metal ions. Consequently, the heterogeneous nature is often questioned, and the search for heterogeneous catalysts with unique activities, selectivities, and operational stability in liquid phase oxidations is ongoing.

Ruthenium oxide-based catalysts supported on activated carbon (AC) and zeolite ZSM-5 were shown to be active for the degradation of aqueous phenol. RuO_2/AC showed superior performance to $RuO_2/ZSM5$ [46]. Complete phenol degradation and 60% total organic carbon (TOC) removal were achieved within one hour. The catalysts activate peroxymonosulfate and effectively generate sulfate radicals that are responsible for phenol degradation. Phenol degradation followed a pseudo-first-order kinetics with activation energies of 61.4 kJ mol^{-1} for RuO_2/AC and 42.2 kJ mol^{-1} for $RuO_2/ZSM5$.

Ruthenium cations, in combination with microcrystals of cobalt hydroxide and cerium oxide, catalyze the oxidation of various types of alcohols to carbonyl compounds. Using atmospheric oxygen, the reaction occurs under mild conditions at atmospheric pressure and 60°C [47]. Notable is the efficient conversion of primary aliphatic alcohols to the corresponding carboxylic acids in high yields.

The selective aerobic oxidation of ethanol to acetic acid is of considerable industrial importance, since acetic acid is a fundamental bulk chemical and food ingredient. The system is also interesting for bioethanol upgrading. Ruthenium-hydroxide on ceria, 1.2 wt % $Ru(OH)_x/CeO_2$, provided acetic acid in quantitative yields under optimal conditions (150°C, 10 bar O_2, 12 h reaction time, molar ratio Ru/substrate 0.23) [48]. Ceria was found to be the most effective support on different support materials (titania, alumina, ceria, and spinel).

Ru/Al$_2$O$_3$ is a good catalyst for the oxidation of alcohols to carbonyl compounds [49]. The catalyst uses molecular oxygen as the oxidant and tolerates both activated and nonactivated alcohols, even those containing sulfur or nitrogen atoms or a carbon-carbon double bond. Oxidation of alcohols under atmospheric conditions has been achieved without the need for additives.

Water-tolerant catalysts are required to overcome the current limitations for practical lignin valorization. In this context, ruthenium supported on γ-alumina or silica has been shown to be an effective catalyst for the oxidation of veratryl alcohol, a compound formed by cleavage of β-O-4 linkages [4] in lignin, to veratraldehyde [50]. The Ru/Al$_2$O$_3$ catalyst, prepared with ruthenium(IV)oxide hydrate, showed superior catalytic activity, yielding 89% yield in veratraldehyde in water at 160°C under 5 bar air pressure after 8 hours. Longer reaction times resulted in significant decarbonylation of veratraldehyde to veratrol. The use of methanol as a solvent instead of water prevented the oxidation of the hydroxyl group in veratraldehyde, indicating that methanol has a protective effect. Catalysts with other transition metals (Mn, Co, Cu, and Ag) showed significantly lower activities compared to Ru/Al$_2$O$_3$.

2.6 Synthesis of fine chemicals

Due to their exceptional catalytic activity, selectivity, and stability, ruthenium catalysts are poised to improve the synthesis of fine chemicals, increasing efficiency and sustainability in this sector of the chemical industry.

The use of ruthenium catalysts shall be exemplified in two distinct contexts for the synthesis of fine chemicals, the hydrogenation of α-amino acids and the epoxidation of olefins using hydrogen peroxide as a 'green' reoxidant [51]. A bimetallic Ru/Re sponge catalyst was used for the stereoretentive hydrogenation of α-amino acids in aqueous medium. The bimetallic catalyst was supported on carbon. Efficient synthesis of amino alcohols with high enantiomeric excess was achieved. Relatively low temperatures prevented racemization. For epoxidation, ruthenium pyridine-2,6-dicarboxylate complexes with tridentate *N*-donor ligands served as homogeneous catalysts and provided protocols for both asymmetric and nonasymmetric reactions. This study underscores the principles of green chemistry, emphasizing the atom efficiency of this conversion and the use of water as a solvent.

Ruthenium catalysis often has distinct capabilities over other catalytic systems such as palladium, rhodium, iridium, or cobalt complexes. Meta-selective remote C − H bromination on aryl-substituted purines has been catalyzed using the heterogeneous ruthenium Ru/SiO$_2$ catalyst [52]. This exemplifies the utility of ruthenium-catalyzed C − H activation and paves the way for novel strategies in direct nucleobase fluorescent labeling of purines, a relevant area in biochemistry and molecular biology. It also highlights the synthetic advantages of ruthenium-catalyzed C − H activation and illustrates the unique potential of ruthenium catalysts in the synthesis of fine chemicals.

