Electronic supplementary information

Highly selective one-pot continuous synthesis of 2-methoxyethanol via hydrogenation of dimethyl oxalate on Cu/ZrO_2 catalysts with balanced acid sites

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Experimental

Catalyst preparation

ZrO_2 supports were prepared via the reflux method. The $Zr(OH)_4$ precursor was firstly prepared by boiling 0.4 M solution of zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$) under reflux at 100℃ and 1 atm for 36 h, while maintaining the pH at 10. The resulting precipitate was filtered off, washed several times with deionized water until free from chloride ions, and dried at 100℃for 12 h. The obtained hydrous zirconia sample was powdered and immersed with different concentrations solution (0.1 M, 0.2 M, 0.4 M and 0.8 M) of sulfuric acid. This process was performed under magnetic stirring and maintained at ambient temperature for 2 h. The prepared supports were labeled as xSZ (x=0.1, 0.2, 0.4, 0.8) according to the concentration of sulfuric acid solution. The 0.2SZ samples calcined at different temperatures were denoted as 0.2SZT.

A series of copper catalysts with 10 wt.%Cu loading were prepared by the AE method.[1] The samples were dried at 100℃ for 12 h and subsequently calcined at 450℃ for 4 h in air, pelletized, crushed, sieved to 40–60 meshes, and denoted as 10Cu-xSZT correspondingly.

1 L. F. Chen, P. J. Guo , M. H. Qiao. *J. Catal.* 2008, 257, 172.

Catalyst characterizations

The BET surface area (S_{BET}) was measured using N_2 physisorption at -196℃ on a Micromeritics TriStar 3000 apparatus. The X-ray diffraction (XRD) patterns were collected on a Bruker AXS D8 Advance X-ray diffractometer using Cu *Kα* radiation (λ = 0.15418 nm). The tube voltage was 40 kV, and the current was 40 mA.

The particle size and distribution were observed by transmission electron microscopy (TEM; JEOL JEM2011). The surface species were detected by X-ray photoelectron spectroscopy (XPS; Perkin Elmer PHI 5000C). The spectra were recorded with Mg *Kα* line as the excitation source (*hv* = 1253.6 eV). The binding energy (BE) values were referenced to the C 1s peak of contaminant carbon at 284.6 eV with an uncertainty of ± 0.2 eV.

The temperature-programmed desorption of NH_3 was conducted on a Micromeritics Auto Chem II instrument. The sample, about 100 mg, was pretreated at 200℃ for 1 h by passing very pure helium (99.999%, 30 mL/min) through it. After pretreatment of the sample, it was saturated with NH_3 in a flow of 10% NH_3-He mixture at 120℃ for 90 min at a flow rate of 75 mL/min and was subsequently flushed at 120℃ for 2 h to remove physisorbed NH_3. TPD analysis was carried out from ambient temperature to 800℃ at a ramping rate of 10℃/min.

Catalytic reaction

The activity test was conducted on a continuous flow unit equipped with a stainless-steel fixed-bed tubular reactor. The catalyst bed had an inner diameter of 10 mm with a height of approximate 40 mm. Both sides of the catalyst bed were packed with quartz powders (20–40 meshes) to ensure a plug flow profile of the feed. The catalyst was activated in a 5% H_2/Ar atmosphere at 300℃ for 4 h at a ramping rate of 2℃/min. After cooling to the reaction temperature of 220℃, 10 wt.% DMO (purity >99%) in methanol and H_2 were fed into the reactor at a H_2/DMO molar ratio of 150

and a system pressure of 3.0 MPa. The products were condensed and analyzed by a gas chromatograph (Finnigan Trace GC ultra) fitted with a 30 m HP-5 capillary column and a flame ionization detector (FID).

Table S1. The distribution and strength of acid sites in different catalysts.

Catalysts	The amount of acid site (mmol/g)		
	Weak and Medium	Strong	Total
10Cu-Z500	1.29	-	1.29
10Cu-0.2SZ	1.06	0.29	1.35
10Cu-0.2SZ300	1.88	0.48	2.36
10Cu-0.2SZ500	1.71	0.47	2.18

Table S2 The distribution and strength of acid sites in different catalysts.

