[Supporting Information]

Effect of Feedstock Solvent on the Stability of Cu/SiO_2 Catalyst for Vapor-phase Hydrogenation of Dimethyl Oxalate to Ethylene Glycol

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1. Experimental

The preparation method of 25wt%Cu/SiO_2 catalysts with 25 wt% copper loadings was described as follows. 9.51 g of $Cu(NO_3)_2$•$3H_2O$ (AR) was dissolved in 200 mL of deionized water, and 28% ammonia aqueous solution was then dropped into it. The mixed solution was stirred for 30 min and formed a copper ammonia complex solution with pH value of 10. 25.0 g of silica sol (JN-40, Qingdao Ocean Chemical Engineering Limited Company) was subsequently dropped into the copper ammonia solution and stirred for another 30 min, all of which were operated at room temperature. Then, the suspension was preheated at 363 K to evaporate ammonia and deposited the copper species on silica. When pH value of the suspension decreased to 5-6, the evaporation process was terminated. The precipitate was washed with deionized water several times and dried at 393 K overnight. The catalyst precursors were calcined in air at 723 K for 4 h, pelletized, crushed, sieved to 40–60 meshes.

The catalytic performance of 25wt%Cu/SiO_2 catalyst for the synthesis of EG was investigated for the continuous vapor-phase hydrogenation of DMO. Prior to the hydrogenation reaction, the 25wt% Cu/SiO_2 catalyst was reduced in H_2 flow at 623 K for 2 h. After cooling to 473 K, 10 wt% DMO-methanol or DMO-ethanol and H_2 were fed into the reactor at a H_2/DMO molar ratio of 80 and a reaction pressure of 3.0 MPa. The liquid hour space velocity (LHSV) of DMO was 0.6 h^{-1}. The products were condensed and analyzed by a gas chromatograph (Shimadzu GC2010) fitted with a 30 m KB-WAX capillary column and a flame ionization detector (FID).

The in-situ X-ray diffraction (XRD) measurements of the samples were performed on a Panalytical X`pert Pro Super X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm). The tube voltage was 40 kV and the current was 30 mA. The 2θ angular regions between 10◦ and 80◦ were recorded at a scan rate of 0.0167◦ for 15 s. The full width at half maximum (FWHM) of Cu (111) diffraction at a 2θ of 43.2 ^{o} was used to calculate the Cu crystallite size using the Scherrer equation. For in-situ XRD measurement, a catalyst was placed in a stainless steel holder and covered with a beryllium plate having a thickness of 0.1 mm. Then a 5% H_2-95% Ar mixture was introduced at a flow rate of 30 mL/min^{-1}. Temperature ramping programs were performed from room temperature to 523 K at a rate of 10 K/min^{-1}. The XRD patterns were collected after samples reached 523 K for 5 min.

Transmission electron microscopy (TEM) micrographs were obtained on a JEM-2100 apparatus operated at 200 kV. The catalyst samples were ultrasonically dispersed in ethanol at room temperature for 30 min. The as-obtained solution was dropped onto the copper grid for TEM.

A Nicolet 6700 FTIR spectrometer equipped with a MCT/A detector was used in this study. For each spectrum, 32 scans were normally recorded in the absorbance mode and at a 4 cm^{-1} resolution. A 13-mm diameter self-supporting disk of Cu/SiO_2 was reduced at 723 K for 2 h under hydrogen flow (30 mL/min) in IR cell. After pursing with He at 723 K for 1 h and cooling down to 473 K, a flow of He-methanol or He-ethanol was introduced into the IR cell until a steady state was reached. The spectra were collected at 473 K under He-methanol or He-ethanol flow.

2. Effect of copper sizes on hydrogenation of DMO to EG over Cu/SiO_2 catalyst

Tab. s1 Copper sizes and activities of hydrogenation of DMO to EG over Cu/SiO_2 after reaction under DMO-methanol-H_2 stream for different time

Reaction time/h	Copper size/nm*	Con (DMO)/%	Sel (EG)/%	Sel (MG)/%
0	4.7	-	-	-
5	6.7	99.95	98.17	0.72
8	6.9	100	97.43	1.75
10	7.0	100	90.12	9.03
11.5	10.6	97.63	79.07	22.62
13.5	10.8	88.4	36.24	62.27
15	11.0	70.75	13.81	84.52

* Calculation by the Scherrer equation, MG: Methyl glycolate

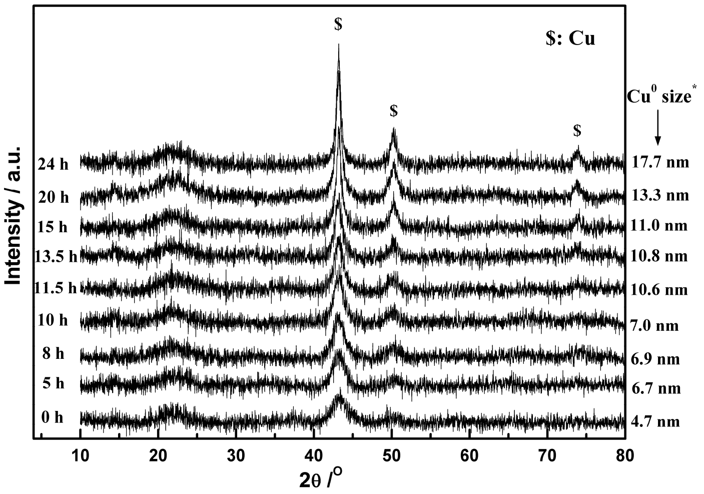

Fig. S1 XRD patterns of $Cu\text{-}SiO_2$ catalysts after reaction under DMO-methanol-H_2 stream for different time

