Carbon Dioxide Reduction

A Rhenium-Functionalized Metal–Organic Framework as a Single-Site Catalyst for Photochemical Reduction of Carbon Dioxide

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Abstract: A metal–organic framework (MOF) based on (bpy)Re(CO)3Cl-containing elongated dicarboxylate ligands and Zr6(μ3-O)4(μ3-OH)4 clusters was synthesized and used as an effective single-site catalyst to photochemically reduce carbon dioxide to carbon monoxide and formate and to provide mechanistic insights into the photocatalytic CO2 reduction process.

Introduction

As a new class of crystalline hybrid materials with high specific surface area, tunable pore size, and pore walls that can be functionalized, metal–organic frameworks (MOFs) have attracted great attention for potential applications in gas storage,[1] nonlinear optics,[2] compound separation,[3] heterogeneous catalysis,[4] drug delivery,[5] biomedical sensing,[6] and other areas. MOFs can be functionalized through ligand doping, post-synthetic modification, or using predesigned functional bridging linkers.[7] Using the doping strategy, we successfully incorporated [Re(CO)3(5,5′-dcbpy)Cl] (at 4 % wt doping level; 5,5′-dcbpy is 5,5′-dicarboxy-2,2′-bipyridine) into the UiO-67 MOF built from Zr6(μ3-O)4(μ3-OH)4 secondary building units (SBUs) and 4,4′-biphenyldicarboxylate (BPDC) ligands.[8] The resulting doped UiO-67 MOF was found to be a good heterogeneous photocatalyst for CO2 reduction to CO using visible light. However, the open channels in this MOF are very small, which not only limits the diffusion rates of reactants and products in the reaction, but also sets an upper limit on the doping concentration of the sterically demanding active (bpy)Re(CO)3Cl reaction centers. Such drawbacks precluded a more detailed mechanistic study of our first MOF-based molecular photocatalytic system and prompted our interest in building a MOF structure with 100 % photocatalytically active ligands. We envisioned that elongating the Re-based ligands by adding two phenyl spacers to them would open up the interior channels of the MOF material and meet the steric requirements of the (bpy)Re(CO)3Cl moieties.

The stability of MOF materials is the limiting factor for many of their applications. A number of Zr-based UIO MOFs have been synthesized by using tunable dicarboxylate bridging ligands and Zr6(μ3-O)4(μ3-OH)4 cuboctahedral SBUs and are among the most stable MOF materials due to their strong Zr–O bonds.[9] Herein we report a highly stable and porous UIO-type MOF with a framework formula of \( [\text{Zr}_6(\mu_3-O)_4(\mu_3-OH)_4]_n \times n \) based on the elongated linear (bpy)Re(CO)3Cl-containing dicarboxylate ligand (H₂L) and Zr6(μ3-O)4(μ3-OH)4 SBUs [Figure 1a, bpydb is 4,4′-(2,2′-bipyridine-5,5′-diyl) dibenzoate].

![Figure 1](image_url)

Figure 1. Crystal structure of 1 (a) showing an octahedral cage and (b) showing a tetrahedral cage with SBUs depicted as polygons. (c) Structure of 1 as viewed along the [010] direction of the unit cell. (d) PXRD pattern of 1 (black) and that simulated from the CIF file of 1 (red).
Results and Discussion

Synthesis and Characterization

The Re-derived ligand H$_2$L was synthesized by refluxing [Re(CO)$_5$Cl] with 4,4′-(2,2′-bipyridine-5,5′-diyl)dibenzoic acid (H$_2$bpdydb) in methanol in a nitrogen atmosphere for 7 days. Yellow crystals of 1 were obtained by heating H$_2$L with ZrCl$_4$ and TFA in DMF at 100 °C for 3 days (Scheme 1). Single-crystal X-ray structure determination indicated that 1 features a three-dimensional fcu topology as other UiO MOFs (Figure 1a–c).[10] The phase purity of 1 was confirmed by the powder X-ray diffraction (PXRD) patterns of 1 (Figure 1d). Inductively coupled plasma mass spectrometry (ICP-MS) of the digested MOF sample gave a ratio of Zr/Re = 1.17, consistent with that in the crystal structure within experimental error. Thermogravimetric analysis (TGA) of 1 shows a weight loss of about 58 % from 20 °C to about 250 °C, corresponding to the removal of guest solvent molecules in the MOF channel. The TGA trace then continues in a plateau up to 450 °C before the decomposition of the framework (Figure S3).

