

Supporting Information

Uniformly Dispersed Cu Nanoparticles over Mesoporous Silica as a Highly Selective and Recyclable Ethanol Dehydrogenation Catalyst

1. Figures and tables

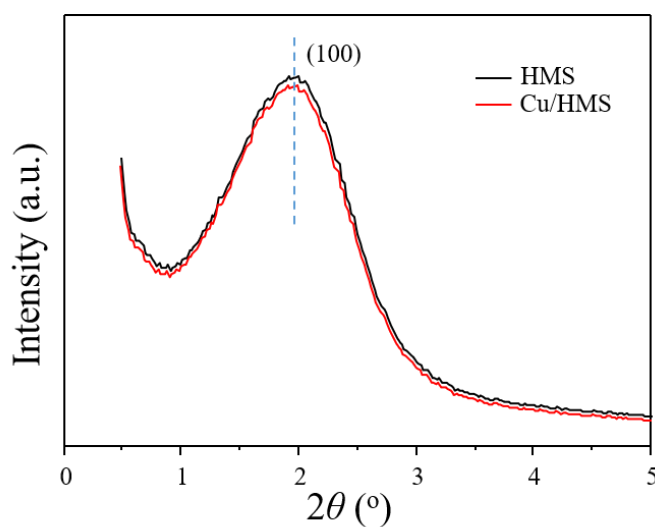


Figure S1. The XRD spectra of HMS and Cu/HMS catalysts.

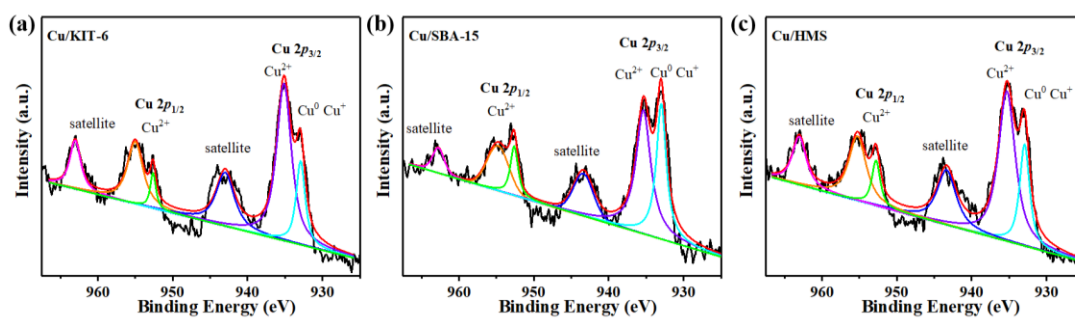


Figure S2. XPS spectra of (a) Cu/KIT-6, (b) Cu/SBA-15, and (c) Cu/HMS catalysts.

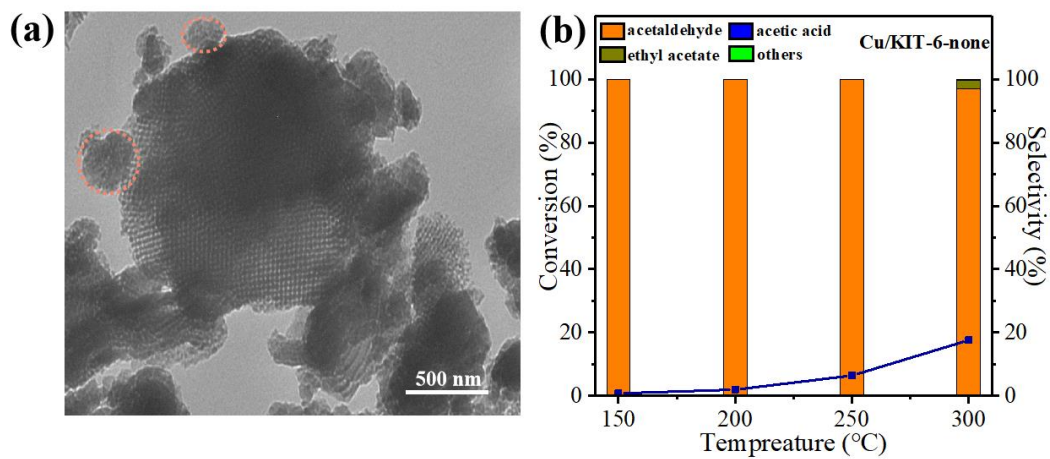


Figure S3. (a) TEM image of Cu/KIT-6-none; (b) ethanol conversion and product selectivity of the Cu/KIT-6-none. Reaction condition: a reactant ethanol stream of 2 kPa balanced by N₂ under atmospheric pressure and WHSV of 13.67 mmol g⁻¹_{Cu} h⁻¹.

