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COMMUNICATION

Construction of Supported Ru Complex on Bifunctional MOF-253 for Photocatalytic CO₂ Reduction under Visible Light

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MOF-253 supported active Ru carbonyl complex (MOF-253-Ru(CO)₂Cl₂) was constructed for photocatalytic CO₂ reduction under visible light irradiations. Its performance can be further improved by immobilization photo-sensitizer. This study highlights the great potential of using MOFs as solid ligand and platform for assembly of complicated catalytic system.

Homogeneous molecular catalysts show high activity in reactions, but suffer from products contaminations and limited recyclability. For practical applications, molecular catalysts are usually immobilized on solid supports for an easy recovery and recycling. Metal-organic frameworks (MOFs), which have already showed a variety of promising applications, are emerging as a new type of ideal support due to their high surface areas and uniform pores for facile diffusion of reactants.¹ By post-synthetic modifications (PSM), MOFs can be endowed with well defined and isolated sites for the anchoring of catalytic species, which makes them especially appealing for constructing supported single site catalysts as compared to other supports which has non-homogeneously scattered sites.² Actually, catalytic active species supported MOF materials prepared via PSM methods have been designed to meet a variety of catalytic purposes.³⁻⁵

However, the anchoring of active catalytic species on MOFs via PSM functionalizations on the ligand sometimes may induce unfavorable interactions between the metal complex and the solid surface, which would lead to decreased performance of the molecular catalysts. The direct construction of metal complexes using the substrate as a solid ligand would be an ideal strategy to develop the supported molecular catalysts without losing their performance. With opening 2, 2'-bipyridine (bpy) moieties in its structure, MOF-253 can be an ideal solid ligand for construction of surface supported metal complex featuring bpy ligands.⁶ Given the

ubiquitous role of the bpy ligand in coordination chemistry, a series of studies have already been done on the functionalization of MOF-253 using its open N, N'-chelating sites.⁷⁻⁹

Ru complexes containing bpy ligand have been widely used as homogeneous photocatalysts and photosensitizers.¹⁰ Especially Ru carbonyl complexes containing 2,2'-bpy are photocatalytically or electrochemically active for CO₂ reduction.¹¹ However, the use of supported Ru complex for photocatalytic CO₂ reduction has not been previously studied. In this communication, we reported for the first time the using of N, N'-chelating centers in the MOF-253 to construct the supported active Ru carbonyl complex (MOF-253-Ru(CO)₂Cl₂) for photocatalytic CO₂ reduction under visible light irradiations and its mechanism. In addition, MOF-253 can also be used as a platform for building of sensitized system with significantly enhanced photocatalytic performance by further incorporation of Ru(bpy)₂Cl₂ as a photo-sensitizer.

Al(OH)(dc bpy) (MOF-253) (dc bpy for 2,2'-bipyridine-5,5'-dicarboxylic acid) was chosen to construct the supported Ru complex since it has open accessible 2, 2'-bipyridine units in its framework, which allows for its coordination to metal centers to develop photo-catalytically active porous materials. MOF-253 was prepared following the previously reported procedures.⁶ The good agreement between the XRD patterns of the as-prepared product and the calculated MOF-253 suggests the formation of pure phase of MOF-253 (Fig. 1a). The Langmuir surface area of the as-obtained product is determined to be 1430 m²g⁻¹, larger than that reported previously (1202 m²g⁻¹), indicating that MOF-253 with high quality has been obtained (Fig. S1).⁸

To prepare MOF-253 supported Ru complex (MOF-253-Ru(CO)₂Cl₂), the as-synthesized MOF-253 was de-solvated first under dynamic vacuum and then reflux in anhydrous methanol solution containing [Ru(CO)₂Cl₂]₂. The XRD pattern of the as-obtained product shows characteristic diffraction peaks of MOF-253 framework, indicating that the introduction of Ru moiety does not

