The effect of supports on hydrogenation and water-resistant of copper-based catalysts

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1.1. Hydrogenation reaction

The effects of support on hydrogenation and water resistance of copper catalysts were studied by ethyl acetate hydrogenation. The performances of copper catalyst were evaluated on a continuous flow unit equipped with vertical stainless steel tubular reactor. The H_2 flow was controlled by Brooks 5850E mass flow controller (MFC). The pressure was always maintained at 2.5 MPa via a back pressure regulator, during the whole evaluation period. After in situ reduction at 300 ^{o}C for 4 h with a H_2 flow rate of 30 ml min^{-1}, the catalysts were cooled to room temperature. Then, the fixed bed reactor was heated to needed temperature at steps of 1 ^{o}C min^{-1}. The liquid reactant (ethyl acetate with 5 wt.% water and 4 wt.% ethanol,) was injected by double-plunger pump, enabling a tunable liquid hourly space velocity (LHSV). After vaporizing by a preheater, the vapor was mixed with H_2. The reaction products were collected in a 5 ^{o}C cooling cool trap and analysed by gas chromatography (Shimadzu GC-14C) using a capillary column (19091n-213, HP-INNOWAX, 0.25 mm × 30 m) with FID and a packed column (TDX-101) with TCD as the detectors. The gas products were analysed by online gas chromatographs (Shanghai Haixin GC-950) with a packed column filled with carbon molecular sieve.

1.2. Characterization

The powder X-ray diffraction (XRD) patterns of the prepared catalysts were recorded by a Shimadzu XRD-6000 diffractometer using Cu Kα radiation

(λ=1.5418Å) in the 2θ scanning range between 10°and 80°. The information of specific surface area and pore sizes of the catalysts was determined by Brunauer-Emmett-Teller (BET) measurements using a Tristar II3020N2 adsorption analyzer. Then, the TPR experiments were performed as follows: the fresh catalysts (20 mg) were placed in a quartz reactor and were reduced by a 5% H_2/N_2 gas mixture with a flow rate of 50 ml min^{-1}, ramping at 10 °C min^{-1} to the final temperature. Meanwhile, hydrogen consumption was recorded using a thermal conductivity detector (TCD). The specific surface area (S_{Cu}), average volume-surface diameter (d_{Cu}) and dispersion (D_{Cu}) of metal copper were measured by N_2O oxidation at 50 °C. The more details could be found from the below. The X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD) was carried out to analyse elemental valance of surface. The changes of morphology of the samples were characterized by means of a high-resolution transmission electron microscope (HRTEM, JEM 2100F). The Raman spectra were recorded on a Horiba-Jobin-Yvon spectrometer equipped with a He-Ne laser light source excited by a wavelength of 632.8 nm.

N_2O-H_2 redox titration procedure

The number of surface metallic copper sites was determined by dissociative N_2O adsorption at 50 °C. [1-2] Catalysts were first reduced by a 5% H_2 / N_2 gas mixture with a flow rate of 50 ml min^{-1}, ramping at 5 °C min^{-1} to 350 °C, and this temperature was hold for 40 min. The amount of hydrogen consumption in first TPR (TPR1) was denoted as X. And then, the catalyst bed was purged with Ar and cooled to 50 °C. Surface copper

atoms were oxidized in a N_2O (50mL/min) at 50 °C for 0.5 h. Finally, samples were flushed with 5% H_2 / N_2 to remove the oxidant for 1 h and then to start another TPR run. Hydrogen consumption in the second TPR (TPR2) was denoted as Y.

