

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

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A short time (3–10 min) of microwave irradiation on the CuO/ZnO/Al₂O₃ oxide precursor can result in a unique tailored microstructural modification on the catalyst, leading to a significantly enhanced performance for H₂ production from steam reforming of methanol.

Catalysts based on copper–zinc mixed oxides are of great importance for industrial scale catalytic processes like low-pressure methanol synthesis and steam reforming of methanol for the production of hydrogen.^{1–3} It is widely accepted that ZnO plays a key role in obtaining and maintaining the “catalytically active” copper in optimal dispersion.^{4–6} The high activity of this particular system is believed to result from a strong interaction of the two phases leading to a specific nature of the active copper metal.⁷ Recently, a positive correlation between the lattice microstrain and the activity of copper nanoparticles supported on ZnO has been identified.^{4,5} Meanwhile, the promotion of Cu(111) surfaces with zinc reveals that the formation of Cu/Zn alloys is also crucial for the generation of active copper material.⁶ All these findings suggest that it is possible to design and develop new efficient catalyst systems with optimized microstructure by tailoring the Cu–ZnO interface properties.^{8,9}

Microwave-assisted catalyst synthesis has attracted tremendous recent attention by providing a much faster, simpler, and more energy efficient technique for fabrication of new catalytic materials with improved microstructures as compared to the conventional

methods.^{10–12} Herein, we present for the first time a unique and unprecedented microwave effect on the microstructural modification of a ternary Cu/ZnO/Al₂O₃ catalyst for hydrogen production from steam reforming of methanol. It was demonstrated that a short time of microwave irradiation on the CuO/ZnO/Al₂O₃ oxide precursor can allow the convenient and favorable modification of the microstructural characteristics of the catalyst, resulting in the creation of highly strained copper nanocrystals in the working catalyst thus leading to a significant enhancement of its performance for steam reforming of methanol.

The CuO/ZnO/Al₂O₃ oxide precursors for the Cu/ZnO/Al₂O₃ catalysts were prepared by a conventional carbonate coprecipitation method followed by calcination of the ternary hydroxycarbonates in air at 360 °C for 4 h.¹³ The as-derived oxide precursors (labeled as CC-PCZA) of about 1.0 g in weight were then processed in a domestic microwave oven (500 W, 2.45 GHz) for a short time of 3–10 min to obtain the final microwave-irradiated CuO/ZnO/Al₂O₃ oxide precursors, referred to herein as a number (denotes the time of the microwave processing) followed by MW-PCZA (see Table 1, molar ratio of Cu/Zn/Al = 45/45/10). Subsequently, all samples of the catalyst precursor were pressed, crushed and sieved to a size of 60–80 mesh for the activity evaluation (for details see ESI†).¹⁴

Table 1 summarizes the textural results, the microstructural properties as well as the catalytic performance of the Cu/ZnO/Al₂O₃ catalysts processed by various times (0–10 min) of microwave irradiation. While the microwave-processed oxide precursors exhibited an almost unchanged BET surface area with respect to that of the conventional material without microwave processing, a dramatic decrease in the specific copper surface area (determined by N₂O titration,^{15,16} the accuracy of which was higher than 95%) from 47 m² g⁻¹ to 30 m² g⁻¹ of the corresponding samples was identified. It is remarkable that the hydrogen-production rates from the microwave-irradiated samples

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Table 1 Physicochemical properties and catalytic performance of various microwave-processed Cu/ZnO/Al₂O₃ catalysts

| Sample | BET area/m ² g ⁻¹ | Cu surface area ^a /m ² g ⁻¹ | | Crystalline size ^b /nm | Microstrain ^b (%) | R _{H2} ^c /mmol g ⁻¹ h ⁻¹ | CO concn. ^c (%) |
|-----------|---|--|--------------------------------|-----------------------------------|------------------------------|--|----------------------------|
| | | A _{Cu} ^{N2O} | A _{Cu} ^{XRD} | | | | |
| CC-PCZA | 58.1 | 47.3 | 50.1 | 5.4 | 2.12 | 280.8 | 0.18 |
| 3MW-PCZA | 59.7 | 39.7 | 47.5 | 5.8 | 3.23 | 291.2 | 0.15 |
| 5MW-PCZA | 60.6 | 36.4 | 41.8 | 6.6 | 4.47 | 310.5 | 0.12 |
| 8MW-PCZA | 61.5 | 33.1 | 40.0 | 6.9 | 5.57 | 330.8 | 0.10 |
| 10MW-PCZA | 57.5 | 30.2 | 36.8 | 7.5 | 4.63 | 315.9 | 0.11 |

