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Hydrogenation of styrene oxide into 2-phenylethanol over nanosized supported copper phyllosilicate catalyst

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Experimental procedure

Catalyst preparation

The 12%Cu/SiO_2 catalyst was synthesized by the method of deposition–precipitation using the thermal hydrolysis of urea (DPU). SiO_2 (‘KSKG’, KhimMed), urea (Acros Organics), $Cu(NO_3)_2\cdot 3H_2O$ (98+, Aldrich) were used as precursors without additional purification. Powdered silica (1000 mg) was suspended in deionized water (21 ml). Then the proper amount (4.72 ml) of copper(II) nitrate (0.45 M aq.) and urea (1.29 g) were added to the suspension, which was then heated to 92 ^{o}C and kept at this temperature for 8 h under stirring. During the DPU synthesis, the probe of mother solution and solid was taken after 1, 3, 4, and 8 h. The pH of mother solution was checked as well as the presence of Cu^{2+} in the solution probe. The qualitative analysis of a mother solution probe with ammonia confirmed the complete copper phase deposition after 3 h. The solid probes were centrifuged and dried at 110 ^{o}C overnight. The probe obtained after 8 h of DPU procedure was additionally calcined at 300 ^{o}C for 4 h. The samples were denoted as Cu/SiO_2-*x*h-*y*, where *x* – the time of DPU synthesis (h), *y* – the temperature of thermal treatment of the sample (^{o}C). The nominal Cu loading was 12% wt.

The 12%Cu/SiO_2-WI catalyst was synthesized by wet impregnation method. Silica (‘KSKG’, KhimMed) and $Cu(NO_3)_2\cdot 3H_2O$ (98+, Aldrich) were used without additional purification. Copper(II) nitrate (0.45 M aq., 4.72 ml) was added dropwise to the powdered support (1000 mg). After that the slurry was dried under vacuum (40 mbar) at 40 °C using rotary evaporator followed by drying in an oven at 110 °C for 12 h. The obtained sample was then calcined at 550 ^{o}C for 4 h. The nominal Cu loading was 12% wt.

Table S1. Characteristics of the samples obtained by DPU method and WI.

Sample	pH $_{ms}$	Cu^{2+} $_{ms}$	Phase	Cell type	*a*, Å	*a* $_{table}$, Å	*D* $_{XRD}$, nm
Cu/SiO$_2$-1 h-110	4.44	+	Rouaite	Monoclinic	5.593×6.079×6.925	5.593×6.069×6.921	> 100
Cu/SiO$_2$-3 h-110	6.06	-	Rouaite				
Cu/SiO$_2$-4 h-110	6.01	-	Rouaite				
Cu/SiO$_2$-8 h-110	7.13	-	Chrysocolla	Orthorhombic	n.d.	5.7×8.9×6.7	5 (TEM)
Cu/SiO$_2$-8 h-300	-	-	Chrysocolla				3 (TEM)
Cu/SiO$_2$-WI	-	-	Tenorite	Monoclinic	4.684×3.425×5.130	4.684×3.423×5.129	25

ms – mother solution

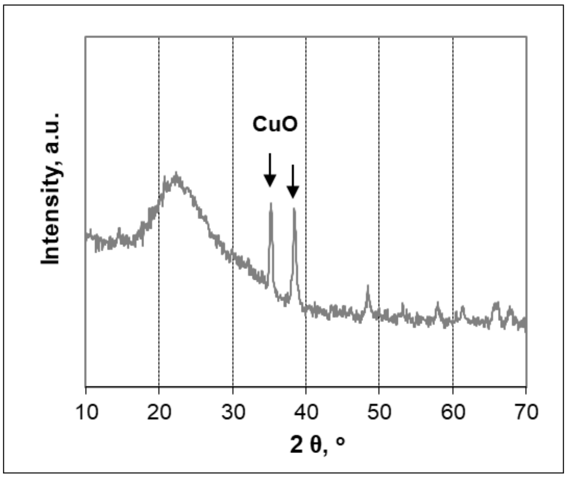


Figure S1. XRD pattern of Cu/SiO$_2$-WI sample.

