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Influence of the component interaction over Cu/ZrO₂ catalysts induced with fractionated precipitation method on the catalytic performance for methanol steam reforming

Jiajia Zhou,^a Ye Zhang,^a Guisheng Wu,^{*}^a Dongsen Mao^{* a} and Guanzhong Lu^{a,b}

A series of binary Cu/ZrO₂ catalysts by choosing different composition ratios and different precipitation sequences have been prepared for the production of hydrogen by steam reforming of methanol (SRM). A variety of characterization techniques including N₂ adsorption, N₂O chemisorption, TEM, TPD and Raman are employed to characterize the physical and chemical properties of the catalysts. The results show that the preparation methods significantly affect the component dispersion, microstructure and adsorption properties. The Cu/ZrO₂ catalysts with 27.3% ZrO₂ loading prepared by fractionated precipitation method displays higher specific surface and interface between copper and zirconia, which not only accelerate decomposition of adsorbed methanol and water, but also promote formation of Cu⁺ and surface oxygen species, accordingly enhance the catalytic activity and stability.

1. Introduction

The production of hydrogen by steam reforming of methanol (SRM) is of great importance for the development of fuel cell powered devices, especially for vehicles¹. A large variety of catalytic materials containing the noble metals of Pt, Pd, Rh²⁻⁵ as well as transition metals of Cu, Ni, $\mathrm{Co}^{6\text{-}10}$ for the steam reforming of methanol have been reported in the literature. Among them, copper based catalysts such as Cu/ZnO and Cu/ZnO/Al₂O₃¹¹ have been attracted the enormous interest for SRM reaction owing to their high activity and selectivity as well as the cheap price relative to the noble metal catalysts. Unfortunately, the shortcomings of the poor catalytic stability and the by-product of a small amount of CO limited them widely used in fuel cell. Therefore, promoting the catalytic stability and suppressing the producing of CO have become the crucial breakthrough for the SRM over Cu-based catalysts. During the last decades, copper supported on ZrO₂ has attracted considerable attention owing to its high activity, enhanced stability and less CO production compared to conventional Cu supported on ZnO/ZnO-Al₂O₃ or SiO₂^{10,12-15}. The promoted performance of zirconia-containing catalysts has been attributed to a higher Cu surface area, better Cu dispersion, and improved reducibility of Cu¹⁶⁻¹⁷. On the other

production of hydrogen from methanol steam reforming. For example, Shimokawabe and coworkers^{18,19} have demonstrated that although a high specific copper surface area is a prerequisite for catalytic activity, it does not account for the observed activity changes alone without taking the particular microstructure of the active Cu particles into account. Based on the corresponding relationship between catalyst activity and the surface oxygen content, Szizybalski et al²⁰ and Oguchi et al.^{21,22} believed that most Cu species were maintained in the transient valence state (Cu₂O) in the presence of a small amount of ZrO2 and the oxygen species bonded with Cu^{\dagger} is the key factors affecting its activity for SRM. In addition, Incorporation of Cu⁺ cation into the ZrO₂ network compensates for the negative charge of vacancies and stabilizes the tetragonal ZrO_2 phase $(t-ZrO_2)^{23}$, which shows much higher catalytic activity for SRM than one with the monoclinic zirconia (m-ZrO₂) as the support due to high dispersed state of copper, rich oxygen vacancies stabilized by Cu^+ ions in Cu/t- ZrO_2^{24} . Therefore, the interface between copper and zirconia has been used to illustrate the high activity of Cu/ZrO₂ for methanol synthesis or methanol reforming because of particular electron interaction and reaction species synergistic effect^{23,24}. Although copper is regarded the active site and is supported over the surface of ZrO₂, accumulation of zirconia over Cu/ZrO2 pretreated at high calcination or reduction temperature can promote the catalytic activity, in spite of larger crystal size of copper or zirconia²⁵. We have also reported that both model catalysts of ZnO/Cu and ZrO_2/Cu

hand, the other factors except the essential nature of metallic

copper should be taken into consideration for the catalytic

^{a.} Research Institute of Applied Catalysis, School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, PR China. E-mail: <u>gswu@sit.edu.cn</u>; dsmao@sit.edu.cn;

^{b.} Key Laboratory for Advanced Materials and Research Institute of Industrial Catalysis, East China University of Science and technology, Shanghai 200237,PR China

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prepared by impregnated $Zn(NO_3)_2$ or $Zr(NO_3)_4$ over macro-size of copper powder exhibited much higher catalytic activity and stability significantly than pure Cu catalyst²⁶.

