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Authors: Amit Kumar and Chang Gao

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Homogeneous (De)hydrogenative Catalysis for Circular Chemistry – Using Waste as a Resource

Amit Kumar*, Chang Gao
Abstract: Increasing production and usage of several consumer products and energy sources have resulted in the accumulation of substantial amount of waste products that are toxic and/or difficult to biodegrade, thus creating a severe threat to our planet. With the recently advocated concepts of circular chemistry, an attractive approach to tackle the challenge of chemical waste reduction is to utilize these waste products as feedstocks for the production of useful chemicals. Catalytic (de)hydrogenation is an atom-economic, green and sustainable approach in organic synthesis, and several new environmentally benign transformations have been reported using this strategy in the past decade, especially using well-defined transition metal complexes as catalysts. These discoveries have demonstrated the impact and untapped potential of homogeneous (de)hydrogenative catalysis for the purpose of converting chemical wastes into useful resources. Four types of chemical waste that have been (extensively) studied in recent years for their chemical transformations using homogeneous catalytic (de)hydrogenation are CO₂, N₂O, plastics, and glycerol. This review article highlights how these chemical wastes can be converted to useful feedstocks using (de)hydrogenative catalytic mediated by well-defined transition metal complexes and summarizes various types of homogeneous catalysts discovered for this purpose in recent years. Moreover, with examples of hydrogenative depolymerisation of plastic waste and the production of virgin plastic via dehydrogenative pathways, we emphasize the potential applications of (de)hydrogenation reactions to facilitate closed-loop production cycles enabling a circular economy.

1. Introduction

A vast majority of the current chemical production industry is based on a linear economic model of take-make-dispose. This model results in a deficit of important resources, and huge amounts of accumulated waste, which threatens our biosphere. Economists, policymakers, and scientists have thus advocated the concept of a circular economic model based on make-use-reuse-recycle to keep material at its highest utility and value at all times. Chemistry lies at the centre of the production of food, energy, materials, and pharmaceuticals, and thus is crucial to the movement from linear to a circular economic model. Recently, Slootweg has proposed twelve principles of circular chemistry to optimize resource efficiency across chemical value chains. Perspectives on the utilization of innovative green chemical strategies for circular chemistry have also been reviewed recently. A fundamental aspect of circular chemistry is to treat waste as a resource to enable a closed-loop production cycle. This specific aim of circular chemistry is the focus of this review.

Reactions based on (de)hydrogenative catalysis are green and sustainable routes for organic synthesis because (a) they are atom-economic, (b) they do not produce any stoichiometric waste as compared to conventional reductants or oxidants, and (c) H₂ can be produced from renewable sources such as by electrolysis of water using electricity produced from solar or wind energy. Moreover, chemical production methods based on (de)hydrogenative catalysis offer a strategic theoretical pathway where products can be converted back to the starting materials with the release or chemical capture of hydrogen gas. This unique trait has been exploited for the development of several Liquid Organic Hydrogen Carriers (LOHCs) where hydrogen gas can be produced from the catalytic dehydrogenation of a charged fuel, which later can be regenerated by hydrogenation of the spent fuel. The ability to perform the (de)hydrogenation reactions in both directions offers an opportunity to design our production route using (de)hydrogenation process so that the products, which become wastes after use, can be converted back to the starting materials using the reverse reaction. And in doing so, the hydrogen gas produced at the dehydrogenation step can also be recycled for the hydrogenation step (Figure 1).

In the previous two decades, several new green organic transformations based on catalytic (de)hydrogenation reactions have been reported. Given the substantial amount of research output, this area has been well-reviewed in recent years from the perspective of both homogeneous and heterogeneous catalysts. Despite the challenge of catalyst separation associated with homogeneous catalysis that limits its industrial applications, the area of homogeneous catalysis, in contrary to heterogeneous catalysis, allows deeper mechanistic studies strengthening the fundamental understanding of catalyst design and catalytic cycle. Because of this, several new green and sustainable catalytic processes have been developed using homogeneous catalysts. A recent surge of research output has emerged from the catalysis community in the direction of homogeneous (de)hydrogenative catalysis enabled by earth-abundant metals. This direction has enhanced the potential of well-defined molecular complexes towards practical applications.

Our interests lie in both homogeneous catalysis and circular chemistry; in this article, we review the impact that well-defined molecular catalysts have made in recent years to enable closed-loop production cycles using the approach of catalytic (de)hydrogenation. The review focuses on recent advances in catalytic methods to convert waste into useful resources. From the perspective of the impact of the homogeneous (de)hydrogenative catalysis, we have identified four chemicals/materials that have been considered as wastes, either because of their higher supply compared to the demand or because they are harmful to our ecosphere/planet or both. These are CO₂, N₂O, plastics, and glycerol.

Here, we review the (de)hydrogenative catalytic transformation of these four wastes to useful chemical feedstocks.
Amit Kumar is currently working as a Leverhulme Trust Early Career Researcher at the School of Chemistry, University of St. Andrews. He completed his DPhil (2012-2016) as a Rhodes Scholar under the supervision of Prof. Andrew Weller at the University of Oxford, UK. He received the PBC fellowship (Planning & Budgeting Committee, Israel) to carry his postdoctoral research with Prof. David Milstein at the Weizmann Institute of Science, Israel where he was promoted to Senior Postdoctoral Fellow in 2019. Amit was awarded the FGS (Feinberg Graduate School) Prize for the outstanding achievements in postdoctoral research 2018 by the Weizmann Institute of Science, Israel. His research interests are organometallic catalysis, energy storage, and circular chemistry.

Chang Gao is currently a fourth-year Chemistry student at the University of St. Andrews studying towards an integrated master’s degree. During her fourth year, she is working as an industrial placement student at Johnson Matthey, Cambridge. She was awarded the Dean’s List Prize by the University of St. Andrews for the 2018-19 and 2019-20 academic years. Her main interests include organometallic chemistry and sustainable chemistry.

2. Carbon dioxide

Carbon dioxide is the final product formed upon the burning of fossil fuels (coal, natural gas, and oil) and organic waste. Growing industrial production and our dependence on fossil fuels have increased the production of CO$_2$ over time. For example, in 2019, 33 gigatons (Gt) of CO$_2$ were produced globally from the energy sector alone.\textsuperscript{[17]} The ever-rising atmospheric concentration of CO$_2$ is held responsible for climate change giving rise to problems of global warming and ocean acidification. Converting CO$_2$ to useful chemicals and fuels presents an attractive opportunity to reduce accumulating waste as well as to lower our dependence on fossil fuels. Several chemicals such as urea, salicylic acid, and polyols are produced industrially using CO$_2$. However, there is a considerable gap in the amount of CO$_2$ produced and that consumed. Thus, there is an urgent need to develop efficient technologies to capture and sequester or valorise CO$_2$. Indeed, there has been an appreciable effort in the area of reactivity of CO$_2$ with various organic compounds such as alkenes, alkynes, arenes, epoxides, alcohols, amines, boranes, and silanes.\textsuperscript{[18-25]}

In the interest of this review as discussed above, here, we summarize recent results in CO$_2$ valorisation enabled by catalytic hydrogenation pathways using molecular hydrogen. A few other review articles have also been written on the topic of CO$_2$ hydrogenation using homogeneous catalysts in past years.\textsuperscript{[26-29]}

2.1 Hydrogenation of CO$_2$ to formic acid

Formic acid (FA) is an important chemical feedstock and has a global demand of around 800, 000 tonnes, with substantial applications in textile, food, and agrochemical industries.\textsuperscript{[30]} It can also be used as a fuel in the FA fuel cell to produce energy. Recently, FA is being advocated as a potential Liquid Organic Hydrogen Carrier (LOHC) for use in a future hydrogen economy.\textsuperscript{[31,32]} Thus, the production of FA from waste CO$_2$ is an attractive process from the perspective of the circular economy.

Hydrogenation of CO$_2$ to formic acid or a formate salt was first accomplished using a heterogeneous catalyst in 1914\textsuperscript{[33]} and several heterogeneous catalysts have been studied since then. These catalysts can be divided into three parts: (a) unsupported bulk (e.g. Pd Black and Raney Ni) or nanometal (e.g. Ru or Pd nanoparticles) catalysts, (b) supported bulk or nanometal catalysts (e.g. Pd/Act. carbon, Pd/graphite, Au/Al$_2$O$_3$, and Au/TiO$_2$), and (c) heterogenized molecular catalysts immobilized on grafted solids or porous polymers. In general, the supported metal catalysts showed superior catalytic activity compared to the unsupported ones. The details on the catalytic conditions and outcome of heterogeneous catalysts for hydrogenation of CO$_2$ to HCOOH or a formate salt have been reviewed recently.\textsuperscript{[34,35]} Although heterogeneous metal catalysts allowed easy separation and recycling of catalysts, the catalytic activity remains poor in most cases. For example, the maximum TOF obtained using supported or unsupported metal catalyst was found to be 836 h$^{-1}$ using Pd/Act. carbon. Since these catalysts involve precious metals, a high activity or the use of earth-abundant metals is desirable for economic viability. In comparison to the heterogeneous catalysts, the number of reports on homogeneous catalytic systems involving both precious and earth-abundant metals is significantly higher. Homogeneous catalysts have also demonstrated much higher catalytic activities such as TONs up to 3 500 000\textsuperscript{[36]} and TOFs up to 1 100 000 h$^{-1}$\textsuperscript{[37]} compared to any heterogeneous catalyst and is the focus of the review in the following section.