influence the structure of MOF-253 (Fig. 1a). The slight decrease of the diffraction intensity of the resultant product as compared with the parent MOF-253 is probably due to the existence of disorder within the crystal structure after the immobilization process. The presence of $\text{Ru}(\text{CO})_2\text{Cl}_2$ in the as-prepared product was confirmed by its FT-IR spectrum (Fig. 1b). As compared with the parent MOF-253, two additional peaks at 2073 cm^{-1} and 2010 cm^{-1} was observed, which can be assigned to the asymmetric vibration of CO in $\text{Ru}(\text{CO})_2\text{Cl}_2$, indication of the formation of MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$. The coordination of Ru(II) to the free N, N-chelating sites in MOF-253 leads to a slight red shift of the asymmetric vibration of CO as compared with those in the original $[\text{Ru}(\text{CO})_2\text{Cl}_2]_2$ (2093 cm^{-1} and 2071 cm^{-1}). The formation of Ru-N bonds between $\text{Ru}(\text{CO})_2\text{Cl}_2$ and N, N-chelating sites in MOF-253 is also evidenced by the extended X-ray absorption fine structure (EXAFS) analyses. The experimental Fourier transform spectrum of EXAFS (FT-EXAFS) shows the Ru-N distances to be 2.16 \AA and 2.20 \AA , while the Ru-Cl distance to be 2.36 \AA and 2.40 \AA , respectively (Fig. 1c). These distances are in good agreement with the Ru(II)-N and Ru(II)-Cl bonds observed in similar Ru(II) bpy complexes.¹² The amount of Ru incorporated in MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ was determined by inductively coupled optical emission spectrometer (ICP-OES) analysis. The Ru/Al ratio (6.3%) in the as-obtained MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ determined by ICP is a little lower than that added into the reaction system (with Ru/Al at 10.0%). N_2 adsorption/desorption isotherm analysis shows that the as-obtained MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ still shows a relatively high Langmuir specific surface area of $1085\text{ m}^2\text{g}^{-1}$, indicating the existence of the permanent porosity (Fig. S1). The slightly decrease of the surface area is attributed to the partial blocking of the open pores in MOF-253 by Ru carbonyl complex, rather than the collapse of the framework.

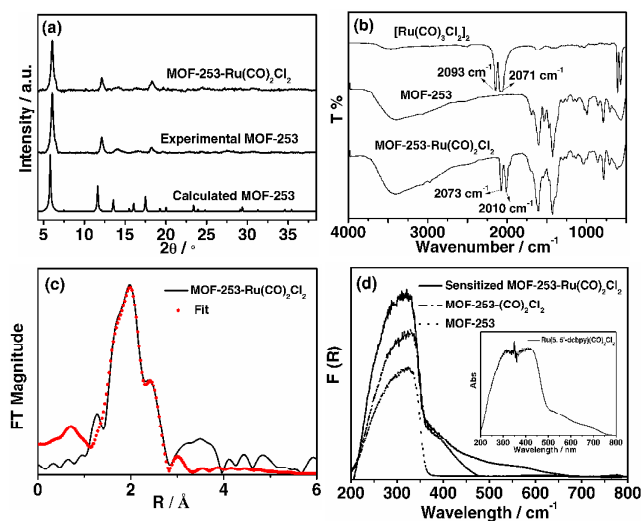


Fig. 1 (a) XRD patterns of the as-prepared samples together with that of the calculated MOF-253; (b) FT-IR spectra of prepared samples; (c) Fourier transform magnitude of the EXAFS spectra (FT-EXAFS) for MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$; (d) UV/Vis spectra of prepared samples. The inset is the UV/Vis absorption spectrum of homogeneous $\text{Ru}(5, 5'-\text{dcbpy})(\text{CO})_2\text{Cl}_2$.

The UV/Vis DRS spectra of the as-obtained MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$, compared with that of pure MOF-253 and $\text{Ru}(5, 5'-\text{dcbpy})(\text{CO})_2\text{Cl}_2$, were shown in Fig. 1d. $\text{Ru}(5, 5'-\text{dcbpy})(\text{CO})_2\text{Cl}_2$ shows absorption edge extending to about 470 nm , in accordance with its bright yellow-greenish color (Fig. 1d inset). The absorption in the visible light region observed over $\text{Ru}(5, 5'-\text{dcbpy})(\text{CO})_2\text{Cl}_2$

can be ascribed to the metal-to-ligand ($\text{Ru}^{\text{II}} \rightarrow \text{bipyridine } \pi^*$) charge transfer (MLCT) transition. Pure MOF-253 alone does not show absorption in visible light region. However, when coordinated to Ru(II) via N, N-chelating sites, the absorption edge of the as-prepared MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ extends to 470 nm , in accordance with its yellow color.

