

Effect of preparation method on the hydrogen production from methanol steam reforming over binary Cu/ZrO₂ catalysts

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Abstract

Several methods (impregnation, oxalate gel–coprecipitation and conventional aqueous coprecipitation) have been comparatively examined for the preparation of binary Cu/ZrO₂ catalysts for the catalytic production of hydrogen by steam reforming of methanol (SRM). A variety of techniques including N₂ adsorption, XRD, N₂O chemisorption, XRD, H₂-TPR, and XPS were used to characterize the physical and chemical properties of the as-obtained catalysts. The results show that the preparation method significantly affects the component dispersion, microstructural properties and the resulting catalytic performance with respect to methanol conversion, H₂ production and CO concentration. The catalyst with higher specific copper surface area and component dispersion shows higher activity for methanol conversion at lower temperature. The best Cu/ZrO₂ catalyst has been prepared by an oxalate gel–coprecipitation method, which shows much higher catalytic activity and enhanced long-term stability in the SRM reaction as compared to the catalysts prepared by conventional aqueous–coprecipitation and impregnation methods.

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1. Introduction

The production of hydrogen by steam reforming of methanol (SRM) is currently of great interest for the development of fuel cell powered devices, especially for mobile applications [1,2]. A large variety of catalytic materials for the steam reforming of methanol have been reported in the literature [3–7]. Among them, copper-containing catalysts such as Cu/ZnO and Cu/ZnO/Al₂O₃, which are traditionally used for methanol synthesis and low-temperature water gas-shift reaction, have been the most frequently studied systems [8–12]. Despite their high activity and selectivity for the SRM reaction, shortcomings of the conventional Cu/ZnO-based catalysts have been noted as the problems with long-term stability, low resistance to contaminants and the formation of poisonous CO as a byproduct [6–13]. Therefore, the development of new efficient catalyst systems that exhibit an improved long-term stability and selectivity toward hydrogen production are highly desired.

The use of ZrO₂ other than ZnO or alumina as an attractive support material for the activation and stabilization of copper is well documented in the field of methanol synthesis, mainly due to its unique amphoteric character and redox properties [14]. The activity of these catalysts is known to be critically dependent on several factors including the preparative route, composition, and constitution [15–18]. Recently, Shimokawa et al. have reported that highly active Cu/ZrO₂ catalysts for the steam reforming of methanol could be prepared by impregnation of ZrO₂ support with an aqueous solution of tetrammine copper(II) nitrate [16,17]. It was found that the Cu/ZrO₂ catalysts exhibited significantly higher activities than their silica-supported counterparts. More recently, Breen and Ross studied the steam reforming of methanol using prerduced zirconia-containing Cu/ZnO/Al₂O₃ catalysts [18]. They found that using zirconia as a support for Cu and ZnO produces a more active catalyst than Cu/ZnO/Al₂O₃ for the SRM reaction. The stability of the catalyst was improved if a small amount of Al₂O₃ was added, most likely because the amorphous zirconia phase was stabilized. The better performance of zirconia-containing catalysts has been attributed to a higher Cu surface area, better Cu dispersion,

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and improved reducibility of Cu as compared to Cu/ZnO/Al₂O₃ catalysts [7].

Regarding the synthesis of active and selective Cu/ZrO₂ catalysts for methanol synthesis or methanol reforming, various synthetic methods including coprecipitation of metal salts, impregnation of copper onto a zirconia support, the formation of amorphous aerogels and the polymer templating technique have been proposed [15–20]. Maintaining the amorphous nature of zirconia under calcination and reaction conditions as well as a high copper/zirconia interfacial area has been found to be very important for the generation of highly active copper material with improved stability [18]. Recently, we have reported that copper and zirconia could be effectively dispersed by an easily controlled approach based on the gel–coprecipitation oxalate precursor from alcoholic solution, resulting in the formation of highly active nanostructured zirconia-containing Cu/ZnO catalyst featured by a much higher surface area with improved copper dispersion [21]. The Cu/ZnO/ZrO₂ catalyst prepared by the oxalate gel–coprecipitation method is found to be highly efficient for methanol synthesis from CO₂ hydrogenation. In view of the microscopic reverse nature of the SRM reaction (CH₃OH + H₂O → 3H₂ + CO₂) with respect to the methanol synthesis from CO₂ hydrogenation, it is conceivable that the oxalate gel–coprecipitation method may also provide an attractive alternative for fabricating new efficient catalyst system for the steam reforming of methanol [21].

In the present work, in an attempt to develop new efficient binary Cu/ZrO₂ catalysts with a high surface area for methanol steam reforming, the preparation of a series of binary Cu/ZrO₂ catalysts by exploring different methods including impregnation, gel–coprecipitation of oxalate precursor and conventional aqueous coprecipitation synthesis as well as their performance in the SRM reaction is reported. Special attention was paid to the effect of preparation methods and the relationship between the catalytic performance and physicochemical properties such as the nature and dispersion of the copper in the catalysts. In addition, the synergistic effects between Cu and ZrO₂ were discussed on the basis of TPR, XRD and XPS analyses.

