CO_2 hydrogenation to methanol over $Cu/ZnO/Al_2O_3$ catalysts prepared by a novel gel-network-coprecipitation method

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Received 13 December 2001; accepted 3 April 2002

A novel gel-network-coprecipitation process has been developed to prepare ultrafine $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis from CO_2 hydrogenation. It is demonstrated that the gel-network-coprecipitation method can allow the preparation of the ultrafine $Cu/ZnO/Al_2O_3$ catalysts by homogeneous coprecipitation of the metal nitrate salts in the gel network formed by gelatin solution, which makes the metallic copper in the reduced catalyst exist in much smaller crystallite size and exhibit a much higher metallic copper-specific surface area. The effect of the gel concentration of gelatin on the structure, morphology and catalytic properties of the $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis from hydrogenation of carbon dioxide was investigated. The $Cu/ZnO/Al_2O_3$ catalysts prepared by the gel-network-coprecipitation method exhibit a high catalytic activity and selectivity in CO_2 hydrogenation to methanol.

KEY WORDS: gel-network-coprecipitation; $Cu/ZnO/Al_2O_3$ catalysts; methanol synthesis; CO_2 hydrogenation; gelatin polymer.

1. Introduction

During the past decade, the effective utilization of CO_2 has attracted considerable attention due to the global recognition that there has been a continuous increasing of the concentrations of greenhouse gases in the earth's atmosphere [1]. Great efforts have been made in an effort to prevent the atmospheric CO_2 build-up by reduction of carbon dioxide to various useful chemical products in the past decade [2]. One promising approach of CO_2 utilization may be the synthesis of methanol from the direct hydrogenation of CO_2, which has been considered as one of the most economical processes for chemical transformation of CO_2.

The use of the commercial $Cu/ZnO/Al_2O_3$ catalysts for the catalytic synthesis of methanol from CO_2 hydrogenation has gained much attention since CO_2 is currently used as an additive in the synthesis of methanol from CO and H_2 [3]. Moreover, several investigations have provided evidence that methanol is synthesized predominantly from carbon dioxide [4]. However, it has been found that the $Cu/ZnO/Al_2O_3$ catalysts prepared by conventional coprecipitation methods, which have exhibited a high performance for syngas (CO/H_2) to methanol synthesis, have only shown a very poor activity in the methanol synthesis from hydrogenation of CO_2 [5–7]. Although the $Cu/ZnO/Al_2O_3$-based catalysts have been subject to numerous investigations, the nature of the active sites and the involved reaction steps continue to be discussed in the literature.

The influence of the preparation variables on the catalytic behavior of $Cu/ZnO/Al_2O_3$ catalysts has been intensively investigated. Recently, Inui *et al.* [1] reported that the Cu–Zn–Cr–Al oxide catalyst prepared by an intrinsic uniform gelation method showed a higher activity for methanol synthesis from CO_2 hydrogenation. The effect of ultrasonic treatment on the methanol synthesis activity of a $Cu/ZnO/Al_2O_3$ catalyst was also investigated by Li and Inui [8]. They found that insonation of the suspension during coprecipitation and aging steps can appreciably enhance the activity of the catalyst, and along with the increase of the frequency of the ultrasound the enhancement grew stronger. This suggests that the catalytic activity was greatly influenced by the preparation methods. Moreover, numerous recent investigations have revealed the presence of a linear correlation between the specific copper surface area and the methanol synthesis activity on the $Cu/ZnO/Al_2O_3$ catalysts [9,10], and it is believed that that the role of ZnO is to maintain an adequate copper surface area in the catalyst by preventing the sintering of metallic copper particles.

Considering the catalytic performance of a methanol synthesis catalyst closely related to the copper surface area, it is therefore very important to develop new efficient catalytic systems for CO_2 hydrogenation reaction with attractive structural properties such as a larger copper surface area [6,7,11,12]. Recently, it has been reported that porous $Cu/ZnO/Al_2O_3$ catalysts with meso- and macroporous structures can be synthesized by employing water-swellable polymer networks (WSPNs) obtained by *in situ* polymerization of the monomer in the precipitation process. The gel of WSPNs has a three-dimensional network with cavities

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of the order of 10 nm in size, which can function as water reservoirs for lodging water-soluble inorganic salts [13]. Ruckenstein and Hong [14] have successfully employed the WSPNs as nano-reservoirs to prepare a series of $Cu/ZnO/Al_2O_3$ catalysts with different surface area and structures. However, a high-temperature treatment (>450 °C) is needed to completely eliminate the polymer included in the mixed oxides, which often leads to unattractive agglomeration, i.e., size increment, of the oxide particles.