A recent study examined the use of ruthenium catalysts for the Meerwein–Ponndorf–Verley reaction and the isomerization of allylic alcohols to saturated ketones. In this study, a ruthenium metal-organic framework (Ru/MOF) catalyst was modified through defect engineering and hydrogen pretreatment [53]. This enhancement was achieved by using a mixed-linker approach on the Ru-MOF [Ru$_3$(BTC)$_2$A$_n$]·G$_m$ (where BTC represents benzene-1,3,5-tricarboxylate; A is a

counterion; G stands for a guest molecule). The mixed-linker approach introduced structural defects at the Ru paddlewheel nodes, resulting in the formation of partially reduced Ru-nodes and enhanced catalytic activity. Hydrogen pretreatment further enhanced the catalytic activity.

Several features make ruthenium catalysts of particular interest for the synthesis of fine chemicals: The versatility of ruthenium catalysts makes them useful for the synthesis of many different types of fine chemicals. Ruthenium catalysts can often provide high levels of chemo-, regio-, and stereoselectivity, enabling the production of fine chemicals with precise structural features. Ruthenium catalysts are generally tolerant of a wide range of functional groups and reaction conditions, allowing for broad substrate scope and operational simplicity. Together with the general aspects discussed above, these factors make ruthenium catalysts an attractive option for the synthesis of fine chemicals, contributing to greener and more sustainable chemical processes.

3. Interaction of ruthenium particles with the support

A study of the nature of the catalyst challenged previous claims of homogeneous benzene hydrogenation with Ru(arene) precatalysts [54]. The study provided evidence that the real catalyst in benzene hydrogenation is bulk ruthenium metal particles, not a homogeneous metal complex or a soluble nanocluster. The reaction was initiated with $Ru(II)(\eta^6\text{-}C_6Me_6)(OAc)_2$ as the precatalyst. Evidence that the catalysis is based on nanoparticles is provided by (i) the nucleation and autocatalytic surface-growth mechanism; (ii) the formation of bulk ruthenium metal during hydrogenation; (iii) the high activity of bulk ruthenium metal; (iv) inactivity of the filtrate until bulk metal is formed; (v) complete inhibition of catalysis by Hg(0), a known poison for heterogeneous catalysts; and (vi) absence of detectable nanoclusters under conditions where they are typically found. The study suggests that a similar investigation be conducted for other benzene hydrogenation catalysts derived from Ru(arene) precatalysts.

In accordance, supported ruthenium nanoparticles are used as heterogeneous catalysts. Metal nanoparticles must always be stabilized against agglomeration [55]. To stabilize the ruthenium nanoparticles in a supported ruthenium nanoparticle catalyst, an intimate interfacial contact between the Ru nanoparticles and the support is required for stable performance. Such interactions can be induced by appropriate choice and modification of the oxide or carbon support. A suitable method for preparing supported ruthenium catalysts usually involves special thermal reduction protocols.

A study of the selective oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid underscores the importance of support materials in the design of efficient catalysts for the sustainable conversion of biomass-derived compounds into valuable chemicals. HMF is a biomass-derived chemical typically produced by the dehydration of sugars and polysaccharides. Heterogeneous ruthenium-based catalysts have been shown to be very effective for the oxidation of HMF with molecular oxygen in the absence of a base and in water as a solvent [56]. Among a wide range of support materials, including various metal oxides, magnetite, spinel, hydrotalcite, and hydroxyapatite, ruthenium-hydroxide species supported on cerium oxide exhibited superior catalytic activity and selectivity compared to those using titanium dioxide as support.

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In the case of carbon supports, Ru precursors were deposited on carbon materials and then reduced to Ru nanoparticles, resulting in catalysts with exceptional performance in the hydrogenation of benzene and toluene [57]. Remarkably, these thermally treated Ru catalysts operate up to 24 times faster than their conventionally prepared counterparts and exhibit impressive resistance to oxidation, reduced leaching, and well-distributed dispersion on carbon materials.

A magnetically separable ruthenium-hydroxide catalyst on magnetite ($Ru(OH)_x$/ Fe_3O_4) has been used for three types of reactions: aerobic oxidation of alcohols, aerobic oxidation of amines, and reduction of carbonyl compounds to alcohols using 2-propanol as a hydrogen donor [58]. This shows that the catalyst is effective for a wide range of substrates, including aromatic, aliphatic, and heterocyclic substrates. A significant advantage of this catalyst is its magnetic separability: the $Ru(OH)_x$/Fe_3O_4 catalyst can be easily separated from the reaction products using a permanent magnet, with a recovery of more than 99%. The study confirmed the intrinsic heterogeneity of the catalysis for these reactions and showed that the $Ru(OH)_x$/Fe_3O_4 catalyst retained its activity after multiple reuses.