2. Experimental

2.1. Catalyst preparation

Four Cu/ZrO₂ catalysts, all with a Cu/Zr mole ratio of 4/1 were prepared by different methods. A typical procedure to prepare the gel–coprecipitated oxalate precursor CZ-01 is as follows: an alcoholic solution of 20% excess of oxalic acid is injected rapidly into a mixed alcoholic solution (each 0.1 M) of copper nitrate and zirconium nitrate at room temperature at vigorous stirring. The gel-like precipitates are formed and separated by centrifuge, then dried at 110 °C overnight, which show significant volume shrinkage during the drying process. The procedure to prepare precursor CZ-02 is similar to the procedure for preparing the precursor CZ-01, while the only difference is that an aqueous solution is used as a replacement of the alcoholic solution as described above. The precursor CZ-03 is prepared by the conventional carbonate coprecipitation

method. Briefly, a mixed aqueous solution of copper nitrate and zirconium nitrate (each 0.1 M) and a solution of sodium carbonate (0.1 M) were added slowly and simultaneously into 150 mL of deionized water at 80 °C with vigorous stirring. The pH was kept constant at 6.5–7.0. The precipitates were aged at 50 °C for 30 min under vigorous stirring, then filtered and thoroughly washed with warm deionized water. The precipitates were dried overnight in air at 110 °C. The precursor CZ-04 is prepared by an aqueous impregnation of a zirconia support (64 m² g⁻¹), which is prepared by oxalate gel–coprecipitation of zirconium nitrate as described above, with aqueous solution of zirconium nitrate (0.1 M) followed by drying at 120 °C for 12 h in air. All precursors were calcined in a muffle oven at 150 °C for 1 h, 200 °C for 1 h, 250 °C for 1 h, 300 °C for 1 h and 350 °C for 4 h.

2.2. Characterization of the samples

The textural parameters have been measured using the BET method by N₂ adsorption and desorption at 77 K in a Micromeritics TriStar system. The scanning electron microscope (SEM) images were obtained using a Philips XL 30 microscope operating at 30 kV. The X-ray powder diffraction (XRD) of the samples was carried out on a Germany Bruker D8Advance X-ray diffractometer using nickel filtered Cu K α radiation with a scanning angle (2θ) of 10–80°, a scanning speed of 2° min⁻¹, and a voltage and current of 40 kV and 20 mA. Crystallite sizes of CuO or Cu were calculated using Debye–Scherrer equation: $d_{\text{Cu}} = 0.9\lambda/\beta \cos \theta$, where λ is the wavelength of radiation (1.5418 Å), β the line broadening of the peak due to small crystallites (rad 2θ), and θ is the corresponding angle of the diffraction peak. The full width at half maximum (FWHM) of (1 1 1) reflection of CuO or copper was measured for calculating crystallite sizes [22]. The instrumental broadening was corrected by $\beta = (B^2 - b^2)^{0.5}$, where B is the total broadening, and b is the instrumental broadening. The catalysts after reaction were retrieved under Ar gas atmosphere, and then rapidly measured using XRD. The specific area of metallic copper was calculated from the total amount of N₂O consumption with 1.46×10^{19} copper atoms/m² [23]. The accuracy of the metallic copper surface area measurement was higher than 95%. TPR profiles were measured under the following conditions: heating rate 5 °C min⁻¹, flow-rate 40 mL min⁻¹ 5% H₂/Ar. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Perkin-Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg K α , $h\nu = 1253.6$ eV) was used. The C 1s line (284.6 eV) was used as the reference to calculate the binding energies (BE).

2.3. Catalytic activity measurements

The catalytic test was conducted using a fixed-bed flow reactor at 180–250 °C under atmospheric pressure. A 0.5 g sample of the catalyst diluted with 0.5 g quartz sand (both in 40–60 mesh) was packed in a stainless steel tubular reactor with

an inner diameter 6 mm. After reduction in a H_2/Ar (5/95) flowing of 80 mL min^{-1} at 250°C for 6 h, premixed water and methanol with a certain $H_2O/MeOH$ molar ratio were fed into the pre-heater maintained at about 250°C by means of a micro-feeder. The vaporized feed entered the reactor with a stream of Ar gas, which had a speed of 30 mL min^{-1} , and then began the steam reforming reaction at the designated reaction temperature. The reaction products were first passed through a cold trap, then the gaseous products such as H_2 , CO , CO_2 , CH_4 were detected on-line by the gas chromatograph (Type GC-122, Shanghai Analysis) equipped with thermal conductivity detectors and TDX-01 column; the liquid products such as water, methanol were detected by the same Gas Chromatograph equipped with thermal conductivity detectors and Porapak-Q column. Unless otherwise mentioned, the catalytic activity was evaluated from the data collected between 5 and 6 h of the on-stream operation by methanol conversion (X_{MeOH}), CO_2 selectivity (S_{CO_2}) and CO volume content (V_{CO}) in the outlet.