Scheme 1. Synthesis of MOF-1.

Photochemical Reduction of CO$_2$

The series of Re(CO)$_3$(bpy)X (X = halide) complexes are well known for their ability to selectively photocatalyze the reduction of CO$_2$ to CO.[11] The photocatalytic activity of 1 towards CO$_2$ reduction was carefully evaluated in CO$_2$-saturated organic solvents with triethylamine (TEA) as a sacrificial reducing agent and a 410 nm LED as the light source. The yellow crystals turned green after irradiation with LED light for 5 min, indicating rapid activation of the precatalyst to initiate catalytic turnover (Figure 2d). The amount of CO and H$_2$ generated in the reaction was quantified by analyzing the headspace gas by GC with CH$_4$ as an internal standard. The amount of formate generated in the reaction was quantified by $^1$H NMR spectroscopy by using a deuterated solvent in the reaction.

Previous mechanistic studies on the [Re(CO)$_3$(bpy)Cl]-catalyzed reduction of CO$_2$ suggested either a unimolecular pathway involving a [Re(bpy)(CO)$_2$(COOH)] intermediate[12] or bimolecular pathways involving a CO$_2$-bridged Re dimer, ([CO$_3$(bpy)Re]$^+$)[CO$_2$][Re(bpy)(CO)]$_3$,$^{13}$ or outer-sphere redox reactions between two Re molecules[14] in the catalytic cycle. The presence of multiple catalytic pathways in one system makes it difficult to attribute the catalytic selectivity and activity to any single reaction pathway. The present CO$_2$ reduction catalyzed by 1 can only occur by the unimolecular mechanism as a result of site-isolation of the catalyst immobilized in the MOF framework. This study provides us a unique opportunity to examine the activity and selectivity of single-site Re catalysts without interference from bimolecular mechanisms.

The photocatalytic turnover numbers (TONs) of CO and H$_2$ in the reactions catalyzed by 1 are listed in Table 1. The product selectivity of CO vs. H$_2$ of the reaction depends on the reaction medium. CO$_2$ reduction to CO was preferred over H$_2$ production when acetonitrile (MeCN) was used as the solvent, while proton reduction to H$_2$ was favored in tetrahydrofuran (THF) (see Table 1 entry 1 vs. entry 2). As shown in Table 1, the CO TON of 1 in 6 hours (6.44) is much higher than that of the homogeneous counterpart (1.12). This enhanced TON is presumably due to the stabilization effect of active-site isolation of the immobilized single-site Re catalysts in the framework. The homogeneous control can not only undergo both the unimolecular and bimolecular catalysis but is also more prone to deactivation/decomposition by bimolecular pathways. This stabilization effect in the framework is consistent with our previous observation of the shorter Re-ligand-doped UiO-67 MOF.[8]

Control experiments in the absence of CO$_2$ or LED light led to no CO detection (Table 1, entries 5 and 6), confirming that the CO detected in the catalytic runs did not come from the chemical or photochemical decomposition of the Re(CO)$_3$Cl centers. As expected, in the absence of sacrificial reducing agent, only noncatalytic amounts of CO were generated (Table 1, entry 4). Interestingly, we found that addition of water to acetonitrile can significantly enhance the activity of 1. The optimized solvent system for the maximum TON for CO is an
acetonitrile solution with a water concentration of 0.83 m (Figure 2a). At a higher water concentration, the crystals appeared to partially dissolve, leading to less stable homogeneous catalysts with significantly lower TONs (Figure 2a).

Luminescence spectra of 1 were also taken to shed light on the details of the photochemical process. An emission peak at around 643 nm was observed, upon excitation at 465 nm, due to a MLCT state of the Re ligand, which is around 643 nm was observed, upon excitation at 465 nm, due to a MLCT state of the Re ligand, which is adding triethylamine to the suspension effectively quenched the emission intensity resulting from a redox reaction between triethylamine and the MLCT state of the Re ligand, which is the first step of Re-catalyzed CO2 reduction. There was also a blueshift in the emission spectra (Figure S5). On the other hand, adding triethylamine to the suspension effectively quenched the emission intensity, indicating a fast turnover by GC. The TONs for CO quickly reached 5.7 in 1 hour and 6.44 in 6 hours, indicating a fast turnover.

