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Supplementary information

Copper nanoparticles socketed *in situ* into copper phyllosilicate nanotubes with enhanced performance for chemoselective hydrogenation of esters

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1. Experimental Details

Synthesis of copper phyllosilicate nanotubes (CSNTs): The CSNTs were prepared by a hydrothermal method. 5 mmol $Cu(NO_3)_2·3H_2O(s)$ and 30 mmol $NH_4Cl(s)$ were placed into a glass flask and the deionized water was added to dissolve the salts at room temperature with stirring constantly. Subsequently, 5mL of $NH_3·H_2O$ was added to this clear solution. Then, the water solution of silica colloidal was added dropwise. The mixture was transferred into stainless steel autoclave and then the autoclave was put in an oven at 473 K for 48 h. The products was collected by filtration and washed with deionized water several times. Finally, the filtrate were dried overnight under vacuum at 333 K, and calcined for 4 h at 723 K in an air atmosphere.

Synthesis of comparison catalysts. According to the literature, the comparison catalysts with the similar content were prepared by ammonia evaporation hydrothermal (AEH), urea-assisted gelation (UG) and deposition precipitation (DP) methods labeled as A-Cu/SiO_2, U-Cu/SiO_2 and D-Cu/SiO_2, respectively.

A-Cu/SiO_2: 2.416 g $Cu(NO_3)_2·3H_2O$ was dissolved in 180 ml deionized water at room temperature and 11.2 g $NH_3·H_2O$ was added under stirring. Then, 3.6 g 40 wt% Ludox as 40 colloidal silica was added into the formed copper ammonia complex solution. After stirring for 12 h at 298 K, the temperature was increased to 353 K to allow for the evaporation of ammonia and the deposition of copper species onto the silica. When the pH value of the suspension decreased to 6–7, the mixture was transferred into stainless steel autolave and then the autoclave was put in an oven at 473 K for 12 h. The products was collected by filtration and washed with deionized water several times. Finally, the filtrate were dried overnight under vacuum at 333 K, and calcined for 4 h at 723 K in an air atmosphere.

U-Cu/SiO_2: 3.5 g of 40 wt% Ludox as 40 colloidal silica was dispersed in 100 ml of aqueous solution containing 2.83 g of urea, and 2.28 g of $Cu(NO_3)_2·3H_2O$ in a round-bottomed flask. The suspension was vigorously stirred at 363 K in an oil bath for 4 h. The light blue precipitate obtained was separated by hot filtration, washed thrice with deionized water, dried overnight under vacuum at 333 K, and calcined for 4 h at 723 K in air, yielding an azure powder of Cu/SiO_2 precursors.

D-Cu/SiO_2: 1.14 g $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 80 ml deionized water at room temperature and 0.7 g SiO_2 power obtained by mechanical lapping was added to form a suspension under stirring at 363 K. 10 mol/mL Na_2CO_3 aqueous solution was added dropwise until the final pH value was 8. The slurry was aged for 4 h at 363 K, filtrated and washed with deionized water, dried overnight at 393 K, and then calcined for 4 h at 723 K in air, yielding an azure powder of Cu/SiO_2 precursors.

2. Catalyst characterizations

The actual metallic content of catalysts was determined by X-ray fluorescence spectrometry (XRF) using a Bruker S8 TIGER spectrometer.

X-ray diffraction (XRD) patterns were collected on a PANalytical X′pert Pro Super X-ray diffractometer using Cu Kα radiation (λ=0.15418 nm), operating at 40 KV and 30 mA with scanning angle (2θ) ranging from 10º to 90° at room temperature. And the data were analyzed using JADE software.

Transmission electron microscopy (TEM) was performed on a Philips Analytical FEI Tecnai 30 electron microscope at an acceleration voltage of 300 kV and fitted with an ultrahigh resolution pole piece. The catalyst powders were lightly ground and reduced in a sealed flask. After cooling to room temperature, ethanol was injected into the flask and the catalyst powders were ultrasonically dispersed without air exposure. The as-obtained suspension was then loaded onto holey Cu grid supported with carbon films. Mean crystallite sizes were obtained by counting more than 200 nanoparticles in a spherical model.

N_2 adsorption-desorption measurements were taken on a Micrometrics TriStar II 3020 system. The surface area and Pore size distributions were calculated from desorption branch according to the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

Hydrogen temperature-programmed reduction (H_2-TPR) for the as-prepared catalyst samples was performed using a Micromeritics Autochem II ASAP 2920 instrument with a thermal conductivity detector (TCD).