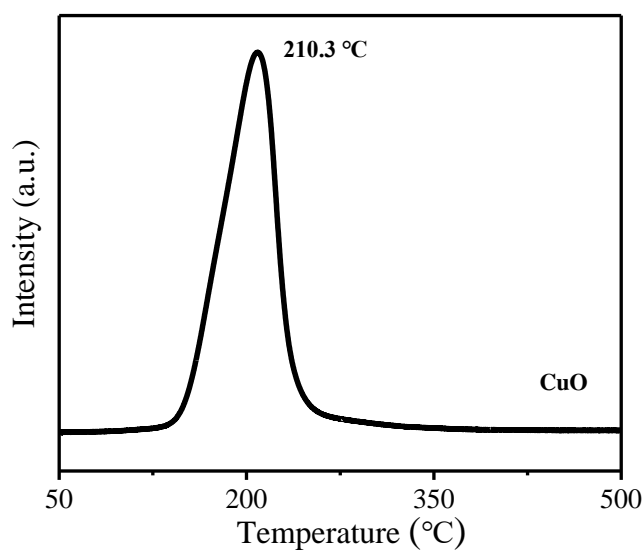


Figure S4. H₂-TPR analysis of the CuO sample.

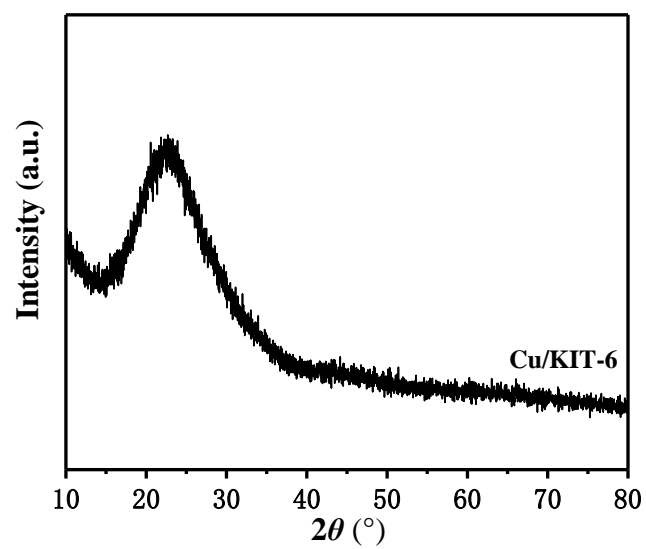


Figure S5. XRD pattern of the spent Cu/KIT-6 catalyst after running for 96 h.

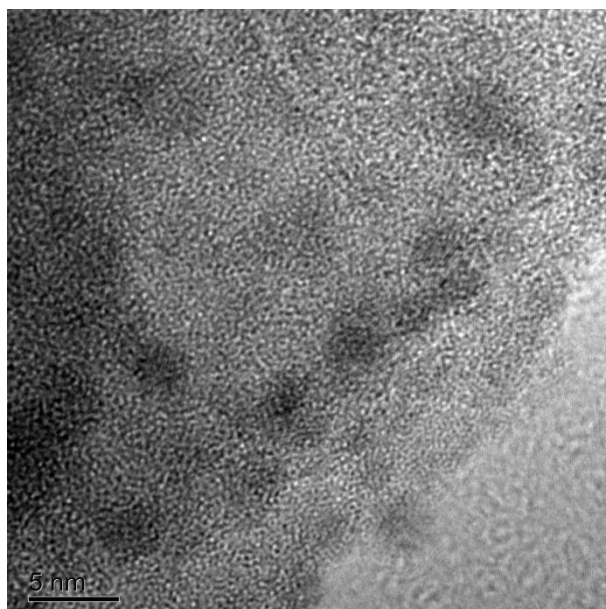


Figure S6. TEM image of the spent Cu/KIT-6 catalyst after running for 96 h.