In this paper, a novel process utilizing the gel-network-coprecipitation method is proposed to prepare a $Cu/ZnO/Al_2O_3$ ultrafine catalyst. Gelatin, a natural polymer, which is present in a three-dimensional gel-network state by attracting the molecular chains using hydrogen bonds or van der Waals forces at a lower temperature (lower than 10 °C), but can be easily dissolved in water at higher temperature (higher than 70 °C), was used as the polymer providing the solution reservoir to prepare the precursor of $Cu/ZnO/Al_2O_3$ methanol synthesis catalysts using oxalate acid as precipitator. The utilization of gelatin as a polymer network can offer the advantage of easy elimination of the polymer by washing several times at 70 °C instead of by calcining the mixture at high temperature, thus avoiding the agglomeration of particles during high-temperature calcination. The effect of the gel concentration of gelatin on the structural and the catalytic properties of the $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis from hydrogenation of carbon dioxide was investigated. The results show that the gel-network-coprecipitation method can produce new types of ultrafine $Cu/ZnO/Al_2O_3$ catalysts with a high metallic copper surface area, exhibiting high catalytic activity and selectivity in CO_2 hydrogenation to methanol.

2. Experimental

2.1. Catalyst preparation

Various $Cu/ZnO/Al_2O_3$ catalysts with a same composition (molar ratio of copper:zinc:aluminum = 45:45:10) were prepared by three different methods. The preparation procedure of the gel-network-coprecipitation method (see figure 1) is described as follows. Briefly, an appropriate amount of gelatin polymer (M_W = 15 000–90 000, from Shanghai Chemical Reagent Works) was added into a mixed aqueous solution of copper nitrate, zinc nitrate and aluminum nitrate (100 ml) at 70 °C. Then a green homogeneous "gelatin gel" containing the nitrate salts was obtained by cooling down the resolved hot gelatin aqueous solution to allow gel formation. After being divided into small pellets, the gelatin gel was dipped in an oxalic acid solution at 5 °C for 24 h to accomplish the coprecipitation process. After that, the gelatin was re-dissolved by putting the gel in hot water (70 °C) to obtain a slurry of coprecipitated oxalates mixture. Thus most of the gelatin polymer can be separated from the precipitate by centrifugation. Finally, the precipitate was dried overnight at 110 °C. The resulting catalyst precursors obtained by using various gelatin concentrations are denoted as PCZA1x (x = 1–5) as seen in table 1.

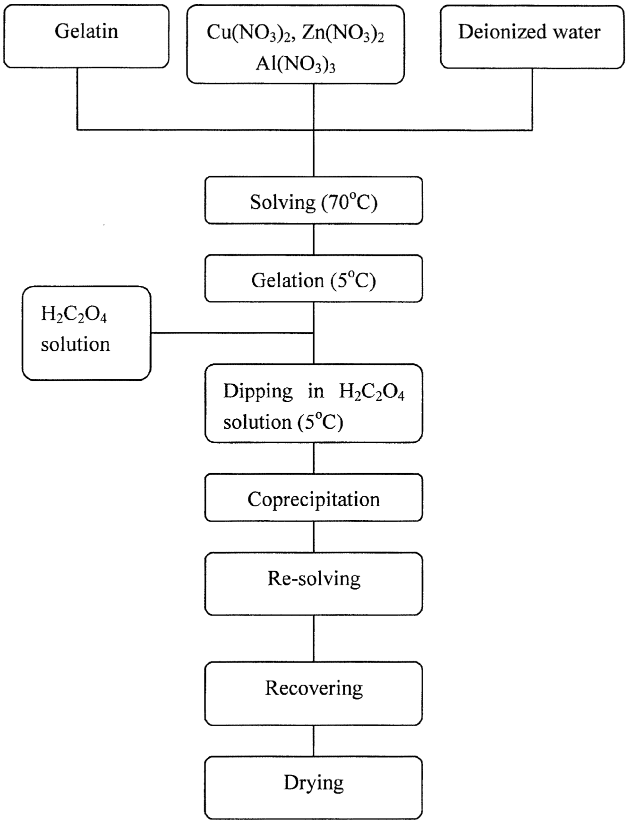


Figure 1. The preparation process of the $Cu/ZnO/Al_2O_3$ catalysts by the gel-network-coprecipitation method.

