Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Ethanol-induced transformation of furfural into 1,4-pentanediol over a Cu/SiO2 catalyst with enhanced metal-acid sites by copper phyllosilicate

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1 EXPERIMENTAL SECRION

1.1 Materials.

$Cu(NO_3)_2·3H_2O$ (A.R., Macklin Ltd.), 28% ammonia aqueous solution (A.R., Guangzhou Chemical Reagent Factory), silica sol (Shandong Yinfeng Nano New Material Co. Ltd), fumed SiO_2 powder (Sigma-Aldrich). 1,4-pentanediol (98%), furfural (99%), furfuryl alcohol (97%), 2-ethoxymethyl-furan (98%), ethyl levulinate (98%), γ-valerolactone (98%), 3-acetyl-1-propanol (95%), 2-methyltetrahydrofuran (99.5%), 2-methyl furan (98%), cyclopentanone (99.5%), cyclopentanol (99.5%), tetrahydro furfuryl alcohol (99%) and ethanol (100%) were purchased from Aladdin Ltd. Furfural and furfuryl alcohol were purified by distillation in vacuum at 80℃ before used. Other chemicals were used without further purification.

1.2 Catalyst characterizations.

ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) was used to determine the Cu loading of the catalysts with a Perkin-Elmer OPTIMA 8000 instrument. Textural properties were examined utilizing N_2 physical adsorption at -196 ℃ on a Micromeritics instrument (Tristar II 3020). Prior to tests, the samples were degassed under vacuum (10^{-3} torr) at 200 ℃ for 12 h. The crystalline structures of the catalysts were characterized by XRD (X-ray diffraction) using a MiniFlex 600 instrument with Cu Kα radiation (λ = 1.54059 Å). XRD patterns were collected with a scanning range of 10-80° and step size of 0.02°/s. The IR spectra were recorded on a Nicolet NEXUS 470 in the range of 4000-400 cm^{-1} with a 4 cm^{-1} resolution. H_2-TPR (H_2-temperature programmed reduction) of the catalysts were conducted using a chemisorption analyzer (AutoChem II 2920, America Micromeritics) equipped with a thermal conductivity detector (TCD). Prior to the experiments, all of the catalysts (20 mg) were dried in flowing He (30 mL/min) at 100 °C for 30 min. After cooling down to room temperature, the flow was changed to 30 mL/min of 10%H_2/Ar. Subsequently, the catalysts were heated to 500 °C in H_2 with a rate of 10 °C/min, and the TCD signal was recorded. TEM (transmission electron microscopy) was tested on a FEI Talos F200S (accelerating voltage of 200 kV). "The average particle size was calculated using an equation of $d = \sum n_i d_i^3 / \sum n_i d_i^2$, where n_i is the number of particles with diameter of d_i. The particle size distribution was determined by measuring 100-200 particles." The acidity of the catalysts was analyzed by NH_3-TPD (NH_3-temperature-programmed desorption) with a TP-5080 (China Xianquan) instrument. Firstly, the catalysts (200 mg) were reduced with hydrogen at 260 °C for 2 h and then were purged with He at 300 °C for 1 h to remove the adsorbed H_2. After that, the catalysts were saturated with NH_3 at 100 °C and purged with He to remove the physisorbed NH_3. Finally, the samples were heated to 500 °C in He with a rate of 10 °C/min.

1.3 Products analysis.

In this work, carbon balance, conversion and products yields were calculated by the following equations:

$$\text{Carbon balance (C–mol\%)} = \frac{\sum \text{Mole of carbon in the product}}{\text{Moles of carbon in the initial substrate}} \times 100\%$$

$$\text{Conversion} = 100\% - \frac{\text{Moles of carbon in the } products}{\text{Moles of carbon in the initial substrate}} \times 100\%$$

$$\text{Yield} = \frac{\text{Moles of carbon in } a\ spesific \text{ product}}{\text{Moles of carbon in the initial substrate}} \times 100\%$$

Table S1. Chemical, abbreviation and condensed structural formulas.

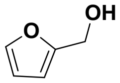
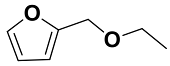
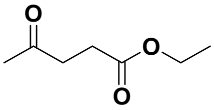
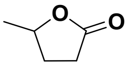
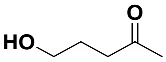
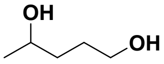
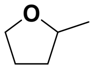
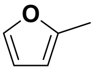
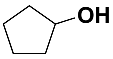
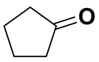
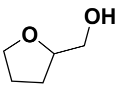
Chemical	Abbreviation	Condensed structural formulas
furfuryl alcohol	FOL	
2-ethoxymethyl-furan	2-(EoM)F	
ethyl levulinate	EL	
γ-valerolactone	GVL	
3-acetyl-1-propanol	3-AP	
1,4-pentanediol	1,4-PeD	
2-methyltetrahydrofuran	2-MTHF	
2-methylfuran	2-MF	
cyclopentanol	CPL	
cyclopentanone	CPO	
tetrahydrofurfuryl alcohol	THFOL	

Table S2. Transformation of the substrates over the reduced 20Cu/SiO_2-AE catalyst.