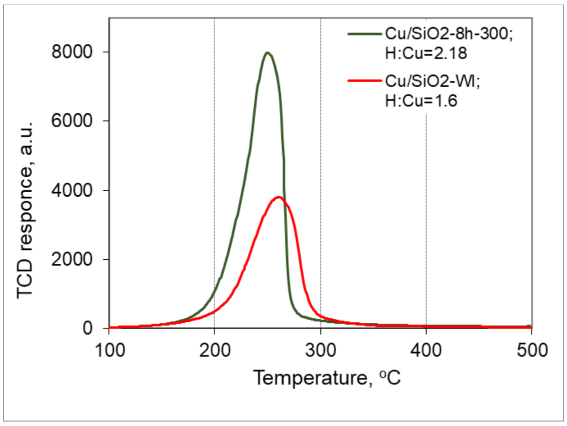


Figure S2. TPR-H$_2$ curves for Cu/SiO$_2$-8h-300 and Cu/SiO$_2$-WI samples**.**

Catalyst characterization

XRD

X-ray diffraction patterns were recorded using an ARL X'tra diffractometer (Thermo Fisher Scientific) equipped with a theta-theta goniometer (CuKa radiation, 40 kV, 40 mA) in the range of $2\theta = 10^o – 80^o$ at a scanning speed of 1 deg min^{-1}. Phase identification was performed by comparing the position and intensity of the peaks with data from the International Diffraction Data Center files.

TEM, SEM

Target-oriented approach was utilized for the optimization of the analytic measurements [V. V. Kachala, L. L. Khemchyan, A. S. Kashin, N. V. Orlov, A. A. Grachev, S. S. Zalesskiy, V. P. Ananikov, *Russ. Chem. Rev.*, 2013, **82**, 648-685]. Before measurements the samples were mounted on a 25 mm aluminum specimen stub, fixed by conductive carbon tape, and coated with a 30 nm film of carbon. The observations were carried out using Hitachi Regulus8230 field-emission scanning electron microscope (FE-SEM). Images were acquired in backscattered electron mode (compositional contrast) at a 10kV accelerating voltage.

Samples morphology was studied using Hitachi HT7700 transmission electron microscope. Images were acquired in bright-field TEM mode at 100 kV accelerating voltage. Before measurements the samples were deposited on the 3 mm grids.

N_2 adsorption-desorption

The N_2 adsorption-desorption isotherms at 77 K were measured by the Micromeritics ASAP 2020 Plus System. Prior to acquisition of the adsorption isotherm, the calcined sample (0.2–0.3 g) was degassed for 3 h at 110 or 300 °C under a residual pressure of 0.8 Pa. The BET method was used to calculate the specific surface area of the sample. Pore size distributions for mesopores were determined by Barret-Joyner-Halenda (BJH) method applied to the desorption isotherms with Harkins and Jura thickness curve. The total pore volume was evaluated at $p/p^o = 0.99$. The cumulative volume at desorption in the BJH method was taken as a mesopore volume. The micropore volume was calculated by t-plot method and DFT method (model: N_2 - Cylindrical Pores - Oxide Surface). The mesopore specific surface area was calculated as cumulative at desorption in the BJH method. The micropore size distribution was calculated according to the Horwath-Kawazoe model in assumption of a cylinder shape of the pores.

Catalytic experiment

The hydrogenation of styrene oxide **2** was carried out in a stainless-steel autoclave with glass liner at 150 °C and initial hydrogen pressure of 10 atm. Styrene oxide (0.4 mmol) and catalyst (50 mg) were placed into glass liner, then THF (2.2 ml) were added. The glass liner was placed in the autoclave. The autoclave was closed and purged with hydrogen (10 atm) for five times to remove the residual air. After that, the reaction volume was filled with hydrogen under a pressure of 10 atm, and the autoclave was placed on an oil bath preheated to the desired temperature. The reaction was carried out at a stirring speed of 1000 rpm for 5-9 h. At the end of the experiment, the autoclave was cooled in an ice bath and de-pressured slowly. The liquid phase was separated from the catalyst *via* centrifugation, and samples were taken to analyse the reaction products.