^a Specific copper surface area measured by N₂O titration and calculated from the XRD data. ^b Crystalline size, lattice parameter and microstrain of the copper nanoparticles in working catalyst estimated from Cu(111) line measured at 250 °C. ^c Activity data obtained at 250 °C (Detailed reaction conditions: catalyst loading: 0.5 g; carrier gas of Ar: 60 mL min⁻¹; liquid feed (H₂O/CH₃OH = 1.1 molar ratio): 3.4 mL h⁻¹; WHSV ~5.8 h⁻¹; pressure ~0.1 MPa).

were much higher than those of the conventional sample despite a much lower specific copper surface area of the former. Particularly, it is seen that the 8MW-CZA catalyst derived by a 8-min microwave processing exhibited the highest performance in terms of hydrogen-production rate as compared to other samples. Additionally, it is noticed that a significant reduction in the CO production was also achieved for the present microwave-promoted Cu/ZnO/Al₂O₃ catalysts. It should be noted that the activity data shown in Table 1 were taken after 6 h on stream reaction, at which point the product composition was found to be stable. A more detailed durability test of the above samples is in progress to clarify the effect of microwave-irradiation on the catalytic stability of the Cu/ZnO/Al₂O₃ catalysts.

To gain an insight into the microstructural changes of the active Cu/ZnO/Al₂O₃ catalyst under working conditions, *in situ* X-ray diffraction investigations of the various catalysts were performed (ESI†).^{4,17–19} As shown in Fig. 1, the X-ray diffraction patterns showed no significant changes in the phase composition of two of the active Cu/ZnO/Al₂O₃ catalysts (0 and 8 min processing). However, dramatic deviations in the individual copper diffraction lines as a function of microwave processing time were observed. A detailed analysis of the Cu(111) diffraction line reveals a progressive increase in copper particle size from 5.4 nm (0 min) to 7.5 nm (10 min). Nevertheless, a significantly different variation behavior of the microstrain as a function of processing time has been observed in the copper particles (see Table 1). The values for microstrain show a maximum on the catalyst obtained by 8-min processing, suggesting the optimal modification of the Cu–ZnO interaction or Cu/ZnO interface achievable in the active 8MW-CZA sample. Furthermore, the analysis of the X-ray patterns of various copper catalysts yields a distinct anisotropy in both particle size and microstrain, demonstrating dramatic changes in the morphology of the particles as a function of microwave processing.

Fig. 2 compares the effect of the microwave processing time on the hydrogen production rate as well as the specific copper surface area as determined by surface titration with N₂O and estimated by the XRD crystallite size, where the larger Cu surface area obtained from XRD crystallite size calculations compared to N₂O titration

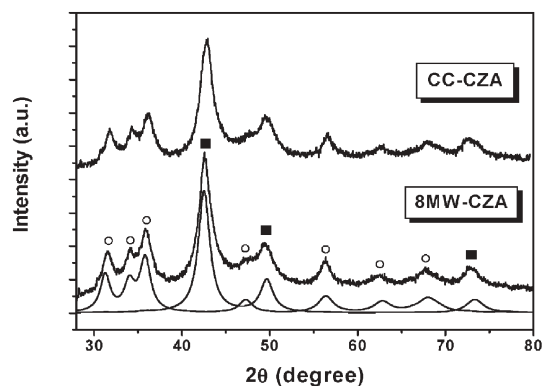


Fig. 1 *In situ* X-ray powder diffraction patterns of two Cu/ZnO/Al₂O₃ catalysts (■ Cu phase; ○ ZnO phase) obtained from original and microwave-irradiated (for 8 min) oxide precursors measured at 250 °C under simulated methanol steam reforming conditions. The disordered structure leads to a broadening of the signals for the Cu and ZnO phases. The Pawley method was employed to simulate the experimental patterns by a sum of profile functions and a background polynomial.