3. Results and discussion

3.1. Catalytic activity for steam reforming of methanol

The SRM experiments were conducted with steam in excess of stoichiometry ($H_2O/CH_3OH = 1.3$ molar ratio), ensuring complete methanol conversion and suppressing CO formation by the reverse water-gas shift (RWGS) reaction: $CO_2 + H_2 \rightarrow H_2O + CO$. Fig. 1 shows a typical set of results for SRM over the CZ catalysts. It is clear that the preparation methods have a significant influence on the performance of the catalyst for hydrogen production from steam reforming of methanol. Among them, CZ-01 exhibits the highest methanol conversion and H_2 production rate throughout the temperature range studied. It is remarkable that a total conversion of methanol could be achieved over the CZ-01 sample at a relatively low-temperature of 260°C . It is also highly interesting to make a comparison of the selectivity toward CO formation for all four catalysts. As shown in Fig. 1, the outlet CO concentration is observed to be less than 1.0% over CZ-01 and CZ-04 in the temperature range of $180\text{--}300^\circ\text{C}$, however, CZ-02 and CZ-03 show relatively higher selectivity for CO formation. These results imply that the highly active CZ-01 catalyst prepared by oxalate gel-coprecipitation can effectively retard the formation of CO and exhibit high selectivity for CO_2 during methanol steam reforming.

The effect of reaction temperature on the catalytic performance of Cu/ZrO_2 catalysts is also illustrated in Fig. 1. It can be seen that methanol conversion and H_2 production rate increase with increasing reaction temperature, while methanol is converted almost completely into H_2 and CO_2 accompanied with trace amount of CO up to 260°C over the CZ-01 catalyst. At lower temperature reactions, especially at 220°C , CZ-01 exhibits much higher activity as compared with CZ-02, CZ-03 and CZ-04, methanol conversion is up to 53.9%. On the other hand, the outlet CO concentration increases with increasing reaction temperature. This indicates that it is difficult to suppress CO evolution at high methanol

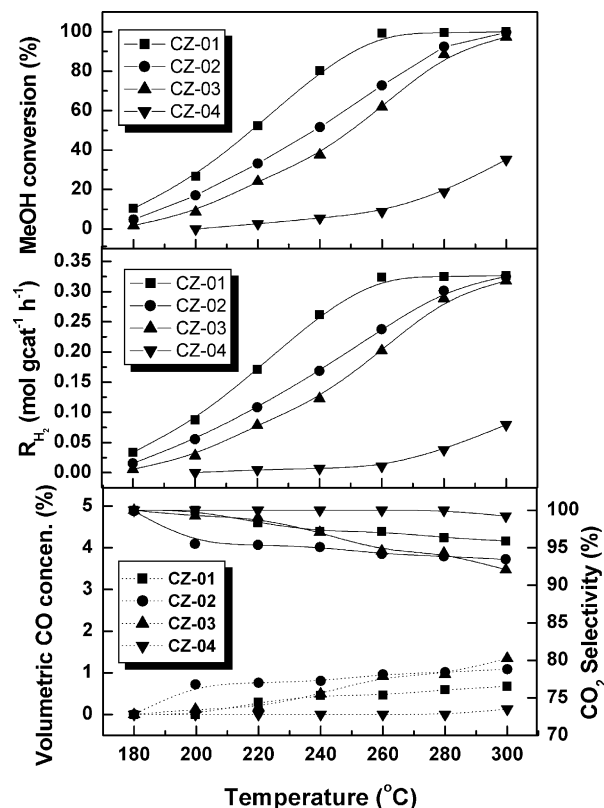


Fig. 1. Effect of reaction temperature on catalytic activity over CZ catalysts prepared by various methods. Dotted lines are the volumetric CO content in the outlet (reaction conditions: $H_2O/CH_3OH = 1.3$ molar ratio, $WHSV = 5.4 \text{ h}^{-1}$, $p = 0.1 \text{ MPa}$).

conversion region due to the presence of RWGS reaction at a higher temperature.

The catalytic activity of the CZ catalysts is also found to be strongly dependent on the contact time (W_{cat}/F_M) of the liquid feeding. Fig. 2 shows the methanol conversion as a function of W_{cat}/F_M , with W_{Cu} indicating the mass of catalyst and F_M the

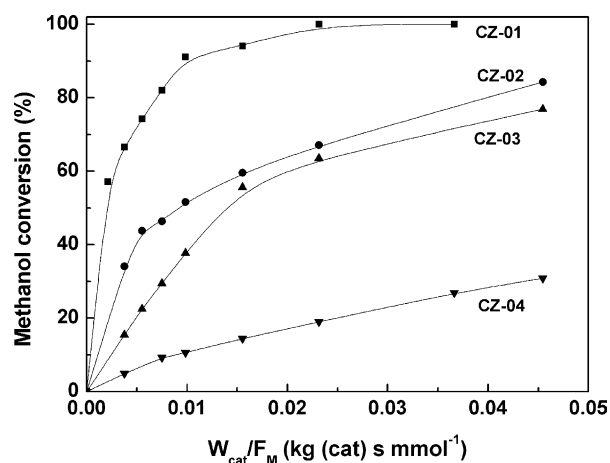


Fig. 2. Methanol conversion as a function of W_{cat}/F_M ratio over the CZ catalysts at 260°C during steam reforming of methanol. The data for catalyst CZ-04 is obtained at reaction temperature of 300°C ($H_2O/CH_3OH = 1.3$ molar ratio, $p = 0.1 \text{ MPa}$).

flow rate of methanol. For these measurements, the contact time was varied by changing the liquid flow rate of methanol/water mixture between 0.04 and 0.75 mL min⁻¹. It is seen that methanol conversion increased rapidly with increasing contact times for all samples. Previous investigations concerning the effect of space velocity or contact time of the feed on the SRM performance of Cu/ZnO/Al₂O₃ catalysts have revealed the similar trend for methanol conversion and H₂ production [6]. The results also show that catalyst CZ-01 is significantly more active than all the other samples, further confirming the superior performance of the oxalate gel-coprecipitation derived binary CZ system for the methanol steam reforming reaction.