NMR

The structure of the obtained products was determined by ^{1}H and ^{13}C NMR spectroscopy on a Bruker Fourier 300HD (300.1 and 75.5 MHz) spectrometer in DMSO-d_6. The yield of the product was determined by ^{1}H NMR spectra of the obtained sample probe with the external standard (1,1,2,2-tetrachloroethane). The yield of the product (Y) was calculated according to the equations 1-2:

$$n\,prod = n\,st \cdot \frac{I\,prod}{Hprod} \cdot \frac{H\,st}{Ist} \qquad (1)$$

n - amount of standard (st) or product (prod) in the probe, mol:

I – the intensity of a characteristic signal in ^{1}H NMR spectrum

H – the number of protons correlated to the characteristic signal in ^{1}H NMR spectrum;

$$Y = \frac{n\,prod}{n\,t} \cdot \frac{m}{m\,prod} \cdot 100\% \qquad (2)$$

n t – theoretical amount of the target product, mole;

m prod – mass of the probe taken to NMR analysis, g;

m – total mass of the dried sample obtained in the reaction, g;

SEM images

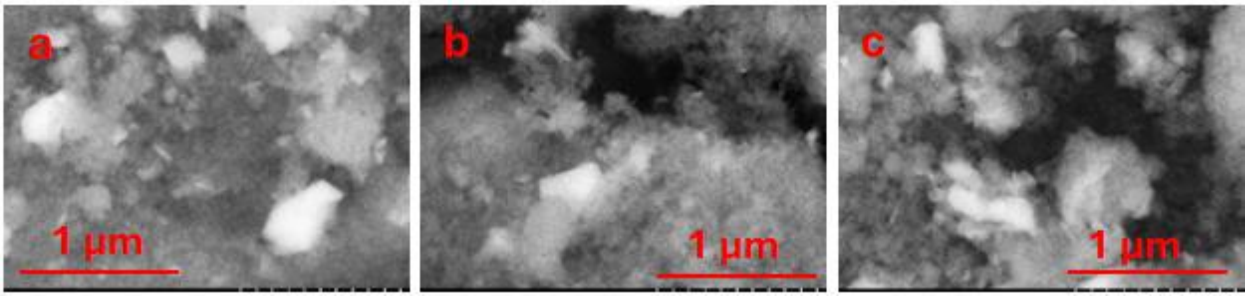


Figure S3. SEM images of (*a*) Cu/SiO$_2$-1h-110, (*b*) Cu/SiO$_2$-3h-110, and (*c*) Cu/SiO$_2$-4h-110 samples.