Catalysts	The amount of acid site (mmol/g)		
	Weak and Medium	Strong	Total
10Cu-0.1SZ300	1.59	0.53	2.12
10Cu-0.2SZ300	1.88	0.48	2.36
10Cu-0.4SZ300	1.55	0.91	2.46
10Cu-0.8SZ500	1.44	0.93	2.37

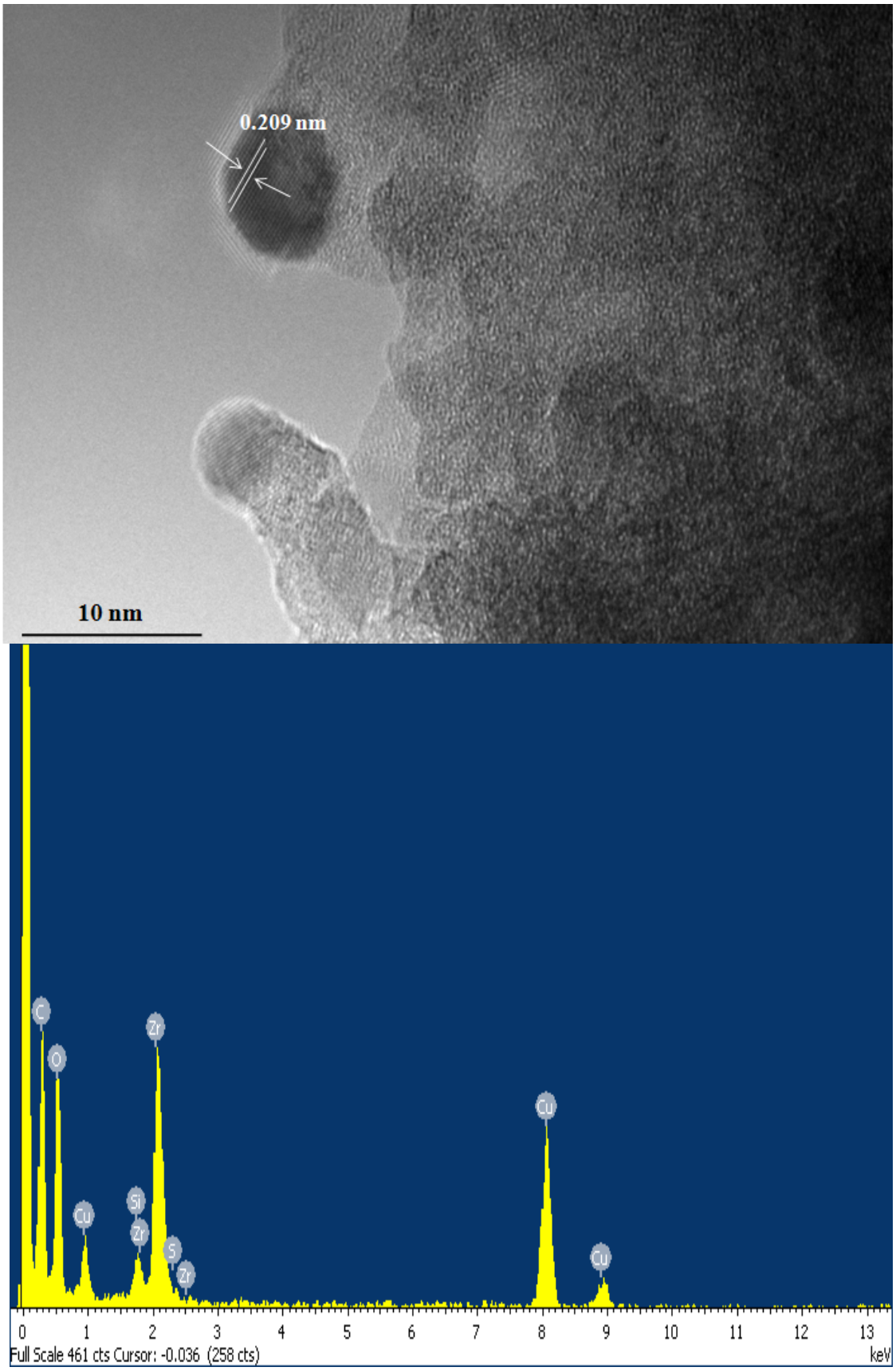

Fig. S1. HR-TEM image and EDX spectrum of 10Cu-0.2SZ300 catalyst.

