

Supported Information

Continuous synthesis of methanol: heterogeneous hydrogenation of ethylene carbonate over Cu/HMS catalyst in fixed bed reactor system

Xi Chen^a, Yuanyuan Cui^a, Chao Wen^a, Bin Wang^a and Wei-Lin Dai^a

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, People's Republic of China

I. Catalysts preparation

Mesoporous siliceous HMS was prepared according to a well-established procedure delineated by Tanev et al.¹ using tetraethylorthosilicate (TEOS) as silica source and dodecylamine (DDA) as template agent. Typically, the HMS materials were prepared by dissolving 5.04 g of DDA in 53.33 g of H₂O and 39.42 g of ethanol under stirring before the addition of 21.39 g of TEOS dropwise. The solution mixture was then stirred at 313 K for 0.5 h. The resulting gel was aged for 18 h at ambient temperature to afford the crystalline templated product. After that, the resulting solid was recovered by filtration, washed with deionized water, and dried at 373 K, followed by calcination at 923 K in air for 3 h to remove the residual organic template materials, yielding the final mesoporous HMS materials.

The xCu/HMS (x denotes the copper loading), 50Cu/TiO₂, 50Cu/ZrO₂, 50Cu/SiO₂, 50Ni/HMS and 50Co/HMS catalysts were prepared by ammonia evaporation (AE) method. A defined amount of Cu(NO₃)₂·3H₂O, adjusted to yield 20, 30, 40, 50, 60 wt.% of Cu in the final catalysts, and 25 wt.% ammonia aqueous solution dissolved in deionized water were mixed and stirred for 30 min. HMS was then added to the copper ammonia complex solution and stirred for 4 h. The initial pH of the suspension was 11~12. All the above operations were performed at room temperature. The suspension was heated in a water bath preheated to 363 K to allow for the evaporation

of ammonia, the decrease of pH, and the consequent deposition of copper species on HMS. When the pH value of the suspension decreased to 6-7, the evaporation process was terminated. The obtained precipitates were naturally cooled to room temperature and filtrated. The filtrate was washed with deionized water three times and ethanol once followed by drying at 393 K overnight. The catalyst precursors were calcined at 723 K for 4 h, pelletized, crushed, sieved to 40–60 meshes. The final calcined sample was designed as $x\text{Cu}/\text{HMS}$ catalysts.

For comparison, catalyst containing 50 wt.% Cu/SiO_2 , Cu/TiO_2 , Cu/ZrO_2 , Ni/HMS and Co/HMS catalysts were prepared by AE method. The precursors of $50\text{Ni}/\text{HMS}$ and $50\text{Co}/\text{HMS}$ catalysts were $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ respectively and adjusted to yield 50 wt.% of Ni or Co in the final catalysts. For the Cu/SiO_2 , Cu/TiO_2 and Cu/ZrO_2 catalysts, the silica sol, titanium sol and zirconium sol were used as carriers and the amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was adjusted to yield 50 wt.% of Cu in the final catalysts.

II. Catalyst characterization

Nitrogen adsorption-desorption isotherms were measured using a Micromeritics Tristar 3000 instrument at 77 K after the samples were outgassed at 423 K to remove physically adsorbed species. The specific surface areas were calculated following the BET method. Pore size distribution were calculated by the BJH method according to the desorption isotherm branch.

The wide-angle XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer using nickel-filtered Cu K α radiation ($\lambda = 0.15406$ nm) with a scanning angle (2θ) range of 20–80°, a scanning speed of 4° /min with a voltage of 40 kV, and a current of 20 mA. The particle size of copper was calculated by X-ray broadening technique using the Scherrer's equation.

The copper loadings are determined by the inductively coupled plasma (ICP) method using a Thermo Electron IRIS Intrepid II XSP spectrometer.

TEM images of the samples were obtained on a JEOL JEM2011 electron microscope. Before being transferred into the chamber, the samples dispersed in

ethanol were deposited on the sample holder and then quickly moved into the analysis chamber.