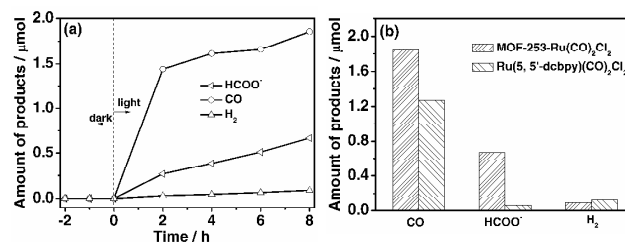


Fig. 2 (a) The amount of products produced as a function of irradiation time over MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$; (b) The amount of products produced over $\text{Ru}(5,5'-\text{dcbpy})(\text{CO})_2\text{Cl}_2$ and MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ after 8h irradiations. Photocatalysts: 5 mg, MeCN/TEOA (10/1, 6ml).

Table 1 TON for photocatalytic CO_2 reduction over different samples after irradiated for 8h.

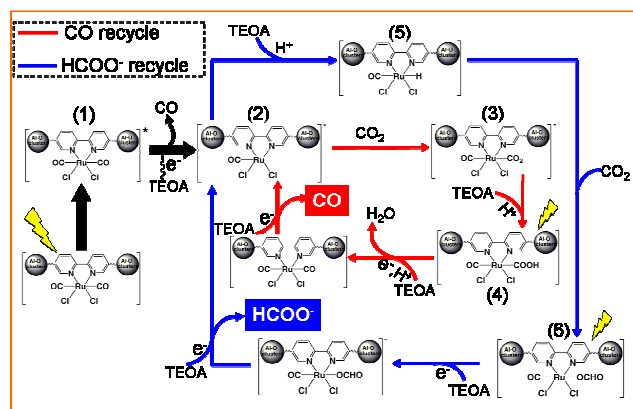
Photocatalyst	Reaction time /h	TON			
		HCOO^-	CO	H_2	Total
$\text{Ru}(\text{dcbpy})(\text{CO})_2\text{Cl}_2$	8	0.3	4.5	0.5	5.3
MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$	8	2.9	7.1	0.4	10.4
sensitized MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$	8	35.8	7.3	11.9	55.0

TON for H_2 and HCOO^- is defined as mole of the evolved H_2 and HCOO^- over per amount of ruthenium, while TON for CO is defined as the number of evolved CO after deduction of those from carbonyl.

Since bpy containing Ru carbonyl complexes have been previously reported to be photocatalysts for CO_2 reduction,¹³ we investigated the photocatalytic CO_2 reduction over the as-obtained MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ in a mixture of MeCN/TEOA (10/1) under visible light irradiations. As shown in Fig. 2a, HCOO^- , CO and H_2 were produced over the as-prepared MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ and the amount of the products increased with the irradiation time. About $0.67\text{ }\mu\text{mol}$ of HCOO^- , $1.86\text{ }\mu\text{mol}$ of CO as well as $0.09\text{ }\mu\text{mol}$ H_2 were produced after irradiated for 8 h. The calculated TON for the formation of HCOO^- , CO and H_2 is 2.9, 7.1 and 0.4, respectively (Table 1). No products were detected over pure MOF-253 or MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ without light irradiations, indicating that the formation of the products is truly induced by the photocatalysis over MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$. The photocatalytic CO_2 reduction over the homogeneous $\text{Ru}(5, 5'-\text{dcbpy})(\text{CO})_2\text{Cl}_2$ revealed that only $0.06\text{ }\mu\text{mol}$ of HCOO^- , $1.27\text{ }\mu\text{mol}$ of CO and $0.12\text{ }\mu\text{mol}$ of H_2 were produced under similar condition (Fig. 2b). The amount of both CO and HCOO^- produced over the homogeneous $\text{Ru}(5, 5'-\text{dcbpy})(\text{CO})_2\text{Cl}_2$ is lower than that over MOF supported Ru complex. The even better performance observed over MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ as compared with its homogeneous counterpart is possibly due to the formation of some intermediates inactive for the photocatalytic CO_2 reduction over homogeneous $\text{Ru}(5, 5'-\text{dcbpy})(\text{CO})_2\text{Cl}_2$.¹⁴ This suggests that the construction of the MOF-253 surface Ru complex via coordination with its N, N'-chelating sites is an efficient strategy to

develop the supported molecular catalyst. Although the ICP analysis revealed that about 6.2% of incorporated Ru leached into the reaction filtrate after 8 h reaction, the filtrate experiment has shown that only about 0.1 μmol of CO and 0.02 μmol of HCOO^- were produced over the filtrate irradiated for 4h (Table S1), a confirmation of the heterogeneous nature of the MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ in photocatalytic CO_2 reduction. Besides this, the XRD of the MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ did not change after the reaction, indicating that the photocatalyst is stable during photocatalytic CO_2 reduction (Fig. S2).