As a comparison with the above method, a conventional oxalate coprecipitation procedure to prepare a precursor PCZA2 is as follows: an aqueous solution of 20% excess of oxalic acid is added rapidly to a mixed aqueous solution (total 0.1 M) of copper nitrate, zinc nitrate and aluminum nitrate at room temperature under vigorous stirring. The precipitates are formed and separated by centrifuge, then dried at 110 °C. The catalyst precursor prepared by the conventional carbonate coprecipitation method is referred to as PCZA3. A mixed aqueous solution of copper nitrate, zinc nitrate and aluminum nitrate (total 0.1 M) and a solution of sodium carbonate (0.1 M) are added slowly and simultaneously into 100 ml of deionized water at 70 °C with vigorous stirring. The pH is kept constant at 6.5–7.0. The precipitates are aged at 70 °C for 30 min under gentle stirring, and then filtered and thoroughly washed with hot deionized water. The precipitates are dried overnight at 110 °C.

Table 1
Physicochemical properties of $Cu/ZnO/Al_2O_3$ catalysts prepared *via* various methods

Catalysts	Composition Cu/Zn/Al (at%)	Weight percent of gelatin	BET surface area (m^2/g)	Pore volume (ml/g)	Cu metal surface area (m^2/g)	Cu metal crystallite size (nm)
CZA11	45/45/10	12.7	63.4	0.27	28.2	10.8
CZA12	45/45/10	8.9	57.8	0.25	24.8	12.3
CZA13	45/45/10	7.5	55.4	0.23	21.3	14.3
CZA14	45/45/10	6.1	54.1	0.21	18.4	16.5
CZA15	45/45/10	4.6	52.1	0.20	15.6	19.5
CZA2	45/45/10	–	46.8	0.20	11.5	26.3
CZA3	45/45/10	–	48.7	0.13	17.2	17.3

All dried precipitates were finally 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 finally 350 °C for 4 h to decompose the precursor [15]. This calcination procedure can allow the full decomposition of the residue gelatin contained in the PCZA1*x* precursors. The calcined oxides are denoted as CZA1*x*, CZA2 and CZA3, respectively.

2.2. Catalyst characterization

Full nitrogen adsorption/desorption isotherms at −196 °C were obtained after outgassing of the sample under vacuum at 150 °C for 4 h, using a Micromeritics ASAP 2000 physical adsorption apparatus. X-ray diffraction patterns of the catalyst samples were recorded using nickel filtered Cu K_α radiation on a Bruker D8 Advance diffractometer. Nitrous oxide experiments were carried out using a pulse technique similar to that reported by Evans *et al.* [16]. The apparatus for the temperature-programmed reaction (TPR) studies has been described previously [9]. TPR profiles were measured under the following conditions: heating rate 5 °C/min, flow-rate 40 ml/min 5% H_2/Ar. Transmission electron microscopy (TEM) was carried out using a Joel 200CX electron microscope.

2.3. Catalytic tests

The catalytic activities of the $Cu/ZnO/Al_2O_3$ catalysts for hydrogenation of CO_2 were measured with a continuous tubular fixed-bed microreactor [7]. The catalyst (40–60 mesh size, 0.5 ml) was packed into a stainless steel reactor (6.0 mm i.d.) and reduced in a premixed H_2/Ar (5/95) flow of 40 ml/min (NTP). The temperature was raised to 240 °C at a rate of 1 °C/min and held there for 10 h. After the reduction, the gas feed was switched to the reactant gas ($CO_2/H_2 = 1/3$). The reaction was carried out at a pressure of 2.0 MPa in the temperature range 180–300 °C with a space velocity (SV) of 3600 or 7200 h^{-1}. The flow rate of reactant gas was regulated by a mass flow controller. The products were analyzed by an on-line gas chromatograph equipped with a thermal conductivity detector, in which two parallel-connected columns, Porapak-Q and TDX-01, were employed to separate the reaction products.

3. Results and discussions

3.1. Characterization of the oxalate precursors

The XRD patterns of the catalyst precursors prepared by conventional oxalate coprecipitation and the present gel-network-coprecipitation method are shown in figure 2. For convenience, only one representative XRD pattern of PCZA11 from samples prepared by the new method is presented. The major diffraction peaks for the samples prepared by conventional methods were observed at 2θ angles of 18.7, 22.9 and 23.7°, which were identified as diffraction lines of α-$ZnC_2O_4 \cdot 2H_2O$, $CuC_2O_4 \cdot xH_2O$, and β-ZnC_2O_4, respectively. Obviously, the diffraction peaks of sample PCZA11 are much broader than those of PCZA2, which indicates that the average particle size of the precipitates prepared by the novel method are much smaller than those of the conventional method. It is also seen that the diffraction bands corresponding to zinc-containing phases are very