The copper dispersions of the samples were measured by H_2-N_2O titration experiments on a Micromeritics Autochem II 2920 apparatus with a TCD. The steps as follows: (1) Samples were reduced in a 5%H_2-95%Ar atmosphere at different temperature for 4 h and the area of hydrogen consumption denoted as A_1. (2) The surface copper atoms were oxidized to Cu_2O by N_2O. (3) The surface Cu_2O were reduced to copper by 5%H_2-95%Ar atmosphere and the area of hydrogen consumption denoted as A_2. The dispersion (D) of copper was calculated by $D = (2*A_2/A_1)*100\%$.

In-situ X-ray photoelectron spectroscopy (XPS) was performed using a PHI QUANTUM 2000 Scanning ESCA Microprobe instrument with an Al-Kα radiation source (hν = 1486.6 eV) and binding energy referenced to C 1s (284.6 eV). Prior to measurements, each sample was put in a chamber and pre-reduced by 5%H_2-95%N_2 mixture gas at different temperature for 4 h.

3. Catalytic Activity Evaluation and Product Analysis

Chemoselective hydrogenation of DMCD was carried out in a fixed bed in a high-pressure reaction system equipped with a computer-controlled auto sampling system under continuous flow mode. In a typical method, 100 mg of catalyst precursor (40−60 meshes) was sandwiched between the inert layers of quartz powder (40−60 meshes) in the center of the reactor. Prior to initiating the reaction, the catalyst was reduced in 5% H_2−95% N_2 atmosphere (50 mL/min) at 523-823 K for 4 hours at a ramping rate of 2 K/min. The catalyst bed was cooled to reaction temperature, pure H_2 was introduced into the reactor, and pressure was maintained at 5.0 MPa by using a back-pressure regulator. A 5%wt DMCD−methanol solution was injected into the catalyst bed by using a high-pressure liquid feed pump (Series III digital HPLC pump, Scientific Systems, Inc.). Finally, the products were analyzed by an Agilent GC7890A gas chromatograph equipped with flame ionization detector and HP-5 capillary column.

The initial turnover frequency (TOF) of the reaction was measured at the DMCD conversion below 30% by increasing the LHSV. The value of TOF indicates the activity of the catalyst per surface Cu site and is calculated according to the following equation:

$$TOF = \frac{V \times C_{DMCD} \times X_{DMCD}}{D \times NM}$$

Where V is the flow rate of the DMCD methanol solution (L/h), C_{DMCD} is the DMCD concentration in the DMCD methanol solution (mol/L), X_{DMCD} is the measured DMCD conversion, D is the dispersion of Cu particles, and N_M is the mole of Cu loading amount. Thus, the TOF number equals to the number of mole of DMCD converted per hour per mole of metal site on the catalyst surface (simply for h^{-1}).

Table S1. Physiochemical properties of Cu-based catalysts.

Catalyst	Metal loading [a] / wt%	Average metallic size [b] / nm	S_{BET} / $m^2 g^{-1}$	V_p [c] / $cm^3 g^{-1}$	D_p / nm	Cu dispersion [d] / %
CSNTs	29.2	–	486.9	1.22	8.3	–
CSNTs-523	29.2	4.9	465.4	1.13	8.1	32.3
CSNTs-623	29.2	4.6	469.1	1.15	8.1	35.4
CSNTs-723	29.2	5.0	446.3	0.95	7.7	28.4
CSNTs-773	29.2	5.0	430.8	0.82	7.7	22.4
CSNTs-823	29.2	5.2	404.5	0.77	7.2	21.1
D-Cu/SiO_2	30.3	3.0	322.5	0.47	4.4	28.7
U-Cu/SiO_2	29.6	4.3	378.9	0.70	8.5	31.6
A-Cu/SiO_2	30.5	5.2	465.9	0.97	8.3	27.9

[a] Determined by XRF. [b] Calculated by Scherrer Equation. [c] Obtained from P/P_0=0.99. [d] Cu dispersion was calculated by N_2O titration.

Table S2. Thermal stability of Cu-based catalysts [a].

Catalyst	STY_F [b] / h^{-1}	STY_T [c] / h^{-1}	Ratio of STY_T / STY_F
D-Cu/SiO_2	0.68	0.37	0.55
U-Cu/SiO_2	1.50	1.32	0.88
A-Cu/SiO_2	1.88	1.74	0.93
CSNTs-623	1.90	1.89	0.99

[a] Reaction conditions: $P(H_2)$ = 5.0 MPa, T = 493 K, LHSV = 2.0 h^{-1}, and H_2/DMCD molar ratio = 260. [b] STY_F represents the space time yield of CHDM for the fresh catalysts, grams of product per gram of catalyst per hour (g g_{-catal}^{-1} h^{-1}, for short h^{-1}). Data were collected after on stream of 4 h. [c] STY_T represents the space time yield of CHDM for the catalysts after a 24 h thermal treatment at 623 K. Data were collected after time on stream of 4 h.

