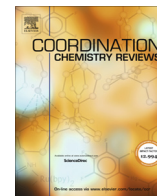




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Review

Reaction mechanisms of catalytic photochemical CO₂ reduction using Re(I) and Ru(II) complexesYusuke Kuramochi^a, Osamu Ishitani^{b,*}, Hitoshi Ishida^{c,*}^a Department of Chemistry, Faculty of Science Division II, Tokyo University of Science, 1-3, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan^b Department of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1-NE-1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan^c Department of Chemistry, Graduate School of Science, Kitasato University, 1-15-1 Kitasato, Minami-ku, Sagami-hara, Kanagawa 252-0373, Japan

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ABSTRACT

Reduction of CO₂ is one of the most important reactions that might solve the problems of global warming and shortage of fossil-fuel resources simultaneously. Metal complex catalysts are sometimes called molecular catalysts because they can be designed and synthesized on the molecular level. Some metal complexes are quite efficient and selective for CO₂ reduction. Recently, such complexes have been applied as semiconductor photocatalysts to yield hybrid metal complex/semiconductor systems. Compared to heterogeneous catalysts, metal complexes are more advantageous for elucidating reaction mechanisms. This review summarizes the reaction mechanisms that have been proposed for the photochemical CO₂ reduction reaction catalyzed by rhenium and ruthenium complexes. Rhenium complexes efficiently reduce CO₂ to selectively produce CO under various reaction conditions. On the other hand, ruthenium complexes yield CO and HCOOH, and the product selectivities are strongly dependent on the reaction conditions. Numerous reaction mechanisms have been proposed; however, no universal mechanism that can completely explain the activities and product selectivities of these catalysts exists. Why are two important intermediates, the η^1 -CO₂ adduct and the hydride complex, proposed? How does the η^1 -CO₂ adduct produce HCOOH? Does the hydride complex yield CO via the formate complex? What is the second electron source for the intermediate that produces CO and HCOOH? This review highlights what is already known about photocatalytic CO₂ reduction reaction mechanisms and what remains to be clarified.

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Abbreviations: 6Mesbpy, 6,6'-mesityl-2,2'-bipyridine; BIH, 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole; BNAH, 1-benzyl-1,4-dihydronicotinamide; bpy, 2,2-bipyridine; CV, cyclic voltammetry; dmb, 4,4'-dimethyl-2,2'-bipyridine; D, electron donor; DMA, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; DMSO, dimethylsulfoxide; EtOH, ethanol; HPLC, high-performance liquid chromatography; IR, infrared; MLCT, metal-to-ligand charge transfer; MOF, metal-organic framework; NMP, N-methyl-2-pyrrolidone; N[^]N, diimine ligand; OERS, one-electron reduced species; phen, 1,10-phenanthroline; ppy, 2-phenylpyridine; PS, photosensitizer; SCE, saturated calomel electrode; SHE, standard hydrogen electrode; TEA, triethylamine; TEOA, triethanolamine; TOF, turnover frequency; TON, turnover number; tpy, 2,2':6'2''-terpyridine.

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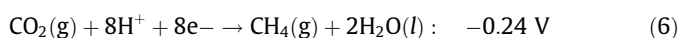
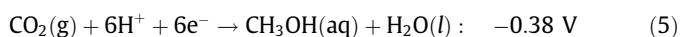
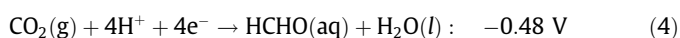
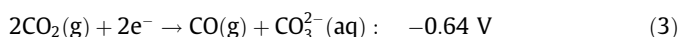
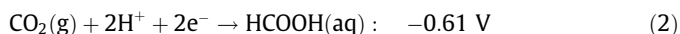
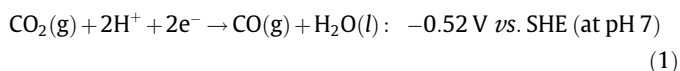
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1. Introduction