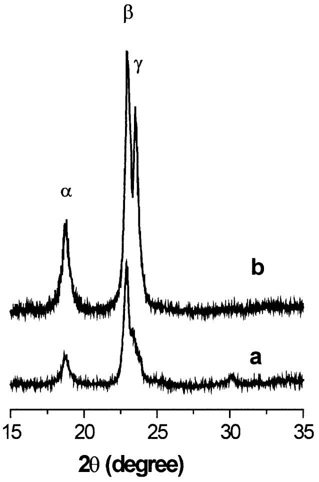
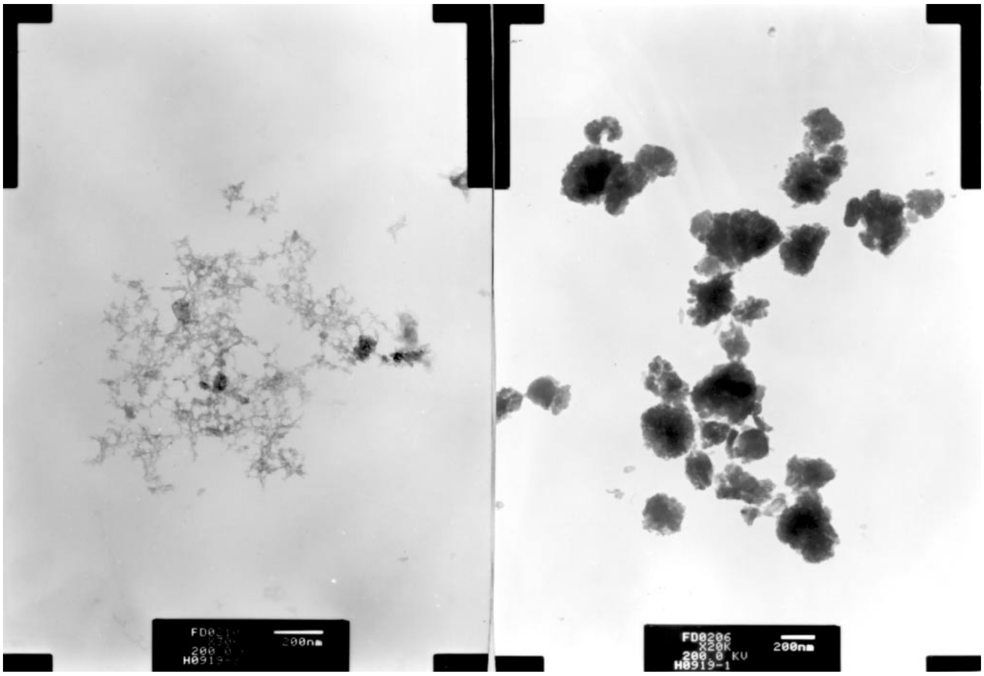


Figure 2. XRD patterns of oxalate precipitates derived from (a) PCZA11 and (b) PCZA2. (α) α-$ZnC_2O_4 \cdot 2H_2O$, (β) $CuC_2O_4 \cdot xH_2O$, and (γ) β-ZnC_2O_4.



a b

Figure 3. TEM graphs of catalyst precursors derived from (a) PCZA11 and (b) PCZA2.

weak and broadened in the XRD pattern of sample PCZA11, indicating that zinc exists in very fine crystallites and most zinc was well-incorporated into the $CuC_2O_4{\cdot}xH_2O$ structure.

The morphological properties of the oxalate precursors have been studied by TEM. It was noted that, upon gelatin addition, the catalyst precursors undergo a significant morphology change from the aggregated nanoparticles to a high degree of cross-linked texture with a decrease in average size. The TEM photograph in figure 3(a) clearly reveals that the ultrafine particles in nanometer scales with a highly cross-linked structure were formed in the precursor sample of PCZA11 derived from the gel-network-coprecipitation process. It can be seen that the as-prepared catalyst precursor of PCZA11 is highly porous in nature, which consists of narrowly distributed nanoclusters of cross-linked particles smaller than 5 nm. In contrast, figure 3(b) shows that much larger particle aggregates are detected in the catalyst precursor of PCZA2 prepared from the conventional precipitation method, in good agreement with the XRD data.

3.2. *Structure and morphology of calcined catalysts*

The XRD patterns of the calcined catalyst precursors obtained by various methods are presented in figure 4. It is shown that only broad diffraction lines corresponding to CuO and ZnO are observed, indicating the chemical homogeneous nature of the calcined samples. It is noticeable that no peaks of Al_2O_3 could be observed, which suggests that the particles of Al_2O_3 are either amorphous in phase or very fine and highly dispersed in the catalyst. As shown in figure 4, the diffraction peaks of sample CZA11 are much broader those of than CZA2. This indicates that the crystallite sizes of ZnO and CuO in catalyst precursor of CZA11 are much smaller than in precursor CZA2.

