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.

N₂O 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 1.46×10¹⁹ 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 Kα-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° 2θ, step width 0.02° 2θ, 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”).¹² 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/Al_2O_3 oxide precursors (■, CuO phase; ○, 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 $d$ (●) and microstrain (▼) 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 (■, Cu phase; ○, 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