In order to promote the performance of Cu/ZrO₂ catalysts for methanol synthesis or methanol reforming, various preparation methods, such as co-precipitation of metal salts²⁷, impregnation of copper onto a zirconia support^{18,19}, the formation of amorphous aerogels 28, 29 and the polymer templating technique^{30,31} have been proposed. The different pretreatment processes including being calcined or reduced at different temperatures^{25,32}, being pretreated at microwave irradiation³³ have also been put forward. Maintaining the high surface by stabilizing the amorphous nature of zirconia or t-ZrO₂ phase 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 ¹⁰. In view of active sites of Cu/ZrO₂ and preparation methods, the efficient catalyst systems with cheap price and simple preparation process as well as the high Cu-ZrO₂ interface should be highly desired.

In the present work, in order to develop the facile and efficient binary Cu/ZrO₂ catalysts with a high Cu/Zr interface and the unique component interaction for methanol steam reforming, the Cu/ZrO₂ catalysts with fractionated precipitation method are chosen and compared one with co-precipitation method. Moreover, their performance in the SRM reaction is determined herein. Special attention is paid to the relationship between the catalytic performance and physicochemical properties such as the interaction between copper and zirconia species as well as adsorption ability to methanol and water in the catalysts. In addition, the synergistic effects between Cu and ZrO_2 and the role of zirconia were discussed on the basis of TEM, TPD, Raman analyses and in-situ Diffuse Reflectance infrared spectroscopy.

2. Experimental

2.1. Catalyst preparation

2.1.1 Co-precipitation method

The certain stoichiometric aqueous mixtures of $Cu(NO_3)_2$ (A.R., Sinopharm Chemical Reagent Ltd.) and ZrOCl₂ (A.R., Sinopharm Chemical Reagent Ltd.) as well as aqueous solution of Na₂CO₃(0.5 M, A.R., Sinopharm Chemical Reagent Ltd.) were dropped to the precipitating reactor under vigorous stirring at 60 °C, while the pH value of the reaction medium was kept at 9. Subsequently, these reaction media were aged under stirring for 1 h at 60 °C and cooled statically for 1 h. After filtration and washing with de-ionized water until the filtrate was neutral, the precursor was dried at 120 °C for 12 h, calcined at 450 °C for 4 h.

2.1.2 Fractionated precipitation method

The aqueous solution of $Cu(NO_3)_2$ (0.5 M) and the aqueous solution of Na_2CO_3 (0.5 M,) were dropped to the precipitating reactor under vigorous stirring at 60 °C and pH 7.5 at first, after finishing the addition of $Cu(NO_3)_2$ solution, the solution of $ZrOCl_2$ and the solution of Na_2CO_3 were added under the same

precipitation conditions except that pH was maintained at 9.0. The subsequently processing procedure of the suspension liquid was as same as one described in 2.1.1.

The prepared catalysts are labeled as CZ-x-y-c/f, among which x : y represents the atomic ratio of copper and zirconium in Cu/ZrO_2 catalysts but c and f represents the coprecipitation and fractionated precipitation method, respectively. In addition, the pure copper catalyst prepared by precipitation is labeled as C-1-c.

2.2. Catalyst characterization

The metallic copper surface area (S_{cu}) of the catalyst was determined using a nitrous oxide chemisorption method³⁴. The catalyst samples (0.2 g) were reduced up to 280 °C in a 5% H₂/He stream (40 ml/min) for 1 h, and then were cooled to 60 °C in He stream. Subsequently, the flow of 1% N₂O/He (1 ml/min) was passed through the sample with the temperature being maintained at 60 °C, while the signals of the thermal conductivity detector (TCD) signal were recorded. The surface copper atoms density of 1.46 × 10¹⁹ copper atoms per m² assuming Cu:N₂O=2:1 was used for the calculation of the copper surface area³⁵. The surface areas of the catalysts were measured by N₂ adsorption at -196 °C using a Micrometrics ASAP 2020 apparatus and calculated by the Brunauer–Emmett–Teller (BET) method.