The physicochemical properties of the calcined CuO/ZnO/Al_2O_3 catalysts prepared by the gel-network-coprecipitation method utilizing various gelatin concentrations during the network formation process are summarized in table 1. For comparison, the physicochemical properties of the catalysts obtained by the conventional methods using oxalic acid as well as sodium carbonate as precipitation agents are also included. One can see that both the BET specific surface

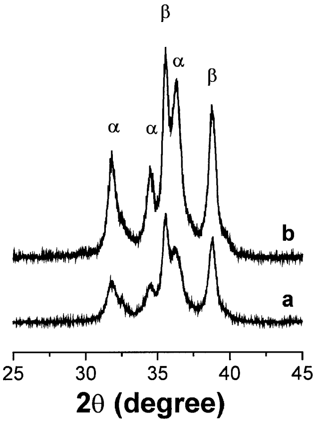


Figure 4. XRD patterns of calcined catalysts obtained by (a) CZA11 and (b) CZA2. (α) ZnO, (β) CuO.

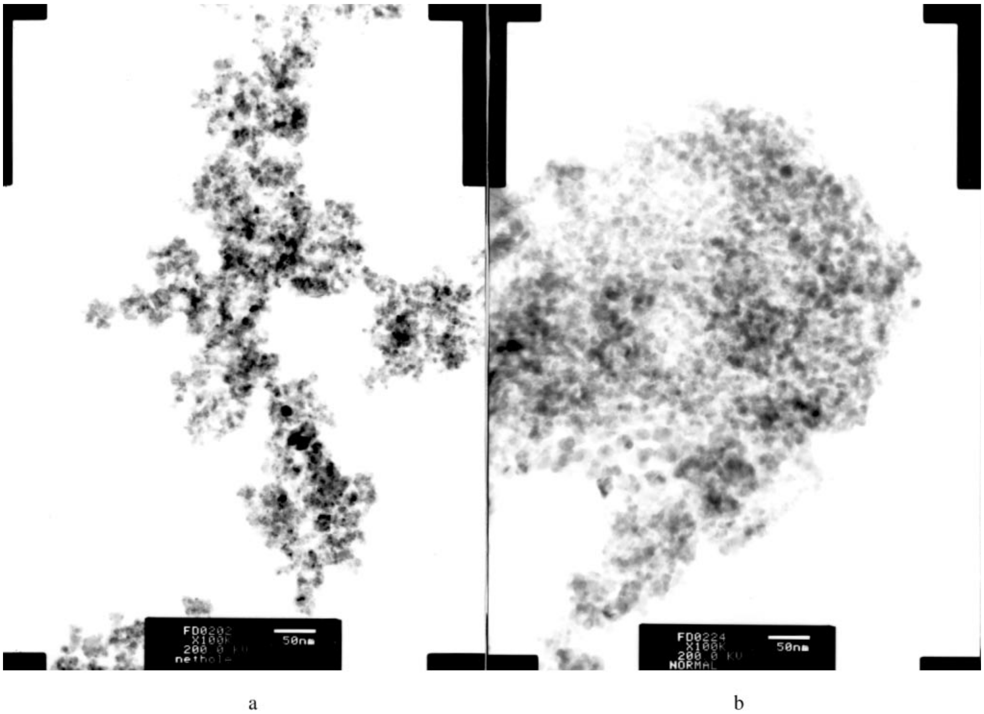


Figure 5. TEM photographs of calcined catalysts derived from (a) CZA11 and (b) CZA2.

area and the copper metal surface area of the catalysts prepared by the present gel-network-coprecipitation method are significantly higher than those prepared by the conventional precipitation methods. The data of the metallic copper surface area in table 1 demonstrate clearly that the copper dispersion in the $Cu/ZnO/Al_2O_3$ catalysts prepared by the gel-network-coprecipitation method is much higher than that of the catalyst prepared by conventional methods. It is therefore expected that the catalysts derived by the gel-network-coprecipitation method can provide catalytically active centers consisting of copper nanoparticles with a much smaller crystallite size for CO_2 hydrogenation.

From table 1, it is also noticeable that the metallic copper surface area as well as the total specific surface area of the $Cu/ZnO/Al_2O_3$ catalysts prepared *via* the gel-network-coprecipitation method increases as a function of the gelatin concentration. With increasing gelatin concentration, a decrease in the average size of the nanocrystalline copper particles in the catalysts is also observed. The dependence of the catalyst behaviors on the gelatin concentration implies that the structure of the $Cu/ZnO/Al_2O_3$ catalyst can be finely tuned simply by a variation of the gelatin concentration in the preparation process. The TEM images of a gel-network-coprecipitation-method-derived $Cu/ZnO/Al_2O_3$ catalyst and a conventional-method-derived catalyst after calcination are shown in figure 5. The morphology of the two calcined catalysts clearly demonstrates that the catalyst obtained by the conventional coprecipitation method consists of much larger particles of similar shape, which often appeared in much larger agglomerates than the gel-network-coprecipitation-method-derived catalyst.