Thermodynamically, direct hydrogenation of CO$_2$ to HCOOH is an endothermic process (Scheme 1, $\Delta G = +7.6$ kcal mol$^{-1}$).\textsuperscript{[38]} Therefore, most of the catalytic processes use a stoichiometric amount of base to drive the reaction forward by producing the more stable formate salt.\textsuperscript{[39-42]} Despite highly active and selective catalysts developed for the hydrogenation of CO$_2$ to formate salt (such as one by Nozaki with TOF 1 500 000 h$^{-1}$ at 200 °C, 50 bar and TON 3 500 000 at 120 °C),\textsuperscript{[43]} use of (i) stoichiometric base and then (ii) stoichiometric acid to produce HCOOH from formate produces significant salt waste, which presents a challenge in the commercialization of this technology.

\begin{equation}
\text{CO}_2(g) + \text{H}_2(g) \rightarrow \text{HCOOH} \quad \Delta G = +7.6 \text{ kcal mol}^{-1} \\
\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOO}^- \quad \Delta G > 0 \\
\text{CO}_2 + \text{H}_2 \rightarrow \text{H}^+ \text{OH}^- \text{solvent} \quad \Delta G < 0
\end{equation}

\textbf{Scheme 1. Thermodynamics of hydrogenation of CO$_2$ to HCOOH.}
To achieve a circular economy that advocates for the elimination of waste, it is important to develop catalytic processes for the hydrogenation of CO₂ to HCOOH without using a stoichiometric amount of additive. An early example for the hydrogenation of CO₂ to free HCOOH dates back to 1990 using [Rh(NB)₂(PPh₃)₃]BF₄ complex albeit with a lower TON of 10-60/day.[43] With the new catalyst design, it has been possible to perform hydrogenation of CO₂ to HCOOH under acidic conditions. In 2004, Fukuzumi and Ogo reported the first example of hydrogenation of CO₂ under acidic conditions without using any stoichiometric additive. A water-soluble ruthenium catalyst [(η⁶-C₆Me₆)Ru(η(L)(OH))SO₄ (L = 2,2'-bipyridine or 4,4’-dimethoxy-2,2'-bipyridine) was used for the hydrogenation of CO₂ (pH/pCO₂ = 5.5/2.5 MPa) in water under acidic conditions (pH = 2.5-5.0) to produce HCOOH.[44] However, the activity of the catalyst was significantly lower than those used under basic conditions, and a TON of up to 50 was obtained in 70 h. Later, Fukuzumi and Ogo in 2006 reported iridium aqua complexes [Cp*Ir(L)(OH)₂]⁺ (Figure 2, Ir-1, Cp* = η⁶-C₅Me₅, L = 2,2'-bipyridine) and ruthenium aqua complexes [(η⁶-C₆Me₆)Ru(L)(OH)₂]⁺ (Ru-1, L = 2,2'-bipyridine, 4,4’-dimethoxy-2,2'-bipyridine) for the hydrogenation of CO₂ to HCOOH under acidic conditions.[45]

![Catalysts working under acidic conditions](image)

**Catalysts working under acidic conditions**
- **Ir-1**
- **Ru-1** (R = H, OMe)

Fukuzumi and Ogo, 2006

**Catalysts used with ionic liquid**
- **Ru-2**
- **Ru-2**

Albrecht and Sans, 2020

![Catalysts with DMSO as solvent](image)

**Catalysts with DMSO as solvent**
- **Ru-3**
- **Ru-4**

Laurenczy, 2014; Li, 2016

Figure 2. Catalysts for the additive-free hydrogenation of CO₂ to HCOOH.

An approach based on using ionic liquids (ILs) as solvents has also been used for the additive-free hydrogenation of CO₂ to HCOOH.[46] ILs have a high capacity to dissolve CO₂. More importantly, ILs bearing basic anions such as 1,3-propyl-2-methylimidazolium formate (PPMI·O₂CH) can enhance the yield of reaction by thermodynamically stabilizing the product. Sans and Dupont reported hydrogenation of CO₂ to HCOOH using [Ru₂(μ-CO₂)]₂ and an imidazolium-based IL associated with the acetate anion.[47] Based on the experimental observations, the authors suggest a dual role of IL: (i) it assists in the formation of catalytically active Ru-H species, and (ii) it acts as an acid buffer driving the reaction equilibrium towards the formation of free HCOOH. A high TON of 17,000 was observed and a good yield (1.2 M) of HCOOH was observed. Ruthenium catalysts (Ru-2, Figure 2) based on pyridylidene amide (PYA) ligand have also been utilized to perform hydrogenation of CO₂ to HCOOH recently by Albrecht and Sans. A TON of up to 4,520 was observed in H₂O/DMSO solvent mixture in the presence of an IL.[48]

In the direction of additive-free hydrogenation of CO₂ to HCOOH, the use of polar solvents such as H₂O or DMSO for performing catalysis has also shown promising results. These solvents can stabilize HCOOH by performing hydrogen bonding thus driving the reactions forward (Scheme 1). Laurenczy has reported that using a homogeneous ruthenium catalyst [RuCl₂(PTA)] (Ru-3, PTA = 1,3,5-triazole-7-phosphaadamantane, Figure 2), CO₂ can be hydrogenated in H₂O or DMSO to form HCOOH without using any additive.[49] A 0.2 M HCOOH can be produced in H₂O at 200 bar and 60 °C whereas in DMSO, 1.9 M HCOOH can be obtained. The catalyst was found to be very stable and could be recycled multiple times without loss of activity. Soon after, Li reported an iridium catalyst (Ir-2, Figure 2) bearing an N,N’-dimine ligand for the direct hydrogenation of CO₂ to HCOOH without using any additive.[50] A TON of >10,000 was obtained at 40 °C and 76 bar (7.6 MPa) of H₂CO₂ (1:1) in H₂O. Along this line, Leinert reported ruthenium acrylides pincer catalyst (Ru-4, Figure 2) for the hydrogenation of CO₂ to HCOOH in H₂O or DMSO solvent that exhibits a TON of up to 4,200 and TOF of up to 260 h⁻¹ at 60 °C and 80 bar H₂ and 40 bar CO₂.[51] However, the lower yield of HCOOH (up to 0.33 M) was obtained compared to that of Laurenczy (up to 1.9 M). The lower product yield was attributed to the product-dependent catalyst inhibition and was overcome by the addition of acetic buffer. This resulted in a high concentration of free HCOOH of 1.27 M. DFT calculations support the stabilization of HCOOH by hydrogen bonding from solvents – H₂O or DMSO.

2.2 Hydrogenation of CO₂ to methanol and higher alcohols

![Hydrogenation of CO₂ using amines](image)

**Figure 3. Hydrogenation of CO₂ to CH₃OH using amines.**

Methanol, with a global demand of more than 75 million tons annually, is one of the most important feedstocks of chemical industries such as for the production of formaldehyde, acetic acid, methyl tert-butyl ether (MTBE), hydrocarbons, and olefins.[52] It
also has several applications in the energy sector, for example, as fuel in internal combustion engines, as energy carriers, and for the production of biodiesel. Thus, the topic of producing methanol from CO₂ is highly attractive and has been intensively studied by the catalysis community. The concept of ‘Methanol Economy’ for the sustainable production of methanol from CO₂ has been advocated by the Nobel Laureate Prof. George A. Olah and Prof. Surya Prakash. Hydrogenation of CO₂ to methanol is an endothermic process and therefore requires a high temperature. Almost all the catalysts reported to date for the direct and additive-free hydrogenation of CO₂ to methanol are heterogeneous in nature. Heterogeneous catalysts have also been commercialized for the production of methanol by the hydrogenation of CO₂. For example, Cu/ZnO/Al₂O₃ catalyst that operates at 220–300 °C and 5–10 MPa was commercialized by Imperial Chemical Industries in the 1960s. Since then, Cu-ZnO-based materials have attracted substantial attention, and still remain the most investigated type of heterogeneous catalysts for the catalytic hydrogenation of CO₂ to methanol. Cu-ZnO-based catalysts have also been utilized in the Mitsui Process by the RITE and NIRE (Japan), and the Lurgi Process by Lurgi for the conversion of CO₂ to methanol. A few years ago, in 2012, the Carbon Recycling International started the production of 100% renewable methanol from the direct hydrogenation of CO₂ (captured from emission) to methanol where hydrogen gas was produced by the electrolysis of water using renewable electricity. Despite the industrial applications of heterogeneous catalysts, catalysts based on well-defined molecular complexes have demonstrated promising activity for the hydrogenation of CO₂ to methanol especially under relatively milder reaction conditions (e.g. temperature <150 °C).

Hydrogenation of CO₂ to methanol using homogeneous catalysts have been demonstrated using indirect sequential approaches except for the example discussed in Scheme 3. This sequential concept was first realized by Milstein and co-workers (2011) who reported ruthenium pincer catalysts (e.g. Ru-5, Figure 3) for the hydrogenation of formates, organic carbonates, and organic carbamates to methanol. As these species can be readily formed by the reaction of CO₂ with alcohols/amines, their hydrogenation to methanol provides an alternative strategy for the indirect conversion of CO₂ to methanol using molecular hydrogen. Since then, several homogenous catalysts have been utilized for the hydrogenation of CO₂ to methanol in the presence of additives such as amines and alcohols. The first example of the hydrogenation of CO₂ to methanol via cascade catalysis was demonstrated by Sanford. A three-step methodology was used – (i) Hydrogenation of CO₂ to HCOOH in the presence of (PMe₃)₂Ru(Cl)(OAc) (ii) esterification of HCOOH in the presence of Sc(OTf)₃ catalyst and (iii) hydrogenation of formed formate ester to methanol in the presence of a RuPNN pincer catalyst (Ru-5, Figure 3). Although an overall transformation of CO₂ to methanol was successfully demonstrated, a low TON (up to 21) was observed. Recently, Goldberg has used the same approach and obtained a higher TON (428) using the catalytic combination of Ru(H₂)[P(CH₃)₂CH₂PPh₂]₃/Sc(OTf)₃/tri-1BuPCP/CO₂. After the seminal works of Milstein and Sanford, several examples have been reported where CO₂ is captured by a nucleophile such as amines and alcohols to form a species whose hydrogenation to methanol is more favourable compared to the direct hydrogenation of CO₂ to methanol.

Hydrogenation of CO₂ to methanol in the presence of amines was first demonstrated by Sanford in 2015 using NHMe₂ and a ruthenium-Macho catalyst (Ru-6, Figure 3). NHMe₂ in the presence of CO₂ (2.5 bar) and H₂ (50 bar) formed dimethylammonium dimethylcarbamate (DMC) and dimethylformamide (DMF) which was subsequently hydrogenated to methanol. The overall process was also demonstrated as a single step where CO₂ (2.5 bar) was hydrogenated (50 bar) to methanol (TON = 550) in the presence of the ruthenium pincer catalyst (Ru-6, 0.03 mol%). Figure 3). K₂PO₄ (0.25 mmol) and NHMe₂ (7.6 mmol). Around a similar time, Milstein reported the capture of low-pressure CO₂ (1 atm) using amino-ethanol followed by subsequent ruthenium (Ru-5, Figure 3) catalysed hydrogenation to form methanol with the release of amino-ethanol. Using this approach, Ding reported hydrogenation of CO₂ to methanol in the presence of morpholine and ruthenium-Macho pincer catalyst (Ru-6, Figure 3) in two steps via the formation of N-formylimorpholine. Using a new avenue in this direction, the group of Prakash and Olah demonstrated for the first time in 2016 an integrated process by combining CO₂ capture and hydrogenation. In this approach, CO₂ is first captured from the air (CO₂ concentration 400 ppm) using a scrubbing agent such as polyamines to form mixtures of carboxamides and carbonates/bicarbonates and then subsequently hydrogenated using a ruthenium-Macho pincer catalyst (Ru-6, Figure 3) to form methanol. A very good yield of CH₃OH (79%) was obtained and recyclability of the catalyst was also demonstrated for up to five times exhibiting a TON > 2000. A proposed mechanism for this transformation has been outlined in Scheme 2. CO₂ is captured by a polyamine to form a carbamate (step 1) which subsequently gets hydrogenated in the presence of the ruthenium pincer catalyst to form a formate salt (step 2). Dehydration of the formate salt results in the formation of a formyl intermediate (step 3) which then is converted to methanol via ruthenium catalysed hydrogenation process (step 4). A more detailed mechanism for the final step i.e. hydrogenation of formamide to methanol using an analogous ruthenium complex has been reported recently by the same group.

