

Electronic Supplementary Information

Solvent feedstock effect: the insights into the deactivation mechanism of Cu/SiO₂ catalyst for hydrogenation of dimethyl oxalate to ethylene glycol

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1 Catalyst preparation

All the reagents are purchased from Sinopharm Chem. Reagent Ltd. without further purification, unless otherwise specified.

The Cu/SiO₂ catalyst with 15 wt.% copper loadings is prepared by ammonia evaporation method (AE).¹ Firstly, 2.83 g of Cu (NO₃)₂•3H₂O are dissolved into 250 ml of deionized water, then, about 20 ml of aqueous ammonia (25 wt.%) are added to the above solution and the pH is adjusted to 11.0, After that, 12 ml of silica sol (JN30, Qingdao Haiyang Chem. Co., Ltd) is added dropwise into the solution. The as-obtained suspensions is kept stirring for 6 h at room temperature, and then the temperature is risen to 363 K to decompose the cuprammonia until the pH value reached to 6-7. After then, the filtrate is washed with deionized water for five times and dried at 373 K overnight. Finally, the catalyst precursors were calcined in static air at 723 K for 4 h, then pelletized, and grounded to 40–60 meshes. The catalyst will go through hydrogen treatment under 573 K for 4 h with a ramping rate of 2 K min⁻¹ from the room temperature for pre-activation.

2 Catalyst characterization

2.1 Specific surface area analysis: Specific surface areas of the samples are measured by nitrogen adsorption-desorption method at 77 K (Micromeritics Tristar ASAP 3000) using Brunauer-Emmett-Teller (BET) method. The micropore structures of the catalysts are analyzed by using the Quantachrome Autosorb-iQ analyzer by nitrogen adsorption-desorption method at 77 K using NLDFT adsorption branch model.

2.2 Elemental analysis: The copper loadings are determined by the inductively coupled plasma method using a Thermo Electron IRIS Intrepid II XSP spectrometer.

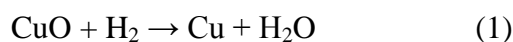
2.3 X-ray diffraction (XRD) analysis: The wide-angle XRD patterns are collected on a Bruker D8 Advance X-ray diffractometer using nickel-filtered Cu K α radiation

($\lambda = 0.15406$ nm) with a scanning angle (2θ) range of $20\sim 90^\circ$, a scanning speed of $2^\circ \cdot \text{min}^{-1}$, and a voltage and current of 40 kV and 40 mA, respectively. The full width at half maximum (FWHM) of Cu (111) reflection is measured for calculating crystallite sizes using the Scherrer equation.

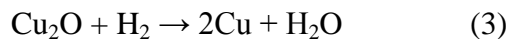
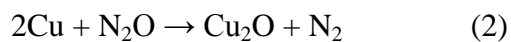
2.4 Transmission electron microscopy (TEM): TEM micrographs are obtained on a JOEL JEM 2010 transmission electron microscope. The samples for electron microscopy are prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids.

2.5 Temperature-programmed reduction (TPR): TPR profiles are obtained on a Tianjin XQ TP5080 auto-adsorption apparatus. 40 mg of the catalyst is outgassed at 473 K under Ar flow for 2 h. After cooling to room temperature under Ar flow, the in-line gas is switched to 5 % H_2/Ar , and the sample was heated to 773 K at a ramping rate of $10 \text{ K} \cdot \text{min}^{-1}$. The H_2 consumption was monitored by a TCD detector. The TPR profiles of the catalysts after reaction are also conducted. The reacted catalysts should be cooling to the room temperature and drying at 373 K overnight before the TPR measurement.

2.6 Dissociative N_2O adsorption measurement: The copper dispersion and the Specific surface area of metallic copper of the catalyst are measured by dissociative N_2O adsorption.² The N_2O chemisorption process consists of three sequential steps:



hydrogen consumption = A_1



Hydrogen consumption = A_2

Step 1 represents reduction of CuO in the catalyst. In this step, a flow of 5 vol.% H_2/Ar (30 mL/min) is used as the reducing agent, and the temperature is raised from room temperature to 773K with a heating rate of 10 K /min. Step 2 represents oxidation of surface Cu to Cu_2O by N_2O , which is a well-known method to evaluate the dispersion and crystallite size of Cu catalysts.³ This step is initiated after the reduced catalyst is cooled to 333K in Ar (30 mL/min) and purged with Ar for 30 min. Then, pure N_2O (40 mL/min) is introduced to the catalyst at 333K for 0.5 h. Subsequently, the catalyst is purged with Ar (30 mL/min) for 0.5 h to remove the residual N_2O . Step 3 represents reduction of Cu_2O surface species. In this step, a flow of 5 vol.% H_2/Ar (30 mL/min) is also used as the reducing agent, and the temperature was raises from room temperature to 773K with a heating rate of 10 K /min. The dispersion (D) of Cu, was calculated as follows:

$$D = \frac{2A_2}{A_1} \times 100\%$$

which has extensively been used in literature. The specific area of metallic copper was calculated from the amount of H₂ consumption (A_2) with 1.46×10^{19} copper atoms per m².⁴