Entry	Substrate	Conv. (%)	Yield (%)				Carbon balance (%)
			1,4-PeD	3-AP	2-MTHF	Others^a	
1	1,4-PeD	24.0	-	0.0	19.0	5.0	99.9
2	2-MF	24.9	7.5	0.6	16.8	0.0	99.9

Reaction conditions: 300 mg 20Cu/SiO_2-AE catalyst, 5.2 mmol substrate, 12.0 mL H_2O/ethanol (9:3 volume ratio), 4.0 MPa H_2, 180 °C, reaction for 8 h.

[a] Including 1-pentanol, 2-pentanol and humins.

1,4-PeD = 1,4-pentanediol, 3-AP= 3-acetyl-1-propanol, 2-MTHF = 2-methyltetrahydrofuran, 2-MF = 2-methylfuran.

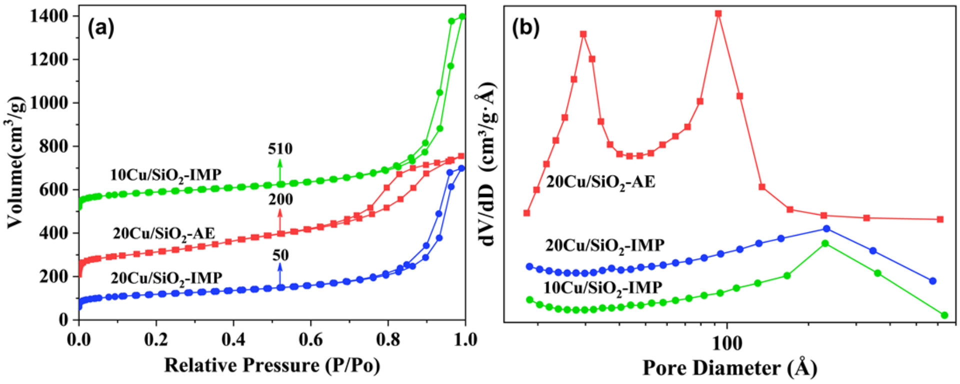


Figure S1. (a) N_2 adsorption-desorption isotherms; (b) Pore distribution curves of the calcined catalysts.

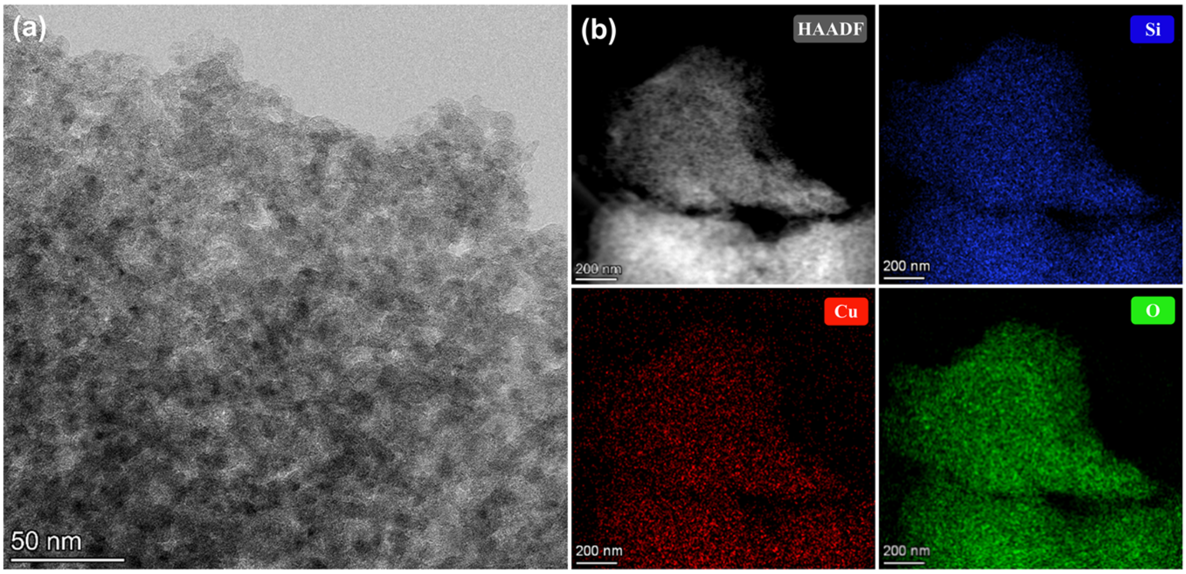


Figure S2. (a) TEM image of the reduced 20Cu/SiO_2-AE catalyst; (b) High annular dark-field scanning TEM (HAADF-STEM) and the corresponding elemental mapping images of the reduced 20Cu/SiO_2-AE catalyst.