One of the main problems using the conventional Cu/ZnO/Al₂O₃ catalyst in SRM is the deactivation with time-on-stream. The stability of the present four CZ catalysts during the SRM reaction was investigated over 48 h of on-stream operation at 260 or 300 °C and the results are displayed in Fig. 3. The activity of the CZ-04 catalyst was low even at the beginning of the reaction and declined continuously during the reaction for 48 h. It is clear that the two catalysts of CZ-02 and CZ-03 showed enhanced activity and stability as compared to CZ-04. For the catalyst CZ-01, no appreciable decrease in the activity was observed even after 48 h of time-on-stream, suggesting the excellent catalytic stability of the present oxalate gel-coprecipitated copper-zirconia sample for SRM reaction. Purnama et al. have recently compared the deactivation behavior of a novel template-derived Cu/ZrO₂ catalyst with a commercial Cu/ZnO/Al₂O₃ sample during a continuous operation of 250 h time-on-stream under SRM conditions [13]. A much smaller extent of deactivation was identified for the Cu/ZrO₂ catalyst prepared by polymer templating, which has been attributed to the fact that the copper particles in the zirconia catalyst are less prone to sintering during the steam reforming reaction.

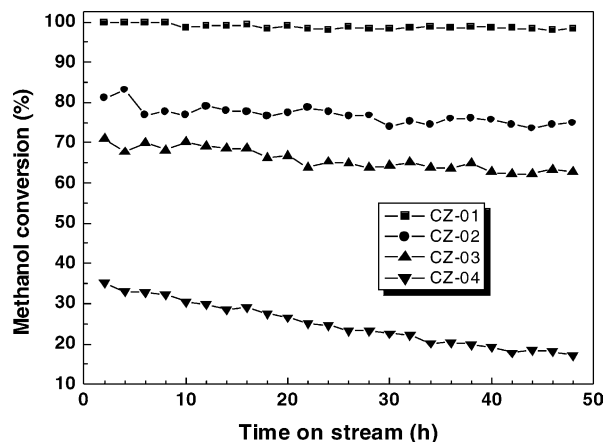


Fig. 3. Methanol conversions during SRM of four CZ catalysts as a function of time-on-stream (reaction conditions: $T = 260$ °C, $H_2O/CH_3OH = 1.3$ molar ratio, $WHSV = 5.4$ h⁻¹, $p = 0.1$ MPa). The data for catalyst CZ-04 is obtained at 300 °C.

3.2. Characterization of the CZ catalysts

Fig. 4 compares the surface morphology of the four CZ catalysts prepared with different methods. Distinct particles in the form of spherical or irregular aggregates of various shape and size are observed in all four samples. The particles composing the catalysts CZ-01 and CZ-02 are spherical and the distribution of the main active particles for both samples seems to be practically uniform with average size less than 0.5 μm. It is notable that the sample CZ-03 obtained by conventional carbonate coprecipitation afforded the massive agglomerates apparently much larger than those of the oxalate-derived samples. An absolute different surface morphology is observed for catalyst CZ-04 prepared by the aqueous impregnation of the amorphous zirconia support. The SEM micrographs show the

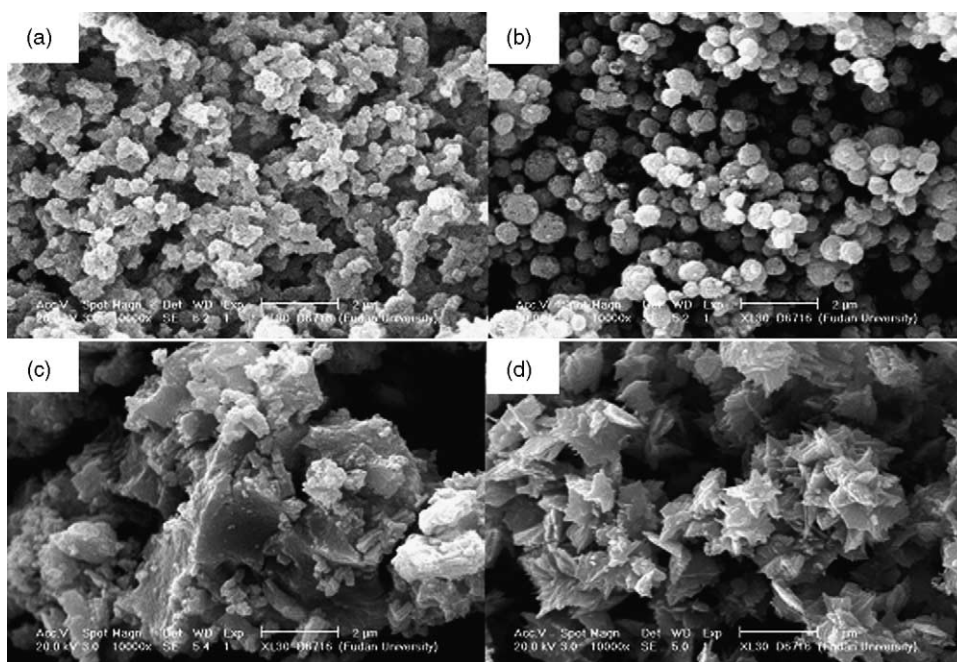


Fig. 4. SEM images of the oxide precursors of the CZ samples prepared by various methods: (a) CZ-01; (b) CZ-02; (c) CZ-03; (d) CZ-04.