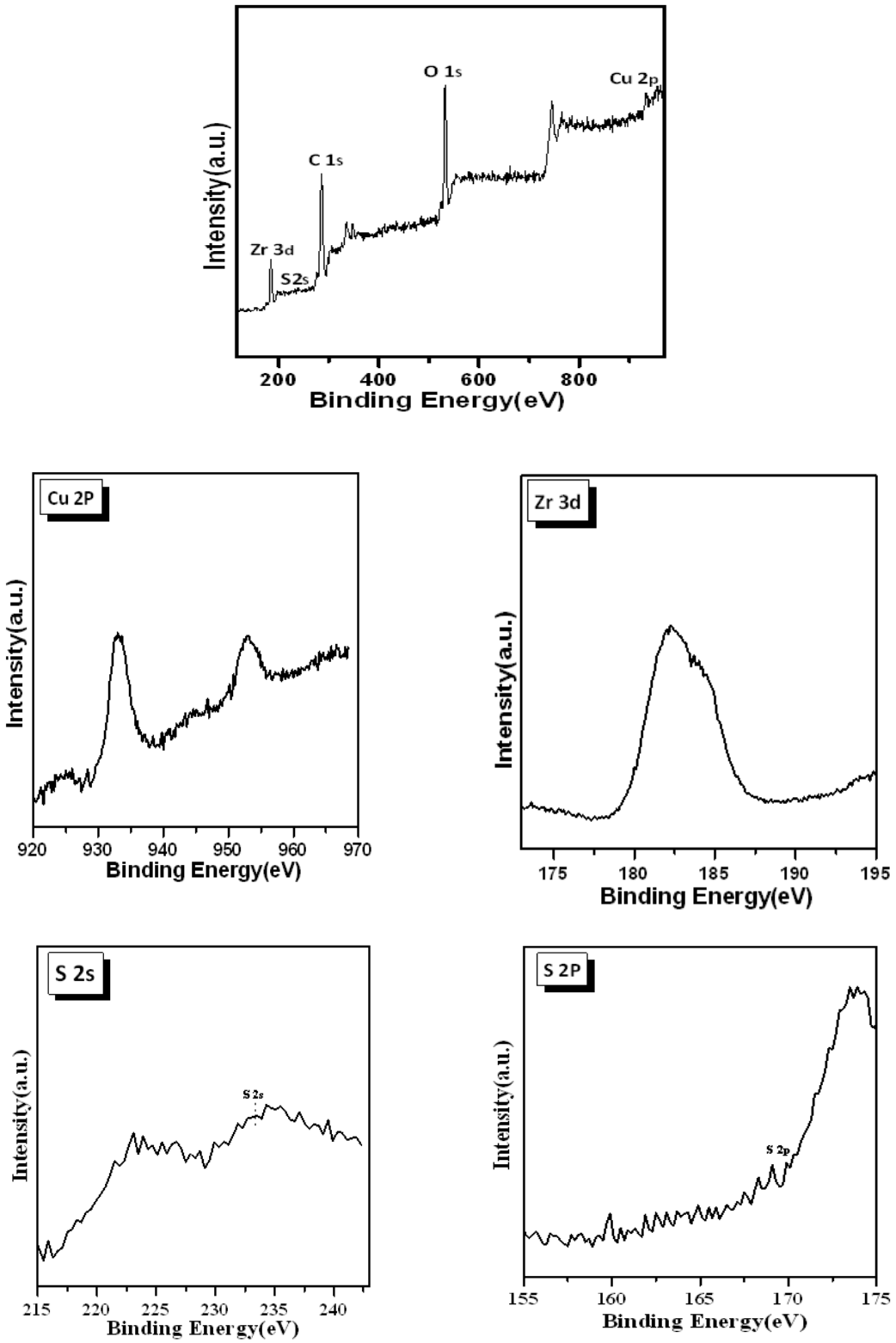

Fig. S2. XPS profiles of 10Cu-0.2SZ300 (Reduced) catalyst.