Table S3. Cu LMM deconvolution results of Cu-based catalysts before and after thermal treatment.

Catalyst	K. E. / eV [a]		A. P. / eV [b]		X_{Cu+} / %
	Cu^+	Cu^0	Cu^+	Cu^0	
Fresh D-Cu/SiO_2	914.0	918.0	12679.2	12578.3	50.2
Used D-Cu/SiO_2	914.0	918.0	8595.5	11004.2	43.9
Fresh U-Cu/SiO_2	914.3	918.2	10526.4	8680.6	54.8
Used U-Cu/SiO_2	914.0	918.0	7630.5	8044.1	48.7
Fresh A-Cu/SiO_2	914.2	918.1	14550.5	9441.4	60.6

Used A-Cu/SiO_2	913.9	918.0	17099.16	13495.1	55.9
Fresh CSNTs-623	914.2	918.0	28960.5	14948.9	65.9
Used CSNTs-623	914.0	917.9	11037.2	6940.2	61.4

[a] Kinetic energy. [b] Auger parameter. [c] Intensity ratio between Cu^+ and (Cu^++Cu^0) by deconvolution of Cu LMM XAES spectra.

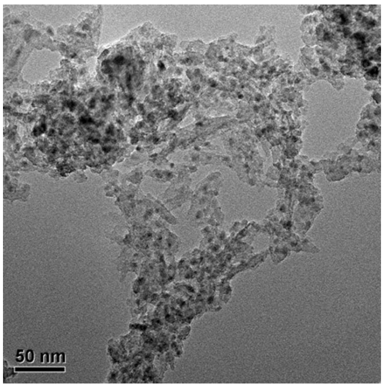

Fig. S1. TEM image of CSNTs-773.

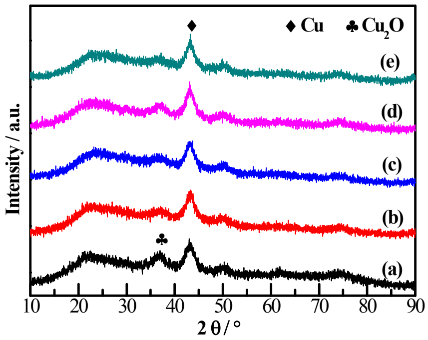

Fig. S2. The XRD patterns of CSNTs reduced under different temperature. (a) CSNTs-523, (b) CSNTs-623, (c) CSNTs-723, (d) CSNTs-773, and (e) CSNTs-823.

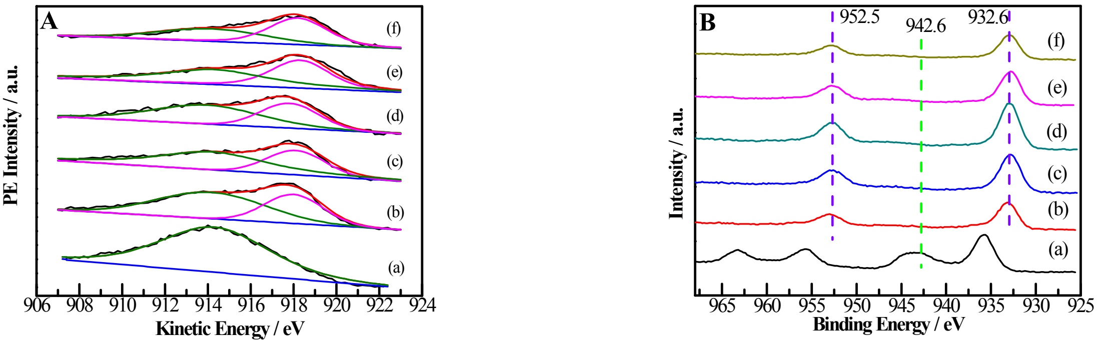

Fig. S3. (A) Cu LMM XAES and (B) Cu 2P XPS spectra of CSNTs under different reduction temperatures. (a) as-prepared CSNTs, (b) CSNTs-523, (c) CSNTs-623, (d) CSNTs-723, (e) CSNTs-773, and (f) CSNTs-823.