Table 1
Physicochemical properties of the CZ catalysts prepared by various methods

Catalyst	S_{BET} (m^2/g)	Pore volume (cm^3/g)	S_{Cu}^{a} (m^2/g)	D_{Cu}^{b} (nm)	$d_{\text{CuO}}^{\text{c}}$ (nm)	d_{Cu}^{c} (nm)
CZ-01	71.5	0.26	18.4	21.0	9.1	21.9
CZ-02	36.2	0.10	5.0	77.4	20.8	33.2
CZ-03	64.2	0.14	3.5	110.6	17.1	35.9
CZ-04	13.1	0.05	1.0	387.2	24.4	48.4

^a Cu surface area measured by N_2O method after 5% H_2/Ar reduction.

^b D_{Cu} calculated from the copper surface areas by using a quasi-sphere model.

^c d_{CuO} and d_{Cu} calculated from XRD data based on Scherrer equation.

agglomeration of interconnected plate-shaped crystalline CuO randomly distributed on the external surface of the zirconia support. Thus, the present SEM results suggest that the oxalate gel-coprecipitation technique is more effective than other methods in preparation of nanostructured Cu/ZrO₂ catalysts with high component dispersion.

Table 1 summarizes the physicochemical properties of the CZ catalysts prepared by various methods. One can see that both the BET specific surface area and the pore volume of the CZ-01 catalyst prepared by the oxalate gel-coprecipitation method are significantly higher than that prepared by the conventional methods. It is noticeable that sample CZ-04 prepared by aqueous impregnation exhibits the lowest BET surface area and smallest pore volume. Copper metal surface areas measured by nitrous oxide titration are also included in Table 1. By using a quasi-sphere model, the average copper metal crystallite sizes (D_{Cu}) were calculated from the copper surface areas. The data of the metallic copper surface area in Table 1 demonstrate clearly that the copper dispersion in CZ-01 catalyst is much higher than those of the catalysts prepared by the conventional methods, thus providing catalytically active centers consisting of copper nanoparticles with much smaller crystallite size for hydrogen production from steam reforming of methanol reaction. Note that the specific copper surface areas for the present binary Cu/ZrO₂ catalysts were far smaller than that of the binary Cu/ZnO catalysts [5] and those of ternary Cu/ZnO/Al₂O₃ catalysts [4], but were very closed to the binary Cu/ZrO₂ materials as reported by Koepfel et al. [15].

The XRD patterns of the catalysts before and after the reaction are shown in Fig. 5. It is shown in Fig. 5A that all calcined precursors of the Cu/ZrO₂ catalysts do not contain any detectable crystalline ZrO₂, suggesting that the particles of ZrO₂ are either amorphous in phase or very fine crystals that could not be detected by XRD. From a comparison of the diffraction peaks of CuO in these catalyst samples, one can find that the diffraction peaks of CuO for catalyst CZ-01 are much broader and lower as compared to those of catalysts prepared by the impregnation, conventional oxalate and carbonate coprecipitation methods. The mean crystal sizes of CuO are estimated by using the Scherrer equation and summarized in Table 1. The CuO crystal size of CZ-01 is about 9 nm, while those of CZ-02, CZ-03 and CZ-04 are much larger in the range of from 17 to 25 nm.

To establish a correlation between the catalytic performance and the active phase, XRD patterns of the catalysts after the reaction were recorded and are shown in Fig. 5B. Only

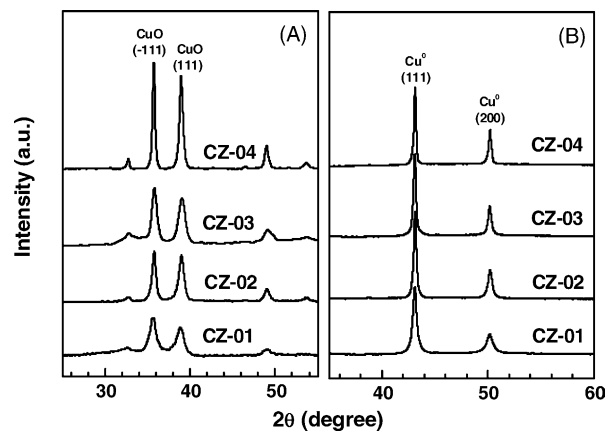


Fig. 5. X-ray powder diffraction patterns of the CZ catalysts before (A) and after (B) the SRM reaction.

diffraction peaks corresponding to metallic Cu are identified, indicating metallic copper is the active phase of the present Cu/ZrO₂ catalysts for SRM reaction. Assuming that Cu particles were spherical, the average copper metal crystallite sizes were calculated from the FWHM of Cu (1 1 1) diffraction lines. The calculation results reveal a much smaller copper particle size for CZ-01 (21.9 nm) as compared to CZ-02 (33.2 nm), CZ-03 (35.9 nm) and CZ-04 (48.4 nm). It should be noted that the copper particle size of sample CZ-02 is found to be smaller than that for CZ-03, in contrast to the relatively larger CuO particle size in CZ-02 as compared to CZ-03, possibly due to the different Cu–ZrO₂ interaction behavior in the two samples. It is also noticeable that for sample CZ-01, the copper crystallite size calculated from the copper surface area as determined by surface titration with N_2O is in good agreement with the results obtained from XRD crystallite size calculations. However, the copper crystallite sizes obtained from XRD are observed to be much smaller than those as determined by N_2O titration. These discrepancies could be due to the interactions of the copper particles with ZrO₂ or deviations from a spherical morphology.

