Microporous Materials

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Photochemical Reduction of Low Concentrations of CO_2 in a Porous Coordination Polymer with a Ruthenium(II)–CO Complex

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Abstract: *Direct use of low pressures of CO_2 as a C1 source without concentration from gas mixtures is of great interest from an energy-saving viewpoint. Porous heterogeneous catalysts containing both adsorption and catalytically active sites are promising candidates for such applications. Here, we report a porous coordination polymer (PCP)-based catalyst, PCP-Ru^{II} composite, bearing a Ru^{II}-CO complex active for CO_2 reduction. The PCP-Ru^{II} composite showed improved CO_2 adsorption behavior at ambient temperature. In the photochemical reduction of CO_2 the PCP-Ru^{II} composite produced CO, HCOOH, and H_2. Catalytic activity was comparable with the corresponding homogeneous Ru^{II} catalyst and ranks among the highest of known PCP-based catalysts. Furthermore, catalytic activity was maintained even under a 5% CO_2/Ar gas mixture, revealing a synergistic effect between the adsorption and catalytically active sites within the PCP-Ru^{II} composite.*

Use of CO_2 as a C1 source is an important contemporary research topic for various reasons, such as reducing CO_2 emissions and developing an alternative energy feedstock for fossil fuels. Transformations of CO_2 into organic chemicals have been studied extensively.[1] Among these processes, CO_2 reduction (hydrogenation) is of particular interest because the products (for example CO, HCOOH, MeOH, and CH_4) are regarded as energy carriers and are key materials in C1 chemistry. Although several homogeneous and heterogeneous catalysts with high efficiency have been developed for such reactions, they usually require high temperature and/or high CO_2 pressures,[1,2] which is unfavorable from both energetic and economic viewpoints. In this context, direct use of low partial pressures of CO_2 without concentration from gas mixtures, such as flue gas (5–15% CO_2) and air (400 ppm CO_2),[2] are interesting from an energy-saving perspective.

Porous heterogeneous catalysts containing both adsorption and catalytically active sites are promising candidates for catalyzed CO_2 transformations. Porous coordination polymers (PCPs), also known as metal–organic frameworks (MOFs),[3] are a new class of porous heterogeneous catalysts with highly tailorable characteristics.[4] Several research groups have reported PCP-based catalysts for CO_2 reduction,[5–8] with a characteristic focus upon the stability of heterogeneous catalysts over extended periods, or their recyclability. Although CO_2 capture and separation have been actively investigated within the PCP research field[9] the adsorption properties of these materials have not been adequately correlated with their catalytic properties. Herein, we report a new PCP-based catalyst with a Ru^{II}-CO complex, $[Ru^{II}(bpy)(terpy)(CO)](PF_6)_2$ (**1**; bpy = 2,2′-bipyridine, terpy = 2,2′:6′,2′′-terpyridine; Supporting Information, Scheme S2),[10] incorporated in the form of a metallolinker. After integrating the CO_2 reducing catalyst **1** into a CO_2-adsorptive PCP, the resulting PCP-Ru^{II} composite produced CO and HCOOH with high turnover numbers (TONs), and especially at low CO_2 concentrations. Notably, differing product selectivity was observed between the PCP-Ru^{II} composite and **1**.

To incorporate **1** into a PCP, we designed and synthesized a new derivative, $[Ru^{II}(H_2bpydc)(terpy)(CO)](PF_6)_2$ (H_2**RuCO** or **2**; bpydc = 2,2′-bipyridine-5,5′-dicarboxylate), bearing carboxy substituents (Supporting Information, Scheme S2). Complex **2** was characterized by ^1H, ^{19}F, and ^{31}P NMR spectroscopy, IR spectroscopy, high-resolution mass spectrometry, and X-ray single-crystal structural analysis (Supporting Information, Figure S1 and Table S2). As the parent framework we chose a Zr^{IV}-based PCP, UiO-67, formulated as $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(bpdc)_6]_\infty$ (Zr-bpdc; bpdc = biphenyl-4,4′-dicarboxylate; Scheme 1) because 1) the structure of the organic linker bpdc in the PCP is quite similar to that of bpydc in **2**; 2) it has large enough three-dimensional pores to incorporate the bulky metallolinker **2**; and 3) it shows relatively high thermal and chemical stability among the reported PCPs.[11] We found that **2** was successfully incorporated into Zr-bpdc by utilizing the post-synthetic exchange (PSE) method,[12] yielding a PCP-Ru^{II} composite Zr-bpdc/**RuCO** (**3**). Suspension of Zr-bpdc