Transmission electron microscopy (TEM) images were obtained using a FEIG2F30 microscope operated at 100 kV. The samples were suspended in ethanol and supported onto a holey carbon film on a Cu grid.

Temperature programmed desorption (TPD) of methanol and water was performed in a quartz tube reactor system equipped with a quadrupole mass spectrometer (QMS200, Balzers OmniStar) under atmospheric pressure. 100 mg sample in 40-60 mesh was reduced in a 5% of H₂/He flow (40 ml/min) at 280 °C for 1 h and then cooled to room temperature in 40 ml/min He flow. Subsequently, the flow of the mixture (40 ml/min) of methanol vapour and He was passed through the sample for 60 min, ensuring obtaining a saturated adsorption of methanol over the catalysts. After that, the sample was swept with 40 ml/min He stream, until no signals of methanol was determined. Eventually, the sample was heated in 40 ml/min He flow from ambient temperature to 700 °C at the ramping rate of 15 °C/min. The m/e signals of 2, 28, 28, 30, 32 and 44 corresponding to H₂, CO, CH₂O, CH₃OH and CO₂ were monitored by an on-line quadrupole mass spectrometer. With regards to TPD of water, adsorption of steam and purging with He flow were carried out at 230 °C and the m/e signals of 18 corresponding to H₂O were monitored in order to illustrate the adsorption and activation of water at the reaction temperature of SRM.

In situ Diffuse Reflectance infrared spectroscopy was performed using a Nicolet 6700 FTIR spectrometer. The powdered samples were held in a Harrick Scientific (HS) high-temperature reaction chamber, the temperature of which was controlled by a HSI temperature controller. The samples was reduced at 300 °C in 5%H₂/N₂ flowing at 50 mL/min for 30 min. After cooling to room temperature in N₂ purge at 50 mL/min,

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the samples were pumped to 1×10^{-2} Pa, and then the spectra of background was collected. Subsequently, about 20 mL CO (0.1MPa) was introduced by one pulse injection and then the adsorption timer started. In situ absorbance spectra referenced to a spectrum of background described earlier by collecting 64 scans at 4 cm⁻¹ resolution.

Raman spectroscopy was recorded using a DXR Raman spectrometer equipped with a ~100 mW, 785 nm diode laser. The powdered samples were held in a Harrick Scientific (HS) high-temperature reaction chamber, the temperature of which was controlled by a HSI temperature controller. The surface species over the samples reduced at different time at 300 °C as well as exposed in steam for 30 h at 230 °C were monitored online using Raman spectroscopy.

2.3. Catalytic activity testing

The catalytic activities were tested in a fixed-bed reactor under atmospheric pressure. 0.5 g sample of the catalyst is reduced in a 5% H_2/N_2 flow (50 mL/min) at 280 °C for 1 h and then cooled to 230 $^{\circ}C$ in N_{2} flow. After that, the mixture of water and methanol with a volume ratio of 1.2 fed into by an injection pump was preheated at about 200 °C to ensure full vaporization before being introduced in reactor. The tail gas from reactor was passed through a cold trap cooling by icewater bath, then were analyzed on-line by the gas chromatograph (GC 2060) 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.

3. Results

In order to illustrate the effect of ZrO₂ on the catalytic activity over Cu/ZrO₂, Fig. 1 shows the variation trends of catalytic activity and CO selectivity with different ZrO₂ loadings as well as different preparation methods. It is clear that the ZrO₂ loading has a significant influence on the performance of Cu/ZrO₂ for hydrogen production from steam reforming of methanol. At first, the catalytic activity and selectivity of Cu/ZrO₂ prepared by fractionated precipitation are compared. C-1-c reveals low catalytic activity with 32.4 % of methanol conversion and 0.046 mol.gcat⁻¹.h⁻¹ of hydrogen production rate. With increase of ZrO₂ loading, the methanol conversion and hydrogen production rate increase remarkably and achieve the highest values over CZ-8-3-f with 27.3 % of ZrO₂.