In order to investigate the reducibility of the copper species in the Cu/ZrO₂ catalysts prepared by various methods, TPR measurements were carried out and reported in Fig. 6. All the samples exhibit a broad reduction profile together with shoulders in the temperature range 200–350 °C. The reduction of bulk CuO is featured by a single reduction peak at a considerably higher temperature of 320 °C (not shown). It is thus concluded that there is a Cu/Zr interaction which facilitates the reduction of the supported copper species. In order to gain a

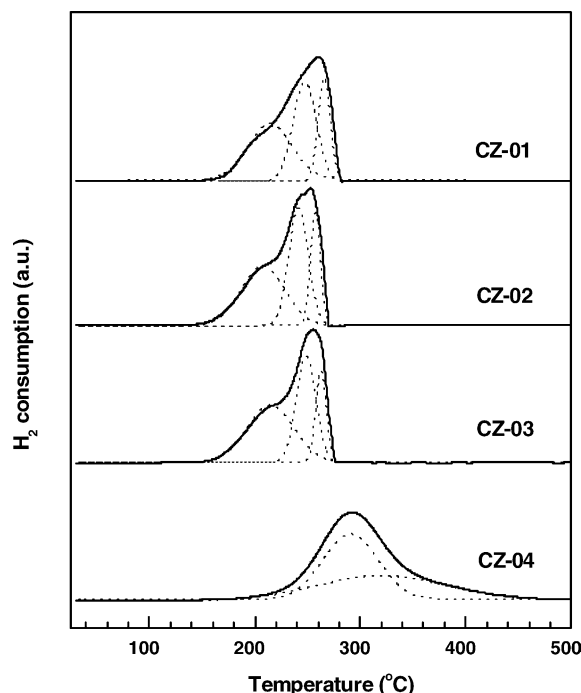


Fig. 6. TPR profiles of the CZ catalysts prepared by various methods. Solid lines are experimental curves and dotted/broken lines are deconvoluted curves.

further insight into the TPR results, the profiles are deconvoluted using a computer program [24]. The peak positions and their contributions derived from deconvolution are summarized in Table 2. The original TPR profile can be deconvoluted into at least two or three peaks in all cases. This suggests the presence of at least two or three types of CuO phase in the Cu/ZrO₂ samples, where highly dispersed CuO phase (α peak), crystallized copper oxide (β and γ peaks) weakly or strongly with the ZrO₂ surface co-exist. The fraction of high temperature reduction peaks, i.e., the β and γ peaks, is observed to be the highest and shifted to higher temperatures for sample CZ-01 as compared to other coprecipitated samples, indicating the presence of a stronger Cu/Zr interaction in the sample prepared by oxalate gel-coprecipitation. A similar shift of the reduction maximum toward higher temperature has been previously observed by Robinson and Moi in a TPR study of the interaction of CuO and ZnO [25]. They have attributed this phenomenon to the presence of a specific type of CuO strongly interacted with the ZnO lattice.

Table 2

TPR peak positions and concentrations of reducible species in the Cu/ZrO₂ catalysts as determined by the deconvolution of TPR profiles

Catalyst	TPR peak position (temperature °C) and concentration (%) ^a		
	Peak α	Peak β	Peak γ
CZ-01	213 (40.8)	247 (38.3)	266 (21.0)
CZ-02	208 (43.4)	243 (38.0)	258 (18.6)
CZ-03	215 (46.9)	248 (36.2)	262 (16.9)
CZ-04	–	291 (52.8)	320 (47.2)

^a Values in parentheses are the contribution (%) of each species.

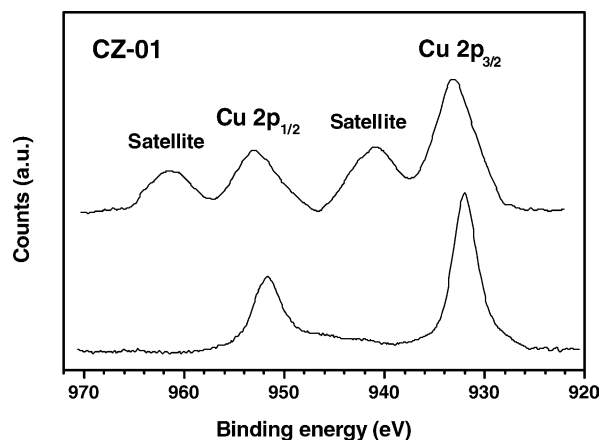


Fig. 7. Cu 2p_{3/2} photoelectron spectra of catalyst CZ-01 after calcination (top), and after exposure to reaction conditions (bottom).