Later, Prakash in 2018 employed a biphasic 2-MeTHF/water solvent system that allowed easy separation and
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recycling of both amine and catalyst.\textsuperscript{[86]} Utilising this strategy, not only a higher yield of CH$_3$OH (>90\%) was obtained but more efficient recycling of both amines and the catalyst was demonstrated with 95\% of the catalyst activity after four cycles. To further enhance the recyclability of amines, in 2019, Prakash employed amines that were immobilized onto a solid support.\textsuperscript{[87]} A highly active ruthenium catalyst (Ru-7, TON up to 8900, Figure 3) was reported by Everett and co-workers for the hydrogenation of CO$_2$ to methanol via formamide in the presence of amines.\textsuperscript{[88]} Prakash has also used a polyamide for the hydrogenation of CO$_2$ to methanol in the presence of a ruthenium-Macho pincer catalyst (Ru-6, Figure 3) exhibiting a TON of up to 9900.\textsuperscript{[89]} Along this line, the use of poly(ethyleneimine) has also been recently reported by Kayaki for the hydrogenation of CO$_2$ to methanol in the presence of a ruthenium-Macho pincer catalyst (Ru-6, Figure 3).\textsuperscript{[90]} For all these above-mentioned systems, the hydrogenation mechanism is proposed to be assisted by metal-ligand cooperation.

Other than ruthenium, some base-metal complexes have also been employed for the amine-assisted hydrogenation of CO$_2$ to methanol. Prakash reported an air-stable Mn(I)-PNP pincer catalyst (Mn-1, Figure 3) for hydrogenation of CO$_2$ to methanol via the formation of formamide using an amine such as morpholine or benzylamine.\textsuperscript{[91]} Although a high yield of methanol (84\% with benzylamine and 71\% with morpholine) was obtained, the TON was significantly lower (up to 36) compared to ruthenium systems. More active catalysts in this direction were reported using iron complexes by the groups of Martins (Fe-1, Figure 3) and Bernskoetter (Fe-2, Figure 3).\textsuperscript{[66-67]}

\[
\text{CO}_2 + \text{H}_2 \xrightarrow{\text{[Ru]}} \text{CH}_3\text{OH}
\]

![Figure 4. Hydrogenation of CO$_2$ to CH$_3$OH in the presence or absence of alcohols.](image)

Other than amines, alcohols have also been utilized for the purpose of CO$_2$ capture and subsequent hydrogenation to methanol. After Sanford’s seminal discovery in 2011\textsuperscript{[89]} of the hydrogenation of CO$_2$ in 2012, Klankermayer, Leitner, and co-workers demonstrated hydrogenation of CO$_2$ to methanol using ethanol as an additive.\textsuperscript{[91]} In the presence of ethanol, hydrogenated CO$_2$ was captured as ethyl formate and subsequently hydrogenated to methanol. A combination of ruthenium(II)-triphos complex and a Lewis acid bis(trifluoromethane)sulfonimide (HNTf$_2$) was used as a catalyst that exhibited a TON of 221. The ruthenium(II)-triphos complex could be generated either in situ from Ru(acac)$_3$ and Triphos (Ru-8, Figure 4) or from the readily accessible ruthenium(ii)-complex [(Triphos)Ru(TMM)] precursor (Ru-9, Figure 4). Recycling of the catalyst was demonstrated in a biphasic system of 2-MeTHF-water and an overall TON of 769 was achieved after 4 cycles. Interesting insights into the mechanism were reported later by experiments and DFT calculations by Klankermayer and Leitner.\textsuperscript{[72]} Experimental studies revealed that the role of co-catalyst HNTf$_2$ is to form the cationic complex Ru-10 (Figure 4) which was confirmed to be the active species. Based on this insight, an analogous complex [(Triphos)Ru(11\^{OAc})(S)](NTf$_2$) (Ru-11, with S being a free coordination site or weakly bound solvent molecule, Figure 4) was synthesized. Remarkably, complex Ru-11 or complex Ru-9 with HNTf$_2$ (1 equivalent) was able to catalyse the hydrogenation of CO$_2$ to CH$_3$OH even in the absence of alcohol additive exhibiting a TON up to 348 (140 °C, reaction time 24 h). Recyclability of the catalyst was also demonstrated reaching a TON of 769 after 4 cycles. Notably, this was the first example of the direct hydrogenation of CO$_2$ to CH$_3$OH using a homogenous molecular catalyst without needing an additive. A mechanism as outlined in Scheme 3 was proposed on the basis of DFT calculations. Catalysis starts with the ruthenium hydride complex Ru-10A that can be generated from the hydrogenation of complex Ru-10 or Ru-11. The insertion of CO$_2$ to Ru-10A results in the formation of the ruthenium-formate complex Ru-10B that was also spectroscopically characterised. The reaction of Ru-10B with one equivalent of H$_2$ results in the formation of ruthenium–hydroxymethanolate complex Ru-10C which subsequently gets hydrogenated to form ruthenium–methanolate complex Ru-10D. The reaction of Ru-10D with H$_2$ eliminates CH$_3$OH and regenerates the ruthenium hydride complex Ru-10A.

![Scheme 3. Proposed catalytic cycle for the hydrogenation of CO$_2$ to methanol using Ru-10 catalyst. P$_3$Ru denotes the Triphos–Ru(II) fragment.](image)

Using a similar ligand system, Beller in 2017 reported hydrogenation of CO$_2$ to methanol in THF/EtOH enabled by a homogeneous catalyst of base-metal formed from the combination of [Co(acac)$_3$], Triphos, and HNTf$_2$.\textsuperscript{[78]} A TON of 50 was obtained at 100 °C at 20 bar of CO$_2$ and 70 bar of H$_2$. Later, Beller reported a higher TON of up to 125 using modified triphos ligands, [Co(acac)$_3$], and HNTf$_2$.\textsuperscript{[74]} Along a similar direction, Klankermayer in 2019 reported that a combination of Ru-
In addition to methanol, the synthesis of higher alcohols (C2–C6) from CO2/H2 is also of significant interest because of their potential applications in fuels, additives, and as chemical feedstocks. However, producing higher alcohols from the hydrogenation of CO2 is more challenging than producing methanol. Moreover, most of the catalysts reported for this transformation are heterogeneous in nature operating under harsh reaction conditions. The first example of a homogeneous catalyst for hydrogenation of CO2 to higher alcohols was reported by Tomina and co-workers using a ruthenium-cobalt bimetallic system at 200 °C resulting in the formation of a mixture of methanol, ethanol, methane, and methyl formate.[81] Qian and Han reported in the presence of a homogeneous bimetallic catalyst Ru3(CO)12/Rh3(CO)12 with LiI as a promoter, CO2 can be hydrogenated at 160 °C to give a mixture of higher alcohols such as ethanol, propanol, 2-methyl propanol, butanol, and 2-methyl butanol in addition to methanol.[82] Higher activity was reported by replacing Rh2Cl2(CO)4 with Co2(CO)8.[83] Utilizing the bimetallic catalyst [Ru2Cl2(CO)8/Co2(CO)8] and LiI as a promoter, the same group reported the efficient synthesis of ethanol using homologation of methanol using CO2 and H2.[84] Later, the same group reported that in the presence of a monometallic Ru3(CO)12 catalyst, ethanol can be synthesized under milder conditions (temperature 120 °C) with high selectivity from methanol and H2 in the ionic liquid, 1-butyl-3-methylimidazolium chloride ([bmim]Cl), using LiCl and LiI as promoters.[85] The mechanistic studies revealed that RWGS reaction first produces CO which is subsequently consumed to form ethanol by methanol homologation reaction. Interestingly, the ionic liquid e.g. [bmim]Cl was also found to promote the RWGS reaction to generate a small amount of CO under reaction conditions. Ionic liquid also assisted in the regeneration of catalyst by allowing the removal of water (under vacuum at 80 °C) which was speculated to poison the catalyst. The catalyst could also be recycled with a TON of ethanol reaching 180 after five cycles.

Expanding on the catalytic applications of the bimetallic systems Qian and Han reported the selective synthesis of ethanol from the hydrogenation of paraformaldehyde using the bimetallic system of Ru(acac)3 and CoBr2 with Li as a promoter in 1,3-dimethyl-2-imidazolidinone (DMI) under mild conditions.[86] A temperature of more than 140 °C was needed and the TOF (based on Ru metal) reached up to 17.9 h⁻¹ at 180 °C. Based on the mechanistic investigations authors suggested that the reaction proceeds via (i) hydrogenation of paraformaldehyde to methanol, (ii) reverse water gas shift reaction, and (iii) methanol homologation to form ethanol. Later, in 2019, another catalyst system Ru2(CO)12/Rh2(CO)12Cl/Li was reported to perform this transformation under relatively mild conditions.[84] Along this direction, the same group in 2018, reported a new strategy for the synthesis of ethanol from dimethyl ether, CO2, and H2 using Ru–Co bimetallic catalyst using LiI as a promoter in 1,3-dimethyl-2-imidazolidinone (DMI) solvent.[87] A high selectivity (up to 94.1%) of ethanol in the liquid products could be achieved. A more detailed review on the synthesis of higher alcohols (C1–C4) from CO2/H2 using homogeneous catalysts has been recently reported by Klankermayer, Leitner, and Liu.[88]
pharmaceutically active compounds. For example, N, N-dimethylformamide (DMF) has applications in pharmaceutical, textile, and agrochemical industries. Thus, the utilization of CO$_2$ for the synthesis of formamides is relevant to circular chemistry. The reaction has been proposed to proceed via the hydrogenation of CO$_2$ to ammonium formate followed by thermal condensation to form formamide with the elimination of water (Figure 6).\cite{27} The first report on the synthesis of DMF from the reaction of dimethylamine with CO$_2$ and H$_2$ dates back to 1969 by Haynes and co-workers.\cite{89} The best results were obtained by cobalt and iridium phosphine complexes that exhibited a TON>1000. After this seminal discovery, several ruthenium-based homogeneous catalysts were reported for the synthesis of formamides from amines using CO$_2$ and H$_2$ \cite{90,92} A highly active catalyst based on a Ru-Macho pincer complex (Ru-14, Figure 6) exhibiting TON of up to 1.94 million was reported by Ding for the N-formylation of various amines using CO$_2$ and H$_2$.\cite{93} Moreover, recycling of the catalyst was also demonstrated for up to 12 cycles for the production of N,N-dimethylformamide without significant loss of activity. Tu has recently reported a solid molecular catalyst based on the iridium-NHC coordination assembly (Ir-3, Figure 6) for the N-formylation of a variety of amines using CO$_2$ and H$_2$.\cite{94} A solid molecular catalyst allowed easy recovery of the catalyst by a simple filtration process that could be used more than 10 times without loss of activity for the production of DMF in solvent-free conditions.

