

Communication

Photo-Activation of Cu Centers in Metal-Organic Frameworks for Selective CO Conversion to Ethanol

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Photo-Activation of Cu Centers in Metal-Organic Frameworks for Selective CO₂ Conversion to Ethanol

Lingzhen Zeng,¹ Zhiye Wang,¹ Yongke Wang,¹ Jing Wang,¹ Ying Guo,¹ Huihui Hu,¹ Xuefeng He,¹ Cheng Wang,^{1*} and Wenbin Lin²

¹College of Chemistry and Chemical Engineering, iCHEM, State Key Laboratory of Physical Chemistry of Solid Surface, Xiamen University, Xiamen 361005, P.R. China

²Department of Chemistry, The University of Chicago, 929 E 57th Street, Chicago, Illinois 60637, United States

Supporting Information Placeholder

ABSTRACT: CO₂ hydrogenation to ethanol is of practical importance but poses a significant challenge due to the need of forming one C-C bond while keeping one C-O bond intact. Cu^I centers could selectively catalyze CO₂-to-ethanol conversion, but the Cu^I catalytic sites were unstable under reaction conditions. Here we report the use of low-intensity light to generate Cu^I species in the cavities of a metal-organic framework (MOF) for catalytic CO₂ hydrogenation to ethanol. X-ray photoelectron and transient absorption spectroscopies indicate the generation of Cu^I species via single-electron transfer from photoexcited [Ru(bpy)₂]²⁺based ligands on the MOF to Cu^{II} centers in the cavities and from Cu^o centers to the photoexcited [Ru(bpy)₃]²⁺-based ligands. Upon light activation, this Cu-Ru-MOF hybrid selectively hydrogenates CO₂ to EtOH with an activity of 9650 μ mol g_{Cu⁻¹}h⁻¹ under 2MPa of H₂/CO₂=3/1 at 150 °C. Lowintensity light thus generates and stabilizes Cu^I species for sustained EtOH production.

Conversion of CO₂ to platform chemicals such as methanol (MeOH), formic acid, and ethylene,1-3 is of significant scientific interest. Among these, ethanol (EtOH) synthesis from CO₂ hydrogenation is of economic value.⁴⁻⁶ EtOH has much higher energy density than MeOH as a fuel or an auxiliary fuel. Cu-based catalysts such as Cu/ZnO_x, Cu/ZrO_x , and Cu/CeO_x can efficiently catalyze hydrogenation of CO₂ to MeOH,7-10 but their selectivity towards EtOH is usually low.¹¹⁻¹² Recently, we found that it is possible to achieve a high EtOH selectivity (over 99%) by using Cu^I instead of Cu^o centers as the catalytic sites.¹³ However, limited stability of the Cu^I under reaction condition presents a challenge towards sustained EtOH production from CO₂.13

Cu^{II} species can be photochemically reduced to Cu^I via single-electron transfer (SET).¹⁴⁻¹⁵ We posited that it might be possible to generate and stabilize Cu^I using light during CO₂ hydrogenation. Metal-organic frameworks (MOFs) provide a platform to design new heterogeneous catalyst.¹⁶⁻²⁰ Photoactive MOFs with molecular photosensitizers as ligands are used for various types of photocatalysis.²¹⁻²³ We were intrigued by possible use of photoactive MOFs to generate Cu¹ centers from Cu¹¹ and/or Cu^o species via SET in MOF cavity. The interconnected nanochannels of MOFs further facilitate diffusion of CO₂, H₂ and EtOH (or MeOH) for catalytic conversion.²⁴

We prepared a photoactive MOF of the UiO-67 structure (Ru-UiO) by reacting $ZrCl_4$ and a mixture of $[Ru^{II}(BPY)_2(H_2BPYDC)]Cl_2$ (BPY=2,2'-bipyridine; H_2BPYDC=2,2'-bipyridine-5,5'-dicarboxylic acid, see Figure S1, Supporting Information [SI]) and biphenyl-4,4'-dicarboxylic acid (H_2BPDC) in DMF at 120 °C (Figures 1a&b).²¹



