Effect of ZnO/SiO₂ ratio on structure and catalytic activity of Cu/SiO₂ and Cu/ZnO catalyst in water-containing ester hydrogenation

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1.1. Hydrogenation of ester reaction

The effect of water on hydrogenation performance of Cu/SiO_2 and Cu/ZnO catalysts were studied by hydrogenation of ethyl acetate. The performance of Cu/SiO_2 and Cu/ZnO catalysts were performed 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 °C (1°C/min) 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 °C min^{-1}. The liquid reactant (mass ratio: AcOEt / H_2O / EtOH = 91 / 5 / 4) 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 °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) pattern of the prepared catalysts was

recorded on a Shimadzu XRD-6000 diffractometer using Cu Kα radiation (λ=1.5418Å) in the 2θ scanning range between 5° and 85°. The dispersion and specific surface area of Cu^0 (D_{Cu}^0 and S_{Cu}^0) were measured by one-pulse N_2O oxidation at 50 °C. For more details could be found from the below. Fourier transform infrared (FT-IR) spectra was performed in transmission mode from 4000-500 cm^{-1} using a Bruker Vector 22 spectrometer equipped with a DTGS detector and a KBr beam splitter. 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 morphology of the samples were characterized by means of a high-resolution transmission electron microscope (HRTEM, JEM 2100F). The X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD) was carried out to analyze elemental valance of surface.

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 for 4 h. The amount of hydrogen consumption in first TPR 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 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:

$$CuO + H_2 \rightarrow Cu + H_2O, \qquad\qquad \text{hydrogen consumption} = X$$

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

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O, \qquad\qquad \text{hydrogen consumption} = Y$$

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

$$D = (2\,Y\,/\,X) \times 100\% \;;\; S = 1353 \times Y\,/\,X \; (m^2\,Cu\,/\,g\,Cu); \; d_{v.s.\,Cu}{}^0 = 0.5\,X\,/\,Y \; (nm)$$
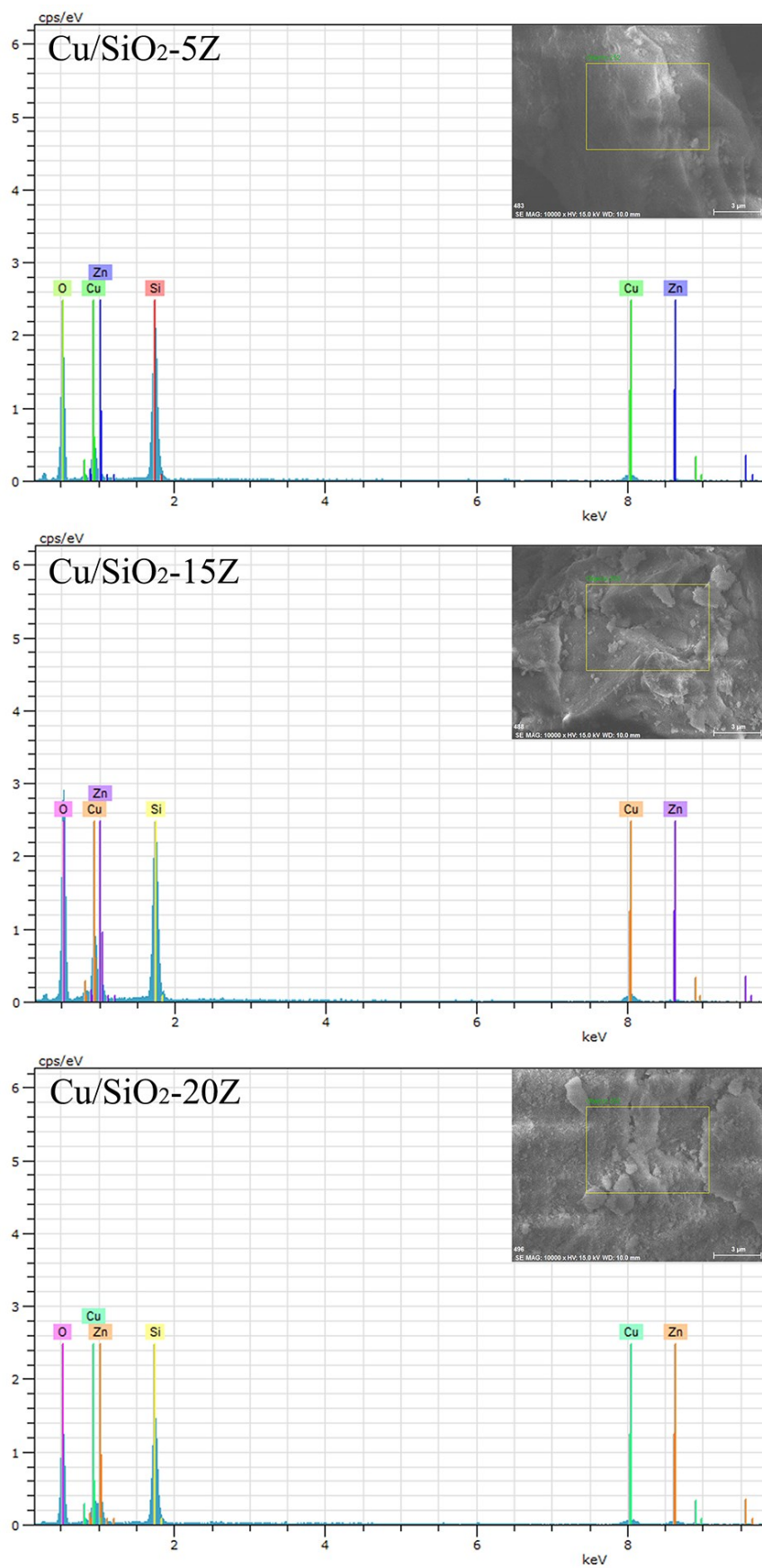
Figure S1. SEM-EDS images of Cu/SiO$_2$ catalysts with different ZnO contents.