X-ray photoelectron spectra were obtained for the Cu/ZrO₂ samples prepared by various methods. In addition to prereaction spectra, postreaction spectra were also recorded for the four samples subjected to time-on-stream tests. As shown in Fig. 7, CuO in the catalyst CZ-01 is reduced by the reactants after being on-stream for about 50 h. While the binding energies of Cu⁰ and Cu⁺ species are not distinguishable on the basis of Cu 2p_{3/2}, these two species can be differentiated by their different kinetic energies in the Auger Cu_{LMM} line position [20,26]. Our data are pointing to the metallic state of copper species, with possible polarization effects due to dispersion or a strong metal–support interaction with the oxide matrix of zirconia. This result is also in line with the present postreaction XRD data thus further confirming that metallic copper is the active phase of the present Cu/ZrO₂ catalysts for SRM reaction. The Cu 2p_{3/2} and Zr 3d_{5/2} binding energies of the four Cu/ZrO₂ catalysts are reported in Table 3. The Zr 3d_{5/2} binding energies of all measured catalysts are between 182.2 and 182.8 eV, in good agreement with the published data for ZrO₂ [27], and with no systematic deviation observed with respect to copper dispersion. In contrast, the Cu 2p_{3/2} binding energy appears to correlate with the copper dispersion, with lower BEs observed for CZ-01 and CZ-02 samples with a higher component dispersion and highest BE observed for CZ-04 sample containing more bulk crystalline CuO.

Table 3

XPS results of the CZ catalysts prepared by various methods

Catalyst	Conditions	Binding energies (eV)		
		Cu 2p _{3/2}	Zr 3d _{5/2}	Atomic Cu/Zr ratio
CZ-01	Fresh	933.1	182.2	1.72
	After reaction	932.0	182.7	1.68
CZ-02	Fresh	933.3	182.7	1.62
	After reaction	932.1	182.4	1.81
CZ-03	Fresh	933.4	182.5	1.56
	After reaction	932.1	182.7	1.86
CZ-04	Fresh	933.6	182.8	6.49
	After reaction	932.3	182.6	7.08

Table 3 also lists the surface Cu/Zr ratios in the four CZ samples. The Cu/Zr ratio of calcined catalysts is falling in the range of 1.56–1.72 for the coprecipitated samples. This value is far below the ratio (~ 4.0) as used in the preparation, inferring a preferential accumulation of the Zr-components occurs during the course of the catalyst preparation. In contrast, a significant higher value of 6.49 is observed for the CZ-04 sample prepared by impregnation, thus pointing to a pronounced Cu-enrichment on the surface. After the time-on-stream tests, the Cu/Zr ratio for samples CZ-02, CZ-03 and CZ-04 increased to a higher value as compared to their calcined case, suggesting a prominent surface Cu-enrichment on exposure to reaction conditions. However, in the CZ-01 catalyst, it is clear that the surface composition of the sample remains essentially unaffected after the reaction, indicating a strong resistance to sintering. Thus, the present finding strongly supports the idea that Cu/Zr ratio of the surface or sub-surface plays a key role in obtaining and maintaining the activity of the Cu/ZrO₂ catalysts for methanol steam reforming.

3.3. Discussion

The methanol steam reforming reaction is essentially the microscopic reverse of the methanol synthesis reaction using CO₂/H₂ as a feedstock over Cu-based supported catalysts [19]. Among various supports, zirconia emerged as an interesting material for copper catalysts. It has been generally accepted that catalysts containing copper and ZrO₂ behave in a bifunctional manner, with copper and ZrO₂ playing complementary but different roles in methanol synthesis reaction [28–30]. A recent in situ FTIR investigation by Fisher and Bell revealed the involvement of similar bifunctional roles of copper and ZrO₂ in the methanol decomposition [29]. Accordingly, methanol interacts with the OH groups of ZrO₂ to form water and methoxide, leading to dehydrogenation into formaldehyde and subsequent decomposition to gas-phase CO₂ and H₂ generation. The main role of copper is to accept the hydrogen released from the surface species located on ZrO₂ and subsequent desorption of molecular hydrogen [30]. In addition, ZrO₂ is known to possess anionic vacancies, which entails a geometric effect that can influence the dispersion and leading to a change in the morphology of the supported copper metal particle [31]. Taking into account these unique features rendered by the ZrO₂ in the supported catalytic systems, it is reasonable that the present binary CZ catalyst systems, in particular the one prepared by the oxalate gel-coprecipitation, are found to be highly active and selective for the production of H₂ via steam reforming of methanol.

On the other hand, it is known in the literature that methanol conversion over copper based catalysts during the steam reforming reaction greatly depends on the status of copper, such as the dispersion, metal surface area and particle size [7,19]. Generally, catalyst with higher copper dispersion shows better performance in methanol steam reforming, whereas the status of metal dispersion is closely related to overall surface area. Unfortunately, the Cu/Zr-based catalysts reported in the literature generally have a limited copper surface area by

conventional preparation methods [15]. In the present work, we have unambiguously demonstrated that the present oxalate gel-coprecipitation method can allow the generation of a new type of Cu/ZrO₂ catalyst with a much higher specific surface area and improved copper dispersion with respect to its conventional counterparts. Accordingly, the CZ catalyst obtained by gel-coprecipitation of oxalate precursor has exhibited a unique catalytic behavior in methanol steam reforming as compared to the catalysts prepared by other methods in terms of methanol conversion, H₂ production and CO concentration. Obviously, the oxalate gel-coprecipitation method, previously established to be an effective technique for the preparation of the ultrafine Cu/ZnO/ZrO₂ catalyst highly efficient for methanol synthesis from CO₂ hydrogenation by our group [21], has been experimentally demonstrated to be particularly useful in generating the highly active Cu/ZrO₂ catalyst for the methanol steam reforming reaction.