The TPR profiles were conducted with a homemade apparatus. During the experiments, each sample (20 mg) was outgassed under flowing Ar at 473 K for 1 h and then cooled to ambient temperature. The TPR profiles are obtained with a 5% H₂/Ar flow (40 mL/min). The temperature was increased from 303 to 773 K at a rate of 10 K/min. The H₂ consumption was monitored using a TCD detector.

The copper dispersion and the specific surface area of metallic copper (S_{Cu}) of the catalysts are measured by dissociative N₂O adsorption². The specific area of metallic copper is calculated from the amount of H₂ consumption with 1.46×10^{19} copper atoms per m²³.

Fourier transform infrared spectroscopy (FT-IR) experiments of the catalysts were performed using a Bruker Vector 22 spectrometer equipped with a DTGS detector and a KBr beam splitter

X-ray photoelectron spectroscopy (XPS) was recorded with a Perkin Elmer PHI 5000 C ESCA system equipped with a hemispherical electron energy analyzer. The Al K α X-ray radiation source ($h\nu = 1486.6$ eV) was operated at 14 kV and 20 mA. The carbonaceous C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BEs).

To prevent the reduced catalysts from being oxidized before XRD and XPS characterizations, the catalysts which were reduced in tube furnace by hydrogen would not be taken out until the temperature of the tube furnace was below 30 degrees. And then these catalysts were protected by loading them immediately into a centrifuge tube full of ethanol which could provide a great effect of isolation from air for these catalysts after reduction.

III. Experimental procedures and thermodynamic calculation

The catalytic activity test was performed using a fixed-bed microreactor. Due to the fact that the boiling point of ethylene carbonate (248°C) is below the reaction

temperature (180°C), the stainless steel tubular reactor was loaded with quartz sand as pre-treatment section with length of 18.3 cm to promote the vaporization of ethylene carbonate. Then, a 1.0 g catalyst (40–60 meshes) sample was loaded into the stainless steel tubular reactor with the thermocouple inserted into the catalyst bed for better control of the actual pretreatment and reaction temperature. Catalyst activation was performed at 573 K for 4 h with a ramping rate of 2 K/min under hydrogen atmosphere. After cooling to the reaction temperature, 5 wt.% EC (purity > 99.0%) in THF (AR purity) and H₂ were fed into the reactor at a H₂/EC molar ratio of 257 and a system pressure of 3.0 MPa. The reaction temperature was first set at 453 K and the room-temperature liquid hour space velocity (LHSV) was set at 0.1 h⁻¹ for MeOH production. The products collected in the condenser were analysed offline by SHIMADZU GC-2010 Plus gas chromatography using a flame ionization detector and the tail gas was analysed online using a flame ionization detector with a six-way valve as gas sampler. The EC conversion and liquid products selectivity were calculated as follows:

$$\text{Conversion (\%)} = \frac{\text{mol of EC charged} - \text{mol of EC left}}{\text{mol of EC charged}} \times 100\%$$

$$\text{Selectivity (\%)} = \frac{m_i}{m_{i(T)}} \times 100\%$$

$$m_i = \frac{f_i}{f_s} \cdot \frac{m_s \cdot A_i}{A_s} = f_{is} \cdot \frac{m_s \cdot A_i}{A_s}$$

$$\text{Yield (\%)} = \text{Conversion} \times \text{Selectivity} \times 100\%$$

$$f_{is} = \frac{f_i}{f_s} : \text{the relative correction factor of product } i$$

f_i : the absolute correction factor of product i

f_s : the absolute correction factor of internal standard substance s

m_i : the content of product i

$m_{i(T)}$: the content of product i derived from the amount of EC reacted

m_s : the content of internal standard substance s

A_i : the peak area of product i in GC test

A_s : the peak area of internal standard substance s in GC test

The gaseous products selectivity were calculated as follows:

$$\text{Selectivity (\%)} = \frac{c_i}{c_{i(T)}} \times 100\%$$

$$c_i = x_i \cdot A_i$$

$$x_i = \frac{c_i}{A_i}$$

$$\text{Yield (\%)} = \text{Conversion} \times \text{Selectivity} \times 100\%$$

c_i : content of product i

$c_{i(T)}$: the content of product i derived from the amount of EC reacted

x_i : absolute correction factor of product i

A_i : peak area of product i in GC test

Table S1 Catalytic activities of continuous hydrogenation of EC over various catalysts^a

^aReaction Conditions: liquid hour space velocity (LHSV) = 0.1 h⁻¹, H₂/EC = 257 (mol/mol), 453 K, 3 MPa.