3. TEM images of Cu/SiO_2 catalysts after reaction under DMO-methanol-H_2 stream for different time

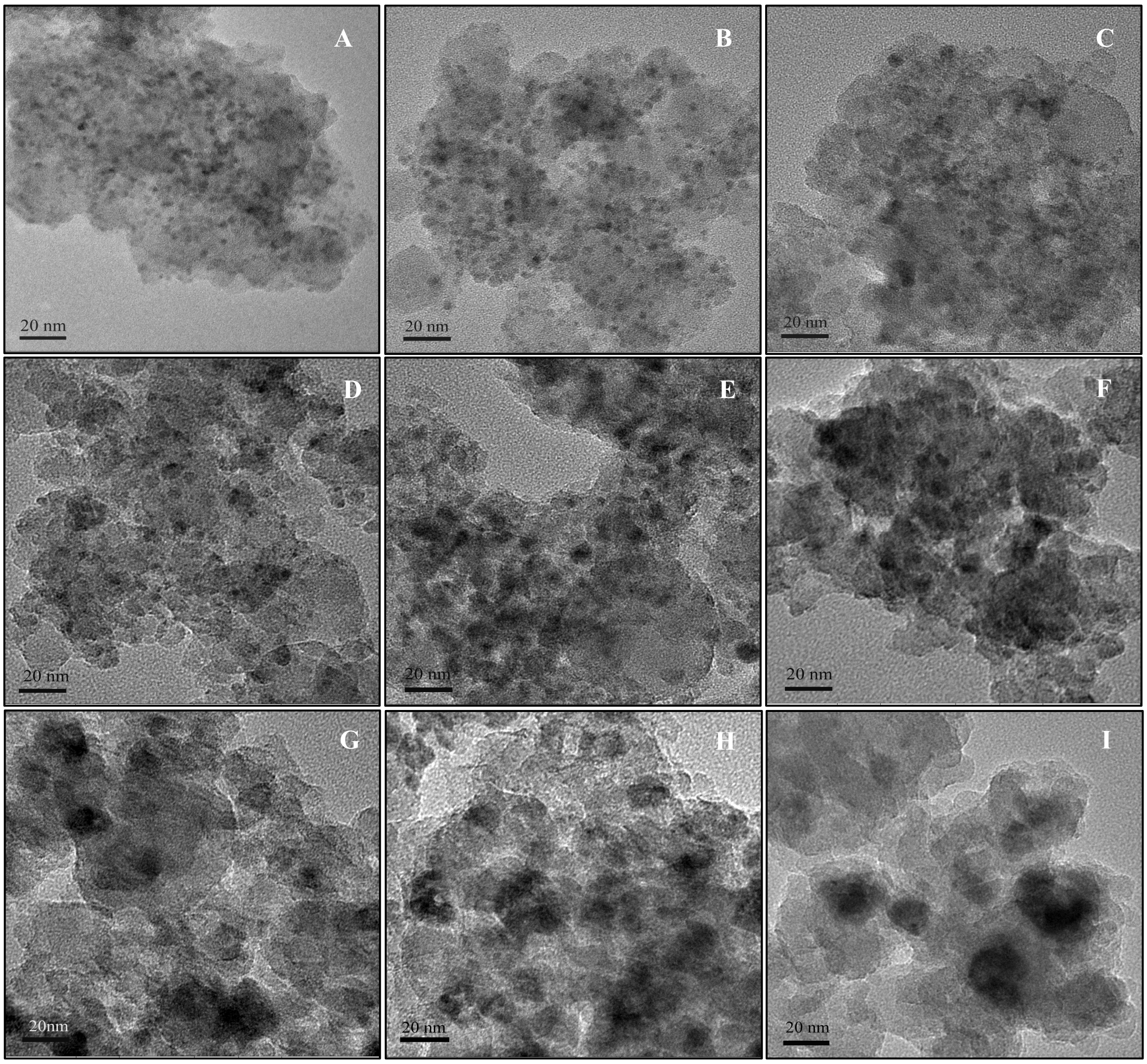

Fig. S2 TEM images of Cu/SiO_2 catalysts after reaction under DMO-methanol-H_2 stream for different time (A: 0 h; B: 5 h; C: 8 h; D: 10 h; E: 11 h; F: 13 h; G: 15 h; H: 20 h; I: 24 h)