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Figure 1. a) Controlling catalytic selectivity of CO₂ hydrogenation using low-intensity light. b) Synthesis and structure of Cu^{II}(H_xPO₄)_y@Ru-UiO. c) PXRD patterns of the precatalysts, catalysts, and catalysts after reactions. d) TEM image and EDXmapping of Ru(cyan), Cu (red), and Zr (yellow) in Cu^{II}(H_xPO₄)_y@Ru-UiO.

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The UiO-67 structure of Ru-UiO was confirmed by powder X-ray diffraction (PXRD) studies (Figure 1c, Figure S2).21 Transmission electron microscopy (TEM) showed that the MOFs adopted octahedral morphology with a diameter of 400 – 700 nm (Figure S₃). The ratio of [Ru^{II}(BPY)₂(BPYDC)] / BPDC in Ru-UiO was determined to be 4.1 by proton nuclear magnetic resonance (1H-NMR) spectroscopy of digested MOFs (Figure S₄). Combined with the Ru/Zr ratio of 1/6 determined by inductively coupled plasma-mass spectroscopy (ICP-MS) and organic weight losses in thermogravimetric analysis (TGA) (Figure S₅), a framework formula of $Zr_6(\mu_3-O)_4(\mu_3-$ OH)₄(bpdc)_{3.7}[Ru^{II}(BPY)₂(BPYDC)]_{0.9}(HCO₂)_{2.8} was obtained for Ru-UiO. The Cu species were then introduced into the MOF channel by a double-solvent impregnation method, in which an aqueous solution of $Cu(NO_3)_2$ was added to a suspension of Ru-UiO in n-hexane under vigorous stirring. A solution of 0.1M NaH₂PO₄/Na₂HPO₄ was then added dropwise to the MOF suspension in hexane to afford $Cu^{II}(H_xPO_4)_v@Ru-UiO.$ $Cu^{II}-H_xPO_4$ connection was confirmed by broadened ³¹P-NMR peaks due to paramagnetic Cu^{II} center (Figure S6). The retention of Ru-UiO PXRD patterns confirms the stability of the MOF during the synthesis of Cu^{II}(H_xPO₄)_v@Ru-UiO. The TEM images together with energy-dispersive X-ray spectroscopy (EDX) images of Cu^{II}(H_xPO₄)_y@Ru-UiO showed that the Cu, Ru, and Zr were evenly distributed (Figure 1d) in the octahedral crystals. The molar ratio of Cu/Ru in the sample was approximately 1 as determined by atomic absorption spectroscopy (AAS).

Table 1. Catalytic performance of different catalysts^a

	Catalyst		Cu wt%	CO₂ conv. %	Productivity (µmolg _{Cu} -1h-1)		Selectivity %	
					EtO H	MeO H	EtO H	MeO H
	1	Cu ^{II} (H _x PO ₄) _y @Ru- UiO	2.1	0.7	9650	N.A.	>99	<1
	2 ^b	Cu ^{II} (H _x PO ₄) _y @Ru- UiO	2.1	5.3	7690	N.A.	>99	<1
	3°	Cu ^{II} (H _x PO ₄) _y @Ru- UiO	2.1	13.2	8739	N.A.	>99	<1
	4 ^{<i>d</i>}	Cu ^{II} (H _x PO ₄) _y @Ru- UiO	2.1	1.1	287	31807	<1	>99
	5	$Cu^{II}(H_xPO_4)_y@UiO$	3.3	<0.1	59	181	25	74
	6	$Cu(H_xPO_4)_y+[Ru(BP Y)_3]^{2+}$	9.9	<0.1	49	29	63	37
	7	Cu ^{II} @Ru-UiO	2.3	<0.1	259	N.A.	>99	<1
	8 ^e	Cu ^{II} (H _x PO ₄) _y @Ru- UiO	1.9	0.7	8420	N.A.	>99	<1