The time-dependent CO2 reduction of the homogeneous system process. This prompted us to examine the decomposition process of the (bpy)Re(CO)3Cl catalysts by precluding bimolecular pathways and isolating the solid catalysts after reactions. We have previously established MOFs as powerful platforms to study the details of the modification and deactivation of single-site molecular catalysts for water oxidation.[110] After photocalysis, 1 was separated from the supernatant by centrifugation and examined by PXRD. The resultant PXRD pattern indicates only partial retention of the ordered framework structure, suggesting significant distortion of the framework during the catalysis (Figure S8), presumably as a result of the deactivation/decomposition of the Re centers in the framework structure.

We have further established the stability of the framework structure during the catalysis by a combination of ICP-MS and PXRD analyses. The framework is very stable when not too much water is added to the reaction mixture. The active MOF catalyst decomposes under the reaction conditions as a result of decomposition of the Re complex instead of the framework structure. When too much water is added to the reaction mixture, however, the framework itself begins to decompose because of the presence of hydroxide from the reaction between water and triethylamine.

ICP-MS analysis of the supernatant indicated that 6 % Zr and 27 % Re leached into the solution. This result was further confirmed by the detection of 91 % Zr and 69 % Re by ICP-MS in the recovered MOF solids. At the same time, both the reaction supernatant and the recovered solids were studied by 1H NMR spectroscopy. Formate was detected in the supernatant with a 1H NMR spectrum in NaOD/D2O solution and D3PO4/D6DMSO solution. 1H NMR spectra in these solvents showed the generation of multiple species with complicated spectra. The different solvents used for NMR spectroscopy analysis gave information on different species from digestion in line with the different solubilities of these species. A singlet peak at 8.45 ppm, which was further confirmed by spiking the sample with sodium formate. The amount of formate generated was quantified with mesitylene as an internal standard, leading to a formate TON of 0.25 and a CO/HCO3− molar ratio of 26.

The recovered MOF solid was dissolved both in 10 % NaOD/D2O solution and D3PO4/D6DMSO solution. 1H NMR spectra in these solvents showed the generation of multiple species with complicated spectra. The different solvents used for NMR spectroscopy analysis gave information on different species from digestion in line with the different solubilities of these species. A singlet peak at 9.3–9.2 ppm in the 1H NMR spectrum of the original Re ligand is associated with the proton adjacent to the nitrogen atom on the pyridine ring. The chemical shift of this proton is relatively sensitive to the coordination of pyridine.

The time-dependent CO2 reduction experiment was performed by analyzing the CO production at different points in time by GC. The TONs for CO quickly reached 5.7 in 1 hour and 6.4 in 6 hours, indicating a fast turnover at the initial stage of the reaction followed by catalyst deactivation. The photocalytic reduction is highly selective toward the initial stage of the reaction followed by catalyst deactivation. The photocatalytic reduction is highly selective toward CO and H2 with a ratio of approximately 15.

The immobilization of the (bpy)Re(CO)3Cl centers in the UiO MOF enhanced the TON for CO by almost six times, but the Re catalyst still decomposed following a fast catalytic activation.

**Table 1. Investigation of MOF-1 for the photochemical reduction of CO2.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>H2-TON(a)</th>
<th>TON for CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MOF-1/MeCN</td>
<td>0.40</td>
<td>6.44</td>
</tr>
<tr>
<td>2</td>
<td>MOF-1/THF</td>
<td>4.15</td>
<td>0.32</td>
</tr>
<tr>
<td>3</td>
<td>Re(CO)3Cl(bpyde)</td>
<td>0.18</td>
<td>1.12</td>
</tr>
<tr>
<td>4</td>
<td>MOF-1/no TEA</td>
<td>0.003</td>
<td>0.19</td>
</tr>
<tr>
<td>5</td>
<td>MOF-1/no CO2</td>
<td>0.73</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>MOF-1/no light</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

(a) The TON was calculated from the results of GC analysis after irradiation for 6 h.

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bpydb was synthesized as previously reported.[16] The A'(2) mode showed up as a shoulder peak. After catalysis, the peak of the A'(2) mode became more prominent, and the peak associated with the A'' mode slightly shifted to 1886 cm⁻¹ (Figure 2c). The presence of only three CO stretching peaks after catalysis indicates that the remaining Re centers are still coordinated with three carbonyl groups and very likely still retain a fac-coordination geometry. The chloride might be replaced by other coordinating ligands.