The dispersion of Cu and exposed Cu surface area are calculated on the equations reported by Van Der Grift et al. [1]

All copper atoms were reduced in the first TPR:

$$CuO + H_2 \rightarrow Cu + H_2O,$$ hydrogen consumption = X

Surface copper atoms that were oxidized to Cu_2O by N_2O at 50 °C were reduced in the second TPR:

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O,$$ hydrogen consumption = Y

And the dispersion of Cu and exposed Cu surface area were calculated as:

$$D = (2\ Y\ /\ X) \times 100\%\ ;\ S = 1353 \times Y\ /\ X\ (m^2\ Cu\ /\ g\ Cu);\ d_{v.s.} = 0.5\ X\ /\ Y\ (nm)$$
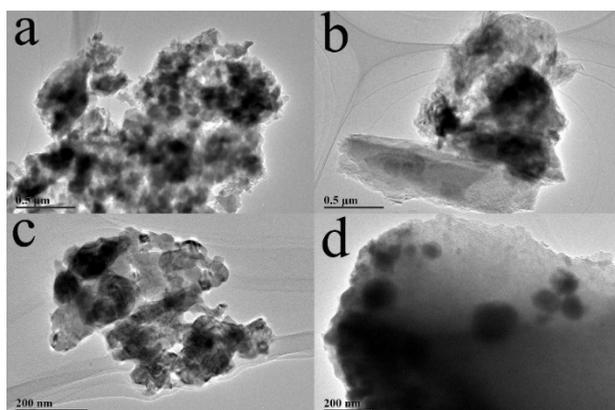
Figure S1. The TEM images of Cu/Al_2O_3 (a, b) and Cu/ZrO_2 (c, d) catalysts before (a, c) and after (b, d) reaction.
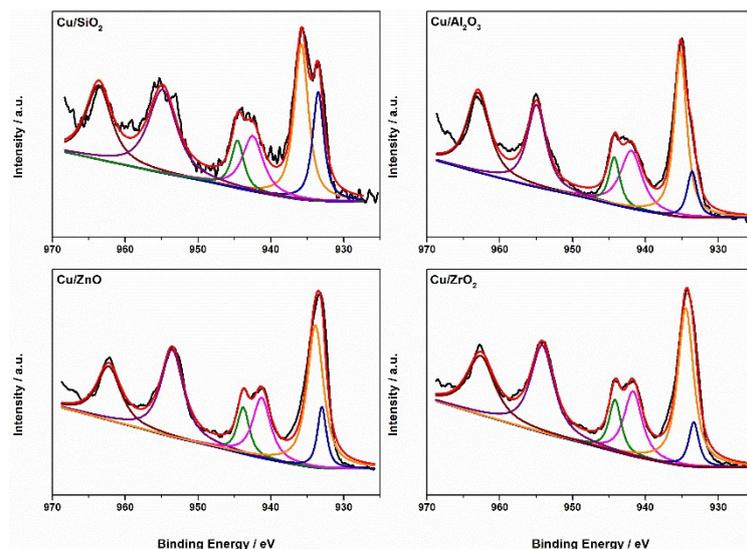
Figure S2. The XPS of Cu/SiO_2, Cu/Al_2O_3, Cu/ZnO and Cu/ZrO_2 catalysts before reaction.
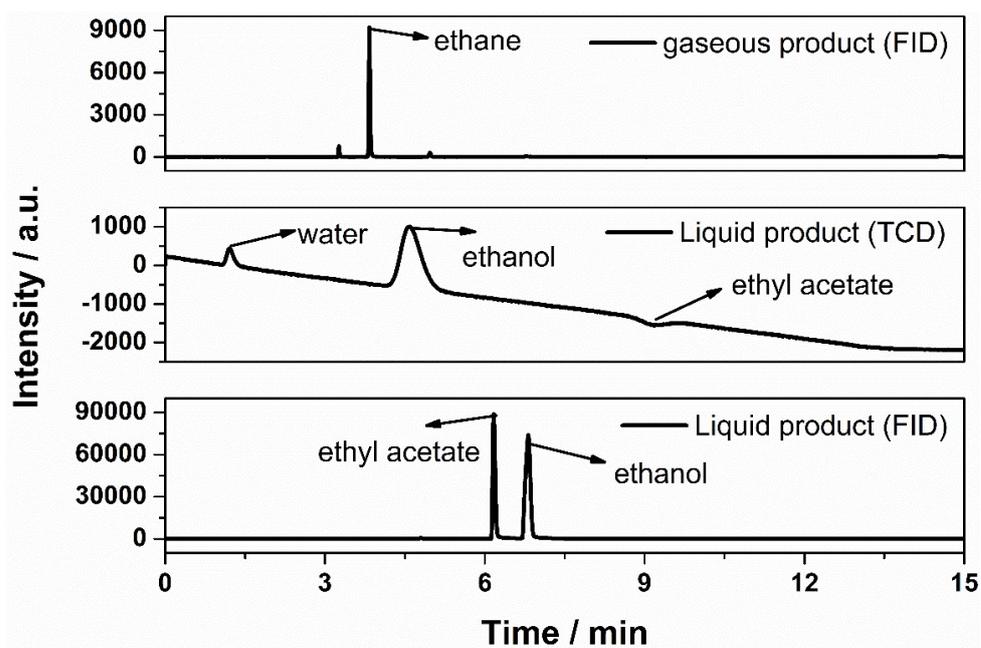
Figure S3. Chromatogram map of Liquid product and gaseous product for ethyl acetate containing water hydrogenation.