^{*a*}Standard reaction conditions: 10 mg catalyst in the high-pressure reactor, 2 MPa, H₂/CO₂ = 3, temp. = 150 °C, time = 24 h, illumination with 450 nm light. ^{*b*}100 mg catalyst ^{*c*}220 mg catalyst ^{*d*}without light. ^{*e*}The buffer pair was changed from NaH₂PO₄/Na₂HPO₄ to KH₂PO₄/K₂HPO₄.

The catalytic activity of $Cu^{II}(H_xPO_4)_y@Ru-UiO$ in CO_2 hydrogenation was tested. A LED at the wavelength of 450 nm was used as the light source to activate the catalyst, followed by CO_2 hydrogenation under 2 MPa of H_2 and CO_2 in a ratio of 3/1 at 150 °C over 24 h. The gaseous products were analyzed by gas chromotography (GC) with a flame ionization detector (FID) (Figures S7-8) and possible liquid products were extracted with 0.5 mL of deuterated solvent after cooling the reactor in an ice bath for quantification by 'H-NMR.

Cu^{II}(H_xPO₄)_y@Ru-UiO with light-activation gave EtOH as the only product (Figure S9). The EtOH production rate reached 9650 µmol $g_{Cu^{-1}h^{-1}}$ (Table 1, Entry 1) and CO₂ conversion reached 13.2 % (Table 1, Entry 3), which compares favorably to other start-of-the-art catalysts under similar conditions (Table S1). The carbon atoms in the EtOH product came from CO₂ as demonstrated by the detection of ¹³CH₃¹³CH₂OH in mass spectrometry (MS) and ¹H-NMR spectroscopy when ¹³CO₂ was used as the reactant (Figures S10-11). In 7 repeated runs, the catalyst did not show significant decrease in activity (Figure S12), and the MOF structure was retained as evidenced by PXRD (Figure 1c) and TEM (Figures S3, S13-14) studies.

Interestingly, the catalytic reaction under similar conditions but without light gave MeOH as the only detected product with a MeOH production rate of 31807 μ mol g_{Cu}⁻¹h⁻¹ (Table 1, Entry 4). $Cu^{II}(H_xPO_4)_y$ -loaded UiO-67 without the doped photosensitizer [Ru^{II}(BPY)₂(BPYDC)]²⁺ gave a mixture of MeOH and EtOH in a 74:25 molar ratio with a low activity of 240 μ mol g_{Cu}⁻¹h⁻¹ under light irradiation (Table 1, Entry 5). EtOH selectivity over 99% can only be achieved when Cu/Ru ratio is below 1.6 (Figure S15). The role of Cu centers as the catalytic sites was supported by lack of catalytic activity for Ru-UiO without Cu loading. Furthermore, a physical mixture of $Cu^{II}(H_xPO_4)_y$ nanoparticle and $[Ru(BPY)_3](PF_6)_2$ gave only a trace amount of EtOH (49 µmol g_{Cu}⁻¹h⁻¹) under light irradiation (Table 1, Entry 6), indicating the importance of the proximity between the Cu centers and the Ru centers in generating Cu^I active sites for EtOH synthesis.



Figure 2. a) Switching the product selectivity of $Cu^{II}(H_xPO_4)_y@Ru-UiO$ between EtOH and MeOH via light illumination. b) EtOH productivity of $Cu^{II}(H_xPO_4)_y@Ru-UiO$ under different light intensities.

Although light illumination and photosensitizer are critical to EtOH production, the process is NOT photocatalytic. Recovered Cu(H_xPO_4)_y@Ru-UiO catalyst from a photo-assisted reaction continued to produce EtOH without light irradiation for several hours (Figure 2a). Selectivity towards EtOH production could also be regained by re-activating the catalyst with light (Figure 2). Furthermore, a thermally-activated MeOH production catalyst could be turned into an EtOH production catalyst by irradiating low-intensity light (11 mW/cm², Table S₂). Finally, reaction under light illumination 1

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at room temperature gave no products. All these results support the role of light in catalyst activation.