Fig. 1 Effects of ZrO₂ loadings on catalytic activity over CZ catalysts prepared by different methods. Circle symbols in a and b represent the production rate of H₂ and CO₂ selectivity, respectively, while the triangle symbols in a and b represent the methanol conversion and the volumetric CO content in the outlet, respectively. Solid and hollow symbols represent the data over CZ catalysts prepared by Fractionated precipitation and co-precipitation, respectively. (Reaction conditions: T = 230 $^{\circ}$ C, p = 0.1 MPa, $H_2O/CH_3OH = 1.2$ molar ratio, WHSV = 4.8 ml.gcat⁻¹h⁻¹).



Fig. 2 Methanol conversions over C-1-C (a), CZ-8-3-c (b) and CZ-8-3-f as a function of time-on-stream (reaction conditions: T = 230 $^{\circ}$ C, p = 0.1 MPa, H₂O/CH₃OH = 1.2 molar ratio, WHSV =4.8 ml.gcat⁻¹.h⁻¹).

With the further increase of ZrO₂, the catalytic activity drop significantly and CZ-8-8-f shows 30 % methanol conversion and 0.041 gcat⁻¹.h⁻¹ of hydrogen production rate. As a comparison,

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the activity results of catalysts prepared by co-precipitation methods are also exhibited in Fig. 1. When ZrO₂ loading is low, Cu/ZrO₂ prepared by fractionated precipitation shows the higher activity, while one from co-precipitation shows higher performance with high ZrO₂ content. For example, compared with methanol conversion, it is found that CZ-8-3-f presents 92 % but CZ-8-3-c 67 %, in contrast, CZ-8-8-f displays 30% but CZ-8-8-c 80%. CO₂ selectivity shows the similar change trend, that is, the selectivity of CO2 first increased and then decreased with the content of ZrO₂, moreover, CO selectivity over all catalysts is maintained below 1.5 %

It is well known that the shortcoming of Cu based catalysts in SRM is the fast deactivation with time-on-stream. The catalytic stabilities of the SRM reaction over C-1-c as well as CZ-8-3-c and CZ-8-3-f were investigated for 24 h at 230 °C (Fig. 2.) The activity of C-1-c lasts for about 2.5 h and then continue dropping significantly to zero after 10h. The methanol conversion of CZ-8-3-c maintains about 71% for first 5 h, and then begins to slightly decline continuously, finally reaches 65 % at the end of 24 h of time-on-stream. For the catalyst CZ-8-3-f, no appreciable decrease in the activity is observed after 24 h of time-on-stream, suggesting the excellent catalytic stability of Cu/ZrO₂ is obtained from fractionated precipitation. Yao et al³⁶ also obtained Cu/ZrO₂ catalysts for MSR through oxalate catalytic gel-co-precipitation with highly dispersed components of copper and zirconia, which could maintain high Table 1 Textural properties of Cu/ZrO2 prepared by different methods

Sample	The molar content	S _{BET} /m ² .g ⁻¹	S _{Cu} /m ² .g ⁻¹
	of zirconia / %		
C-1-c	0.0	8.1	1.0
CZ-8-1-f	11.1	41.0	2.71
CZ-8-2-f	20.0	70.0	5.49
CZ-8-3-c	27.3	65.9	4.62
CZ-8-3-f	27.3	75.5	7.97
CZ-8-4-f	33.3	73.7	7.03
CZ-8-6-f	42.9	83.5	5.93
CZ-8-8-f	50.0	85.2	4.51







Fig. 3 TEM images of CZ-3-8-c (a) and CZ-3-8-f (d). Based on energy spectrum analysis,

Fig. 4 TPD patterns of methanol on C-1-c (a) ZrO₂ (b) and CZ-8-3-f (c), m/e=2, 28, 30, 32, 44, corresponds to the desorbed species of H₂, CO, CH₂O, CH₃OH, CO₂, respectively. Due to the weak desorption over C-1-c, all desorption signs over C-a-c are magnified by 5 times.