In order to investigate the reducibility of the copper species in the $Cu/ZnO/Al_2O_3$ catalysts prepared by various methods, TPR measurements were carried out. The TPR profiles of the $Cu/ZnO/Al_2O_3$ catalysts prepared by gel-network-coprecipitation and conventional coprecipitation methods are reported in figure 6. For comparison, the TPR profile of the catalyst prepared by the conventional carbonate coprecipitation method is also presented. The TPR profiles of these catalysts show that single reduction peaks and the peak maximum

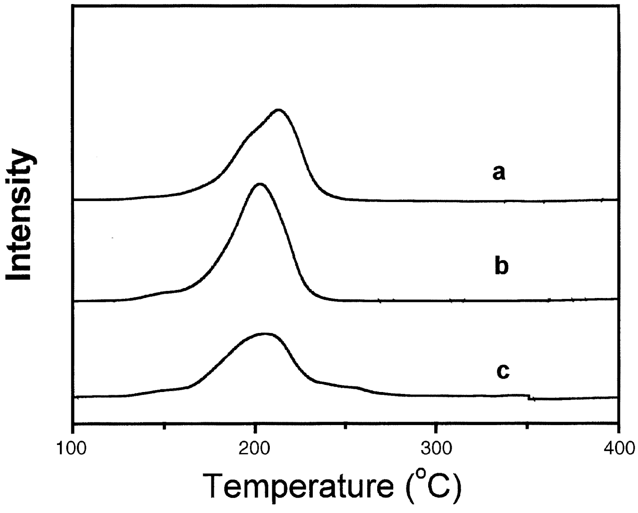


Figure 6. TPR profiles of calcined catalysts derived from (a) CZA11, (b) CZA2 and (c) CZA3.

Table 2
Performance of methanol synthesis from $CO_2 + H_2$ on catalysts prepared *via* various methods

Catalysts	Cu : Zn : Al	SV (h^{-1})	CO_2 conversion (%)	Methanol selectivity (%)	MeOH yield (%)
CZA11	45 : 45 : 10	3600	20.1	31.3	6.3
		7200	17.3	32.4	5.6
CZA2	45 : 45 : 10	3600	19.3	22.3	4.3
		7200	17.4	19.0	3.3
CZA3	45 : 45 : 10	3600	15.8	22.8	3.6
		7200	15.4	19.5	3.0

Reaction conditions: $T = 513\,K$, $P = 2.0\,MPa$, and $CO_2/H_2 = 1/3$.

(T_M) are similar to those observed by Boyce *et al.* [17] for CuO/ZnO based catalysts. It is seen that the reduction peak of CZA11 is centered at 212.9 °C, and those of CZA2 and CZA3 at 203.6 °C and 202.8 °C, respectively. It is noticed that a higher reduction temperature is needed to reduce the CuO in the gel-network-coprecipitated catalyst than the catalysts obtained by conventional coprecipitation. This may be due to the strong interactions of CuO with the ZnO lattice. The shift of the reduction maximum toward higher temperature has been previously observed by Robinson and Moi [18] in a TPR study of the interaction of CuO and ZnO; they attributed this phenomenon to the presence of a strong interaction between CuO and the ZnO lattice.

3.3. *Methanol synthesis by hydrogenation of CO_2*

The catalytic activity and selectivity for methanol synthesis on the catalysts prepared by various methods, which was obtained after the activity was shown to be stabilized, are summarized in table 2. Carbon monoxide and methanol are the only carbon-containing products found under the reaction conditions described above. At higher temperatures, traces of methane and higher hydrocarbons can be detected by gas chromatography. The catalytic results obtained at a lower gas velocity show a higher CO_2 conversion value but a relatively lower selectivity to methanol. As seen in table 2, the catalyst prepared by the gel-network-coprecipitation method exhibits the best catalytic performance for methanol synthesis among all catalysts with the same composition. Comparing the two types of catalysts derived from the conventional methods, it can be found that the catalytic CO_2 conversion on the conventional oxalate-precipitated catalyst is higher than that on a conventional carbonate-precipitated catalyst although the two catalysts exhibit a comparable selectivity for methanol synthesis. It is noticeable that the selectivity to methanol on the catalyst prepared from the gel-network-coprecipitation process is much higher than that from the conventional methods, which results in the highest methanol yield on the catalyst obtained by the new method.