TEM images

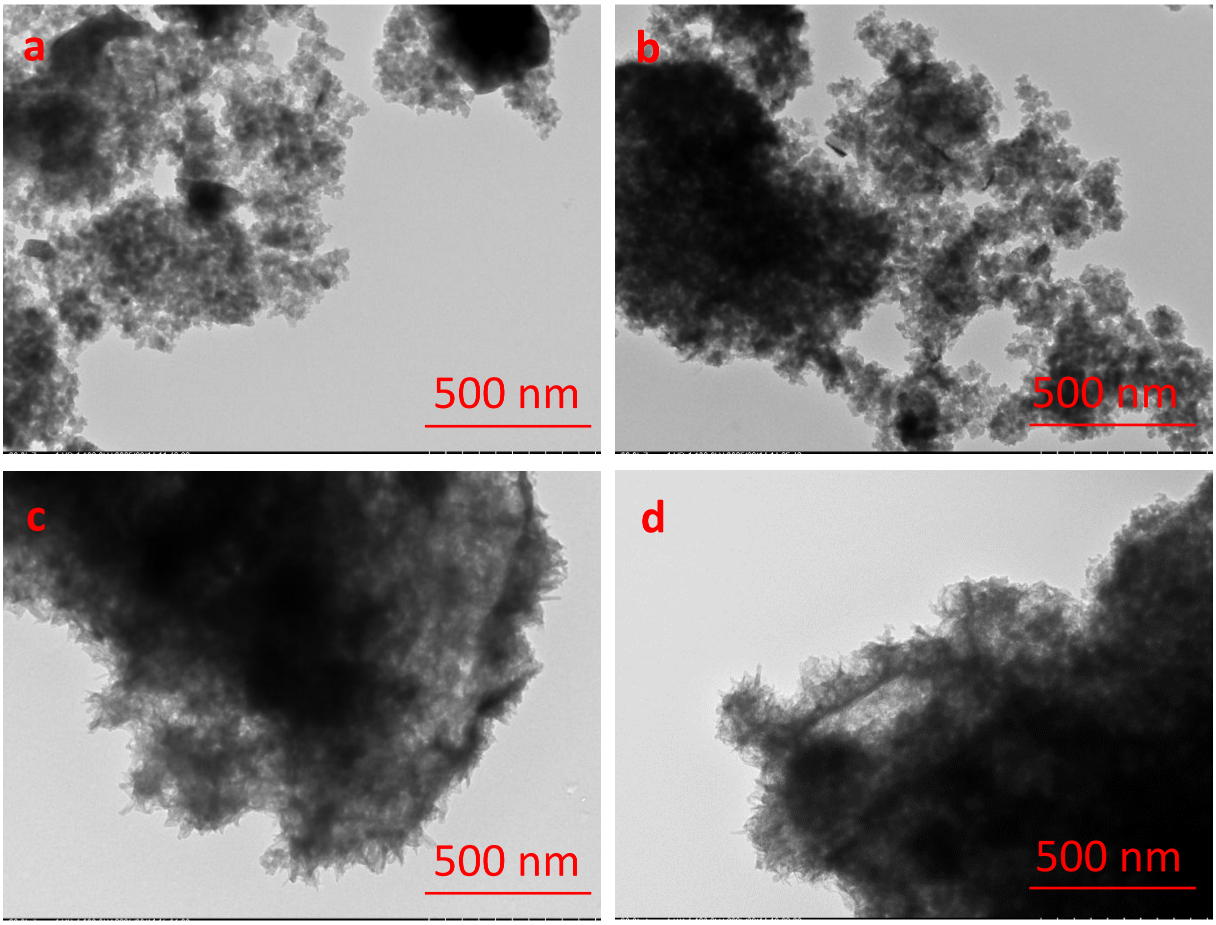
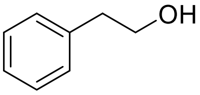


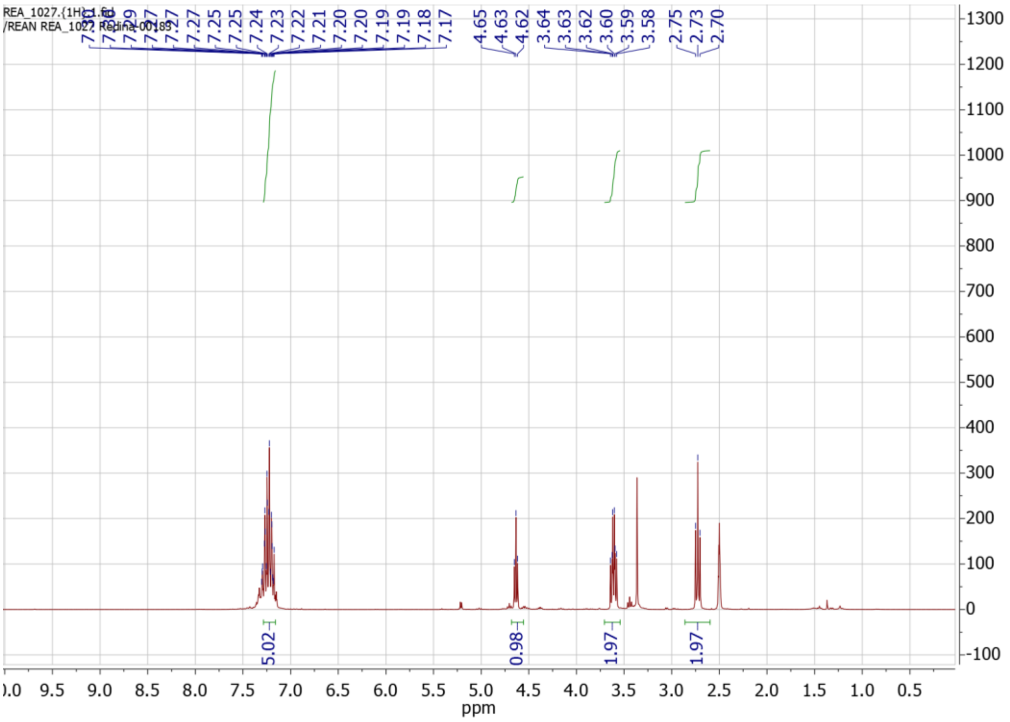
Figure S4. TEM images of (*a*) Cu/SiO_2-1h-110, (*b*) Cu/SiO_2-4h-110, (*c*) Cu/SiO_2-8h-110, and (*d*) Cu/SiO_2-8h-300 samples.