Combining the information from the ¹H NMR and FTIR spectroscopic studies, we envisioned a possible decomposition pathway of the Re catalyst: partial hydrogenation of the pyridine ring followed by Re decomplexation from the ligand. Such a proposal can explain a number of our experimental observations.

One remaining question about this single-site CO₂ reduction catalyst is the origin of the second electron. Two equivalents of electrons are required to reduce CO₂ to CO, but the redox reaction of the ³MLCT state of the Re catalyst is a one-electron process. In the homogeneous system, the second electron can come from another Re molecule through inner-sphere or outer-sphere electron transfer. In the MOF structure with isolated Re centers, however, electron transfer from adjacent Re centers is expected to be slow (although it is still a possible pathway). Alternatively, the decomposition product of triethylamine (TEA) can provide the second electron. After being photooxidized by the ³MLCT state of the Re catalyst, the generated TEA⁺ radical can quickly lose a proton to give an enamine radical with very high reducing power. This species can give the second electron to the Re–CO₂ adduct intermediates to complete the cycle. The resulting enamine is then hydrolyzed to give acetaldehyde and diethylamine, both of which were detected by ¹H NMR spectroscopy in the supernatant of the reaction mixture in CD₃CN.

Conclusions

We have synthesized a new porous Re-functionalized UiO MOF of fcu topology that serves as a highly effective single-site photocatalyst for the reduction of CO₂ to CO and formate. The Re-MOF showed higher TONs for CO than the corresponding homogeneous catalyst, but still underwent decomposition due to partial hydrogenation of the bpy ligand and subsequent Re decomplexation. The incorporation of the Re catalyst into a stable MOF framework affords isolated catalytic sites, which enables detailed studies of the catalytic selectivity and mechanism of the unimolecular catalytic pathway, without interference from parallel bimolecular catalysis in the homogeneous system. This work highlights exciting opportunities in using MOFs as a platform to study the mechanisms and deactivation/decomposition pathways of molecular catalysts.

Experimental Section

4,4′-(2,2′-Bipyridine-5,5′-dily)dibenzoic Acid (bpydb): Ligand bpydb was synthesized as previously reported.[16] Re(CO)₅Cl(bpydb) (H₂L): Re(CO)₃Cl(bpydb) (127.8 mg, 0.354 mmol) and bpydb (140 mg, 0.354 mmol) were added to methanol (75 mL) and degassed for 30 min in a nitrogen atmosphere. The mixture was heated to reflux for 7 d, and the solid product was collected by filtration. Methanol was removed under vacuum to afford the pure product. Yield: 210 mg (86 %). ¹H NMR (400 MHz, CDCl₃): δ = 9.26 (s, 2 H), 9.01 (d, 2 H), 8.77 (d, 2 H), 8.17 (d, 4 H), 8.11 (d, 4 H) ppm. The single-crystal X-ray structure of the compound was also determined (Figure S2 and Table S2).[18] MOF-1: ZrCl₄ (1 mg, 4.29 μmol) and Re(CO)₃Cl(bpydb) (3 mg, 4.29 μmol) were added to a mixture of DMF (300 μL) and TFA (6 μL), sealed in a 2 mL glass vial, and heated at 100 °C for 72 h. After cooling to room temperature, yellow crystals were obtained by centrifugation. They were washed with DMF and methanol. Yield: 2.9 mg (46.6 %).

CCDC 1449520 (for MOF-1) and 1449521 (for H₂L) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

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Keywords: Metal–organic frameworks · Heterogeneous catalysis · Homogeneous catalysis · Photochemistry · Carbon dioxide reduction

References

[10] CCDC 1449520; space group F23; α = 38.7410(2) Å, Z = 8.
[18] CCDC 1449521; space group Cc; a = 27.622(2) Å; b = 9.5198(7) Å; c = 12.8992 Å; β = 106.806(5)°, Z = 4.

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A (bpy)Re(CO)_3Cl-containing metal–organic framework (MOF) acts as an effective single-site catalyst to photochemically reduce carbon dioxide to carbon monoxide and formate. Mechanistic insights into the monomolecular pathway of the photocatalytic CO₂ reduction have been obtained without interference from bimolecular pathways, thanks to site-isolation of the catalytic centers in MOFs.

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