Catalyst	Yields (%)		
	MeOH	CO	CO ₂
50Cu/SiO ₂	65.7	14.4	19.4
50Cu/TiO ₂	-	0.7	35.9
50Cu/ZrO ₂	-	2.1	42.5
50Ni/HMS	13.1	1.1	20.8
50Co/HMS	5.3	0.2	27.9

Table S2 The yields of gaseous products in hydrogenation of EC over various catalysts^a

Catalyst	Yields (%)	
	CO	CO ₂
20Cu/HMS	2.2	41.5
30Cu/HMS	6.6	36.6
40Cu/HMS	5.9	27.6
50Cu/HMS	5.2	19.9
60Cu/HMS	10.1	20.5

^aReaction

Conditions:

liquid hour space velocity (LHSV) = 0.1 h⁻¹, H₂/EC = 257 (mol/mol), 453 K, 3 MPa.

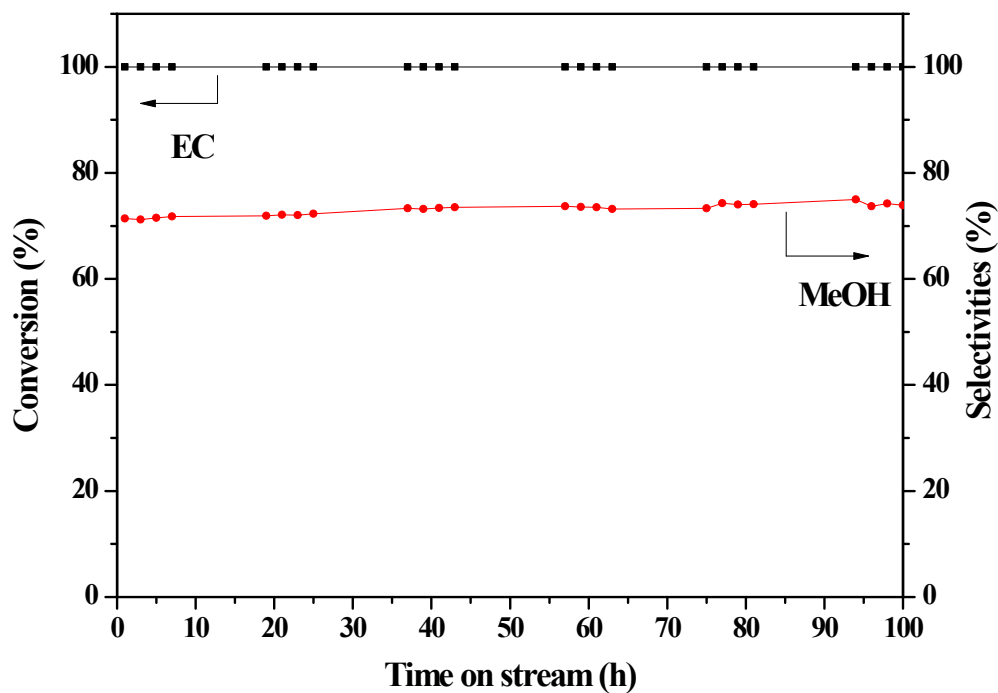


Fig. S1 EC conversion and MeOH selectivity vs. time on stream. Reaction conditions: 453 K, 3.0 MPa, LHSV = 0.1 h⁻¹, and H₂/EC = 257 (mol/mol).