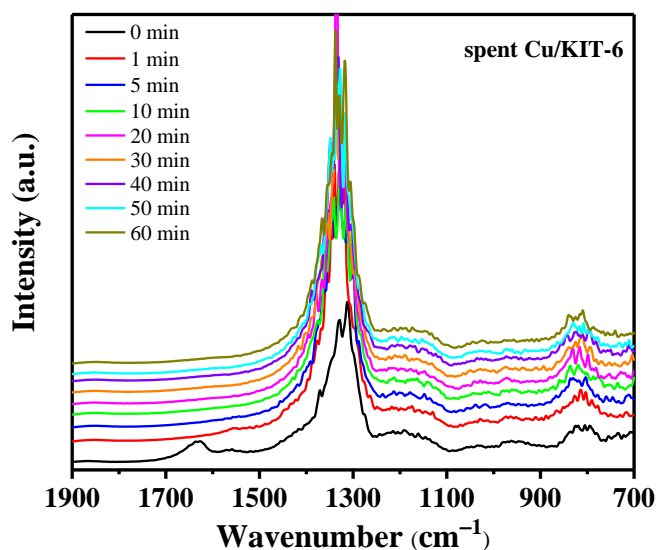


Figure S7. In situ FTIR spectra of the spent Cu/KIT-6 catalyst exposed to 10% O₂/He atmosphere at 250 °C for 1 h.

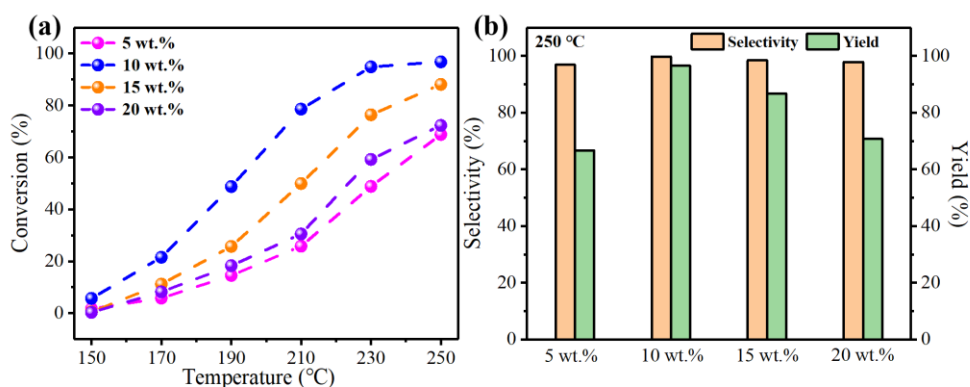


Figure S8. (a) Ethanol conversion and (b) acetaldehyde selectivity and yield of the Cu/KIT-6 catalysts with different Cu loading. Reaction condition: a reactant ethanol stream of 2 kPa balanced by N₂ under atmospheric pressure and WHSV of 13.67 mmol g⁻¹_{Cu} h⁻¹.

2. Synthesis of mesoporous silica

2.1 SBA-15

Typically, 2.0 g of P123 was added into 52.5 mL of deionized water and 10 mL HCl (~ 37 wt.%) solution under vigorous stirring followed by the addition of 4.25 g

TEOS as the silica source. The obtained synthesis solution in each route was stirred continuously at 35 °C for 20 h to allow silica hydrolysis and sol formation and then was crystallized in a Teflon-lined autoclave at 100 °C for 3 days. Afterwards, the solids were filtered, washed with deionized water, dried in air at 50 °C, and finally calcined in a muffle furnace with a heating rate of 2 °C/min until 550 °C with a 6 h dwell time at that temperature.

2.2 KIT-6

Typically, 2.0 g of P123 was added into 62 mL of deionized water, 2.85 mL HCl (~ 37 wt.%) solution, and 2.12 mL n-Butanol under vigorous stirring followed by the addition of 3.68 g TEOS as the silica source. The obtained synthesis solution in each route was stirred continuously at 35 °C for 24 h to allow silica hydrolysis and sol formation and then was crystallized in a Teflon-lined autoclave at 100 °C for 1 day. Afterwards, the solids were filtered, washed with deionized water, dried in air at 50 °C, and finally calcined in a muffle furnace with a heating rate of 2 °C/min until 550 °C with a 6 h dwell time at that temperature.

2.3 HMS

Dodecylamine (DDA, 4.9 mmol) was dissolved in 5 mL of ethanol, and 45 mL of H₂O was then added to afford a 90:10 (v/v) H₂O/EtOH solution of the surfactant at 55 °C. The surfactant solution was heated to the desired reaction temperature, and TEOS (4.08 g) and 7 mL of ethanol were added to give a reaction mixture. The reaction flask was sealed and shaken at 220 rpm in a heated water bath at the desired synthesis temperature for 20 h. Afterwards, the solids were filtered, washed with deionized water, dried in air at 50 °C, and finally calcined in a muffle furnace with a heating rate of 2 °C/min until 600 °C with a 4 h dwelling time at that temperature.