CO₂ emissions from the massive consumption of fossil fuels are seriously changing the global climate: increases in atmospheric CO₂ concentrations cause global warming as well as ocean acidification from the uptake of atmospheric CO₂. The inevitable depletion of fossil fuels and energy shortage problems also confront the world. As fossil fuels are produced from ancient solar energies over a long period of time, the fact that humankind has rapidly consumed so many fossil-fuel resources, both as energy and chemical resources, in a very short period of time should be regarded as a serious problem. To solve these problems, development of systems that convert CO₂ into energy-rich compounds with the aid of solar energy input is desirable. The so-called solar fuels are a more attractive method of solar-energy storage than others, such as solar batteries, from the viewpoint of high energy densities and long-term storage of fuel reserves [1]. Various technologies that indirectly and directly convert CO₂ into solar fuels have already been developed. As examples of indirect conversion, the conversion of biomass into biofuel has been demonstrated on a practical level [2], and the hydrogenation of CO₂ into energy-rich carbon-containing molecules, whose reaction uses hydrogen produced from the electrolysis of water using photovoltaic electricity or solar water splitting using photocatalysts, has been widely investigated [2–4]. In addition, the direct conversion of CO₂ into energy-rich carbon-containing molecules via electrochemical and photochemical reactions has attracted much attention because intermediate energy carriers, which sometimes cause storage and transportation problems, are not necessary. Mostly, the direct conversion of CO₂ has been carried out by reduction in the presence of a catalyst. The one-electron reduction of CO₂, which is not expected to be a productive method for CO₂ utilization, yields a CO₂ radical anion that has a very high potential (−1.9 V vs. SHE for CO₂/CO₂^{•−} in water at pH 7) [5]. However, alternative processes, including two-electron and greater-than-two-electron reduction of CO₂, can yield stable energy-rich products at relatively low potentials: two-electron reduction yields CO and HCOOH; four-, six-, and eight-electron reductions afford HCHO, CH₃OH, and CH₄, respectively. The equilibrium potentials of various CO₂ reductions (pH 7 in water at 25 °C, 1 atmosphere gas pressure, and 1 M for the other solutes) are summarized in the following equations [6,7]:



The CO₂ reductions described in this review are almost entirely limited to the two-electron reduction catalysis that yields CO (Eqs. (1) and (3)) and/or HCOOH (Eq. (2)). Both CO and HCOOH are useful and desired CO₂ reduction products. For example, CO can be converted into liquid hydrocarbons using the Fischer–Tropsch reaction [8]. HCOOH is useful as a liquid storage material for H₂ because HCOOH can be easily converted to H₂ using catalysts under moderate conditions [9].

To achieve CO₂ reduction, catalysts that lower the reduction activation energies are necessary. As the activation energy corresponds to the overpotential in an electrochemical reaction, efficient catalysts might undergo the reaction when the potential is near the equilibrium potential. It should be noted that the two-electron reduction of CO₂ (Eqs. (1–3)) is less thermodynamically favorable compared to H₂ formation from protons (−0.41 V vs. SHE for H⁺/H₂ in water at pH 7). Therefore, CO₂ reduction catalysts require specificity such that they cannot readily reduce water to H₂ but can reduce CO₂. Such catalysts also require properties for driving the multi-electron reduction process for CO₂ reduction, as described above. Metal complexes have multiple accessible redox states in both the central metal and the ligand(s); thus, a multi-electron reduction process becomes feasible. Metal complexes can be synthesized using various designs, which allow us to search for efficient CO₂ reduction catalysts. Various metal complexes have been investigated as CO₂ reduction catalysts to date (Fig. 1) [7,10–28]. The following complexes have been reported as CO₂ reduction catalysts: manganese mono(bipyridyl) tricarbonyl [29–31], cobalt and iron porphyrin [32–37], iron bis(1,10-phenanthroline)bis(thiocyanate) and polypyridyl [38,39], cobalt tris(bipyridyl) [40,41], cobalt macrocycle [42–44], nickel cyclam [45–47], nickel *N*-heterocyclic carbene–isoquinoline [48], nickel S₂N₂-type tetradenate [49], dinuclear copper [50,51], molybdenum and tungsten mono(bipyridyl) tetracarbonyl [52], rhodium bis(bipyridyl) [53,54], palladium phosphine [55], rhenium mono(bipyridyl) tricarbonyl [56–59], osmium mono(bipyridyl) dicarbonyl [60,61], iridium dihydride pincer, iridium poly(pyridyl) [62,63], ruthenium mono(bipyridyl), and ruthenium bis(bipyridyl) dicarbonyl complexes [64–68]. Most of the metal complexes yield CO and/or HCOOH as the two-electron reduction products of CO₂, whereas some complexes produce oxalate (oxalic acid) [46] and methane [37]. Since some of the metal complexes have high activation energies for the proton reduction, a highly selective CO₂ reduction can proceed even under aqueous conditions.

Metal complex catalysts for CO₂ reduction can be applicable in heterogeneous photocatalytic systems. Semiconductor photocatalysts containing metal complexes have recently been developed for CO₂ reduction [69–93]. Various other hybrid systems combining metal complex catalysts with different types of materials, e.g., electrode [94–101], periodic mesoporous organosilicas (PMOs) [102–106], and metal–organic frameworks (MOFs) [107–115], have also been developed in recent years. Some of the hybrid photocatalysts show very high activities and advantageous possibilities for recycling. However, in many cases, the catalytic reaction mechanisms are not yet deeply understood.

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