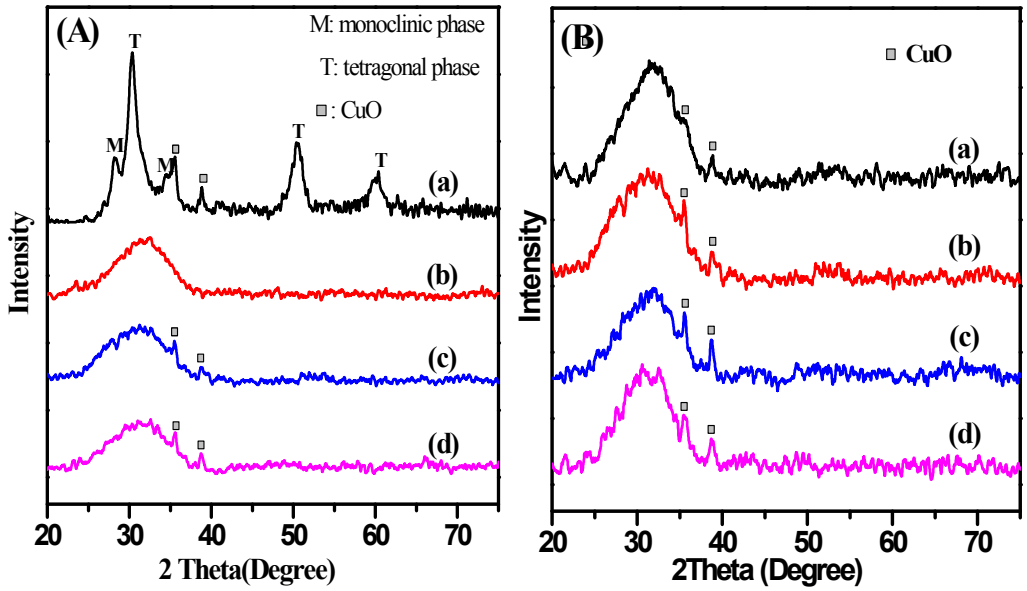

Fig. S3. XRD patterns of (A): (a) 10Cu-Z500, (b) 10Cu-0.2SZ, (c)10Cu-0.2SZ300, (d)10Cu-0.2SZ500; (B): (a) 10Cu-0.1SZ300, (b) 10Cu-0.2SZ300, (c)10Cu-0.4SZ300, (d)10Cu-0.8SZ300.

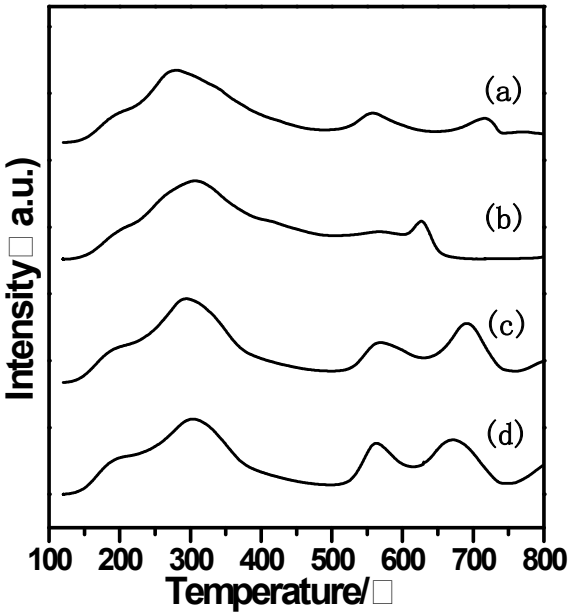

Fig. S4. NH_3-TPD profiles of: (a) 10Cu-0.1SZ300, (b) 10Cu-0.2SZ300, (c)10Cu-0.4SZ300, (d)10Cu-0.8SZ300.