For binding ionic ruthenium complexes [59] and ruthenium clusters, nitrogen-doped carbon materials have attracted attention due to their strong interaction with the active metal species through their nitrogen functionalities. Such nitrogen-doped carbon materials can be prepared from adenine as carbon and nitrogen source and anhydrous magnesium chloride as template [59]. Favorable binding sites include pyridinic and pyrrolic nitrogen moieties (**Figure 2**).

As a biorenewable, biodegradable material with multiple functional groups, chitosan is an attractive candidate for anchoring metal catalysts. Ruthenium supported on chitosan, a natural polysaccharide, has been used as a heterogeneous catalyst for the hydration of nitriles to amides in aqueous media under neutral conditions [60]. The chitosan-ruthenium catalyst offers high yields, excellent selectivity, and easy recoverability, all under neutral, environmentally benign conditions.

Ruthenium macromolecules, such as ruthenium tetraphenylporphyrin [Ru(TPP)], have been shown to be an effective catalyst for the reaction of carbon dioxide (CO_2) with epoxide to form cyclic carbonates [61]. The [Ru(TPP)] catalyst showed excellent performance, following first-order kinetics with respect to epoxide, leading exclusively to cyclic carbonate. Importantly, it offered significantly lower activation energy than previously reported catalysts. For heterogenization, the [Ru(TPP)] complex was grafted onto functionalized SBA-15 molecular sieves. When grafted onto aminosilane-
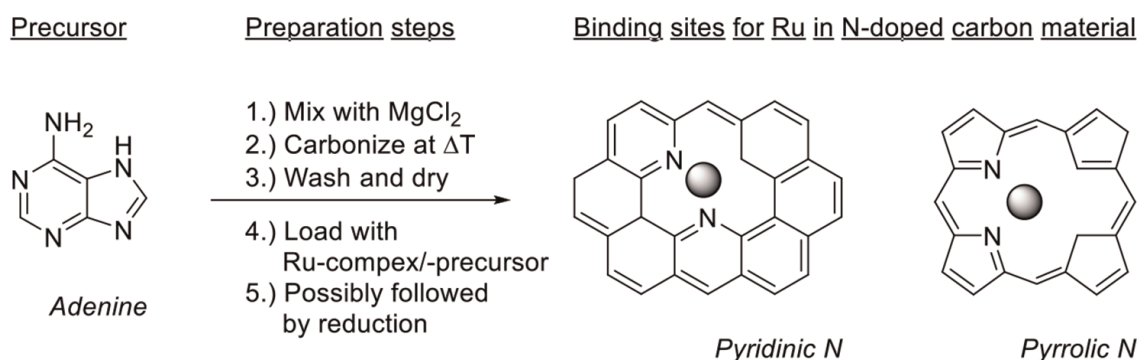

Figure 2.
Synthesis of N-doped carbon materials and binding sites according to [59].

and iodosilane-functionalized materials, [Ru(TPP)] showed promising catalytic activity for the carboxylation of epoxides.

Heterogeneous ruthenium catalysts have a significant potential for efficient and selective chemical transformations with relevance to environmental sustainability. A heterogeneous ruthenium catalyst prepared by adsorption of [$RuCl_2$(*p*-cymene)]$_2$ on activated carbon showed exceptional efficiency and selectivity for the aerobic oxidation of alcohols, hydrolytic oxidation of silanes, and the dehydration of aldoximes [62].

The use of agricultural wastes in the preparation of carbon supports has also been explored as a way to increase the sustainability of catalyst production. One example is a heterogeneous ruthenium catalyst using silica derived from rice husk ash (RHA) [63]. The ruthenium was loaded by precipitation using a metal salt solution in nitric acid followed by high-temperature calcination. The structure varied depending on the calcination protocol. Initial analysis showed that the Ru/RHA catalyst was in an amorphous state. After postcalcination at 700°C, some degree of crystallization was observed. SEM images revealed the formation of nano-sized rods within the amorphous powder. Interestingly, the specific surface area decreased significantly upon postcalcination, consistent with the formation of the rod-shaped crystalline phase. The catalyst exhibited strong metal-oxygen chemical bonding, which is believed to be the key interaction between the metal and the silica support. The inhomogeneous Ru distribution in the initial Ru/RHA catalyst improved upon calcination, as shown by EDX.