Table S1. Metal contents of Cu/SiO$_2$ catalysts with different ZnO content measured by SEM-EDS.

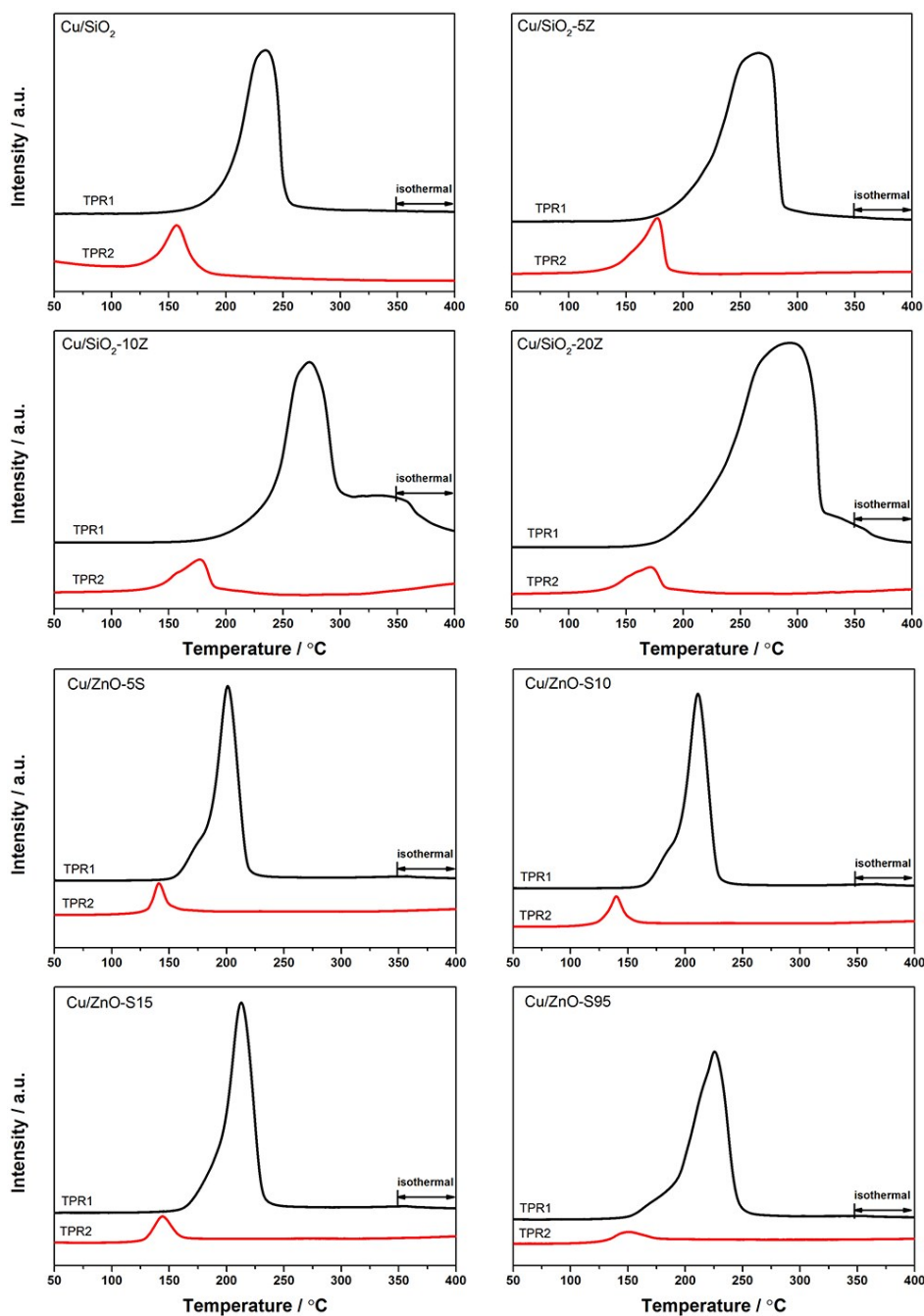| Sample	Cu/SiO$_2$-5Z	Cu/SiO$_2$-10Z	Cu/SiO$_2$-20Z
Cu wt.%	24.48	24.48	17.74
ZnO wt.%	4.7	8.7	21.6

Figure S2. TPR profiles of Cu/SiO$_2$ catalysts with different ZnO content and Cu/ZnO catalysts with different SiO$_2$ content before and after N$_2$O oxidation at 50 °C.