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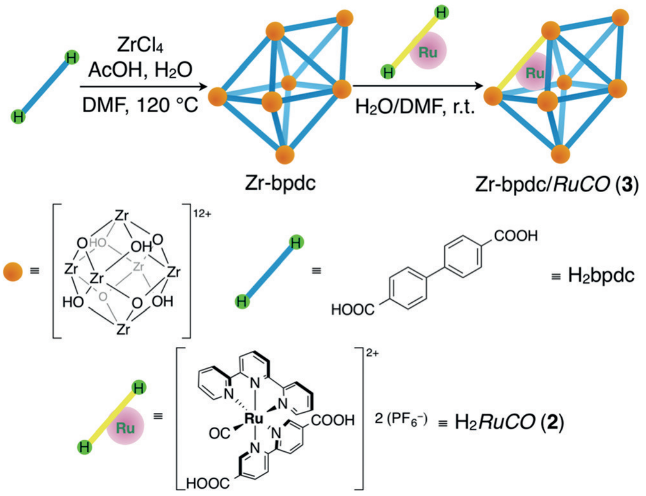

Scheme 1. Synthesis of **3** by the PSE of **2** with bpdc in Zr-bpdc.

and **2** in a H_2O/DMF solvent mixture allowed linker exchange to occur (Scheme 1).

The presence of H_2O was crucial to the exchange reaction. The efficiency of incorporation of **2** was remarkably affected by the H_2O/DMF ratio. While no exchange proceeded in DMF, almost all metallolinker **2** was introduced into Zr-bpdc using a 4:1 (v:v) H_2O/DMF when 10 mol % of **2** was used (Supporting Information, Table S3 and Figure S4). The loaded amount can also be varied by controlling the mixing ratio of **2** and Zr-bpdc. A maximum loading of 23 mol % was achieved when an equimolar amount of **2** was mixed with the parent PCP, although porosity was largely lost at such a high loading because of the bulkiness of **2** (Supporting Information, Table S4 and Figure S5).

Subsequently, we synthesized PCP-Ru^{II} composite **3** with a low loading of **2** to preserve the highly porous properties of Zr-bpdc (Supporting Information, Table S6). Materials were characterized using thermogravimetric analysis (TGA), X-ray powder diffraction (XRPD), IR and UV/Vis spectroscopy, and scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDX). TGA indicates that **3** is thermally stable up to 400 °C, slightly less resilient than the parent Zr-bpdc (Supporting Information, Figure S6). The XRPD pattern of **3** was quite similar to that of Zr-bpdc, indicating retention of the framework structure during the PSE process (Supporting Information, Figure S7). In the IR spectrum, the CO stretching vibration of **3** appeared at a different position from that observed for Ru^{II} complexes **1** and **2** (Supporting Information, Figure S9 and Table S5), suggesting that the -COOH groups in **2** transform to -COOZr in **3**. In the UV/Vis spectrum of **3**, a weak absorption around 380 nm characteristic of Ru^{II}-CO complexes **1** and **2** was observed (Supporting Information, Figure S10). STEM-EDX images of **3** revealed that Ru atoms were uniformly distributed in the crystal (Supporting Information, Figure S11). This implies that linker exchange occurred not only at the crystal surface but also in the inner part of the crystal. As the crystal size of the PCP is not very large (ca. 2 μm; Supporting Information, Figure S11), metallolinker **2** can diffuse into the center of the crystal. Depth dependency of the linker exchange has been reported for a much larger crystal (> 100 μm).[12c]