In addition to precious-metal systems, a few homogeneous catalysts based on earth-abundant metals have also been reported for this transformation. Laurenczy and Beller in 2010 reported the first example of N-formylation of amines with a base-metal homogeneous catalyst [FeH$_2$(H$_2$)(PP$_3$)BF$_4$] (PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$), generated in situ from Fe(BF$_4$)$_2$:6H$_2$O and the tetraphos ligand (PP$_3$).\cite{95} DMF, the only product, was produced in 75% yield with the catalyst's TON of 727 using this strategy. A more active iron catalyst, iron(II)-fluoro-tris(2- (diphenylphosphino)phosphino)phosphino)tetrafluoroborate which could be generated from the combination of Fe(BF$_4$)$_2$:6H$_2$O and a tetradentate phosphate ligand, triis(2- (diphenylphosphino)phosphino)phosphine was reported by Beller in 2012. This showed a TON of up to 5104 with a 74% yield of DMF.\cite{96} A cobalt-based system using a precatalytic combination of Co(BF$_4$)$_2$:6H$_2$O and tetraphos ligand, P(CH$_2$CH$_2$PPh$_2$)$_3$, was used for the formation of DMF in 73% yield from NEt$_3$, CO$_2$ (30 bar) and H$_2$ (60 bar).\cite{97} All these examples of base-metal catalysts were limited to the synthesis of DMF. Han and co-workers for the first time reported a base-metal catalyst based on Cu(OAc)$_2$:4-dimethylamino pyridine (DMAP) for the synthesis of a variety of formamides from the corresponding amines, CO$_2$ and H$_2$.\cite{98} Remarkably, the catalyst was highly selective towards formylation even in the presence of unsaturated functional groups such as carbonyl groups, C=C, and CN bonds which were not affected under catalytic conditions (CO$_2$ and H$_2$ pressures of 40 bars each, temperature of 90 °C). Around a similar time, Miletin also reported a base-metal catalyst based on a cobalt pincer complex (Co-1, Figure 6) for the N-formylation of a variety of primary and secondary amines.\cite{99} In all the catalytic systems reported to date, nucleophilic primary and secondary amines have been formylated with good to excellent yields, however, we do not find any examples of successful formylation of poor nucleophiles such as anilines and their derivatives.

Several examples of heterogeneous catalysts mostly based on precious metals have also been reported in recent years for the N-formylation of amines using CO$_2$ and H$_2$.\cite{100,101,102} However, pincer catalysts, for example, the one reported by Ding (TON of 1.94 million for the N-formylation of morpholine in 97 h at 120 °C and POC$_2$ = PH$_2$ = 35 bar and that by Bemskoetter (TON = 4260 in 4 h at 120 °C and POC$_2$ = PH$_2$ = 34.5 bar) still remain to be more active catalysts in this direction.

### 2.4 Methylation of amines, imines, and arenes using CO$_2$/H$_2$

Methylation is a highly useful strategy in organic synthesis, drug discovery, and materials science. Change of pharmacological properties upon the introduction of a methyl group in heteroarenes, also known as “magic methyl effect” has been well documented.\cite{99} Nevertheless, most routes for methylation either use toxic reagents or produce stoichiometric amounts of waste creating a need for sustainable and green catalytic processes. Similar to formylation, the use of CO$_2$/H$_2$ for the purpose of methylation can be described as green and also may participate in a circular process to mitigate the excess CO$_2$. A mechanism for the N-methylation of amines proceeds first via the formation of formamides using CO$_2$/H$_2$ as discussed above (Figure 6), followed by deoxygenative hydrogenation of formamides to form N-methylated amines.\cite{100} The later step has been reported by a few organometallic catalysts such as Ru-Triphos based systems which were utilized for N-methylation reaction.\cite{101}

N-methylation of amines has been well studied by heterogeneous catalysts starting from the first report on this topic using a copper-alumina heterogeneous catalyst in 1995. Since then, several examples of heterogeneous catalysts using Ni, Pt, Pd, Co, Fe, Cu, Au, Al and Zr have been reported.\cite{102-107} Recently, well-defined molecular complexes have also been utilized for the N-methylation reactions and will be discussed in the following section. In comparison to the homogeneous catalysts, heterogeneous catalysts have demonstrated better activity for N-methylation of amines under milder reaction conditions e.g. 10 bar CO$_2$ and 25 bar H$_2$.\cite{107}

The first example for the homogeneously catalyzed N-methylation of amines using CO$_2$/H$_2$ was reported by Klankemayer and Leitner in 2013 using a catalytic combination (Ru-15, Figure 7) of [Ru(triphos) (tmm)] (tmm = trimethylpenemethane) and Bronsted acid cocatalyst trifluoromethanesulfanylisonitrile (HNTf$_2$).\cite{108} Several primary and secondary aromatic amines were N-methylation in good to excellent yields. As the dimethylaniline is found in many pharmaceutically active compounds, this path was also utilized to synthesize several N,N-dimethylaniline derivatives. Furthermore, a sequential hydrogenation/methylation strategy was
demonstrated to access unsymmetrical methyl/alkyl anilines from the corresponding amides. For example, acetanilide was converted to N-ethyl-N-methylaniline in a 69% yield in presence of CO$_2$/H$_2$ (20/60 bar) at 150 °C. Around a similar time, Beller also reported N-methylation of amines using an in-situ generated catalyst from the combination of Ru(acac)$_3$, triphos, and a Lewis or Bronsted acid (Ru-16, Figure 7).[110] Several aromatic amines were successfully N-methylated using the combination of Ru(acac)$_3$ (1 mol%), triphos (2 mol%), and methanesulfonic acid (MSA, 1.5 mol%). More nucleophilic aliphatic amines were methylated using Lewis acidic LiCl instead of a Bronsted acid such as MSA. This protocol was also applied for the selective monomethylation of aromatic diamines as well as to introduce a $^{13}$C-methyl group in drugs containing amine functionality such as desipramine and nortriptyline. Along this line, Beller demonstrated dual substitution of anilines using the combination of RCOOH that performs alkylation (-transfer of R group) and CO$_2$/H$_2$ that performs the methylation in the presence of Ru(acac)$_3$, triphos and HNTf$_2$.[110]

Utilizing similar catalytic conditions as reported for the N-methylation of amines, Klankermayer and Leitner reported N-methylation of imines using CO$_2$/H$_2$ in the presence of [Ru(triphos) (tmmm)] catalyst (Ru-9, Figure 4).[111] The synthetic application of this strategy was demonstrated by the atom-economic synthesis of an antifungal agent butenafine in one step.

2.5 Reaction of olefins with CO$_2$ and H$_2$

Olefins are useful feedstocks for a variety of reactions utilized in the industry such as alkyoxy carbonylation and hydroformylation where olefins react with CO. Utilisation of CO$_2$/H$_2$ as a CO surrogate for its subsequent reactivity with olefins would be highly green and sustainable. The Reverse Water Gas Shift (RWGS) reaction (CO$_2$ + H$_2$ → CO + H$_2$O) has been mostly studied using heterogeneous catalysts due to the unfavourable thermodynamics ($\Delta H^\circ_{298} = 42.1 \text{kJ/mol}, \Delta G^\circ_{298} = 28.5 \text{kJ/mol}$).[115] The reported heterogeneous catalysts involve precious metals that are expensive leaving the room for development using active catalysts based on earth-abundant metals.[116]

An approach where the in-situ formed CO from the RWGS reaction can be trapped with olefins to form a more stable product has been utilized to overcome the thermodynamic barrier. Some homogeneous catalysts have demonstrated promising results in this direction recently (Figure 8). The first example in this direction was revealed by Sasaki in 2000 who reported the hydroformylation of cyclohexene using CO$_2$ (4.0 MPa) and H$_2$ (4.0MPa) in the presence of H$_2$Ru$_2$(CO)$_{12}$ and LiCl in NMP solvent.[117] The product hydroxymethyl cyclohexane was obtained in 88% yield (Figure 8A). Later in 2009, Haukka reported that oligonuclear and mononuclear ruthenium carbonyl species derived from [Ru(CO)$_3$]$_2$ can catalyse both RWGS reaction and hydroformylation reaction.[118] Using this catalyst, olefins were converted to alcohols in the presence of CO$_2$ and H$_2$ with similar catalytic activity as reported earlier by Sasaki (Figure 8B). Beller and Fleischer, in 2014 reported a more active catalyst based on [Ru$_2$(CO)$_{12}$]$/\phi$ phosphite (0.5 mol% each) that converted several olefins to alcohols using CO$_2$ (30 bar) and H$_2$ (30 bar) at 130 °C (Figure 8C).[119] A few other active catalysts for this transformation have been reported recently.[120,121]
rhodium-catalyzed RWGS reaction and hydroxy carbonylation cycles.

Carboxylic acids have also been shown to be prepared from hydroxy carbonylation of alcohols using CO₂/H₂. Industrially, acetic acid is manufactured from Monsanto or Cativa process through the reaction of methanol with CO in the presence of a rhodium or iridium complex and HI. Qian and Han in 2016 reported hydroxycarbonylation of methanol from CO₂ and H₂ to form acetic acid.¹²² A bimetallic Ru-Rh catalyst bearing imidazolidine ligand was used as a catalyst and Li₂ was used as a promoter. Soon after, the same group reported the synthesis of acetic acid from methanol with CO₂ and H₂ using a simpler system based on Rh₂(CO)₅Cl₂ precursor and 4-methylimidazole (4-MI) in the presence of LiCl and LiI at 150 °C.¹²⁶ Recently, the same group reported the synthesis of higher carboxylic acids from ethers using the IrI₂ catalyst with LiI as a promoter at 170 °C, 5 MPa of CO₂, and 2 MPa of H₂.¹²⁵ More detailed reviews on the topic of carboxylation of alkenes using CO₂ have been reported by Beller¹²⁶ and Zhang¹²⁷ recently.

