Ruthenium-promoted reductive transformation of CO₂

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The reductive transformation of CO₂ to energy related products including formic acid, CO, formamide, methanol and methylamine could be a promising option to supply renewable energy. In this aspect, ruthenium has found wide application in hydrogenation of various carbonyl groups, and has successfully been applied to reductive transformation of CO₂ with high catalytic efficiency and excellent selectivity. In addition, ruthenium complexes have also served as effective photosensitizers for CO₂ photoreduction. Classified by reductive products, this review summarizes and updates advances in the Ru-catalyzed reduction of CO₂ along with catalyst development on the basis of mechanistic understanding at a molecular level.

carbon dioxide chemistry, homogeneous catalysis, reductive transformation, ruthenium, sustainable chemistry


1 Introduction

The concentration of carbon dioxide has been increasing continuously in the atmosphere in recent decades [1]. With the rapid consumption of fossil fuels, it is urgent to develop alternative energy sources in a sustainable way. Therefore, the utilization of CO₂ as a raw material to afford valuable compounds has drawn considerable attention [1g]. During the last decades, CO₂ has been intensively investigated as a promoter [2], reaction media [3] and sustainable chemical feedstock [4] for organic synthesis. Among versatile applications of CO₂, the reduction of CO₂ to formic acid, CO, formamide, methanol, methylamine and CH₄ has aroused increasing interest recently due to potential utilization of CO₂ as a nontoxic, nonflammable, cheap and renewable raw material for chemical production or as an energy vector to store or harvest renewable energy [5]. In this aspect, because of its thermodynamic stability and kinetic inertness [6], activation of both CO₂ and H₂ could be crucial to performing CO₂ reduction successfully.

Among versatile metal catalysts, Ru complexes have been found to be robust with high efficiency to afford various reductive compounds such as formic acid, CO, formamide, methanol, methylamine. From the mechanistic point of view, Ru works in a similar catalytic pathway for the reduction of both CO₂ and other carbonyl compounds [7]. As such, the hydride of the Ru–H species readily moves to the carbon atom of the carbonyl group. As a result, the catalytic species still remains active even in a strong basic environment [8]. On the other hand, heterogeneous ruthenium catalysis has also been established in the early stage to facilitate the noble metal catalysts [9], although homogeneous catalysis provides great efficiency. In addition, Ru complexes have also been utilized for CO₂ electroreduction and photoreduction. In the case of CO₂ photoreduction, the Ru-bpy complex is used as a kind of active heterogeneous photosensitizer [10]. In this minireview, we would like to summarize recent progress in the reductive transformation of CO₂ catalyzed by
Ru complexes, in particular, the activation methodologies for both CO₂ and hydrogen molecules, which leads to the improvement in the reduction efficiency and product selectivity.

2 Reduction of CO₂ to formic acid

Formic acid has been widely employed for the production of leather, textile and latex rubber in industry [11]. On the other hand, formic acid is also considered to be a hydrogen-store material with capacity of resolving or releasing H₂ [12]. Although the hydrogenation of CO₂ with hydrogen produces formic acid with 100% atom efficiency [5e,13], this is thermodynamically unfavorable when CO₂ and H₂ are the gas phase (Scheme 1(a)) [14]. In order to render the reaction smoothly (ΔG<0), an additional base is required (Scheme 1(b)). If water or other solvent that can form hydrogen bonding to stabilize formic acid is employed as reaction media, the reaction can readily perform in a thermodynamically favorable manner (Scheme 1(c)) [5e,13].

The aluminum oxide-supported ruthenium is the first heterogenous catalyst for hydrogenation of CO₂ to formic acid [9], unfortunately the turnover number (TON) is only 120. On the other hand, the first homogeneous Ru catalyst, K[Ru(dii)(EDTA-H)Cl]·2H₂O, was reported in 1989 [15]. In contrast to the Rh-based catalysts [16], Ru shows higher activity. Herein we would like to give an overview on the catalyst development in terms of ligand designing as well as mechanistic analysis.

2.1 Phosphine ligand

In 1994, Jessop et al. [17] introduced RuH₂(PMe₃)₄ and RuCl₃(PMe₃)₃ as the scCO₂-soluble (supercritical CO₂) catalyst for the hydrogenation of CO₂ to formic acid in NEt₃ and MeOH with turnover frequency (TOF) up to 1400 h⁻¹ and TON up to 7200 at 50 °C under 20.5 MPa (scCO₂). The addition of basic additive further improves the reaction efficiency, thus the TOF of 95000 h⁻¹ with RuCl₂(O₂CC₂H₅)(PMe₃)₂ is obtained in the presence of NEt₃ and pentafluorophenol [18]. The in situ nuclear magnetic resonance (NMR) study under pressure shows that the alcoholic additive induces the catalyst precursor to generate the cationic species and the alcohol works as a hydrogen bonding donor. Besides organic bases, inorganic bases are also effective. Laurenczy et al. reported the hydrogenation of CO₂ in NaHCO₃ aqueous solution by employing the water-soluble [RuCl₃(TPMP)$_2$]⁺ (TPPMS=monosulphonated triphenylphosphane) [19] and RuCl₃(PTA)$_4$ (PTA=1,3,5-triaza-7-phosphaadamantane) [20]. In these reactions, HCO$_2^-$ is actually hydrogenated with the maximum TOFs of 807 and 9600 h⁻¹ respectively. The PTA as a ligand plays an important role in CO₂ hydrogenation [20,21]. The nitrogen atom of PTA, which has a strong basicity, can serve as a hydrogen bonding or proton acceptor to activate HCO$_3^-$ . In this context, the formation of [η₅-(C₆H₅)RuH(PTA)$_2$]$^+$ is regarded as the major hydride species, and a possible mechanism involving hydride transfer to bicarbonate is proposed as depicted in Scheme 2 [21b,21c].

Furthermore, biphosphine ligands are also proven to be efficacious. [RuCl₃(C₆H₅)$_2$]: has been reported as a catalyst precursor cooperating with dpmm [bis(diphenylphosphino)methane] for efficient hydrogenation of CO₂ in aqueous NaHCO₃ [22].

2.2 Pincer ligand

Pincer ligands have been widely applied in CO₂ hydrogenation to formic acid with excellent TONs and TOFs, being attributed to the strong chelating abilities. This geometrically restricted structure can affect the coordination of the substrate to metal, thus resulting in enhanced the product selectivity [23]. Recently, the highest TOF (1100000 h⁻¹) has been achieved by using Ru-complex as reported by Pidko and co-workers [24]. The Ru-PNP complex i.e. RuCl₂(H)(CO)(PNP) PNP$^-$=2,6(CH₃PtBu₂);C₆H₅N shares a similar structure to that of Ir-PNP complex (Scheme 3) [25]. DFT calculation and in situ NMR technique have been intensively applied to mechanistic investigation (Scheme 3) [24b]. As speculated, the bis-hydride Ru complex 4 is regarded as the active species, while the ligand-assisted CO₂ adduct 3 is inactive. The two routes that do not involve the metal-ligand cooperation are predicted to be predominant, which can be controlled by changing H₂ pressure. Recently, Ru(Acrrophos)(PPh₃)(Cl)(PhCO$_2$): [Acrrophos=4,5-bis(diphenylphosphino)acridine] has been developed for the hydrogenation of CO₂ to formic acid in dimethyl sulfoxide (DMSO) or DMSO/