To investigate the essential role of the gelatin addition on the catalytic properties of the catalysts prepared by the gel-network-coprecipitation process, the catalytic activities and selectivities of CO_2 hydrogenation to methanol on the catalysts prepared using various gelatin concentrations are presented in table 3. The results show that the catalytic activities and methanol yields of the catalyst increase with increasing gelatin concentration while keeping a high selectivity to methanol for all five catalysts investigated. Coupled with the data of the metal copper surface area listed in table 1, the present catalytic results demonstrate clearly that, for the catalysts prepared *via* the present gel-network-coprecipitation method, one central role influencing the catalytic activities is the specific copper surface area.

Another important aspect of the catalyst prepared by the new method is the improved catalyst stabilities in the reaction condition. For the catalyst CZA11, no significant decrease in the activity was observed in a 100 h on-stream test, as shown in figure 7, where the methanol yield is found to decrease by less than 5% from its

Table 3
Performance of methanol synthesis from $CO_2 + H_2$ on catalysts prepared *via* the gel-network-coprecipitation method using various gelatin concentrations

Catalysts	Cu : Zn : Al	SV (h^{-1})	CO_2 conversion (%)	Methanol selectivity (%)	MeOH yield (%)
CZA11	45 : 45 : 10	7200	17.3	32.4	5.6
CZA12	45 : 45 : 10	7200	16.2	30.9	5.0
CZA13	45 : 45 : 10	7200	15.6	29.5	4.6
CZA14	45 : 45 : 10	7200	15.4	27.9	4.3
CZA15	45 : 45 : 10	7200	15.0	26.7	4.0

Reaction conditions: $T = 513\,K$, $P = 2.0\,MPa$, and $CO_2/H_2 = 1/3$.

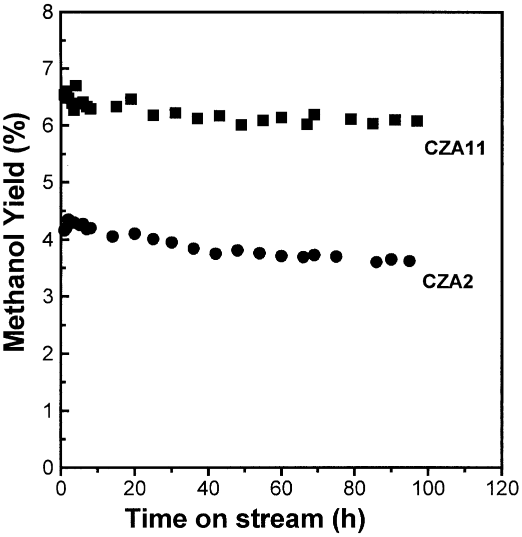


Figure 7. Methanol synthesis activity of $Cu/ZnO/Al_2O_3$ catalysts prepared by various methods as a function of time on stream. Reaction conditions: $T = 250\,°C$, $P = 2.0\,MPa$, $F/W = 3600\,h^{-1}$, $CO_2/H_2 = 1/3$.

initially stabilized value. In comparison, the methanol yield of CZA2 decreased by 16% of its initially stabilized value, from 4.3 to 3.6%. The XRD patterns of the catalysts after reaction showed no significant change as compared with those of the fresh catalysts. Nevertheless, the N_2O titration results showed a decrease of copper specific surface area (14% of its initial value for CZA11 and 20% for CZA2) after 100 h reaction, which may be caused by the water produced during the hydrogenation of carbon dioxide [19]. The improved stability in the CZA11 catalyst may be due to the unique chemical homogeneity associated with the gel-network-coprecipitation-derived catalysts.

3.4. Discussion

It has been well established that methanol synthesis catalysts are highly structure-sensitive [5,20]. It is believed that a small variation in the preparation process may bring about evident changes in the structure and surface properties of a $CuO/ZnO/Al_2O_3$ catalyst and result in subsequently different reaction performances. The significant variation of the catalytic performances is strongly influenced by the choice of the preparation methods and preparation conditions as well as post-processing conditions, which are known to have remarkable influences on the chemical and physical structures of the catalysts. In our case, the results show unambiguously that the present new process utilizing the gel-network-coprecipitation method can allow the preparation of $CuO/ZnO/Al_2O_3$ catalysts with special surface and structural properties significantly different from those of conventional catalysts.