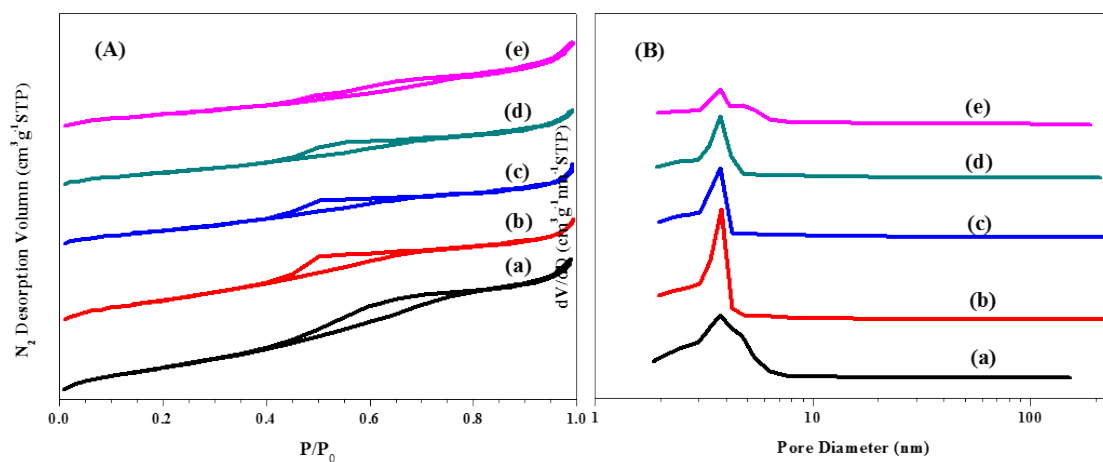


Fig. S2 N₂ adsorption-desorption isotherms of (A) the calcined catalysts and (B) BJH pore size distribution of the calcined catalysts. (a) 20Cu/HMS, (b) 30Cu/HMS, (c) 40Cu/HMS, (d) 50Cu/HMS, (e) 60Cu/HMS.

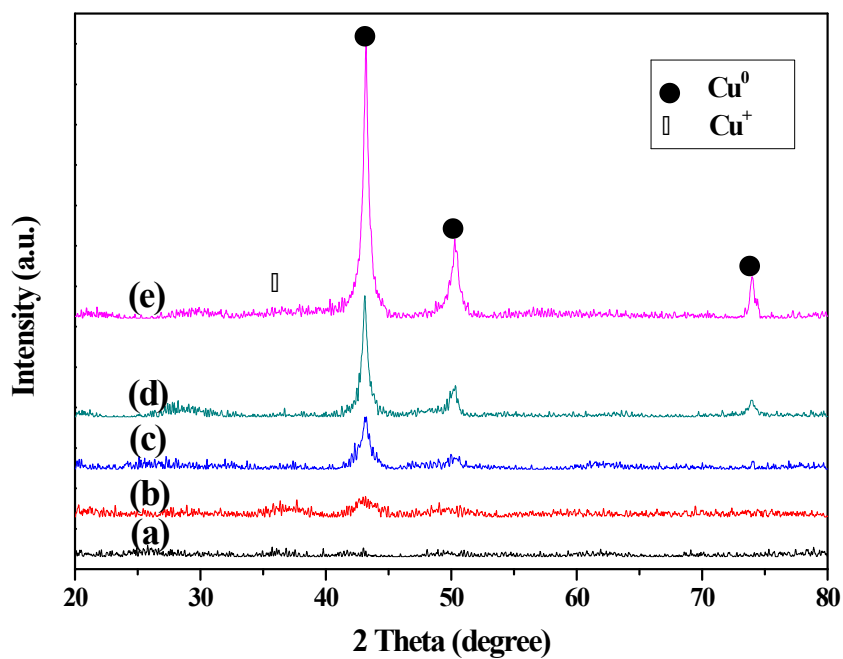


Fig. S3 XRD patterns of the reduced Cu/HMS catalysts. (a) 20Cu/HMS, (b) 30Cu/HMS, (c) 40Cu/HMS, (d) 50Cu/HMS, (e) 60Cu/HMS.