To study the origin of the reaction products, isotopic $^{13}\text{CO}_2$ was used for the photocatalytic CO_2 reaction (Fig. S3-S4). We observed peaks at 164.4 and 158.7 ppm in the ^{13}C NMR spectrum, which can be assigned to HCOO^- and HCO_3^{2-} respectively. This suggests that the as-formed HCOO^- really comes from CO_2 .^{1c} Additional peaks observed at 161.6, 167.5 and 168.6 ppm in the ^{13}C NMR spectrum probably originated from Ru- $^{13}\text{CO}_2$ adducts and intermediates (as shown in Scheme 1) leaching into the solution during the reaction.¹⁵ In the meantime, the GC-MS spectra of the gaseous product from the reaction with $^{13}\text{CO}_2$ showed signals at m/z of 29 and 28, corresponding to ^{13}CO and ^{12}CO respectively. On the contrary, only signal at m/z of 28 was detected in the product from reaction with $^{12}\text{CO}_2$. This clearly indicates that CO_2 was reduced to CO over MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$. The coexistence of ^{12}CO in the gaseous product in the $^{13}\text{CO}_2$ reaction may come from those dissociated from the MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ as elucidated in the mechanism.



Scheme 1 Proposed mechanism for photocatalytic CO_2 reduction over the as-prepared MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ under visible light.

Based on the experimental results and the previous studies on the photocatalytic CO_2 reduction over Ru carbonyl complexes, a possible mechanism for the photocatalytic CO_2 reduction over MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ was proposed (Scheme 1). MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ shows light absorption in the visible light region due to the existence of the MLCT. When irradiated, the excited MLCT state can be reductively quenched by TEOA, giving the one-electron reduced species (1). Previous reports have shown that irradiation of Ru-based complex always induce photochemical ligand substitution to give free CO.¹⁶ The observation of ^{12}CO in the MS spectrum when reaction with $^{13}\text{CO}_2$ and the change of the IR spectrum over MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ after reaction indicated that similar CO dissociation occurred (Fig. S5). The release of CO from the one-electron reduced species can lead to the formation of the penta-coordinated intermediate (2), which would open to the electro-philic attack by CO_2 and result in the formation of a CO_2 adduct (3-4).¹⁵ TEOA can protonate the bound CO_2 in the CO_2 adduct and induce the release of water to complete the catalytic cycle. Such a mechanism leads to the preferential formation of CO as the ultimate product (red cycle in

Scheme 1). An alternative mechanism to the direct CO_2 adduction is the formation of the hydride intermediate (5), which followed by CO_2 insertion into the metal-hydride bond (6) can leading to the formation of HCOO^- ((blue cycle in Scheme 1)). The formation of the Ru hydride intermediate was confirmed in our previous study on the photocatalytic hydrogenation over hybrid of CdS/Ru carbonyl complex.¹⁷ Actually, a similar dependence of the nature of the ligand coordinated to the Ru(II) sites on the ultimately formed products for photocatalytic CO_2 reduction over other Ru complexes was previously reported.¹³

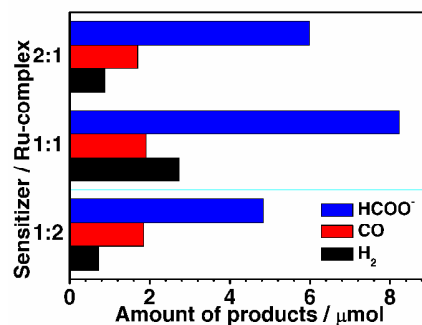


Fig. 3 Products distribution over MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ with different amounts of $\text{Ru}(\text{bpy})_2\text{Cl}_2$.