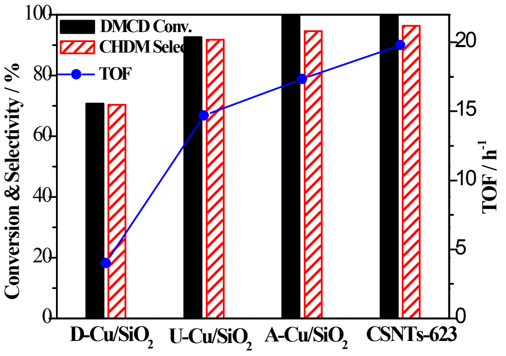

Fig. S4. Catalytic performance of Cu-based catalysts for the selective hydrogenation of DMCD to CHDM. Reaction conditions: $P(H_2)$ = 5.0 MPa, T = 493 K, H_2/DMCD molar ratio = 260, and LHSV = 1.0 h^{-1}.

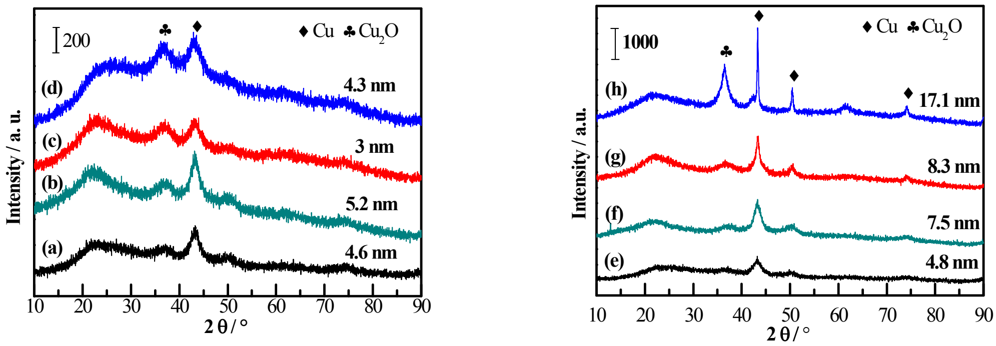

Fig. S5. XRD patterns of (a) fresh CSNTs-623, (b) fresh A-Cu/SiO$_2$, (c)fresh U-Cu/SiO$_2$, (d) fresh D-Cu/SiO$_2$, (e) used CSNTs-623, (f) used A-Cu/SiO$_2$, (g) used U-Cu/SiO$_2$, and (h) used D-Cu/SiO$_2$ catalysts, and the mean particle size was calculated by Scherrer Equation.

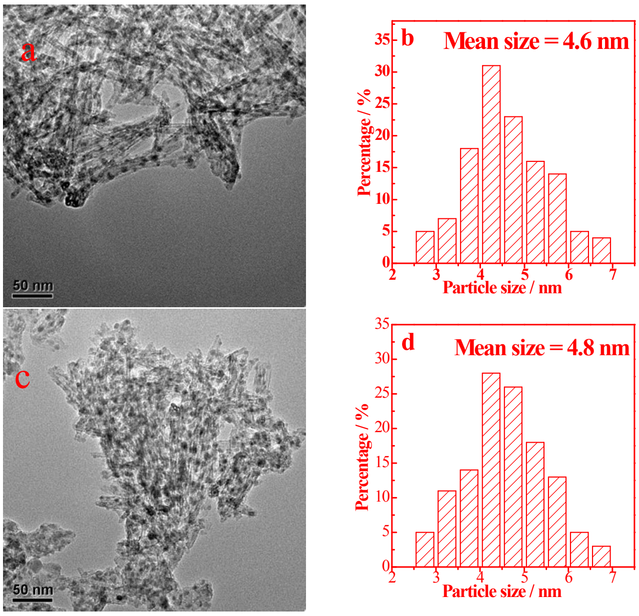

Fig. S6. TEM images and metal particle size distributions of (a), (b) Fresh CSNTs-623 and (c), (d) Used CSNTs-623.