The study thus showcases the successful development of a series of heterogeneous ruthenium catalysts that possess not only comparable activity to homogeneous ones but also offer practical advantages like easy separation and reuse. These catalysts contribute to flexible hydrogen generation and hold the potential for selective and efficient formic acid decomposition in diluted solutions.

An interesting heterogeneous ruthenium catalyst for the selective decomposition of formic acid into hydrogen and carbon dioxide comprised a combination of a Ru(II) *meta*-trisulfonated triphenylphosphine (*m*TPPTS) complex with phosphine-modified mesoporous silica [64]. Variations in the catalyst structure were achieved by changing the length of the alkylene chain connecting the silica to the diphenylphosphine group. The catalysts were highly active, with Ru-*m*TPPTS/MCM41-Si(CH_2)$_2$PPh$_2$ exhibiting a turnover frequency of 2780 h^{-1} at 110°C, comparable to the corresponding homogeneous catalyst. No evidence of ruthenium leaching was detected even after 71,000 turnovers. This shows remarkable durability.

4. Bimetallic catalysts and catalyst mixtures

Alloying ruthenium with other elements imparts unique properties and enhanced reactivity profiles to bimetallic ruthenium catalysts. The integration of additional metals imparts specific properties to ruthenium that profoundly alter reaction pathways compared to their monometallic counterparts.

A review on the synthesis and analysis of polynuclear ruthenium-tin cluster complexes focuses on their transformation into heterometallic nanoparticles [65]. These complexes are then used as catalysts in the hydrogenation of unsaturated organic molecules. The narrative of the study bridges the gap between the molecular design of these clusters and their use in facilitating industrially relevant hydrogenation reactions, reflecting the importance of this class of bimetallic nanoscale heterogeneous catalysts. Unique properties are imparted to the catalyst by the cooperative action of
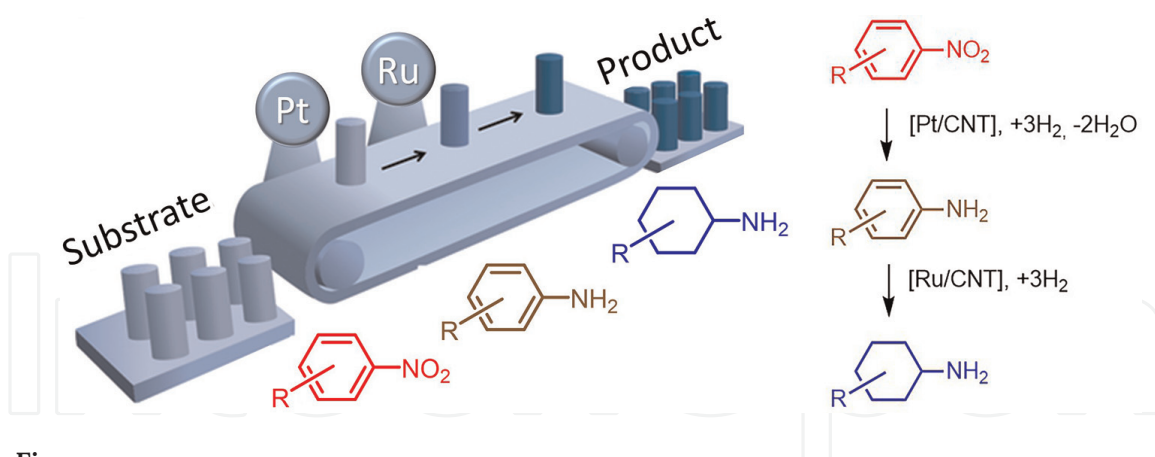
Figure 3.
Concept of a molecular assembly line of a physical mixture of two different heterogeneous catalysts applied to the hydrogenation of nitrobenzene over a Pt/CNT Ru/CNT catalysts mixture.

ruthenium and tin, providing insight into how these properties might be exploited for more efficient and selective hydrogenation processes.

Uniformly distributed bimetallic Ni-Ru nanoparticles on a magnesium-aluminum hydrotalcite support are effective in reducing nitrobenzene under ambient conditions [66], demonstrating that the presence of metallic nickel and ruthenium on the hydrotalcite surface facilitates this process. Kinetic studies indicate a first-order relationship with respect to nitrobenzene. Importantly, the catalyst maintains its activity over multiple cycles and effectively reduces various substituted nitroarene molecules.