The phosphates also played a critical role. $Cu^{II}@Ru-UiO$ without NaH_2PO_4/Na_2HPO_4 treatment showed only low activity to yield a trace amount of EtOH under light irradiation (Table 1, Entry 7). We believe the phosphate or hydrogen phosphate provides an important basic site to form formyl intermediate for EtOH synthesis.¹³ The phosphate/hydrogen phosphate group might also stabilize Cu^{I} catalytic centers. Changing Na^+ in the buffer to K^+ did not affect catalytic activity or selectivity (Table 1, Entry 8). We have also tested other counter anions for the Cu centers in the Ru-UiO, including nitrate, sulfate, borate, and silicate (Table S₃), but none of them can show the same level of activity as the phosphate.

We also characterized the $Cu^{II}(H_xPO_4)_y@$ Ru-UiO after catalysis. TEM showed that catalysts recovered from reactions without light irradiation contained small Cu nanoparticles (NPs) of 5-15 nm in diameter inside the octahedral MOF particles (Figure 3a), which suggests that Cu^o NPs are responsible for MeOH production. This thermally-activated catalyst is denoted Cu-NPs@Ru-UiO. By contrast, no Cu NPs were observed in the TEM images of the catalysts recovered from the reactions with light illumination (Figure 3b).



Figure 3. a,b) TEM image of $Cu^{II}(H_xPO_4)_y@Ru-UiO$ after CO_2 hydrogenation reactions in the absence and presence of light irradiation, respectively. c,d) XPS and Cu-AES spectra of catalysts before and after reactions.

XPS measurements of the catalysts after reaction showed significant shifts of Cu $_{2p_{3/2}}$ binding energy from 934.3 eV for Cu^{II} to around 932.2 eV for reduced Cu species (Cu^I or Cu^o), together with disappearance of shake-up peaks for Cu^{II} at 943.5 eV (Figure 3c).²⁵⁻²⁶ The oxidation state of Cu^I and Cu^o can be differentiated by Auger electron spectroscopy (AES), which indicates the formation of Cu^I after light-activation (912.1 eV) and Cu^o after thermal activation (915.1 eV) (Figure 3d). Zr 3d XPS spectra showed that the oxidation states of Zr did not change during the reaction (Figure S16).

In support of the TEM and XPS results, solid-state UV-Vis diffuse reflectance spectroscopy of the MOF after the thermal activation in dark showed an absorption peak at 580 nm that corresponds to the plasmonic band of Cu NPs (Figure 4d).²⁷⁻²⁸ In contrast, the catalyst after light activation did not have this absorption, indicating the absence of Cu NPs in this sample. Moreover, we have directly incorporated Cu^I salt in pores of Ru-UiO or UiO-67 (Figure S17), which showed activity towards EtOH production in reactions without light illumination (Table S4). The [Ru^{II}(BPY)₂(BPYDC)]^{*} excited state can transfer 1e⁻ to Cu^{II} to (redox generate Cu^I potential: $-0.86V_{NHE}$ for $[Ru^{III}(BPY)_2]^{3+}/[Ru^{II}(BPY)_2]^{2+*}$ vs. -0.153 V_{NHE} for Cu^{II} / Cu^I). This is supported by phosphorescence quenching of $[Ru^{II}(BPY)_3]Cl_2$ by Cu(NO₃)₂ in aqueous solution (Figure 4b) $[Ru^{II}(BPY)_2(BPYDC)]$ by $Cu^{II}(H_xPO_4)_v$ and in $Cu^{II}(H_xPO_4)_v$ @Ru-UiO (Figure 4c), as well as in situ UV-Vis measurement of the catalyst under CO_2/H_2 atmosphere (1) bar) at 140 °C showing disappearance of a 430 nm peak due to Ru^{II} and appearance of a 490 nm peak due to Ru^{III} (Figure S18). On the other hand, the [Ru^{II}(BPY)₂(BPYDC)] phosphorescence is also quenched in Cu-NPs@Ru-UiO, indicating a possible electron injection from Cuº to $[Ru^{II}(BPY)_2(BPYDC)]^*$ to generate Cu^I (redox potential: 0.527) V_{NHE} for Cu^I / Cuº vs. 0.84 V_{NHE} for $[Ru^{II}(BPY)_{2}]^{2+*}/[Ru^{II}(BPY)_{2}(BPY^{-*})]^{+}).$ The $[Ru^{II}(BPY)_2]^{2+*}$ excited state can thus convert both Cu^{II} and Cu^o to Cu^I through SET.