3. Hydrogenation of Nitrous oxide (N₂O)

Recent data show an upward increment in the atmospheric concentration of nitrous oxide (N₂O). Although, its atmospheric concentration (329.9 parts per billion in 2017) is substantially lower than that of CO₂ (405.5 parts per million in 2017), its effect on global warming is significantly higher (300 times that of CO₂).¹²⁸ Around 10-12 trillion grams of N₂O is emitted to the atmosphere annually from various sources such as agriculture (66%), energy and transport sector (15%), biofertilizer burning (11%) and other processes (8%), and with the current emission rate, the amount of N₂O in the atmosphere is going to double by 2050.¹²⁹ Several methods have been reported for the removal or neutralization of N₂O such as (i) adsorption of N₂O on surfaces e.g. activated carbons and complex oxides which upon further treatment with steam can generate nitric acid and concentrated N₂O (ii) absorption of N₂O using various liquid absorbers from some of which it is possible to regenerate N₂O and (iii) catalytic decomposition or reduction of N₂O to N₂.¹³⁰

Although the decomposition of N₂O is thermodynamically downhill, a high barrier of N₂O cleavage (+59 kcal mol⁻¹ in the gas phase) makes the process kinetically unfavourable.¹³¹ Because of the kinetic challenge, most of the examples in literature for the decomposition or reduction of N₂O involves heterogeneous catalysts such as transition metal oxides at high temperature.¹³²

The utilization of N₂O in organic synthesis is also of significant interest to mitigate the excess N₂O (Scheme 5). Heterogeneous catalysts have been employed to utilize N₂O for the synthesis of useful organic compounds. For example, Fe-containing ZSM-5 zeolites have been used for the synthesis of phenol by oxidation of benzene or its derivatives using nitrous oxide.¹³³ Similarly, the transference of ‘O’ atom from N₂O has been demonstrated for the synthesis of methanol from CH₄.¹³³ An interesting application of N₂O has been demonstrated for the synthesis of ketones from alkenes using a non-catalytic approach in the liquid phase.¹³⁴ N₂O has also been explored for the synthesis of azo compounds (Scheme 5). Applications of N₂O as a reagent in organic synthesis has been recently reviewed by Severin.¹³⁵

Neutralization of N₂O using hydrogen gas as a reductant has also been attempted. Seminal reports on the hydrogenation of N₂O has been reported using heterogeneous catalysts at temperatures of 250-500 °C.¹³⁶-¹³⁸ As homogeneous catalysts can enable a reaction to occur under milder conditions, several transition-metal-complexes have been studied for this purpose. Early works on hydrogenation of N₂O to water (N₂O → N₂ + H₂O) using a transition-metal complex have been reported by Bergman,¹³⁹ Caulton¹⁴⁰ and Piets,¹⁴¹ However, in all the cases only stoichiometric activities were reported. The first and the only example for the catalytic hydrogenation of N₂O using a homogeneous catalyst has been reported by Millstein using a ruthenium PNP pincer complex.¹⁴² Screening several ruthenium pincer catalysts for the hydrogenation of N₂O (13 mmol of H₂ in 5 mL of N₂O in THF) revealed the deaeromatized RuPNP complex. Ru-17 (Scheme 6) to be a highly active catalyst resulting in 220 TONs at 65 °C in 36 h. Complex Ru-17 was found to be converted to a new ruthenium hydride hydron oxide complex Ru-19 after the reaction. Interestingly, Ru-19 exhibited even a higher TON of 307 at 65 °C in 37 h. A mechanism was proposed using NMR spectroscopy according to which the deaeromatized complex Ru-17 reacts with H₂ gas to form a trans-dihydride complex Ru-18 that performs mono oxygen transfer of N₂O to form a ruthenium hydride hydroxyl complex Ru-19 liberating N₂ (Scheme 6). Complex Ru-19 can eliminate H₂O via metal-ligand cooperation to regenerate the deaeromatized complex Ru-17. The involvement of complex Ru-18 in the catalysis was further confirmed by using it for the catalytic hydrogenation reaction. The results showed that complex Ru-18 was the most active catalyst for the hydrogenation of N₂O. Detailed mechanistic studies have been reported using DFT by the groups of Poater¹⁴³ and Xie¹⁴⁴ who suggest that H₂O plays an important role in the overall hydrogenation process by lowering the barrier of the oxygen transfer step (Ru-18 → Ru-19).
4. Depolymerisation of plastics using catalytic (de)hydrogenation

Our growing dependence on plastics has resulted in their increased production over the years. Their omnipresence and non-biodegradable nature have caused intense plastic pollution, both on land and in oceans resulting in grievous threats to our biosphere.\textsuperscript{[143][144]} Two approaches have been used to tackle this global challenge: (a) making biodegradable plastic, and (b) recycling current plastic waste. Currently, recycling of plastic is mostly done via mechanical recycling where plastic is mechanically recycled, its quality degrades, and therefore a plastic can only be mechanically recycled a few times before it ends up in a landfill. Because of this, all the plastic produced to date, apart from those incinerated or chemically degraded, still stays in the form of plastic. Thus, mechanical recycling is not a sustainable mode of recycling as it only increases the lifetime of plastic rather than degrading it to its original form. The only sustainable mode of recycling plastic is chemical recycling where a plastic is converted to (a) its monomer from which the same virgin plastic can be made, or (b) useful building blocks that can be used as a chemical feedstock.\textsuperscript{[148][150]} Several methods have been explored for the chemical recycling of plastics such as pyrolysis, hydrolysis, glycolysis, and aminolysis.\textsuperscript{[149]} However, these methods suffer from the drawbacks of harsh reaction conditions (e.g. temperature > 250 °C) and low selectivity. Furthermore, in several cases, pyrolysis and glycolysis do not result in the same monomer which can be used to produce fresh plastic. Approach based on catalytic (de)hydrogenation has been recently utilized for the depolymerisation of plastics and is the focus of this review.

Reactions based on (de)hydrogenation pathways have been used for both the synthesis and degradation of small molecules to form a closed-loop production cycle. For example, esters can be synthesized from the dehydrogenative coupling of alcohols and the same alcohols can be regenerated from esters via the reverse reaction i.e. catalytic hydrogenation reaction (Figure 9A).\textsuperscript{[12][151]} Similarly, amides can be produced from the dehydrogenative coupling of alcohols and amines, and the same alcohols and amines used in the first place can be regenerated back from the catalytic hydrogenation of amides. This unique quality of (de)hydrogenation reactions can also be exploited to develop closed-loop production cycles of plastics such as polyesters and polyamides (Figure 9B). In the direction of the plastic synthesis using catalytic dehydrogenation process, Robertson reported the synthesis of high molecular weight polyesters from the dehydrogenative coupling of diols using Milstein’s RuPNN pincer catalyst (Ru-20, Figure 9C).\textsuperscript{[152]} Using the same RuPNN pincer catalyst (Ru-20), Guan\textsuperscript{[153]} and Milstein\textsuperscript{[154]} independently reported the synthesis of polyamides from the dehydrogenative coupling of diols and diamines (Figure 9C). Later, Keul and Møller reported a dehydrogenative synthesis of polyesters and polyamides using an N-heterocyclic carbene ruthenium complex.\textsuperscript{[155]} The reverse reaction i.e. hydrogenative depolymerisation of polyesters and polyamides have also been reported and is discussed in the following sections. Overall, using catalytic (de)hydrogenation pathways, it is possible to achieve the closed-loop production of plastics.

4.1 Hydrogenative depolymerisation of polyesters

With the global production of more than 50 million tons, polyesters, the most common of which is PET (polyethylene terephthalate), are commonly used plastics with applications in textiles, packaging, and electronics industries.\textsuperscript{[155]} Earlier reports on the chemical recycling of polyesters involve methanolysis, hydrolysis, glycolysis, and aminolysis, which have been well-reviewed in the past.\textsuperscript{[157][158]} Steady progress has also been made in the past few years regarding the degradation of polyester (waste) using the approach based on catalytic hydrogenation. The first example of catalytic hydrogenation of polyesters was...
reported in a patent by Milstein in 2013. Soon after that, in 2014, Robertson reported hydrogenative depolymerisation of polyesters into diols using Milstein’s Ru(II) PNN complexes Ru-20 (Figure 9) and Ru-5 (Table 1). Linear aliphatic polyesters were successfully depolymerised to the corresponding diols with around 80% yield in the presence of complex Ru-20 and hydrogen gas (13.6 atm, 120 °C for 48 h). However, catalyst Ru-20 was ineffective for the hydrogenation of caprolactone and PET which were achieved using RuPNNbipy catalyst Ru-5 (Table 1). To ensure solubility of partially depolymerised products a 50:50 ratio of anisole:THF was used as a solvent along with an elevated temperature. The PET was sourced from a used water bottle, which demonstrated the tolerant nature of the catalysts towards impurities and commercial additives. Higher activity of complex Ru-5 was attributed to the less sterically bulky dipyridyl backbone compared to the dimethylamino methyl arm on complex Ru-20. Catalyst Ru-5 was also able to hydrogenate polylactic acid (PLA) to polyethylene glycol with full conversion under the same conditions as that of PET. Surprisingly, polyesters such as polyhydroxybutyrate (PHB) and poly(3-hydroxypropionic acid) (P3HP), with three or four methylene units, depolymerised to give carboxylic acids rather than diols. Depolymerisation of enantiomerically pure polyhydroxybutyrate (PHB) using catalyst Ru-5 afforded butyric acid in 88% yield as the only product instead of the expected enantiomerically pure R-1,3-butanediol. Similarly, P3HP was depolymerised to propionic acid with a 90% conversion using catalyst Ru-5. The reason that carboxylic acids formed instead of diols is currently uncertain. A plausible mechanism could be via deprotonation of CHZ proton adjacent to the ester (CHZ-OC=O) group and elimination of but-3-enonic acid followed by hydrogenation of C=O bond to form butyric acid. Repetition of this step could result in the depolymerisation of polyhydroxybutyrate to butyric acid.

Table 1. Hydrogenative depolymerisation of PET.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conditions</th>
<th>% Yield</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>[Ru(triphos)tmm)] (Ru-9, Figure 4) and [Ru(triphos-xylo)tmm)] (Ru-22, Table 1)</td>
<td>1.2-propanediol with 1 mol % [Ru(triphos)tmm)] (Ru-9) catalyst and bis(trifluoromethanesulfonyl)imide (HNTf2) cocatalyst at 140 °C in 1,4-dioxane.</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>[Ru(triphos)tmm)] (Ru-9)</td>
<td>64% selectivity towards 1,4-benzene dimethanol and ethylene glycol and polybutylene terephthalate (PBT) was also converted to 1,4-benzene dimethanol and 1,4-butanediol using [Ru(triphos)tmm)] (Ru-9)</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>[Ru(triphos)tmm)] (Ru-9)</td>
<td>1,2-propanediol with 1 mol % [Ru(triphos)tmm)] (Ru-9) catalyst and bis(trifluoromethanesulfonyl)imide (HNTf2) cocatalyst at 140 °C in 1,4-dioxane.</td>
<td>&gt;99</td>
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After seminal reports by Milstein and Robertson, hydrogenative depolymerisation of PET was demonstrated by Clarke using a range of tridentate aminophosphine ruthenium complexes. Out of seven pre-catalysts, complex Ru-21 (Table 1) was found to exhibit the best performance for hydrogenation of two model diesters. This prompted a further study on the performance of complex Ru-21 towards the hydrogenative depolymerisation of PET flakes. Similar to Robertson’s initial work, anisole was used as a co-solvent in a 50/50 mixture of toluene/aniolise to improve polymer solubility. Under 50 bar of hydrogen gas and at 110 °C, 73% conversion of PET to 1,4-benzene dimethanol was obtained.