Although MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ is photocatalytic active for CO_2 reduction, its performance is not satisfactory. Modifying photocatalysts with photo-sensitizer to enhance their light absorption, especially in the visible light region, is a widely adopted strategy to improve their performance. $\text{Ru}(\text{bpy})_2\text{Cl}_2$ was used to prepared photo-sensitized MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ since $\text{Ru}(\text{bpy})_2\text{Cl}_2$ can react with the surface N, N-chelate sites to form MOF-253 supported $[\text{Ru}(\text{bpy})_2(\text{X}_2\text{bpy})^{2+}]$, which shows absorption in visible light region. As shown in Fig. 1d, sensitized MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ shows enhanced absorption in visible light region with the absorption edge extending to 630 nm. The formation of $[\text{Ru}(\text{bpy})_2(\text{X}_2\text{bpy})^{2+}]$ was also confirmed by the higher catalytic activity over MOF-253 supported $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (0.21 μmol of CO, 0.46 of HCOO^- and 0.07 μmol of H_2) than that over pure $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (0.27 μmol of HCOO^- and 0.18 μmol of CO) under similar condition (Table S2). It was found that the photocatalytic activity over the sensitized MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ increases significantly as compared with non-sensitized one. The amount of HCOO^- , CO and H_2 produced in 8 h over sensitized MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ (with a molar ratio of $\text{Ru}(\text{bpy})_2\text{Cl}_2/\text{Ru-complex}$ at 1:2) was determined to be 4.84 μmol , 1.85 μmol and 0.72 μmol , which is much larger than those produced over non-sensitized MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ under similar condition (Fig. 3). ICP analyses showed that about 9.3% of Ru leached into the solution after 8h irradiation. This value is a little higher than that over pure MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ (6.2%), indicating that part of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ leached into the solution. However, the additional amount of Ru leaching into solution showed negligible influence on the photocatalytic activity since homogeneous $\text{Ru}(\text{bpy})_2\text{Cl}_2$ exhibited low activity under similar condition. This indicates that the photocatalytic CO_2 reduction over sensitized MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ is heterogeneous photocatalysis. To give better understanding of the sensitized mechanism, the photocatalytic performance over sensitized MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ and MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ were performed under light irradiation with a wavelength larger than 500 nm. As expected, no products were detected over MOF-253- $\text{Ru}(\text{CO})_2\text{Cl}_2$ since it shows no absorption in this region. Only 0.83 μmol of CO and 0.02 μmol H_2

were detected over sensitized MOF-253-Ru(CO)₂Cl₂. These values are significantly lower than those obtained over wavelength larger than 420nm (1.91 μmol of CO, 8.23 μmol of HCOO⁻ and 2.73 μmol of H₂), indicating that it was induced by the photocatalysis of the sensitizer itself.

It was found that the photocatalytic performance of the sensitized MOF-253-Ru(CO)₂Cl₂ was significantly influenced by the amount of Ru(bpy)₂Cl₂ immobilized and an optimum activity was observed over sensitized MOF-253-Ru(CO)₂Cl₂ when the molar ratio of Ru(bpy)₂Cl₂/Ru-complex was at 1:1. For this system, the amount of the produced HCOO⁻, CO and H₂ reached 8.23 μmol, 2.73 μmol and 1.91 μmol after irradiated for 8 h. Although the amount of CO produced did not change much as compared to the un-sensitized one, the produced HCOO⁻ over the sensitized system was about 12 times as that over un-sensitized one (0.67 μmol), which corresponded to a TON of 35.8 for HCOO⁻ formation (Table 1). This indicates that preparing sensitized MOF-253-Ru(CO)₂Cl₂ by forming surface incorporated [Ru(bpy)₂(X₂bpy)²⁺] can promote the photocatalytic CO₂ reduction over MOF-253-Ru(CO)₂Cl₂. However, further increase in the amount of Ru(bpy)₂Cl₂ resulted in a decrease of the reactivity, probably due to blocking of the MOF-253 pore structure by the Ru(bpy)₂Cl₂ moiety. This implies that MOF-253 not only can act as a solid ligand for construction of supported photocatalyst MOF-253-Ru(CO)₂Cl₂, but also can act as a platform for building the composite photocatalytic system which can promote the charge transfer between the photo-sensitizer and the surface constructed photocatalyst.

In summary, the MOF-253 surface constructed Ru carbonyl complex (MOF-253-Ru(CO)₂Cl₂) shows photocatalytic activity for CO₂ reduction under visible light irradiations. Its performance can be further improved by simultaneous immobilization of photo-sensitizer. This work provides an effective method for the direct construction of surface supported molecular photocatalyst for CO₂ reduction. It also highlights the great potential of using MOFs both as a solid ligand for building supported molecular catalyst and as a platform for assembly of several active moieties into one composite system to achieve complicate functions.

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