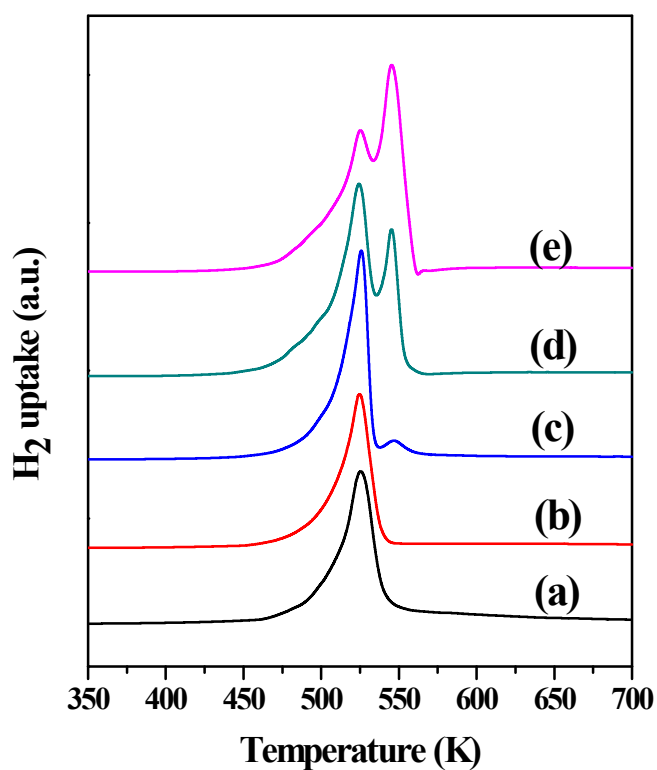


Fig. S4 H₂-TPR profiles of the calcined Cu/HMS catalysts. (a) 20Cu/HMS, (b) 30Cu/HMS, (c) 40Cu/HMS, (d) 50Cu/HMS, (e) 60Cu/HMS.

Table S3 XPS parameters of the Cu/HMS catalysts

Catalyst	KE (eV) ^a		BE of Cu 2p _{3/2} (eV)	X _{Cu⁺} (mol%) ^b
	Cu ⁺	Cu ⁰		
20Cu/HMS	913.6	916.9	932.6	25.1
30Cu/HMS	913.5	916.7	932.6	27.3
40Cu/HMS	913.7	917.2	932.4	31.4
50Cu/HMS	913.7	917.5	932.4	40.1
60Cu/HMS	914.3	918.4	932.2	34.8

a, Kinetic energy.

b, $X_{\text{Cu}^+} = \text{Cu}^+ / (\text{Cu}^0 + \text{Cu}^+) \times 100\%$.