In 2018, Klankermayer reported hydrogenative depolymerisation of a range of polyesters to diols using the [Ru(triphos)tmm)] (Ru-9, Figure 4) and [Ru(triphos-xylo)tmm)] (Ru-22, Table 1) catalysts. Full conversion of polylactic acid (PLA) to 1,2-propanediol was achieved with 1 mol % [Ru(triphos)tmm)] (Ru-9) catalyst and bis(trifluoromethanesulfonyl)imide (HNTf2) cocatalyst at 140 °C in 1,4-dioxane. Polycaprolactone (PCL) was also hydrogenated (complete conversion) to produce 1,6-hexanediol as the only product. Hydrogenative depolymerisation of PET was found to be more challenging. [Ru(triphos)tmm)] (Ru-9) exhibited only 42% conversion of PET with 64% selectivity towards 1,4-benzene dimethanol and ethylene glycol. Polybutylene terephthalate (PBT) was also converted to 1,4-benzene dimethanol and 1,4-butanediol using [Ru(triphos)tmm)] (Ru-9) with only 22% selectivity. Reduced selectivity for PET and PBT was due to further reactions to form ethers favoured by the acid-activated catalyst. To enhance the yields for the hydrogenative depolymerisation of PET and PBT, a modified ruthenium catalyst, [Ru(triphos-xylo)tmm)] (Ru-22) was used. This catalyst showed higher stability and activity, resulting in full conversion of PET with 64% selectivity to the corresponding diols in the presence of 1 mol% catalyst loading and HNTf2 as a cocatalyst at 140 °C in 1,4-dioxane. PBT also showed complete conversion under the same conditions, with a selectivity of >99% towards respective diols. Using this established catalyst system, hydrogenation of commercially available PET flakes from an untreated water bottle was also demonstrated that showed full conversion with excellent selectivity, even at 0.2 mol% catalyst loading. Following this success, the reaction was carried out on PET flakes from a dyed soda bottle, synthetic pillow filling, and yoghurt pots using swollen polymers to improve solubility. Complete conversion of all the consumer products tested at 0.5 mol% catalyst loading resulted in the formation of diols with excellent selectivity. The lack of pre-treatment of the PET highlights the tolerance of this catalyst to commercial additives and pigments. Hydrogenative depolymerisation processes of various consumer products made from polyesters (PLA and PET) and a polycarbonate were also demonstrated on gram scale affording excellent yields of corresponding diols with conversion and selectivity (>99%).

In addition to the ruthenium complexes, a base-metal catalyst based on a Fe-Macho complex (Fe-3) has been utilized by de Vries and co-workers for the depolymerisation of polyesters, although using transfer hydrogenation pathway, unlike the above discussed three catalysts that use molecular hydrogen for the depolymerisation process. Remarkably, EtOH, a renewable feedstock, was used as a hydrogen source compared to the conventionally used isopropanol. In the presence of 5 mol% Fe-Macho complex (Fe-3), Dynacol 7360 which is made from adipic
acid and 1,6-hexanediol, was depolymerised to form 1,6-hexanediol in 87% yield at 100 °C in 24 h (Scheme 7).

![Scheme 7. Transfer hydrogenation of polyester using an iron-pincer catalyst.](image)

Recently de Vries and co-workers have reported an alternative strategy for the recycling of polyesters via catalytic hydrogenation (Scheme 8).[164] Authors utilized a ruthenium-triphos complex as they were earlier demonstrated for the direct reductive etherification of carboxylic acid esters to ethers.[165,166] Catalytic hydrogenation was performed using Ru(acac)3 (1 mol%) precatalyst, Triphos ligand (1.5 mol%), and a Lewis acid as a cocatalyst. The Lewis acid plays a dual role in catalysis by (a) activating the catalyst, and (b) catalysing the etherification step. In support of the latter role, when a catalytic hydrogenation reaction was performed using a 1:1 ratio of Ru(acac)3 and the Lewis acid Al(OTf)3, no ether linkage was obtained despite the full conversion of polyester, and only free diols were detected. This suggests that an additional amount of a Lewis acid is needed for the etherification step. Optimization of catalytic conditions revealed that the best activity was obtained in THF, 140 °C, 40 bar H2, 24 h in the presence of Al(OTf)3 as a cocatalyst. The ratio of the loading of Ru(acac)3 and Al(OTf)3 also showed effects on the catalytic activity. In the presence of a higher concentration of ruthenium, increasing the Al(OTf)3 amount resulted in a lower conversion of the polyester whereas at a lower concentration of ruthenium, increasing the Al(OTf)3 amount resulted in a higher conversion of the polyester. Based on mechanistic investigations such as monitoring molecular weights during catalysis and control experiments, a tandem two-step-pathway involving ruthenium catalysed hydrogenation of polyesters to diols followed by Lewis acid catalysed etherification of diols to polyethers was proposed. The strategy was also extended for the hydrogenation of a broader substrate scope of polyesters.

![Scheme 8. Ruthenium catalysed hydrogenation of polyesters to polyethers.](image)

4.2 Hydrogenative depolymerisation of polycarbonates

Although less than polyesters, polycarbonates (PC) are also commonly used plastics with an annual global demand of more than 4.3 million t with applications in the production of electronic components and construction materials.[167] Several approaches such as solvolysis, hydrolysis, methanolysis, alcoholysis, and glycolysis where PC waste is heated in the presence of a solvent/reagent at high temperature (>300 °C), have been explored for the degradation of PC.[168] With the advancement in the robust and active (de)hydrogenation catalysts, in recent years, a few examples for the hydrogenative depolymerisation of PC has also been reported. The first report on the hydrogenative depolymerisation of PC was made by Ding and co-workers in 2012.[169] In the presence of a ruthenium-Macho complex Ru-14 (15.8 mg, 0.1 mol%), KOBu (1 mol%) and 50 bar H2 (140 °C, 24 h), a sample of poly(propylene carbonate) (PPC; 2.69 g) with a weight-average molecular weight (Mw) of 100698 (Mw/Mn=1.77, >99% carbonate linkages) was depolymerised to form methanol and 1,2-propylene glycol in an almost quantitative yield. A proposed mechanism is outlined in Scheme 9. The precatalyst Ru-14 in the presence of KOBu forms the active species INT1 that activates H2 to form the ruthenium trans-dihydride species INT2 via a transition state (TS1). INT2 hydrogenates the C=O bond of the carbonate group via an outer-sphere mechanism to form an orthoformate intermediate through a transition state (TS2) that further goes to form a formate intermediate. The formate intermediate undergoes the same cycle to form diols and methanol.

![Scheme 9. Proposed catalytic cycle for the hydrogenation of a carbonate group by a ruthenium pincer complex Ru-14.](image)

Later in 2014, Robertson and co-workers used the Milstein RuPNN pincer catalysts Ru-20 (Figure 9) and Ru-5 (Table 2) for the hydrogenative depolymerisation of polypropylene carbonate and polyethylene carbonate.[169] In the presence of 1 mol% ruthenium precatalyst and 2 mol% KOBu under 54.4 bar of H2 at 160 °C, almost complete degradation of polycarbonates was observed to form a mixture of the corresponding diol and methanol in more than 99% yield. A solvent mixture of anisole and THF was used for solubility purposes. Recently, Klankermayer has also demonstrated hydrogenative depolymerisation of commercial PC using [Ru(triphos)mm] and bis(trifluoromethanesulfonyl) imide (HNTf2) (Ru-15, Figure 7) as a catalyst system at 140 °C and 100 bar H2 pressure in the 1,4-dioxane solvent.[162] Poly(bisphenol A carbonate), which is the most common type of polycarbonate, was hydrogenated to produce bisphenol A and methanol in an almost quantitative yield. Moreover, consumer products such as a compact disc (CD) and a regular beverage cup were hydrogenated to form the corresponding diols in quantitative yields in the presence of only 0.33 mol % [Ru(triphos)mm]HNTf2 catalyst (Ru-15, Figure 7). Remarkably, the impurities present in consumer products such as
In addition to ruthenium catalysts, catalysts based on earth-abundant metals have also been exploited for the hydrogenative depolymerisation of PC. Milstein and Rueping arrived at a similar conclusion as Milstein’s system, a catalytic combination of Mn-PNNH complex with an estimation of reaching up to 10.4 million tons by 2027.[173]

Like polyesters and polycarbonates, several approaches such as pyrolysis, hydrolysis, aminolysis, and glycolysis have been explored for the chemical degradation of nylon waste.[174,175] An approach based on catalytic hydrogenation for the chemical recycling of nylons or polyamides has been revealed very recently by Milstein and co-workers using ruthenium pincer complexes.[176] Compared to polyesters and polycarbonates, nylons are more difficult to hydrogenate using a homogeneous catalyst due to the presence of relatively stronger intermolecular hydrogen-bonding that makes nylons insoluble in common solvents. The solvent screening revealed that DMSO was the optimum solvent that could dissolve nylons at high temperatures and also allow the catalytic hydrogenation to occur without binding to the active site. Best catalytic activity was obtained by ruthenium pincer complexes Ru-23 and Ru-24 (2 mol%) with KO'Bu (8 mol%) under 70 bar of H2 at 150 °C that depolymerised commercial resins of nylon 6 (conversion 70-80%) to form 6-amino-1-hexanol in 24-26% yield, the rest being oligoamides (dimer to tetramer) as confirmed by the GC, NMR spectroscopy and mass spectrometry (Scheme 10).

4.3 Hydrogenative depolymerisation of nylons and polyurethanes

More than 8 million tons of nylons are currently produced globally with an estimation of reaching up to 10.4 million tons by 2027.[173]

Like polyesters and polycarbonates, several approaches such as pyrolysis, hydrolysis, aminolysis, and glycolysis have been explored for the chemical degradation of nylon waste.[174,175] An approach based on catalytic hydrogenation for the chemical recycling of nylons or polyamides has been revealed very recently by Milstein and co-workers using ruthenium pincer complexes.[176] Compared to polyesters and polycarbonates, nylons are more difficult to hydrogenate using a homogeneous catalyst due to the presence of relatively stronger intermolecular hydrogen-bonding that makes nylons insoluble in common solvents. The solvent screening revealed that DMSO was the optimum solvent that could dissolve nylons at high temperatures and also allow the catalytic hydrogenation to occur without binding to the active site. Best catalytic activity was obtained by ruthenium pincer complexes Ru-23 and Ru-24 (2 mol%) with KO'Bu (8 mol%) under 70 bar of H2 at 150 °C that depolymerised commercial resins of nylon 6 (conversion 70-80%) to form 6-amino-1-hexanol in 24-26% yield, the rest being oligoamides (dimer to tetramer) as confirmed by the GC, NMR spectroscopy and mass spectrometry (Scheme 10).