activity at 300 °C for 48 h. Purnama et al.³⁷ have investigated the deactivation behavior of a template-derived Cu/ZrO₂, and found that a much smaller extent of deactivation was identified for the Cu/ZrO2 relative to commercial CuZnAI catalysts, therefore attributed the high stability to the fact that the copper particles in the zirconia catalyst were well dispersed and stabilized. Table 1 summarizes the specific surface areas and Cu metal surface areas measured by nitrous oxide titration of the Cu/ZrO₂ catalysts with different ZrO₂ loadings as well as different preparation methods. It is clear that C-1-c shows 8.1 m²/g of BET specific surface and 1.0 m²/g of Cu metal surface areas. The specific surface of Cu/ZrO2 increased significantly to 41.0 m²/g with introduction of 11.1 % ZrO₂, and further continuously increased with rise of ZrO₂ loading. On the other hand, the copper surface area increased with addition of ZrO₂ from 11.1 to 27.3 % and then decreased with further increase of ZrO2. Considering the fact that CZ-8-3-f with 27.3% ZrO₂ shows the highest activity for MSR, one can conclude that both copper surface and the specific surface should be taken into account to ascribe the catalytic activity.

The digital micrographs of Cu/ZrO₂ prepared by different methods are shown in Fig. 3. It is clear that the precipitation

methods have a great influence on the particle size and the distribution of catalysts. Among the two samples, CZ-8-3-c

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exhibits uniform size distribution with some compact structure. However, the lager particles with loose structure are shown in CZ-8-3-f. These results described that the Cu/ZrO₂ catalyst prepared by fractionated precipitation method shows the looser structure which can enlarge the specify surface significantly and coincides with the results of BET surface area. Furthermore, the component distribution maps reveal that Cu and Zr display as well dispersed state in CZ-8-3-f.

In spite of the importance of specific area and copper area to the catalytic activity, they alone cannot illustrate the performance. In order to illustrate the effect of interface between copper and zirconia, the adsorption performance of methanol and water over Cu and Cu/ZrO₂ are further compared.

The TPD profiles of methanol over C-1-c, ZrO₂, and CZ-8-3-f are exhibited in Fig. 4, which reveals the different desorption actions of methanol over the different catalysts. C-1-c shows the weak adsorption ability, illustrated by the fact that a small amount of methanol and CO_2 is desorbed below 200 °C, and the weak and broad desorption peaks of H₂ and formaldehyde simultaneously appears at the range of 200~400 °C. With regard to pure ZrO₂, apart from the desorption of methanol from the ambient temperature to 500 °C, the strong desorption peaks ascribed to CO and H_2 were observed centered 500 °C. Over CZ-8-3-f, however, the desorption temperature of CO and H₂ decreased to 370 °C, furthermore desorption peak of CO₂ is also observed in these temperature range. These results illustrate that the combination of copper and zirconia can accelerate the decomposition of methanol to produce CO and H₂, and promote the formation of CO₂.



Fig. 5 TPD profiles of water over C-1-c (a) and CZ-8-3-f (b).

Besides the adsorption of methanol, the adsorption and activation of the water are of importance to the MSR, hence TPD profiles of water over C-1-c and CZ-8-3-f are shown in Fig. 5. It is clear that C-1-c displayed the poor adsorption capacity and no any perceptible water desorption peaks are observed. In contrast, a strong desorption signal of water is manifested at the temperature range of $350^{\circ}600$ °C over CZ-8-3-f. It is surprised that the desorption of water is above $400^{\circ}600$ °C, which might be due to dehydration of adjacent hydroxyl produced the dissociative adsorption of water over Cu/ZrO₂. These results illustrate that Cu/ZrO₂ shows much stronger

adsorption to water than Cu in the reaction temperautre, which might be accounted for high activity of Cu/ZrO_2 for MSR. In order to illuminate the Cu species over catalysts, CO adsorption is measured with in situ diffuse reflectance infrared spectroscopy, which is shown Fig. 6. When CO was adsorbed over C-Z-c, only a weak band centered about 2146 cm⁻¹ ascribed C-O stretching vibration of gaseous CO was observed, and its intensity did not show any change with the adsorption time, illustrating of low adsorption ability of CO over unsupported Cu catalysts. With regards to CZ-8-3-c, the bands at 2098 and 2133 cm-1 ascribed to CO adsorbed linearly on



Fig. 6 Infrared spectra of CO adsorption over C-1-c (a), CZ-8-3-c (b) and CZ-8-3-f (c)

high-index planes of metallic Cu and Cu^{+ 38}, respectively, appeared at the same time, which increased first and then remained unchanged in intensity with adsorption time. When CO was adsorbed over CZ-8-3-f, much stronger bands at 2105 and 2131 cm-1 were displayed relative to over CZ-8-3-c, furthermore, the intensity of the former deceased while that of the latter increased with the adsorption time. Those findings indicate that CZ-8-3-f not only shows the strong adsorption ability to CO at the active sites of Cu⁰ and Cu⁺, but also exhibits the CO spillover from Cu0 to Cu⁺.

