Electronic Supplementary Information for

"A unique microwave effect on the microstructural modification of Cu/ZnO/Al₂O₃ catalysts for steam reforming of methanol"

Xin-Rong Zhang, Lu-Cun Wang, Yong Cao*, Wei-Lin Dai and Kang-Nian Fan* Department of Chemistry & Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China

Experimental details

Catalytic tests: Catalytic experiments were performed at atmospheric pressure in a continuous flow fixed-bed microreactor consisting of a stainless-steel tube with an internal diameter of 10 mm and a coaxially centred thermocouple with its tip located in the middle of the bed. Prior to each experiment, the catalyst (0.45-0.55 mm, 0.5 g) was reduced at 250 °C for 6 h. The reaction was carried out under the following conditions: pressure: 0.1 MPa; reaction temperature: 250 °C; carrier gas of Ar: 60 mL·min⁻¹; liquid feed (H₂O/methanol = 1.1 molar ratio): 3.4 mL·h⁻¹; WHSV =5.8 h⁻¹. Steady-state measurements were taken at least 6 h after beginning flow to the reactor, at which point the product composition was stable. Data were taken at 250 °C. The reaction products were analysed on-line by a GC (GC122, Shanghai Analysis) equipped with a thermal conductivity detector and two packed columns in series for products analysis. All experimental data were obtained under steady-state conditions.

 N_2O titration: The pulse titration technique was employed in our experiment. N₂ was used as the carrier gas and a thermal conduct detector was used to detect the amount of the consumption of N₂O. The specific area of metallic copper was calculated from the total amount of N₂O consumption by assuming the stoichiometry O:Cu = 1:2 and Cu surface atom density of 1.46×10^{19} Cu atoms·m⁻². The accuracy of the metallic copper surface area measurement was higher than 95%.

X-ray diffraction: In situ X-ray powder diffraction experiments performed on a Bruker AXS D8 Advance X-ray Diffractometer with Cu K α -radiation. Reduction of

the calcined or microwave processed Cu/ZnO/Al₂O₃ precursors in 5 vol% H₂ in argon from room temperature to 250 °C at a ramping rate of 1 °C·min⁻¹ was carried out in a XRK-900 high temperature cell. *In situ* XRD patterns were recorded at 250 °C under simulated methanol steam reforming conditions (c(MeOH) ~ 5 vol%, c(H₂O) ~5.5 vol% in 60 mL·min⁻¹ Ar) (25~80° 2 θ , step width 0.02° 2 θ , counting time: 1s/dp (dp = data point)).

X-ray powder diffraction patterns of the various Cu/ZnO/Al₂O₃ catalysts under reaction conditions were analysed by the Pawley method ("full pattern refinement").^{1,2} A sum of pseudo-Voigt-profile functions and an appropriate background function were refined for the experimental patterns. The crystallite size and microstrain corresponding to the broadening of each *hkl* line was determined from the Lorentzian and Gaussian part of the individual profile functions. The specific copper surface areas as calculated from the crystallite size assuming a spherical particle, are in good agreement with the results of the N₂O titration.



Fig. 1S A linear correlation of the microstrain of copper nanoparticles and the corresponding hydrogen production rate obtained from various CuO/ZnO/Al₂O₃ oxide precursors processed by different time (0-10 min) of microwave irradiation.



Fig. 2S XRD patterns of various Cu/ZnO/Al₂O₃ oxide precursors (\blacksquare , CuO phase; \circ , ZnO phase) obtained by different time (0-10 min) of microwave irradiation: a) CC-PCZA, b) 3MW-PCZA, c) 5MW-PCZA, d) 8MW-PCZA, e) 10MW-PCZA.



Fig. 3S Crystallite size $d(\bullet)$ and microstrain ($\mathbf{\nabla}$) of the CuO nanoparticles (calculated from CuO111 line based on the data shown in Fig. 2S) as a function of microwave processing time *t* on the corresponding oxide precursors.



Fig. 4S. In situ XRD patterns of the working Cu/ZnO/Al₂O₃ catalysts (\blacksquare , Cu phase; \circ , ZnO phase) obtained from the calcined samples via microwave pre-treatment for 0 to 10 min measured at 250 °C under methanol steam reforming conditions: a) CC-CZA, b) 3MW-CZA, c) 5MW-CZA, d) 8MW-CZA, e) 10MW-CZA.

References

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