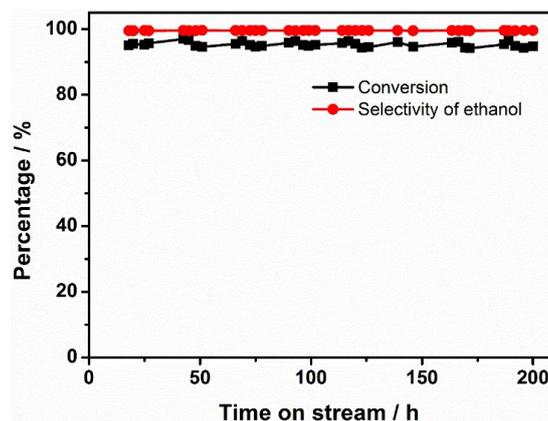
Figure S4. The stability experiment of Cu/ZnO catalyst at reaction condition: T = 240 °C, P = 2.5 MPa, n(H$_2$) / n(ethyl acetate) = 40 (molar ration), m(H$_2$O)/ m(ethyl acetate)/ m(ethanol) =5/ 91/ 4 (mass ration) and LHSV of ethyl acetate = 1h^{-1}.
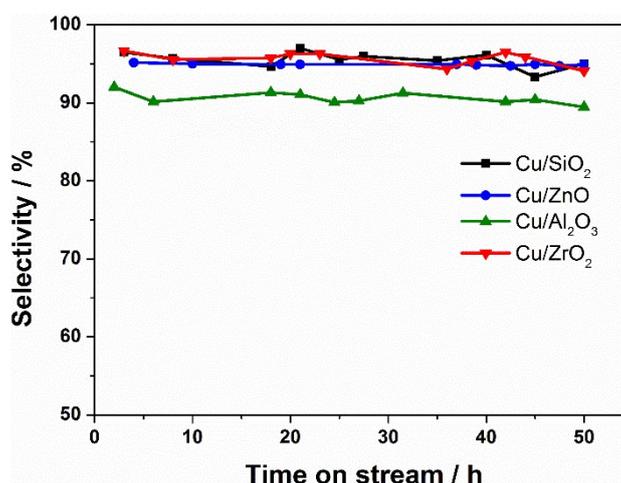
Figure S5. The selectivity of ethanol for all catalyst at reaction condition: T = 240 °C, P = 2.5 MPa, n(H$_2$) / n(ethyl acetate) = 40 (molar ration), pure and LHSV of ethyl acetate = 1h^{-1}.

References

[1]   Van Der Grift, C. J. G.; Wielers, A. F. H.; Jogh, B. P. J.; Van Beunum, J.; De Boer, M.; Versluijs-Helder, M.; Geus, J. W. Effect of the reduction treatment on the structure and reactivity of silica-supported copper particles. *J. Catal.* **1991,** *131*, 178.

[2]   Yuan, Z.; Wang, L.; Wang, J.; Xia, S.; Chen, P.; Hou, Z.; Zheng, X. Hydrogenolysis of glycerol over homogenously dispersed copper on solid base catalysts. *Appl. Catal. B-Environ* **2011,** *101*, 431.