Quantitative conversion of nylon 6 (99%) was obtained using a dual hydrogenation approach where after the first hydrogenation step the catalyst was recharged and the autoclave was pressurized with 70 bar of H2 and heated at 150 °C for 72 h resulting in 37% yield of 6-amino-1-hexanol. Authors observed that 1,4-dioxane is a better solvent than DMSO for the hydrogenation of the amide bond, however, DMSO is needed for dissolving nylon 6. Thus, a higher yield of 6-amino-1-hexanol (48%) was obtained using a dual approach where after the first step of hydrogenation in DMSO, DMSO was removed and the residue was hydrogenated again in 1,4-dioxane solvent after the addition of the fresh catalyst. Other nylons such as nylon 12 and
nylon 66 as well as polyamides containing aliphatic and aromatic moieties were also successfully depolymerized (Table 3). Furthermore, a polyurethane was also hydrogenated to form a mixture of diol, diamine, and methanol. It is noteworthy that polyurethane can be synthesized from CO$_2$ thus this route also represents a proof of concept for the hydrogenation of waste polyurethane (plastic) to a useful chemical and fuel - methanol. In addition, a closed-loop chemical recycling of polyamide was also demonstrated where the monomers obtained from the hydrogenative depolymerisation step was converted back to a polyamide of the same bond-linkage and a similar molecular weight by a ruthenium catalysed dehydrogenation process.

### Table 3. Hydrogenative depolymerisation of nylons. Reproduced with permission from reference 176. Copyright American Chemical Society.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Form</th>
<th>Mol Wt</th>
<th>Conversion</th>
<th>Yield of amino alcohols, diol/diamines</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Powder</td>
<td>10,000</td>
<td>77%</td>
<td>24%</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Powder</td>
<td>11,000</td>
<td>85%</td>
<td>36%</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Resins</td>
<td>-</td>
<td>80%</td>
<td>30%</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Powder</td>
<td>3500</td>
<td>60%</td>
<td>20%</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Powder</td>
<td>1500</td>
<td>80%</td>
<td>42%</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Powder</td>
<td>4000</td>
<td>80%</td>
<td>45%</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Powder</td>
<td>2500</td>
<td>95%</td>
<td>75%</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>Powder</td>
<td>1500</td>
<td>95%</td>
<td>77%</td>
<td></td>
</tr>
</tbody>
</table>

*Catalytic conditions: Polyamide (1 mmol relative to the molecular weight of the monomer), complex Ru-23 (0.02 mmol), KOtBu (0.08 mmol), DMSO (2.5 mL), H$_2$ (70 bar), temperature 150 °C and reaction time 48 h. Two sequential hydrogenation steps both in DMSO. The hydrogenation steps first in DMSO and second in 1,4-dioxane. Ru-24 (0.05 mmol) and KOtBu (0.2 mmol), 72 h, remaining conditions as above.*

4.4 Conversion of polyethylene to fuel using cross alkane metathesis

Polyethylene (PE) is the most commonly used plastic with a global production of more than 100 million tons accounting for around 34% of the total plastic production in the world. The non-polarizable chain and absence of any functional group make PE chemically inert and most of the studies on chemical recycling of PE are based on pyrolysis (direct or catalytic) or hydrothermal processes using strong oxidizing agents such as HNO$_3$. Pyrolysis processes have the drawback of producing a random complex polymeric mixture of products, and it is not surprising that only two examples of the chemical recycling of PE on a commercial scale have been demonstrated. An approach based on catalytic (de)hydrogenation/metathesis has also been explored for the depolymerisation of PE. The concept, commonly known as cross alkane metathesis (CAM), developed by Goldman and Brookhart, is a tandem process involving (i) dehydrogenation of alkanes (a long chain and a light alkane) to
olefins in the presence of a pincer catalyst (ii) metathesis of the generated olefins catalysed by a metathesis catalyst forming new olefins of varied chain length and (iii) hydrogenation of generated olefins in the presence of the same pincer catalyst used earlier for dehydrogenation, to produce alkanes of smaller chain length. This concept was utilized by Guan and Huang for the depolymerisation of PE, which can be treated as a long alkane chain, to produce liquid fuels and waxes (Figure 10A). Utilizing an iridium PCP catalyst Ir-4 (Figure 10B) for (de)hydrogenation and Re$_2$O$_7$/γ-Al$_2$O$_3$ for metathesis resulted in a 56% degradation of HDPE (powder; weight-average molecular weight (Mw) = 3350; polydispersity index (PDI), 1.6) to oil products (C$_{22}$-$C_{40}$) using hexane as a light alkane for cross-metathesis. It is noteworthy that for a PE chain to degrade, the metathesis of an internal double bond is required. Therefore, a higher degradation (up to 98% to oil) of PE was observed when Brookhart’s bis(phosphinite)-ligated (t-BuPOCOP)Ir complexes (Ir-5,6, Figure 10B) were used, which are known for the selective formation of internal olefin, rather than a terminal olefin upon dehydrogenation.

Figure 10. A. Cross-alkane metathesis (CAM) between polyethylene and a light alkane (n-hexane); B. Iridium pincer catalysts used for (de)hydrogenation steps.

The practicality of this methodology was also demonstrated by degrading common plastic wastes without any pre-treatment such as post-consumer polyethylene bottles, bags, and films.

5. Dehydrogenation of glycerol

Glycerol is a cheap and renewable feedstock that is being produced as a by-product of the soap and biodiesel industry. Although glycerol has several applications such as in the food and medical industries, due to the recent increase in biodiesel production, the supply of glycerol has become higher than its demand. With the recent trend of biodiesel production because of its rising popularity as an alternative energy source of fossil fuel, the overproduction of glycerol is going to continue in the future. This creates urgent opportunities to utilise glycerol as a feedstock to produce useful chemicals. Utilization of glycerol for value-added products such as propanediol, acrolein, dihydroxyacetone (DHA), glycric acid (GA), and cyclic acetals or epichlorohydrin has been reviewed in the recent past. An important application is the production of syngas (CO+H$_2$) from the glycerol reforming reaction in the presence of heterogeneous catalysts. Another interesting application is the production of hydrogen gas from the steam reforming of glycerol (C$_3$H$_8$O$_3$+$3H_2$O $\rightarrow$ 3 CO$_2$ + 7H$_2$). However, due to unfavourable thermodynamics (ΔH = 128 kJ/mol), the reaction is performed at a very high temperature (800 °C) in the presence of heterogeneous catalysts. Several homogeneous catalysts have been utilized for the dehydrogenation of glycerol under mild conditions for the purpose of both hydrogen storage and organic synthesis as discussed in the following section. Various products such as dihydroxyacetone (DHA), glyceraldehyde (GAL), 1,2-propanediol (PDO), glycric acid (GA), and lactic acid (LA) can be produced from dehydrogenation type reactions of glycerol (Scheme 12).

Scheme 12. Possible dehydrogenation products of glycerol.

5.1 Acceptorless dehydrogenation of glycerol

Seminal work on the production of acceptorless dehydrogenation of glycerol was reported by Cole-Hamilton in 1988 using rhodium [Rh(bipy)$_2$Cl] (bipy = 2,2’-bipyridine) and ruthenium [RuH$_2$(N$_2$)PPh$_3$)$_2$] catalysts. However, details of the products obtained from the dehydrogenation reaction were not reported. Farnetti reported the synthesis of dihydroxyacetone (DHA) from...
the dehydrogenation of glycerol with a TON of 2-11.\textsuperscript{118} The reaction was catalysed by organoiridium complexes of the type \([\text{HIr(cod)LL}]\) (Ir-7, \text{cod} = 1,5-cyclooctadiene; \(L = \text{Pr}^2-\text{N(CH}_3\text{CH}_2\text{CH}_2\text{PPPh}_2\)), \(\text{Et}_3\text{NCH}_2\text{CH}_2\text{N(CH}_3\text{CH}_2\text{CH}_2\text{PPPh}_2\)), \(\alpha\)-\(\text{Me}_2\text{NC}_6\text{H}_4\text{PPPh}_3\)). Both acceptorless dehydrogenation and dehydrogenation in the presence of a hydrogen acceptor were demonstrated (Scheme 13).

Examples of the conversion of glycerol to lactic acid have been reported using hydrogenolysis under basic conditions in the presence of heterogeneous catalysts.\textsuperscript{189-193} However, these processes suffer from the drawbacks of harsh reaction conditions (temperature \(-200\, ^\circ\text{C}\)) and lower chemoselectivity. Recently, Campos and Crabtree have reported the first example of acceptorless dehydrogenation of glycerol to lactic acid.\textsuperscript{194} Several cationic iridium complexes (0.007 mol\%) were screened for the dehydrogenation of glycerol under basic conditions of 8 M KOH (0.6 equiv. with respect to glycerol) at 115\, ^\circ\text{C} for 15\, h. A TON of 1150 (Ir-8, Figure 11) and 2400 (Ir-9, Figure 11) were obtained. Remarkably, with Ir-10 (Figure 11), a TON of 30,100 was obtained using only 20 ppm of catalytic loading. Furthermore, the selectivity of lactic acid was also found to be excellent (up to 97\%) with propanediol, ethylene glycol, and formic acid being the main side products. In this direction, Tu, in 2015 reported dehydrogenation of glycerol to LA using a coordination polymer of iridium (Ir-11, Figure 11) as a catalyst with a TON of up to 1.24 \times 10^8 even in a large-scale reaction under neat conditions.\textsuperscript{195} Around the same time, Beller reported dehydrogenation of glycerol to lactic acid using ruthenium-pincer catalysts.\textsuperscript{196} The best results were obtained using Ru-Macho catalyst Ru-14 (Figure 11) at 140\, ^\circ\text{C} in N-methylpyrrolidinone solvent under basic condition (NaOH) exhibiting TONs of up to 265,000 and a moderate selectivity of LA (67\%). Soon after, Williams in 2016 reported a highly active iridium catalyst Ir-12 (Figure 11) for the dehydrogenation of glycerol to LA under basic conditions exhibiting the highest TON of 4.56 \times 10^6 for this transformation.\textsuperscript{197} Remarkably, dehydrogenation of crude glycerol obtained directly from a biodiesel refinery was also demonstrated using the catalyst Ir-12 with high selectivity of up to 99\%. Recently, Voutchkova-Kosta has reported a series of water-soluble iridium catalysts for the conversion of glycerol to LA under basic conditions.\textsuperscript{198} The iridium complex \([\text{[(NHCH}_3\text{C}_6\text{H}_4\text{PPh}_3\text{)}_2\text{Ir}\text{(CO)}_2\text{SO}_4\text{]}}\) (Ir-13, Figure 11), was found to be the most active catalyst exhibiting a TOF of 45, 592 h\(^{-1}\) under microwave conditions and performed 2,932,249 turnovers in 8 hours.