The adsorption properties of **3** were investigated using N_2, CO_2, and H_2O isotherm measurements. As expected, **3** with a low loading of **2** (5.5 mol %) produced a high Brunauer–Emmett–Teller (BET) surface area (2174 m^2g^{-1}; Supporting Information, Table S6). By comparison, N_2 (77 K) and CO_2 (195 K) isotherms revealed lower adsorbed amounts for **3** at about 100 kPa than those for the parent PCP (Supporting Information, Figures S14 and S15), showing that the pores in Zr-bpdc were partially occupied by **2** after the linker exchange. On the other hand, **3** adsorbed larger amounts of N_2 and CO_2 in the low-pressure regions (Supporting Information, Figures S14 and S15). More interestingly, CO_2 isotherms at 273 and 298 K revealed increased uptakes for **3** at all pressures up to 100 kPa (Figure 1). These results can be interpreted in terms of a 1) decrease in the pore size and 2) increase in the affinity sites for adsorbates by the loading of **RuCO**. Organic-linker effects on the CO_2 adsorption properties have been reported for Zr-based PCPs.[13] The adsorption amount of CO_2 in **3** is about ten times larger than that of N_2 and Ar at ambient temperatures (Figure 1; Supporting Information, Figure S17), suggesting selective adsorption of CO_2 from gas mixtures. The H_2O (298 K) vapor isotherm of **3** indicates adsorption at a lower pressure than for the parent PCP (Supporting Information, Figure S18) because **RuCO** is more hydrophilic than bpdc. It should be noted that adsorption properties can also be tuned by replacing one or two benzene rings of bpdc with pyridine rings (ppydc, 2-phenylpyridine-5,4′-dicarboxylate, or bpydc; Supporting Information, Figures S19–S26), as pyridine possesses both hydrophilic and Lewis-basic sites.[14]

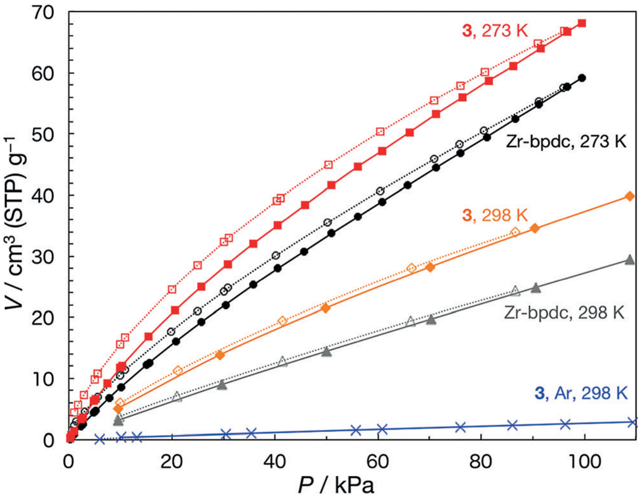

Figure 1. CO_2 isotherms of Zr-bpdc (black and gray) and **3** (red and orange) at 273 and 298 K and Ar isotherms of **3** (blue) at 298 K: closed, adsorption; open, desorption. Connecting lines are provided as visual guides.

To elucidate the effect of hybridization of a CO_2-reductive catalyst and a CO_2-adsorptive PCP, the catalytic behavior of **3** in the photochemical reduction of CO_2 was examined and compared with that of **1**. The reduction proceeded upon irradiation with visible light by using $[Ru^{II}(bpy)_3]^{2+}$ as a photosensitizer (PS) and triethanolamine (TEOA) as an electron donor, giving two-electron reduction products CO and HCOOH together with H_2. When reduced under saturated CO_2, the TON values for **3** were comparable with or slightly lower than those of **1** and **2** (Supporting Information, Table S7), but were among the highest values reported for PCP-based catalysts.[5–8] Control experiments revealed that a catalyst, a sacrificial electron donor and a PS were required for CO_2 reduction, while H_2 production persisted in the presence of a PS without a catalyst (Supporting Information, Table S7).[15] Because absorption of $[Ru^{II}(bpy)]^{2+}$ in the visible region is much larger than that of Ru^{II}-CO **1–3** (Supporting Information, Figure S10 and S32), the photoreduction mechanism can be explained as follows: 1) excitation of a PS; 2) reductive quenching by TEOA; 3) electron transfer from a reduced PS to a catalyst. A similar mechanism has also been proposed for PCP-based catalysts bearing Rh^{III}[7e] and Mn^{I}[7f] complexes.