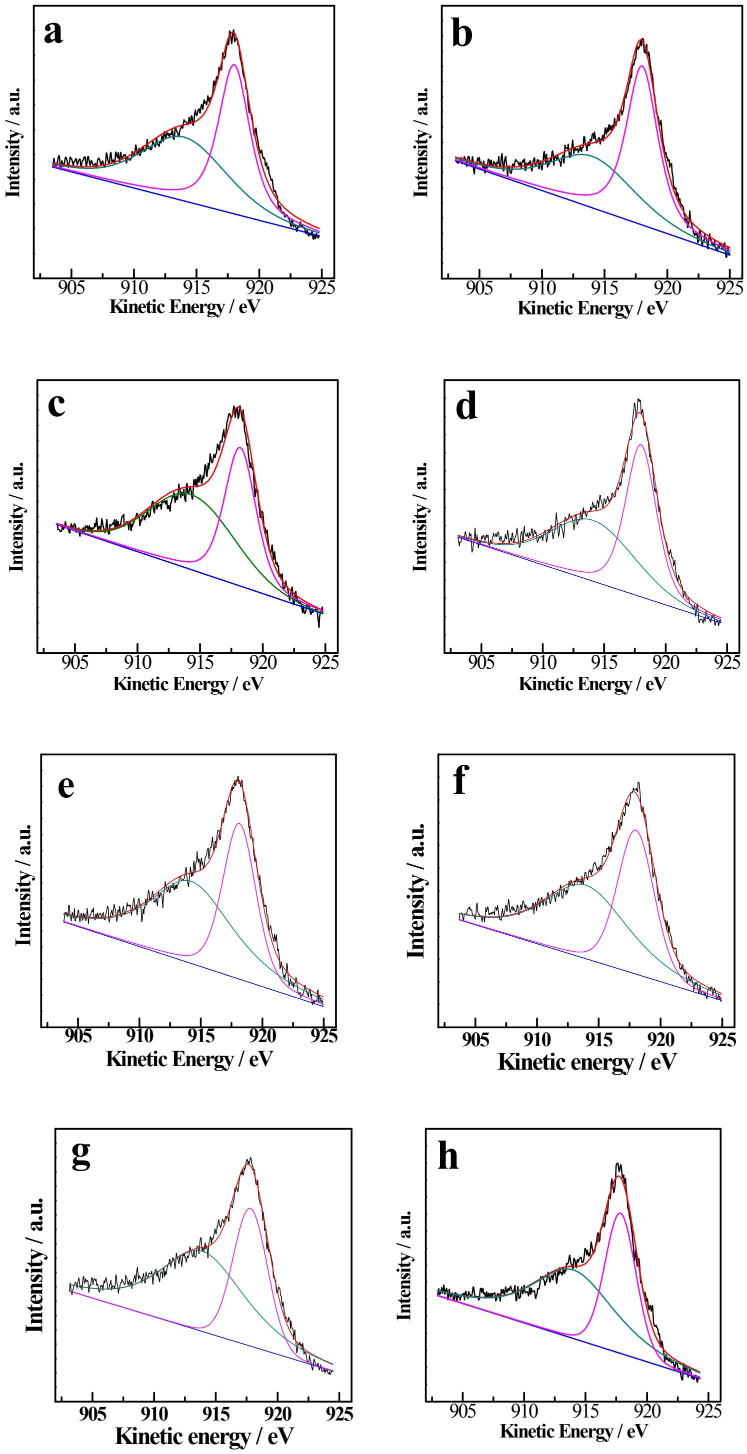

Fig. S7. The Cu LMM XAES spectra of samples: (a) fresh D-Cu/SiO_2, (b) used D-Cu/SiO_2, (c) fresh U-Cu/SiO_2, (d) used U-Cu/SiO_2, (e) fresh A-Cu/SiO_2, (f) used A-Cu/SiO_2, (g) fresh CSNTs-623, and (h) used CSNTs-623.

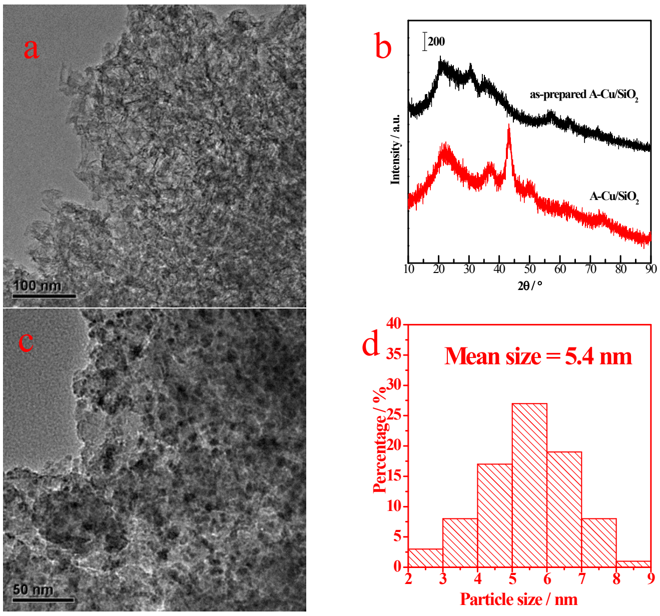

Fig. S8. (a) TEM image of as-prepared A-Cu/SiO_2; (b) XRD patterns of as-prepared A-Cu/SiO_2 and as-reduced A-Cu/SiO_2; (c) TEM image of as-reduced A-Cu/SiO_2; (d) Metal particle size distribution of as-reduced A-Cu/SiO_2.