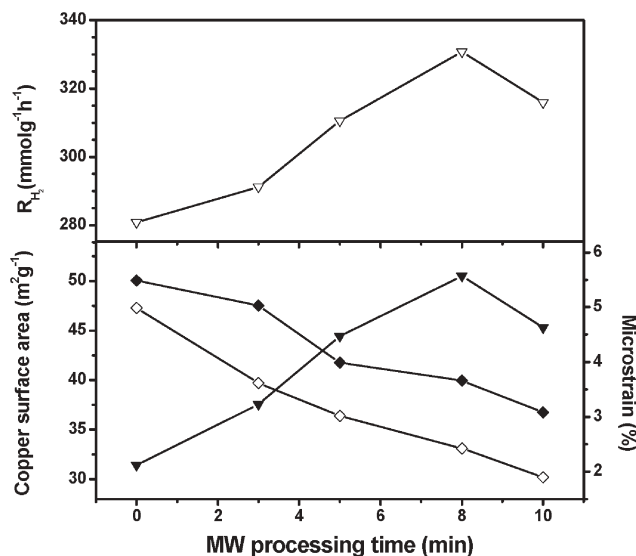


Fig. 2 Hydrogen-production rate R_{H_2} ($\text{mmol g}^{-1} \text{h}^{-1}$), specific copper surface area (◆ calculated from the XRD; ◇ measured by N₂O titration,) and microstrain (▼) of the copper nanoparticles (calculated from Cu(111) line measured at 250 °C) as a function of microwave processing time on the corresponding oxide precursors.

is possibly due to the interactions of the copper particles with ZnO or deviations from a spherical morphology.⁴ Evidently, the increase in hydrogen-production rates does not show correlation with the decreasing copper surface area. However, the increase in activity is observed to correlate well with the increasing microstrain in the copper crystals (ESI†, Fig. 1S), permitting a rational explanation for the present positive microwave effect of precursor processing on the active catalyst.⁴ The excellent correlation of the structural disorder in the copper nanoparticles and the activity unambiguously demonstrates that although a high Cu surface area is a prerequisite for catalytic activity, it does not account for the observed changes in activity and selectivity alone without taking bulk structural changes into account.^{4–6}

Previous investigations concerning the heating of catalytic materials using microwave irradiation revealed, that dielectric heating may result in selective heating of catalytic sites with respect to their direct surroundings, thus leading to “molecular hot spots”.^{20,21} For the ternary system comprising Cu/Zn/Al mixed oxides, only the CuO component is known to be a strong microwave absorber.²² Therefore, hot spot formation at CuO sites embedded in the ZnO–Al₂O₃ matrix thereby inducing pronounced microstructural rearrangement at the Cu–ZnO interface due to selective microwave energy absorbing is possible for the Cu/Zn/Al oxides during the present microwave processing. This may well account for the present excellent correlation between the increase in the structural disorder in the copper nanoparticles and the increase in catalytic activity as a function of oxide precursor microwave processing. In this respect, the microwave processing of the well-mixed ternary Cu/Zn/Al oxides can provide a unique opportunity for generating significant microstructural modification at the Cu–ZnO interface due to the formation of hot spots as a consequence of selective dielectric heating thus leading to the favorable creation of highly strained Cu crystals in the active catalysts.

In summary, we have successfully demonstrated that the tailored microstructural modification of a ternary Cu/ZnO/Al₂O₃ catalyst can be directly achieved by a short microwave irradiation on the oxide precursors. The as-processed catalysts have been found to exhibit remarkably enhanced performance for the methanol steam reforming due to the formation of highly strained copper nanocrystals in the active catalysts.

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