When photochemical reduction of CO_2 was conducted under low CO_2 concentrations (diluted with Ar), the catalytic activity of molecular catalyst **1** was significantly reduced (Figure 2; Supporting Information, Table S8). In stark contrast, PCP-based catalyst **3** showed almost the same catalytic activity even under 5 % CO_2 (Figure 2; Supporting Information, Table S8). These results can be explained by CO_2 enrichment in the pores of **3**. Remarkably, a physical mixture of **1** and Zr-bpdc showed a similar activity to **1** under 20 % CO_2 (Supporting Information, Table S8), which clearly demonstrates the synergistic effect between the adsorption sites and the catalytically active sites in **3**. The catalytic activity of **3** for H_2 production was similar in low CO_2 concentrations, indicating incorporation of TEOA, a proton source, into the pores of **3**.

Product selectivity is another point of interest in our catalytic evaluation. PCP-based catalyst **3** produced a larger amount of H_2 than **1** (Figure 2; Supporting Information, Tables S7 and S8), suggesting that the $Zr_6O_4(OH)_4$ clusters showed photocatalytic activity[16] towards proton reduction in addition to the Ru^{II}-metallolinker. More importantly, the CO/HCOOH ratio for **3** was higher than those for **1** and **2** under all conditions examined (Figure 2; Supporting Information, Tables S7 and S8).[17] One possible explanation for this feature is that reductive disproportionation[18] is favored at the active Ru^{II} sites in the pores of **3** because of CO_2 enrichment. This mechanism is supported by the fact that the CO/HCOOH ratio decreased with decreasing CO_2 concentration (Figure 2; Supporting Information, Table S8). However, other mechanisms such as acid-base equilibrium[18] or a medium effect resulting from the hydrophobic bpdc linkers surrounding the active Ru^{II} sites in **3**, cannot be ruled out at this stage.[19,20]

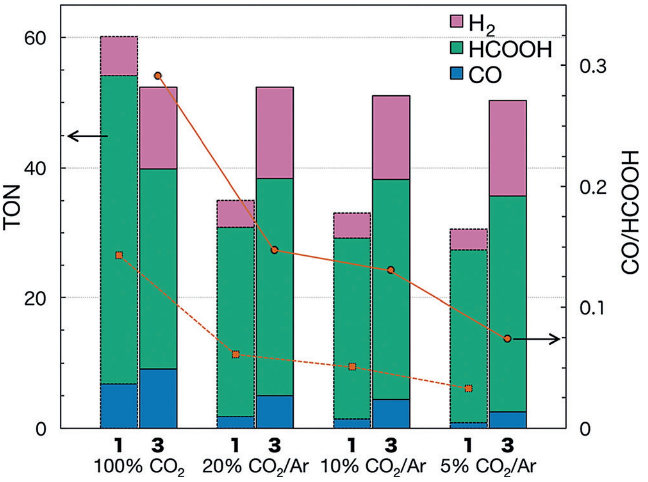

Figure 2. Photochemical reduction of CO_2 with **1** and **3**: left *y*-axis, catalytic activity (bar graph); right *y*-axis, product selectivity (line graph).

Finally, an exhaustive reduction of the CO moiety of **RuCO** in **3** was studied because the electrochemical reduction of CO_2 with **1** has been reported to yield CO and HCOOH, as well as products distinctive for reduction processes requiring more than two-electrons, such as HCHO, MeOH, and C2 molecules.[10] MeOH production was confirmed in the reaction of **3** with excess $NaBH_4$ (Supporting Information, Table S9). The yield was lower than that reported for **1**,[10] probably because of slow diffusion of BH_4^- into the pores of **3** and a competing reaction of BH_4^- with H_2O. In the absence of either **RuCO** or $NaBH_4$ no MeOH was produced (Supporting Information, Table S9). Thus, the Ru^{II}-CO complex in **3**, as well as **1**, were found to have a potential for multi-electron reduction of CO_2.

In summary, we synthesized a PCP bearing a Ru^{II}-CO complex as a metallolinker, Zr-bpdc/**RuCO 3**, by utilizing the PSE method. The resulting PCP-Ru^{II} composite **3** was found to be a good CO_2 adsorbent and to work as a CO_2 reduction catalyst with 1) high catalytic activity under low CO_2 concentrations and 2) different product selectivity compared to its homogeneous counterpart. This work demonstrates the synergistic effect between the gas adsorption properties of a PCP and the catalytic properties of a molecular catalyst, and provides a new strategy for the use of CO_2 as a C1 source from gas mixtures without the need for concentration.

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