Based on our characterization, it is clear that the superior catalytic performance of the gel-network-coprecipitation-derived $Cu/ZnO/Al_2O_3$ catalyst can be attributed to the particularly high copper surface area, the small crystallite size of copper particles and a stronger interaction between the copper species and the ZnO lattice [15,17]. Obviously, the present gel-network-coprecipitation method can offer opportunities to prepare highly dispersed ultrafine $Cu/ZnO/Al_2O_3$ catalysts. One may suggest that the sol-gel methods can also be employed here to obtain chemically mixed oxides at the molecular scale since it is well known that the sol-gel methods can provide opportunities to prepare catalysts with a high dispersion if careful choice of the precursor alkoxides and control of the hydrolysis/condensation conditions can be carried out. However, one major drawback of the sol-gel processes is that they usually require the use of very expensive precursors and thus become economically unattractive for practical reasons. While conventional powder synthesis strategies such as the conventional coprecipitation method or repeated ball milling of a mixture of individual oxide powders offer the advantage of inexpensive precursors, they often result in mixed oxide catalysts with a low dispersion and relatively large crystallite size. As a result, the present novel preparation process employing the gel-network-coprecipitation method can offer advantages to synthesize mixed oxide catalysts combining both the conventional coprecipitation and sol-gel routes while getting away from the disadvantages.

During the gel-network-coprecipitation process for catalyst preparation, we have shown that the use of a gel network generated by using gelatin polymer can allow the preparation of well-mixed oxalate precursors of the $Cu/ZnO/Al_2O_3$ catalysts. This can be understood by taking into account that a preferential "capture" of the mixed metal ions occurred in the "nanoreactors" presented by the three-dimensional network containing numerous hydrophilic functional groups on the backbone of the molecular chains. It is known that the pendant functional groups of the gelatin polymer have a high affinity to the transition metal ions in the aqueous solution. As a result, the gel networks of the gelatin polymer can function as water reservoirs if they are exposed to large amounts of water. Upon absorbing the solution containing the metal salts, the gelatin polymer, which has a three-dimensional network with cavities of the order of 10 nm in size, can be used as "nanoreactors" similar to those created in functionalized emulsion [21] and microemulsion [22]. When dipping the salt-solution-containing gel network in a precipitator solution, the subsequent coprecipitation reaction would result in formation of well-mixed precipitates with a chemical homogeneity in nano-scale particle size confined in the network of the gelatin polymer system.

It is also noticeable that the average size of the "nanoreactors" of the gelatin gel network could be adjusted by simply changing the ratio between polymer and water, that is, by increasing the ratio between polymer and water, the size of the "nanoreactors" for the coprecipitation reaction increases. In our case, this may be reflected by the fact that the particle size of the final precipitates in the nanoscale can be conveniently controlled by variation of the gelatin concentration. We note that the present method may be easily extended to the efficient preparation of other type of catalysts consisting of well-mixed oxides, where the natural polymer employed is not necessarily the gelatin. It should also be noted that the present method for catalyst preparation is quite different from the process previously proposed by Ruckenstein and Hong [14] using a series of water-swellable polymer networks (WSPNs) as nano-reservoirs to prepare $Cu/ZnO/Al_2O_3$ catalysts with various surface area and structures. In our process, the residual gelatin polymer occluded in the coprecipitated oxalate precursors can be easily removed by thoroughly washing the precipitates with hot water. In contrast, a high-temperature treatment above 450 °C has to be carried out to completely remove the residual polymer included in the as-prepared mixed oxides using the WSPN methods, which would inevitably lead to an unattractive increment in the crystallite size of the oxide particles.

5. Conclusions

A novel oxalate gel-network-coprecipitation method has been proposed to prepare ultrafine $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis from CO_2 hydrogenation. The $Cu/ZnO/Al_2O_3$ catalysts prepared by the oxalate gel-network-coprecipitation process exhibit a much higher activity and selectivity for methanol synthesis from hydrogenation of CO_2 than those prepared by conventional methods. We have demonstrated that the present gel network consisting of the natural polymer of gelatin and water can offer opportunities to prepare catalysts with several desirable features including a high dispersion of Cu species, a higher copper surface area, a smaller crystallite size of Cu and a stronger interaction between Cu and the ZnO lattice. It is shown that the proper choice of the gel concentration of the natural polymer of gelatin can offer opportunities to optimize the structural properties such as the surface area and the crystallite size of the final $Cu/ZnO/Al_2O_3$ catalysts. The results show that the present oxalate gel-network-coprecipitation method provides a new way to prepare ultrafine $Cu/ZnO/Al_2O_3$ catalysts for more efficient hydrogenation of CO_2 to methanol.

Acknowledgments

Financial support from the National Natural Science Foundation of China (Project No. 29873010), the Committee of Shanghai Science and Technology (Project No. 0112NM076) and the State Key Laboratory of Coal Conversion (Open Funds of 2002-2003) is gratefully acknowledged.

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