2.7 Gas chromatography/mass spectrometry (GC/MS) analysis

Chromatography was performed on a Thermo Focus DSQ gas chromatograph with a mass-selective detector with electron impact ionization. Analytes were separated using a VF-5MS capillary column of 30 m×0.25 mm with a phase thickness of 0.25 μm from HP, which was inserted directly into the ion source of the MS system. The temperature program used for analysis was as follows: the initial temperature was 60 °C for 2 min, which was increased to 300 °C at 30 °C/min; 300 °C was maintained for 2 min. Helium (99.999%) was the carrier gas maintained at a flow-rate of 1 ml/min. The split rate was 100:1 and inlet volume was 1.0 μL. The electron impact ionization conditions were: ion energy 70 eV and the mass range scanned was 41–400 a.m.u in the full-scan acquisition mode. Compounds were identified using the NIST Mass Spectral Search Program (National Institute of Standards and Technology, Washington, DC, USA).

3 Catalytic activity measurement

The catalytic activity test is conducted using a fixed-bed reactor. Typically, 0.9 g of catalyst (40-60 meshes) sample is packed into a stainless steel tubular reactor (i.d. = 5 mm) with the thermocouple inserted into the catalyst bed. Catalyst activation is performed at 573 K for 4 h with a ramping rate of 2 K·min⁻¹. After cooling to the reaction temperature, 15 wt.% DMO (purity > 99%) in methanol or ethanol and H₂ are fed into the reactor at a H₂/DMO molar ratio of 150 and a system pressure of 3.0 MPa. The reaction temperature is firstly set at 473 K and the room-temperature LHSV of DMO was set at the value ranging from 0.2 to 1.5 h⁻¹. The products are condensed, and analyzed on a gas chromatograph (Finnigan Trace GC ultra) fitted with an HP-5 capillary column and a flame ionization detector (FID). The identification of the products is performed by using a GC-MS spectrometer.

Table S1 Physicochemical property of the catalysts

Catalyst	Cu loading ^a (Wt. %)	S _{BET} (m ² ·g ⁻¹)	D _{Cu} ^b (%)	S _{Cu} ^b (m ² g ⁻¹ _{cat})	d _{Cu} ^c (nm)
15Cu/SiO ₂	14.9	144.5	52	43.3	n.d.
MeOH-DMO -150h	15.6	132.6	44	36.4	5.5
MeOH-DMO-300h	16.8	119.2	34	28.2	7.2
EtOH-DMO -150h	15.1	145.5	48	39.8	3.3
EtOH-DMO -300h	15.3	128.6	40	33.5	5.2

^a Cu loading determined by ICP measurement ^b Dispersion of copper species and copper surface area determined by N₂O titration method. ^c Cu particle size detected by XRD.

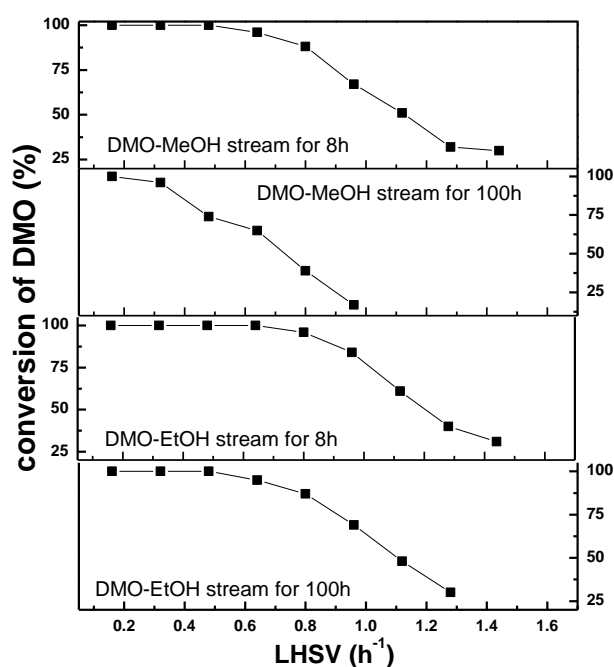


Fig. S1 Conversion of DMO on the LHSV with the Cu/SiO₂ catalyst after reaction in the DMO-MeOH stream and DMO-EtOH stream respectively. Reaction condition: P_{H₂} = 3.0 MPa, T = 473 K, H₂/DMO = 150 (mol/mol).