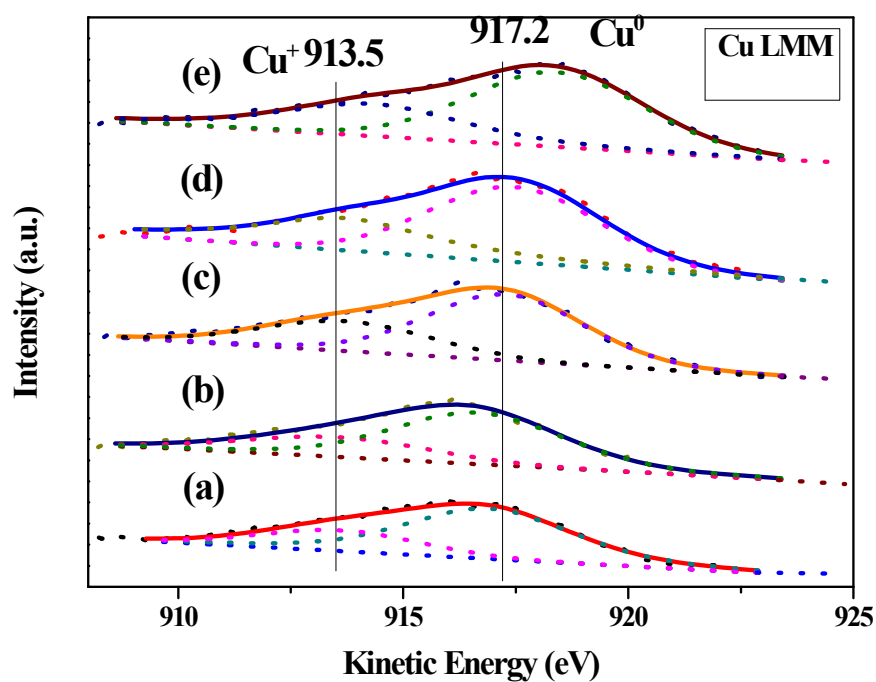


Fig. S5 Cu LMM Auger spectra of the reduced Cu/HMS catalysts. (a) 20Cu/HMS, (b) 30Cu/HMS, (c) 40Cu/HMS, (d) 50Cu/HMS, (e) 60Cu/HMS. The Auger features due to Cu⁰ and Cu⁺ are indicated.

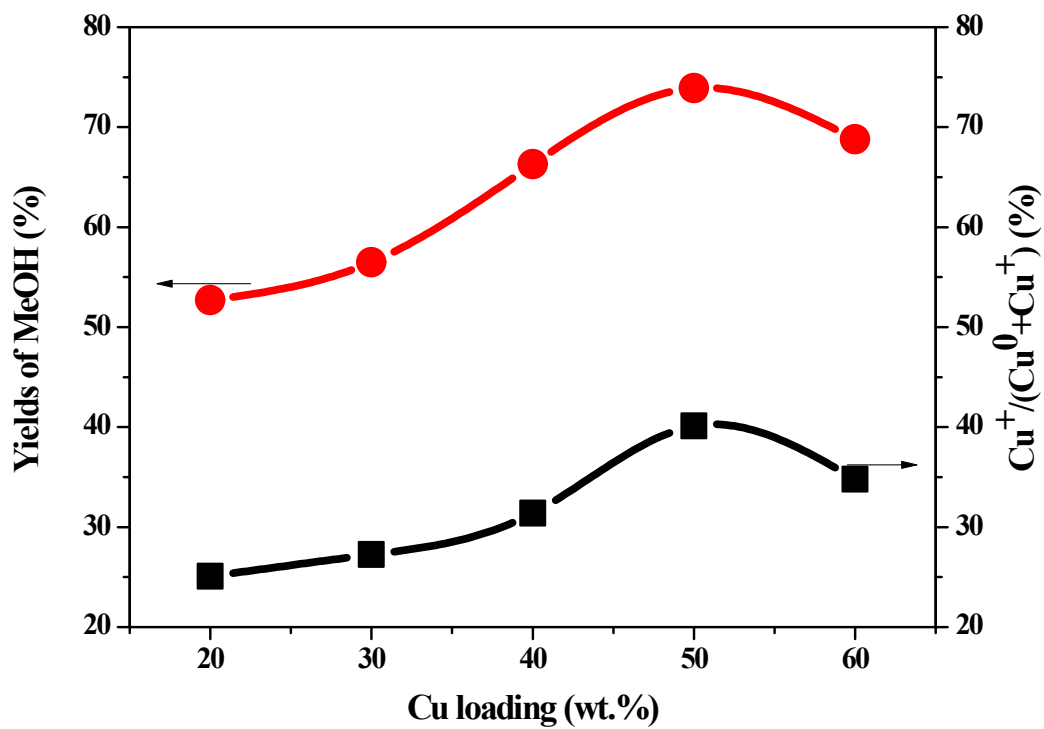


Fig. S6 Yield of MeOH and $\text{Cu}^+ / (\text{Cu}^0 + \text{Cu}^+)$ against copper loadings.