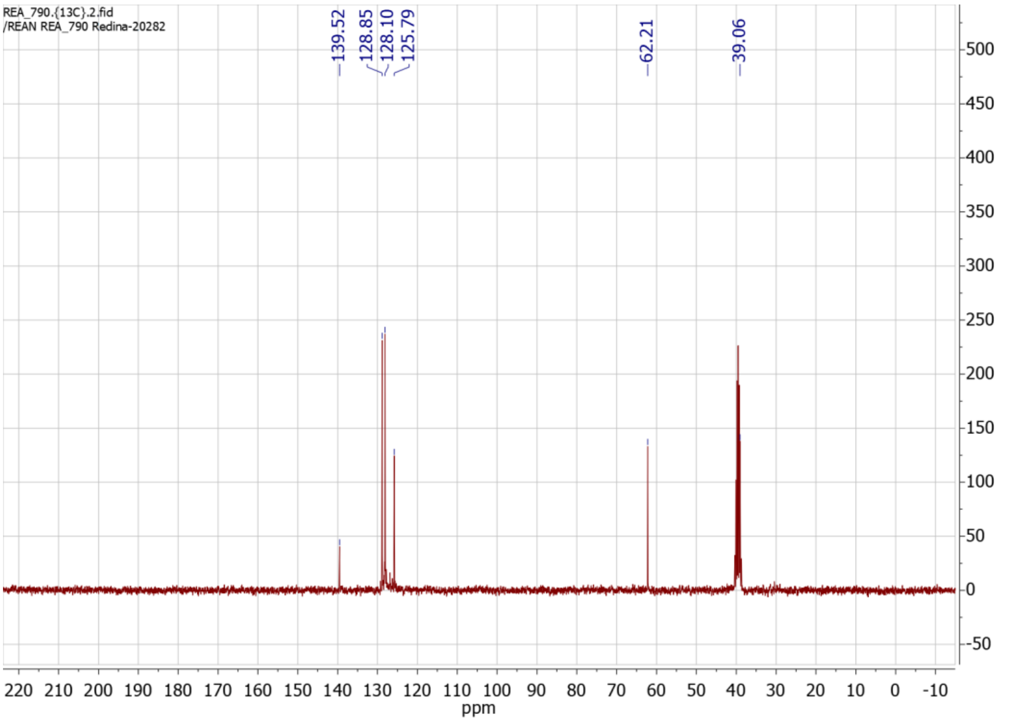
NMR spectra

^{1}H, ^{13}C NMR spectra of the reaction mixture obtained over Cu/SiO_2-8h-300 after 9 h of the styrene oxide hydrogenation and evaporated under vacuum 10 torr at 30°C; colorless viscous liquid with a rose scent.

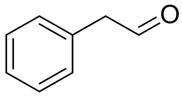


2-Phenylethanol **1** ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.40 – 7.13 (m, 5H), 4.63 (t, *J* = 5.2 Hz, 1H, *OH*), 3.61 (td, *J* = 7.1, 5.1 Hz, 2H, *CH₂*), 2.73 (t, *J* = 7.1 Hz, 2H, *CH₂*). ^{13}C NMR (75 MHz, DMSO-d_6) δ 139.5, 128.9, 128.1, 125.8, 62.2, 39.1





^{1}H, ^{13}C NMR spectra of the main reaction product obtained over Cu/SiO_2-WI after 9 h of the styrene oxide hydrogenation.



Phenylacetaldehyde **3** ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.69 (t, J = 2 Hz, 1H, *CHO*), 7.43 – 7.29 (m, 5H), 3.76 (d, J = 2 Hz, 2H, *CH_2*). ^{13}C NMR (75 MHz, DMSO-d_6) δ 200.5, 132.8, 129.7, 128.6, 126.9, 49.5.