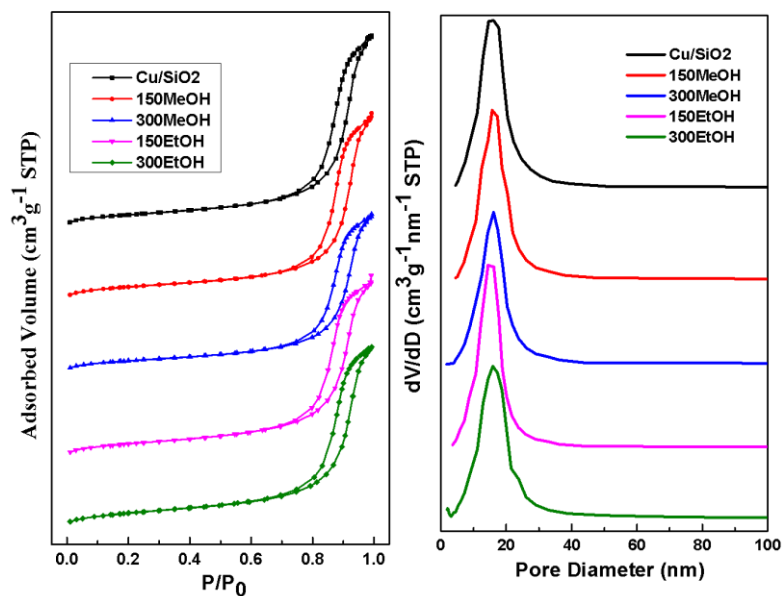


Fig. S2 N_2 adsorption-desorption isotherms and the BJH pore size distribution of the fresh and spent catalysts.

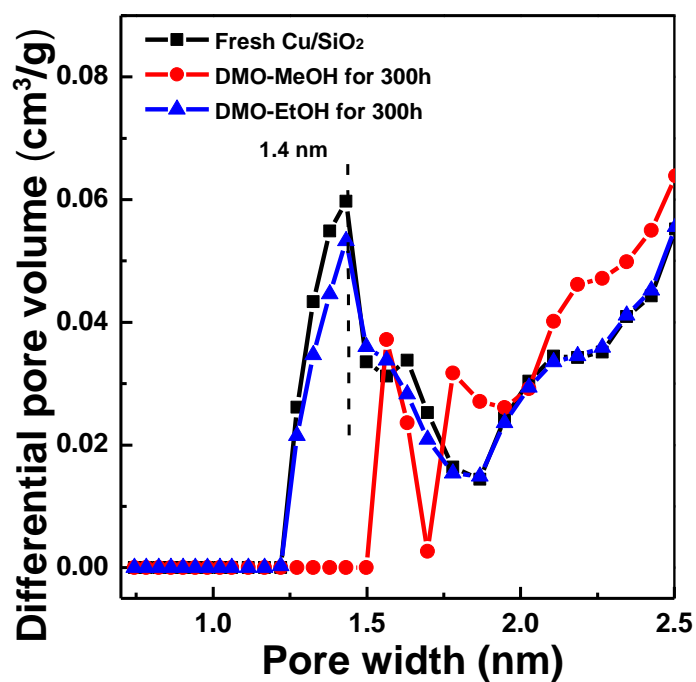


Fig. S3 Micropore size distributions of the fresh and spent catalysts using NLDFT method