In addition to the precious metals, one example of the base-metal catalyst for the dehydrogenation of glycerol to LA has also been reported by Crabtree and Hazari in 2015.\textsuperscript{199} Several iron PNP pincer catalysts (0.02 mol\%) were screened under basic conditions (NaOH) at 140\, ^\circ\text{C} for 3\, h revealing pincer borohydride and formate complexes Fe-3 and Fe-5 (Figure 11) to be the most active catalysts, exhibiting TON of up to 1050. A mechanism involving an amide complex Fe-2 and a dihydride complex Fe-3A was proposed as outlined in Scheme 14. Complex Fe-2 can be formed from Fe-4\('\) by amine-deprotonation and the concomitant loss of chloride. Complex Fe-3A can be formed by base-assisted loss of BH\(_3\) from Fe-3 or a Lewis acid assisted decarboxylation of Fe-5. The amide complex Fe-2 dehydrogenates glycerol to form glyceraldehyde and the dihydride complex Fe-3A. Glyceraldehyde is converted to lactic acid through a series of base-catalysed reactions – dehydration, tautomerization, and intramolecular Cannizaro reaction as shown in Scheme 14. Lactic acid is trapped as a corresponding salt in the presence of a base and the dihydride complex Fe-3A releases H\(_2\) via metal-ligand cooperation to regenerate complex Fe-2.

5.2 Glycerol as a hydrogen source for the transfer hydrogenation reactions

An important research topic in the area of catalytic transfer hydrogenation (TH) is to find a renewable, abundant, and nontoxic chemical that can act as a hydrogen source. Glycerol with the current market stage of overproduction fits well in these criteria. Moreover, it has a number of advantages to be used as a solvent. For example, (a) it has a high solubility of inorganic salts, acids, and bases, and (b) because of its high boiling point, reactions can be carried at high temperatures, and products can be easily distilled out from the reaction. A few examples have been reported for using glycerol in TH reactions using...
homogeneous catalysts (Figure 12). The first example was reported by Crotti in 2009 using organoiridium complexes of the type $\text{Ir}($dienen$)($N-H)X$ (dienen = 1,5-hexadiene, 1,5-cyclooctadiene; N-H = 2,2'-bipyridine, 1,10-phenanthroline and substituted derivatives; X = Cl, I) under basic conditions.$^{[200]}$

![Figure 12. Transfer hydrogenation of organic compounds using glycerol as a hydrogen source.](image)

Acetophenone was hydrogenated to phenyl ethanol at 100°C using glycerol as a hydrogen donor source, where glycerol was transformed into dihydroxyacetone. In the same year, Tavor reported transfer hydrogenation of aldehydes and ketones using glycerol in the presence of $[\text{Ru}(p$-cumene)Cl$_2$]$_2$ as a catalyst.$^{[200]}$ Along this direction, Farnetti in 2010 reported transfer hydrogenation of acetaldehyde, cyclohexanone, styrene, and aldehyde using glycerol in the presence of organoiridium catalysts. In 2011, Mata and Peris reported transfer hydrogenation of aldehydes and ketones using glycerol as a hydrogen donor and solvent.$^{[201]}$ Remarkably, the selective reduction of olefinic double bonds was observed for $\alpha,\beta$-unsaturated ketones. The reaction was catalysed by Ir(III) complexes Ir-14 and Ir-15 (Figure 13) featuring electron-rich chelating bis-NHC ligand and tethered sulfonate group that enhances the solubility of catalyst in glycerol. Soon after that in 2012, Mata and Colacino reported more active iridium NHC catalysts Ir-16 and Ir-17 (Figure 13) for the transfer hydrogenation of aldehydes and ketones using glycerol.$^{[202]}$ Dihydroxyacetone was observed as the main dehydrogenation product of glycerol.

In 2017, Voutchkova-Kosta reported a series of ruthenium(II) and iridium(III) N-heterocyclic carbene (NHC) complexes functionalized with sulfonates for the transfer hydrogenation of aldehydes, ketones, and imines using glycerol.$^{[203]}$ Catalyst Ru-15 (Figure 13) was found to be the most active for the TH of ketones whereas catalyst Ir-18 (Figure 13) was found to be the most active for the TH of imines and aldehydes.

In addition to the TH of aldehydes, ketones, imines, and olefins, glycerol has also been utilized for the TH of levulinic acid which can be derived from biomass. Recently, Voutchkova-Kosta reported highly active catalysts based on iridium N-heterocyclic carbene (NHC) complex for the TH of levulinic acid to Y-hydroxycarboxylic acid (GHV) using glycerol as a hydrogen donor under basic conditions (KOH) at 150°C.$^{[204]}$ A quantitative yield of GHV was obtained using just 1 ppm of catalyst Ir-13 (Figure 11) exhibiting a TON of 101,100 and TOF of 50,550 h$^{-1}$. Glycerol was dehydrogenated to form lactic acid.

![Figure 13. Homogeneous catalysts for transfer hydrogenation using glycerol as a hydrogen source.](image)

Along the direction of utilizing glycerol as hydrogen donors for the TH reactions, Voutchkova-Kosta reported TH of CO$_2$ to formate under basic conditions catalysed by a water-soluble ruthenium-NHC complex (Ru-16, Figure 13).$^{[205]}$ The catalytic activity was found to be dependent on the pH as under low pH conditions the reverse reaction i.e. dehydrogenation of HCOOH to CO$_2$ was also operative. A higher pH was achieved by reducing CO$_2$ pressure as the solubility of KOH would increase on decreasing CO$_2$ concentration. Indeed, reducing CO$_2$ pressure from 48 bar to 26 bar almost doubled the catalytic activity. Similarly, the catalysis was found to be dependent on temperature as at a higher temperature thermal decomposition of potassium carbonate formate was more favorable. Thus, the best activity was obtained by optimizing both the temperature and the base concentration. At 150°C, CO$_2$ (26 bar) was hydrogenated in the presence of Ru-16 (Figure 13), KOH (2 M), and glycerol (6.85 M) to produce an equimolar amount of lactate and formate (~600 turnovers). Additionally, carbonate salts such as K$_2$CO$_3$ can also be hydrogenated under the same conditions to form the same products with an even higher rate exhibiting TONs of 42,610 (lactate), 3,588 (formate), and 5,649 (1,2-propanediol). Recently, Choudhury has also reported TH of CO$_2$ to formate using an iridium catalyst of the type [Cp$^*$$\text{Ir}$(NHC–benzimidazolato)] (Ir-19, Figure 13).$^{[206]}$ Compared to the system reported by Voutchkova-Kosta that operates at 26 bar CO$_2$ and gives TOF of 44 h$^{-1}$ (24 h), Choudhury’s system can work under 1 bar CO$_2$ pressure exhibiting a higher TOF of 90 h$^{-1}$ (12 h) at 150°C. Very recently, Jung and Jang have developed a superior catalyst for the TH of inorganic carbonates (K$_2$CO$_3$, KHCO$_3$, Na$_2$CO$_3$, NaHCO$_3$) using all carbonates as hydrogen donors.
glycerol to form formates and lactates exhibiting higher TONs and TOFs for formates (TON 16,856 and TOF 843 h⁻¹) and for lactates (TON 32,609 and TOF 1630 h⁻¹). The reaction is catalysed by Ir(bis-carbene) complexes where catalytic activity was found to be strongly dependent on the structural properties of biscarbene ligands, such as the length of the alkyl chain between two carbene moieties.[207]

6. Summary and Outlook

Processes based on catalytic (de)hydrogenation present attractive opportunities to transform chemical waste products into valuable resources or feedstocks enabling a circular economy. However, a central challenge remains on the production route of hydrogen gas. Most of the hydrogen gas is currently produced from fossil fuels that emit CO₂ in the atmosphere. Thus, in order to utilize (de)hydrogenation technologies for circular economy and sustainable reactions, it is crucial to develop parallel economic and efficient green technologies for the production of hydrogen gas such as water electrolysis using renewable energy or production of hydrogen gas from biomass.

Although it cannot be claimed that conversion of CO₂ to useful feedstock can solve the burning issues of climate change, but it would certainly allow us to be less dependent on fossil fuels and cut the carbon emission to a significant extent. Plenty of research has been developed which consumes CO₂ using (de)hydrogenation pathways to make several highly useful chemical feedstocks such as formic acid and methanol. Due to unfavorable thermodynamics, direct hydrogenation of CO₂ to HCOOH under neutral conditions is challenging, and therefore most of the active catalytic systems are based on using a stoichiometric amount of a base posing an economic and sustainability hindrance in front of commercialization of this process. In the case of methanol, a few catalysts, although heterogeneous ones have been demonstrated at the pilot plant scale for the hydrogenation of waste CO₂ to methanol. The ‘greenest’ renewable methanol in the world is produced by Carbon Recycling International (CRI) using hydrogenation of CO₂ where H₂ is produced from a renewable source. Utilizing Emission to Liquid technology, the plant has the annual capacity of producing 50,000–100,000 tons of methanol.[208]

Whereas substantial efforts have been dedicated towards CO₂ reduction, the area of N₂O reduction has received scant attention. Only one example has been reported for the direct hydrogenation of N₂O using a homogeneous catalyst (Scheme 6). A new and challenging direction in the area of N₂O reduction could be direct hydrogenation of N₂O to NH₃ or N₂H₄ using molecular hydrogen.

The crisis of plastic pollution is one of the biggest growing concerns of recent times, and in the past decade, several processes have been demonstrated for the closed-loop recycling of plastics. Methods based on catalytic (de)hydrogenation using molecular complexes have also been explored for both production and degradation of plastics although only at the proof of concept level as discussed above. More efforts need to be diverted towards developing active, inexpensive, and recyclable catalysts that could lead to the commercialization of such processes.

Likewise, although dehydrogenation of waste glycerol for the production of dihydroxyacetone and lactic acid have been reported, there are several scopes of development of efficient catalyst and new dehydrogenative coupling reactions involving glycerol such as dehydrogenative coupling of glycerol to make useful plastic such as polyesters, polyamides, and polycarbonates. Moreover, glycerol which is a renewable hydrogen-rich liquid has not yet been demonstrated for a Liquid Organic Hydrogen Carrier. New ligand design could facilitate the discovery of new (de)hydrogenation catalysis involving glycerol.

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Keywords: Homogeneous Catalysis • Hydrogenation • Dehydrogenation • Circular Chemistry • Green Chemistry

REVIEW


[73] J. Schneidewind, R. Adam, W. Baumann, R. Jackstell, M.


REVIEW


Our current dependence on rapidly depleting resources and the growing accumulation of chemical waste have become a grave concern to our society. This has sparked interest in the contemporary catalysis community to develop green technologies for the chemical conversion of waste products to valuable feedstocks enabling the circular economy. This article reviews the applications of homogeneous (de)hydrogenative catalysis for the conversion of chemical waste products – CO₂, N₂O, plastics, and glycerol to useful chemical feedstocks.