

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 $Zr_6(\mu_3-O)_4(\mu_3-OH)_4$ clusters was synthesized and used as an ef-

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 $Zr_6(\mu_3-O)_4(\mu_3-OH)_4$ 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 %

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201600064. fective single-site catalyst to photochemically reduce carbon dioxide to carbon monoxide and formate and to provide mechanistic insights into the photocatalytic CO_2 reduction process.

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(μ_3 -O)₄(μ_3 -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 {Zr₆(O)₄(OH)₄-[Re(CO)₃Cl(bpydb)]₆} (1) based on the elongated linear (bpy)Re(CO)₃Cl-containing dicarboxylate ligand (H₂L) and Zr₆(μ_3 -O)₄(μ_3 -OH)₄ SBUs [Figure 1a, bpydb is 4,4'-(2,2'-bipyr-idine-5,5'-diyl)dibenzoate].



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 [100] 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_2L was synthesized by refluxing [Re(CO)₅Cl] with 4,4'-(2,2'-bipyridine-5,5'-diyl)dibenzoic acid (H₂bpydb) in methanol in a nitrogen atmosphere for 7 days. Yellow crystals of 1 were obtained by heating H₂L with ZrCl₄ and TFA in DMF at 100 °C for 3 days (Scheme 1). Single-crystal X-ray structure determination indicated that 1 features a threedimensional 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 CO₂

The series of Re(CO)₃(bpy)X (X = halide) complexes are well known for their ability to selectively photocatalyze the reduction of CO₂ to CO.^[11] The photocatalytic activity of **1** towards CO₂ reduction was carefully evaluated in CO₂-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 H₂ generated in the reaction was quantified by analyzing the headspace gas by GC with CH₄ as an internal standard. The amount of formate generated in the reaction was quantified by ¹H 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 $[Re^{I}(bpy)(CO)_3(COOH)]$ intermediate^[12] or bimolecular pathways involving a CO_2 -bridged Re dimer, $[(CO)_3(bpy)Re^{I}](CO_2)[Re^{I}(bpy)(CO)_3]$,^[13] or outer-sphere redox re-





Figure 2. (a) Plots of CO and H₂ turnover numbers vs. the concentration of water for 1; (b) CO and H₂ turnover number vs. time for 1; (c) FTIR spectra of H₂L (red) and 1 before (blue) and after (black) catalysis; (d) Photo of the color change for 1 before (left) and after (right) light irradiation (the yellow crystals turned green).

actions 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 H₂ in the reactions catalyzed by 1 are listed in Table 1. The product selectivity of CO vs. H₂ of the reaction depends on the reaction medium. CO₂ reduction to CO was preferred over H₂ production when acetonitrile (MeCN) was used as the solvent, while proton reduction to H₂ 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 thise 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)₃Cl 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



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

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Entry	Photocatalyst	H ₂ -TON ^[a]	TON for CO
1	MOF-1/MeCN	0.40	6.44
2	MOF-1/THF	4.15	0.32
3	Re(CO) ₃ Cl(bpyde)	0.18	1.12
4	MOF-1/no TEA	0.003	0.19
5	MOF-1/no CO ₂	0.73	0
6	MOF-1/no light	0	0

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

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 ³MLCT state. Addition of water to the MOF suspension in anhydrous MeCN did not lead to a substantial change in intensity in the luminescence spectra (Figure S5). On the other hand, adding triethylamine to the suspension effectively guenched the emission intensity resulting from a redox reaction between triethylamine and the ³MLCT 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). This blueshift accompanied a color change in the MOF catalyst to green, similar to that observed in the catalytic runs. Following the color change, the species became very sensitive to oxygen and quickly returned to its original yellow color upon contact with air. Given this sensitivity to oxygen, we believe that this species is the reduced Re^I(bpydc⁻⁻)(CO)₃(solvent) with a radical anion on the bipyridine ring. Interestingly, the addition of triethylamine with water quenches the emission intensity far more profoundly than adding triethylamine alone to the anhydrous acetonitrile suspension of the MOF. This is consistent with the observed acceleration effect of water on the CO₂ reduction activity and is possibly related to proton-coupled electron transfer (PCET) in the presence of water.^[15]

The time-dependent CO_2 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 steadily increased to 6.4 in 6 hours, indicating a fast turnover at the initial stage of the reaction followed by catalyst deactivation. The photocatalytic reduction is highly selective toward CO_2 to generate CO and H₂ with a ratio of approximately 15. The time-dependent CO_2 reduction of the homogeneous system shows a very similar trend to that of the MOF (Figure S6).

React-IR was used to monitor the photocatalytic CO₂ reduction in situ. An increased absorption signal for CO together with the decreased absorption for CO₂ and HCO_3^- confirms that the CO comes from the photoreduction of CO₂ and related species (Figure S7).

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



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 singlesite molecular catalysts for water oxidation.^[16] After photocatalysis, **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 CD₃CN as solvent, characterized by a singlet peak at δ = 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/HCO₂⁻ molar ratio of 26.

The recovered MOF solid was dissolved both in 10 % NaOD/ D_2O solution and $D_3PO_4/[D_6]DMSO$ solution. ¹H NMR spectra in these solvents showed the generation of multiple species with complicated spectra. The different solvents used for NMR spectroscopic 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. Without coordination to Re, this chemical shift moves to higher field below 9.0 ppm. In the ¹H NMR spectrum in D₃PO₄/ [D₆]DMSO, peaks at 9.3–9.2 ppm were still observed, suggesting the preservation of Re coordination in some of the molecules (Figure S9). This peak is split into at least three peaks, indicating generation of different Re species. On the other hand, in the ¹H NMR spectrum in NaOD/D₂O, peaks above 9.0 ppm have very small integration areas. Instead, peaks in the δ = 6.0–4.5 ppm range indicate partial hydrogenation of aromatic rings in some of the molecules (Figure S10).

FTIR spectra showed changes of the vibrational frequencies of the carbonyl groups on the Re cores before and after catalysis. There are three CO stretching peaks at 2019, 1910, and 1881 cm^{-1} for the pristine MOF, corresponding to the A'(1), A'





(2), and A" vibrational modes, respectively (Figure S11).^[17] 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 outersphere electron transfer. In the MOF structure with isolated Re ligands, 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 cation 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 CO_2 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'-diyl)dibenzoic Acid (bpydb): Ligand bpydb was synthesized as previously reported.^[16]

Re(CO)₃Cl(bpydb) (H₂L): Re(CO)₅Cl (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 H_2L) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre

Acknowledgments

We thank the National Natural Science Foundation of the P.R. China (21471126), the National Thousand Talents Program of the P.R. China, the 985 Program of Chemistry and Chemical Engineering Disciplines of Xiamen University, and the US National Science Foundation (NSF) (DMR-1308229) for funding support. Y. P. acknowledges support from the China Scholarship Council. We thank Mr. Alexander E. Hess for experimental help.

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

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Received: January 24, 2016 Published Online: ■





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



A (bpy)Re(CO)₃Cl-containing metalorganic 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.

DOI: 10.1002/ejic.201600064