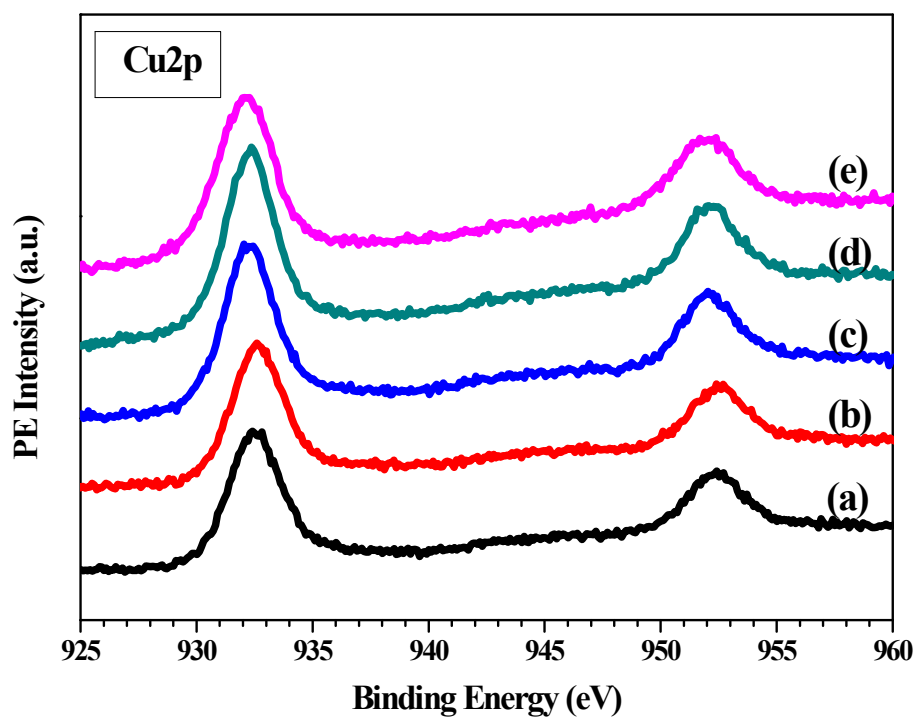


Fig. S7 XPS spectra of the reduced Cu/HMS catalysts. (a) 20Cu/HMS, (b) 30Cu/HMS, (c) 40Cu/HMS, (d) 50Cu/HMS, (e) 60Cu/HMS.

Table S4 The influence of H₂O on heterogeneous hydrogenation of EC to methanol^a

catalyst	amount of adding H ₂ O (wt.%)	yields (%)		
		MeOH	CO	CO ₂
50Cu/HMS	H ₂ O (0%)	74.0	5.2	19.9
50Cu/HMS	H ₂ O (0.1%)	63.5	8.1	26.9
50Cu/HMS	H ₂ O (0.2%)	54.9	10.4	33.0

^aReaction Conditions: liquid hour space velocity (LHSV) = 0.1 h⁻¹, H₂/EC = 257 (mol/mol), 453 K, 3 MPa.

In this work, a phenomenon appeared in this reaction, which is that the oxygen balance exceeded 100% in some catalytic result data (Table S2). To find out the origin of the excess oxygen, a series of experiments were designed to explore its main reason. On account of the strong possibility that H₂O may be the main origin of extra oxygen, we locked our focus on “The omega process”, in which ethylene oxide is reacted with CO₂ to first afford ethylene carbonate, followed by catalytic hydrolysis of the carbonate to selectively produce mono EG⁴. Based on this viewpoint, 5% EC/THF solutions with different amount of H₂O in microscale level were reacted with hydrogen in the same reaction conditions with 50Cu/HMS as the catalyst to test the variation of the products. As can be seen from Table S4, the yield of CO₂ increased with the increase of H₂O largely, suggesting that H₂O played important roles in the production of carbon dioxide and indicating that the extra oxygen is mainly from H₂O. Besides H₂O, another origin might be O₂ dissolved in the solution. From the results of the experiment, it can be inferred that H₂O exists in the solution. In fact, the 5% EC/THF solution after dehydration process as the reactant was also tested and the amount of CO₂ decreased with the yield of MeOH increased with a tiny bit. But taking the operating and reaction conditions into account, it is difficult to eliminate H₂O (moisture absorption or impurity of the reactant) absolutely from the solution confected freshly and keep it detached from the atmosphere, which is also similar to the situation in industrial production. According to the discussion above, it can be found that heterogeneous hydrogenation of ethylene carbonate to MeOH is extremely sensitive to H₂O even in microscale level, resulting from not only this reaction itself, but also the sensitivity of copper catalyst to H₂O⁵, which enlightened us to develop a novel catalyst that is more immune to H₂O and catalytic hydrolysis of the carbonate than Cu/HMS catalyst as the next target.

References

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