3. Catalyst characterizations

3.1 Temperature-programmed desorption of NH₃ (NH₃-TPD)

NH₃-TPD profile was performed on Autochem 2920 II (Micromeritics, Norcross, GA, USA) equipped with a thermal conductivity detector. In total, 150 mg catalyst (Cu/KIT-6(RO), Cu/SBA-15, Cu/HMS) was charged in a U-shaped quartz cell and first pretreated at 350 °C (10% H₂/Ar, ramp rate 10 °C/min) for 1 h, cooled to room

temperature and purged with He for 1 h, and then oxidized at 350 °C (10% O₂/He, ramp rate 10 °C/min) for 1 h, then cooled to 50 °C followed by changing the gas flow to a mixture of 5 vol.% NH₃/He for 30 min. The NH₃-TPD profile was measured by raising the temperature up to 500 °C, using a TCD detector. The OR sample was tested under the same test conditions, except that the pretreatment was first pretreated at 350 °C (10% O₂/He, ramp rate 10 °C/min) for 1 h, cooled to room temperature and purged with He for 1 h, and then reduced to 350 °C (10% H₂/Ar, ramp rate 10 °C/min) for 1 h. The R sample was tested under the same test conditions, except that the pretreatment was pretreated at 350 °C (10% H₂/Ar, ramp rate 10 °C/min) for 1 h. The O sample was tested under the same test conditions, except that the pretreatment was oxidized at 350 °C (10% O₂/He, ramp rate 10 °C/min) for 1 h.

3.2 Temperature-programmed reduction (H₂-TPR)

The temperature-programmed reduction (H₂-TPR) was performed on an Autochem 2920 II (Micromeritics, Norcross, GA, USA) analyzer to determine the reduction properties of the supported catalysts. In total, 80 mg of catalyst (Cu/KIT-6(RO), Cu/SBA-15, Cu/HMS) was loaded into a U-shaped quartz reactor and was first pretreated at 350 °C (10% H₂/Ar, ramp rate 10 °C/min) for 1 h, cooled to room temperature and purged with Ar for 1 h, and then oxidized at 350 °C (10% O₂/He, ramp rate 10 °C/min) for 1 h, then cooled to 50 °C in Ar. The temperature program reduction started from 50 °C to 500 °C at the ramping rate of 10 °C/min in 10% H₂/Ar. The OR sample was tested under the same test conditions, except that the pretreatment was first pretreated at 350 °C (10% O₂/He, ramp rate 10 °C/min) for 1 h, cooled to room temperature and purged with He for 1 h, and then reduced at 350 °C (10% H₂/Ar, ramp rate 10 °C/min) for 1 h. The R sample was tested under the same test conditions, except that the pretreatment was pretreated at 350 °C (10% H₂/Ar, ramp rate 10 °C/min) for 1 h. The O sample was tested under the same test conditions, except that the pretreatment was oxidized at 350 °C (10% O₂/He, ramp rate 10 °C/min) for 1 h.

3.3 Diffuse reflectance infrared Fourier transform spectroscopy of adsorbed CO (CO-DRIFTS)

Diffuse reflectance infrared Fourier transform of samples adsorbing CO (CO-

DRIFTS) was recorded using a VERTEX 70v (Bruker, Billerica, MA, USA) spectrometer equipped with an MCT detector, a diffuse reflectance unit, and a reaction Harrick cell, at a spectral resolution of 4 cm⁻¹ using a total 64 scans per spectrum. Samples (Cu/KIT-6(RO), Cu/SBA-15, Cu/HMS) were first pretreated at 350 °C (10% H₂/Ar, ramp rate 10 °C/min) for 1 h, cooled to room temperature and purged with Ar for 1 h, and then oxidized at 350 °C (10% O₂/He, ramp rate 10 °C/min) for 1 h, then purged with Ar for 1 h. After cooling down to 25 °C, the background spectrum was collected. The sample was filled with a 10% CO/He flow (30 mL/min) for 30 min, and then purged by an Ar flow (30 mL/min) with a heating rate of 10 °C/min. The OR sample was tested under the same test conditions, except that the pretreatment was first pretreated at 350 °C (10% O₂/He, ramp rate 10 °C/min) for 1 h, cooled to room temperature and purged with He for 1 h, and then reduced at 350 °C (10% H₂/Ar, ramp rate 10 °C/min) for 1 h. The R sample was tested under the same test conditions, except that the pretreatment was pretreated at 350 °C (10% H₂/Ar, ramp rate 10 °C/min) for 1 h. The O sample was tested under the same test conditions, except that the pretreatment was oxidized at 350 °C (10% O₂/He, ramp rate 10 °C/min) for 1 h.