Figure 4. a) Generation of Cu¹ via light-induced SET. b) Stern-Volmer plot of $[Ru(BPY)_3]^{2*}$ phosphorescence quenching by $Cu(NO_3)_2$; c) Time-resolved phosphorescence decay trace of Ru-UiO and Cu¹¹(H_xPO₄)_y@Ru-UiO at 640 nm (excited at 377 nm); d) UV-Vis diffuse reflectance spectroscopy of Cu¹¹(H_xPO₄)_y@Ru-UiO before and after reactions; e) transient absorption spectra of different samples.

The rates of SET processes were monitored by transient absorption (TA) spectroscopy (Figures S19-20). Global fitting of the TA spectrum of a Ru-UiO suspension in EtOH gave four-time constants of 210 fs, 46 ps, 1.1 ns, and > 10 ns (Figure S21). The first two components are due to dynamics of the $[Ru^{II}(BPY)_2(BPYDC)]^*$ 3MLCT state involving intraligand electron transfer and vibrational relaxation,²⁹ and the last two are due to quenching of the ³MLCT state by EtOH. The TA spectrum of $Cu^{II}(H_xPO_4)_y@Ru$ -UiO showed similar longtime components but different short time constants of 75 fs, 1.2 ps, and 9.1 ps, indicating fast electron transfer between Cu^{II} and $[Ru^{II}(BPY)_2(BPYDC)]^*$ (Figure 4e, Figure S21). This assignment is supported by increased absorption below 530 nm and decreased absorption above 550 nm due to generation of Cu^I and Ru^{III} at 0.5 ps (Figure S22). On the other hand, TA spectrum of Cu-NPs@Ru-UiO showed distinct dynamics with time constants of 116 fs, 34 ps, 3.6 ns, and > 10 ns. The TA spectrum at 0.5 ps is similar to inversed plasmonic absorption of Cu NPs (Figure 4e, Figure S21), suggesting electron transfer from the Cu NP to $[Ru^{II}(BPY)_2(BPYDC)]^*$ to generate Cu^I.

In summary, we have used low-intensity light to *in situ* activate a $Cu^{II}(H_xPO_4)_y$ @Ru-UiO catalyst for selective CO_2 hydrogenation to EtOH. Under light illumination, [Ru^{II}(BPY)₂(BPYDC)]^{*} undergoes SET to both Cu^{II} and Cu° to generate Cu^{I} for catalytic EtOH production. In contrast, the same catalyst forms Cu° NPs as the active species for MeOH production from CO_2 hydrogenation in the dark. This work suggests new opportunities in using light to stabilize metal centers of an intermediate oxidation state for selective chemical transformations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <u>http://pubs.acs.org</u>. Synthesis and characterization of MOFs, photocatalytic CO_2 reduction procedures, details of ligand synthesis and NMR spectrum.

AUTHOR INFORMATION

Corresponding Author

*chengwangxmu@xmu.edu.cn

Notes

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The authors declare no competing financial interests.

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