Regarding the essential nature of metallic copper for the catalytic production of hydrogen from methanol steam reforming, some studies have experimentally demonstrated that for a given type of catalyst, the catalytic activity is directly proportional to the metallic copper surface area [20]. However, there are also conflicting reports which suggest that the methanol conversion or hydrogen production rate cannot be correlated to the surface area of metallic copper for the Cu-based catalysts [22]. It is therefore highly interesting to make a comparison between the catalytic activity of the present CZ catalysts prepared by various methods and the metallic copper surface area obtained from N₂O decomposition. Fig. 8 shows the effect of the surface area of metallic copper on the hydrogen production rate (R_{H_2}) from methanol steam reforming over the four CZ catalysts obtained by different preparation routes. Apparently, the increase in H₂ production rates does not show linear correlation with the increasing copper surface area for the four CZ catalysts. This demonstrates that although a high Cu surface area is a prerequisite for catalytic activity, it does not account for the observed activity changes alone without taking the powerful synergy between copper and zirconia into account.

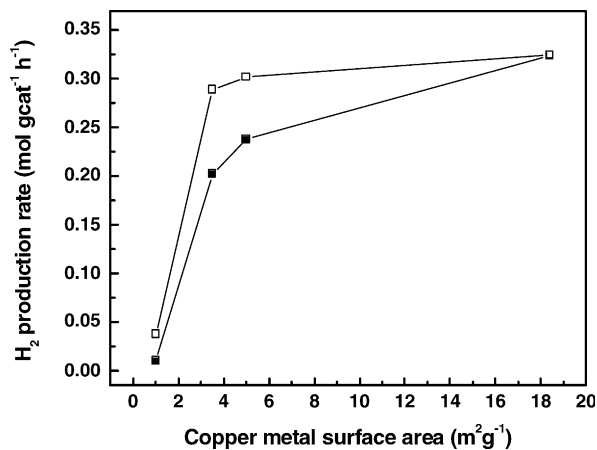


Fig. 8. The relationship between the specific Cu surface area (S_{Cu} , $m^2 g^{-1}$) and hydrogen-production rate (R_{H_2} , $mmol g_{cat}^{-1} h^{-1}$) at 260 °C (■) and 280 °C (□).

The XPS results show that the surface composition of the present CZ catalysts prepared by both the oxalate gel-coprecipitation and conventional coprecipitation methods deviated significantly from the bulk composition. The Cu/Zr ratio of calcined and used samples of CZ-01 remained more or less in the same range and show a correlation with the observed activity and stability. An increase in the Cu/Zr ratio of the surface and sub-surface of methanol steam reforming catalysts during deactivation for the other three samples suggests that an optimal Cu/Zr ratio ~ 1.7 is required to obtain high activity and stability. Similar results were obtained by Kumari et al. [32] on correlation the activity and stability of Cu/ZnO/Al₂O₃ methanol steam reforming catalysts with the surface Cu/Zn ratio obtained by SEM-EDAX analysis.

Based on the present investigation, it is clear that the superior catalytic performance of the oxalate gel-coprecipitation derived Cu/ZrO₂ catalyst can be attributed to the particularly high copper surface area and the small crystallite size of copper particles [22]. Furthermore, the improved synergy effect between active Cu material and ZrO₂ as a consequence of a higher component dispersion and smaller crystallite size of the active component is also thought to be essential for the enhanced catalytic performance in the methanol steam reforming reaction. It should also be pointed out that the most active catalyst CZ-01 prepared by the present oxalate gel-coprecipitation method had the highest TPR peak as compared to other coprecipitated samples. Previous investigations concerning the reducibility of copper based catalysts for methanol synthesis have revealed that a better reducibility is always associated with a higher activity of the catalyst [33]. However, according to a recent investigation by Günter et al. [22], this does not necessarily mean that the reducibility of copper species plays the decisive role in determining the catalytic performance of the present Cu/ZrO₂ samples. One possible explanation is that a less sintering is expected during the reductive activation of catalyst CZ-01 thus leading to the generation of much smaller copper particles in the active catalyst, which however could be the main reason why the less reducible CZ-01 shows an improved performance of for SRM reaction.

4. Conclusion

Several methods including impregnation, oxalate gel-coprecipitation and conventional aqueous coprecipitation were employed for the preparation of binary Cu/ZrO₂ catalyst for methanol steam reforming, and the catalytic results show that the preparation method plays an important role in the steam reforming of methanol. It is shown that the oxalate gel-coprecipitation approach involving the gel-coprecipitation of oxalate precursors can allow the fabrication of highly effective Cu/ZrO₂ catalyst with a large metallic copper surface area as well as high component dispersion, which exhibits a much higher catalytic activity for methanol steam reforming than the catalysts prepared by conventional methods. Combined SEM, XRD, N₂O chemisorption, H₂-TPR and XPS results demonstrated that the superior catalytic performance of the oxalate gel-coprecipitation derived Cu/ZrO₂ catalysts could be

attributed to the generation of highly dispersed copper and zirconia components with a much higher metallic copper specific surface as well as and the beneficial synergy effect due to a stronger interaction between copper and zirconia.

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