Likewise, physical mixtures of different heterogeneous catalysts can alter the course of the reaction. Thus, carbon nanotube-supported Ru/CNT and Pt/CNT catalysts have been effectively employed in the hydrogenation of nitroaromatics to cycloaliphatic amines [67]. Interestingly, Ru and Pt, as metals, share similar atomic radii of 133 and 137 pm, while their static average electric dipole polarizabilities differ [68]. Consequently, the aromatic ring, categorized as "soft" due to its aromatic π-system dispersed over six carbon atoms, tends to adsorb preferentially on the more polarizable ruthenium. The nitro group, deemed "hard" due to its negative charge spread mostly over only two oxygen atoms, tends to adsorb preferentially on platinum, which has highly shielded d-electrons. A combination of 95% Ru/CNT and 5% Pt/CNT provides approximately equal rates for the hydrogenation of the respective moieties and maximum selectivity toward the fully hydrogenated product, cyclohexylamine (**Figure 3**).

Bimetallic ruthenium catalysts, thus, often offer distinct advantages including enhanced catalytic performance and an increased range of reactivity.

5. Conclusions

Ruthenium catalysts have demonstrated a remarkable capacity for a multitude of reactions, encompassing hydrogenation, oxidation processes, and, notably, the contemporary utilization of carbon dioxide. The ability of ruthenium catalysts to convert carbon dioxide into useful chemicals and fuels may not only help to sequester CO_2, a potent greenhouse gas but also produce valuable feedstocks for industry, providing a potential route to carbon-neutral or even carbon-negative processes. Similarly, ruthenium catalysts may play an increased role in the intensified use of bio-derived feedstock. In the field of electrocatalysis, ruthenium shows particular promise in water-splitting technologies, organic electrosynthesis, proton exchange membrane fuel cells,

and metal-air batteries. The metal's propensity to catalyze the oxygen evolution reaction significantly increases the efficiency of hydrogen production.

The interplay between homogeneous and heterogeneous catalysis using ruthenium, as demonstrated in CO_2 conversion, also illustrates the immense potential of the metal to unlock new technologies and sustainable solutions. It is the ability to form bonds of intermediate strength with a variety of ligands, exist in multiple oxidation states, and accommodate both high and low oxidation states that enables this wide range of chemical transformations. Delving deeper into the fundamental atomic-level mechanisms could pave the way for further advances in the design of ruthenium catalysts, thereby expanding their efficacy and applicability. Particularly in the global raw material transition to sustainable feedstocks and the energy transition to more sustainable and cleaner energy systems, ruthenium catalysts offer a range of solutions in key areas that can make a significant contribution to reducing carbon emissions and optimizing energy use.

In summary, the extensive exploration of ruthenium as a catalyst underscores its fundamental role in modern chemistry and materials science. While current advances in ruthenium catalysis are impressive, the breadth of its untapped potential encourages continued exploration and innovation. As researchers develop an even more refined understanding of its properties, ruthenium is likely to continue to be at the forefront of new discoveries and applications, contributing to sustainable solutions in exciting areas of technology.

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Conflict of interest

The author declares no conflict of interest.

Acronyms and Abbreviations

AC	Activated Carbon
CCU	Carbon Capture and Utilization
PP	Bisphosphine
EDX	Energy Dispersive X-Ray Spectroscopy
$\Delta H_r°$	Heat of reaction at standard conditions
$\Delta G_r°$	Gibbs free energy at standard conditions
L	Ligand (L)

LOHC	Liquid Organic Hydrogen Carriers
OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction
PEMFC	Proton Exchange Membrane Fuel Cells
m.p.	Melting Point
MOF	Metal-Organic Framework
n_{H2}	Mols of Hydrogen
MEA	Monoethanolamine
POP	Porous Organic Polymer
RHA	Rice Husk Ash
RCM	Ring-Closing Metathesis
TPD	Temperature Programmed Desorption
TOC	Total Organic Carbon
TEM	Transmission Electron Microscopy
TOF	Turnover Frequency
TON	Turnover Number
Wh	Watthours
w_{H2}	Weight Percentage of Hydrogen
XRD	X-Ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
OAc⁻	Acetate
ZSM-5	Aluminosilicate Zeolite Socony Mobil–5
BTC	Benzene-1,3,5-tricarboxylate
DMF	*N,N*-Dimethylformamide
DMSO	Dimethylsulfoxide
DAMI	Di(*N,N*-dimethylaminoethyl)-2-methylimidazolium
HMF	5-Hydroxymethylfurfural
MCM-41	Mesoporous Material Mobil Composition of Matter No. 41
TPP	Tetraphenylporphyrin
*m*TPPTS	*meta*-Trisulfonated triphenylphosphine

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