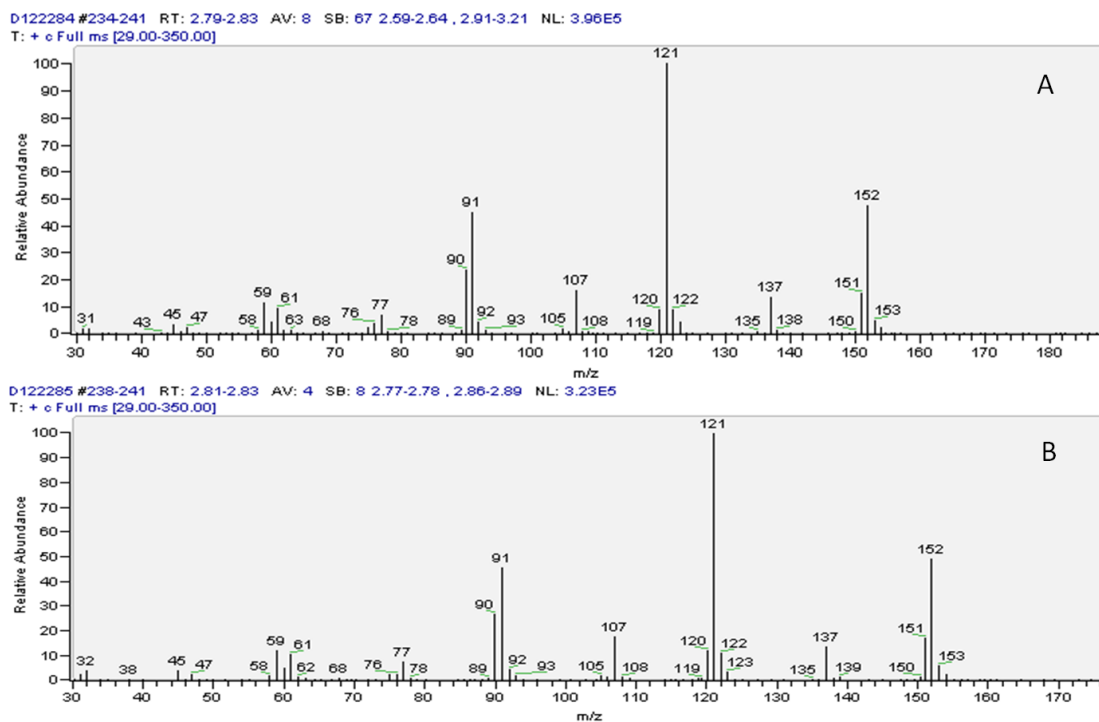


Fig. S4 MS spectrums of TMOS in the DMO-MeOH stream (A) and single MeOH stream (B). The products are collected after catalyst undergoes 100 h of running at LHSV of 0.3 h⁻¹ and 573 K.

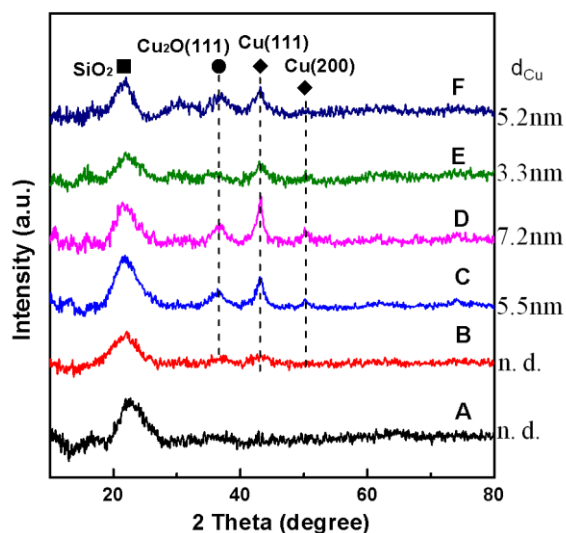


Fig. S5 XRD profiles of the calcinated Cu/SiO₂ (A); reduced Cu/SiO₂(B); Cu/SiO₂ after reaction in DMO-MeOH stream for 150 h (C) and 300 h (D); Cu/SiO₂ after reaction in DMO-EtOH stream for 150 h (E) and 300 h (F)

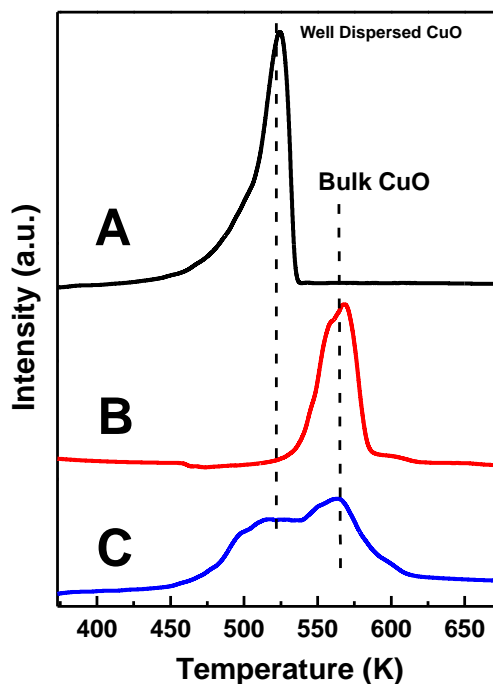


Fig. S6 TPR profiles of the catalyst. A: Calcinated Cu/SiO₂ (A); After 300 h of reaction in DMO-MeOH stream (B); C: After 300 h of reaction in DMO-EtOH stream (C); The catalysts after reaction should be cooling to the room temperature and drying at 373 K overnight before the TPR measurement.

Reference

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3. F. Deng, Q. Sun, Y. L. Zhang, S. Y. Chen, D. Wu, *Appl. Catal. A*, 1996, **139**, 75.
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