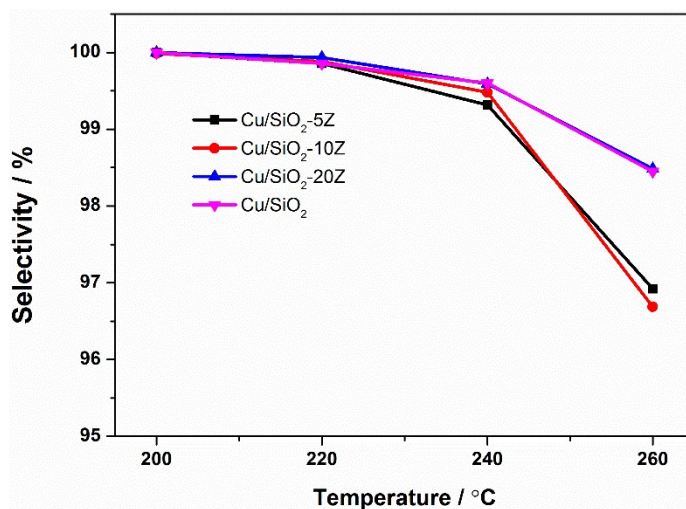
Figure S3. The change of selectivity of ethanol with the increased of reaction temperature for Cu/SiO$_2$ catalysts with different ZnO content. Reaction condition: P = 2.5 MPa, n(H$_2$) / n(AcOEt) = 40 (molar ratio), LHSV of AcOEt = 1h^{-1} and the AcOEt contained 5 wt.% water.

References

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