3.4 N₂O-chemisorption

N₂O-chemisorption was performed to determine the Cu dispersion and the exposed Cu surface area of the catalysts. 80 mg catalyst was loaded into a U-shaped quartz reactor and was pretreated in He at 350 °C for 1 h to remove water and other impurities in the catalysts. After cooling to room temperature in He, the first TPR process was performed in 10% H₂/Ar to 350 °C at the ramping rate of 10 °C/min and the temperature was held at 350 °C for 10 min to fully reduce the samples. Subsequently, the sample was cooled to 60 °C in He. The surface copper atoms were allowed to be oxidized in N₂O at 60 °C for 1 h. Before the second TPR process, the sample was flushed with He to remove the physisorbed oxidant. The peak areas of the first and the second TPR profiles were denoted as *X* and *Y*, respectively. The dispersion of Cu (*D_{Cu}*) and the exposed Cu surface area (*S_{Cu}*) were calculated based on the following equations:

$$D_{Cu} = (2 \times Y / X) \times 100\% \quad (1)$$

$$S_{Cu} = (2 \times Y \times N_{av} \times Cuwt.\%) / (X \times M_{Cu} \times 1.4 \times 10^{19}) \quad (m^2/g_{cat}) \quad (2)$$

where N_{av} is the Avogadro's constant, M_{Cu} is the molecular weight of copper (63.55 g/mol), and 1.4×10^{19} is the average copper surface atom area of 0.0711 nm^2 , which is equivalent to 1.4×10^{19} copper atoms per square meter.

3.5 In situ FTIR spectra of the fresh, spent and regeneration Cu/KIT-6 catalysts

In situ FTIR spectra of the fresh, spent and regeneration Cu/KIT-6 catalysts were recorded on a VERTEX 70v (Bruker, Billerica, MA, USA) spectrometer equipped with an MCT detector, a diffuse reflectance unit and a reaction Harrick cell, at a spectral resolution of 4 cm^{-1} using a total 64 scans per spectrum. Fresh Cu/KIT-6 samples were treated at $350 \text{ }^\circ\text{C}$ (10% H_2/Ar , ramp rate $10 \text{ }^\circ\text{C}/\text{min}$) for 1 h, cooled to room temperature and purged with Ar for 1 h, and then oxidized at $350 \text{ }^\circ\text{C}$ (10% O_2/He , ramp rate $10 \text{ }^\circ\text{C}/\text{min}$) for 1 h, then cooled to $25 \text{ }^\circ\text{C}$ in Ar. In situ FTIR spectra were recorded during treatment. Spent Cu/KIT-6 samples were oxidized at $250 \text{ }^\circ\text{C}$ (10% O_2/He , ramp rate $10 \text{ }^\circ\text{C}/\text{min}$) for 2 h, cooled to room temperature and purged with Ar for 1 h, and then reduced at $250 \text{ }^\circ\text{C}$ (10% H_2/Ar , ramp rate $10 \text{ }^\circ\text{C}/\text{min}$) for 2 h, then cooled to $25 \text{ }^\circ\text{C}$ in Ar, and in situ FTIR spectra were recorded during treatment.

3.6 Other characterizations

N_2 adsorption–desorption isotherms were tested on an ASAP2020 (Micromeritics, Norcross, GA, USA) apparatus at $-196 \text{ }^\circ\text{C}$. Prior to each adsorption experiment, the samples were degassed at $200 \text{ }^\circ\text{C}$ for 6 h to remove the water molecules and other impurities adsorbed on the surface. X-ray diffractometer (Bruker, 40 kV, 40 mA, Billerica, MA, USA) with Cu K_α radiation was performed to analyze the phase composition of the sample. Transmission electron microscopy (TEM) was performed using a JEM-2100 (JEOL, Tokyo, Japan) transmission electron microscope with a field emission gun operated at 200 kV to investigate the morphology and metal crystallite sizes of the catalysts. The Cu content of the sample was determined by an atomic absorption spectrometer (AA700, PerkinElmer, Waltham, MA, USA).