The surface species of C-1-c and CZ-8-3-f in the process of reduction as well as adsorption of water are also characterized with Raman spectrometer, which are shown in Fig. 7. C-1-c displayed three peaks at 291, 335 and 626 cm⁻¹, which is ascribed to A_g , B_g^{-1} and B_g^{-2} of the Raman-active phonon modes in C_{2h}^6 point group of bulky CuO with monoclinic crystal.^{39,40}. After reduction in hydrogen at 300 °C for 30 min, no evident change can be observable with regard to Raman spectra, illustrating that main surface species over copper still is CuO. When reduction time reaching 60 min, the characteristic bands

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of CuO decreased significantly and two bands at 146 and 213 cm⁻¹, which are attributed to the Raman-active phonon modes of Γ_{15}^{-} and 2 Γ_{12}^{-} in Cu₂O crystal⁴¹, emerge. Exposed in steams for 30 min, the surface species over C-1-c remain unchanged. Concerning CZ-8-3-f, only broad bands ascribed to CuO are displayed in Fig 7, but the bands attributed to ZrO₂ crystal is not found, indicating that the crystal size of CuO became small with introduction of ZrO₂ and ZrO₂ species is highly dispersed or is in the form of amorphous state. After reduction in hydrogen at 300 °C for 30 min, the bands of CuO disappeared completely and only slight band at 213 cm⁻¹ ascribed to Cu₂O appeared. After introducing steam, however, the band ascribed to Cu₂O increased. These results illustrate that CuO species in pure CuO particles is difficult to be reduced and then dominant species are Cu₂O as well as CuO. By contrast, Cu/ZrO_2 is much more easily reduced to Cu^0 , hence small amount of Cu_2O remained after reduction at 300 °C for 30 min. The fact that ZrO₂ can promote the reduction of CuO can also be evidenced by TPR results^{12,36}. Even so, IR results of CO adsorption shows that Cu^+ is stabilized on the interface between copper and zirconia, as also is evidenced by Spectroscopic studies of Auger and XPS²³ and X-ray absorption fine structure analysis²⁴. Furthermore, ZrO₂ in Cu/ZrO₂ can also promote the adsorption and activation of water and formation of Cu⁺, whose mechanism is proposed as follows:





The water is adsorbed on the oxygen vacancy site of zirconia and further dissociated and bonded with adjacent oxygen atom to form two hydroxyls. The formed hydroxyl over ZrO_2 can spillover to the surface of copper and subsequently is dehydrogenated to form surface oxygen species and Cu species.

4. Discussion

It is well known that the factors affecting catalytic activity of Cu/ZrO₂ are various, including physical properties, such as the specific area of catalyst, copper surface area, the crystal size distribution and the morphology of Cu/ZrO2, as well as chemical factors between copper and zirconia^{10-19,36}. Despite the various preparation methods of Cu/ZrO₂, it is not difficult to find the aims of almost all methods are to increase the specific area of Cu/ZrO_2 as well as the surface area of Cu^{28} , and to promote the interaction between copper and zirconia $^{\rm 23,24}\,\rm by$ improving copper dispersion in ZrO₂ and maintaining the amorphous nature. In the case, the fractionated precipitation method also enhances the specific surface area as well as copper surface area of Cu/ZrO₂ effectively. Compared with preparation condition, Cu²⁺ precipitated at pH of 7.5⁴³ while the sol-gel containing Zr^{4+} is formed at pH of about 9-10⁴⁴. In the process of co-precipitation of ${\rm Cu}^{2{\scriptscriptstyle +}}$ and ${\rm Zr}^{4{\scriptscriptstyle +}},~{\rm Cu}^{2{\scriptscriptstyle +}}$ was rapidly precipitation to form crystal nucleus at pH of 9, which can accelerate precipitation of Zr^{4+} and hinder the formation of sol-gel containing Zr^{4+} , therefore the particle size shown in TEM is small but compact. In the process of fractionated precipitation, however, Cu^{2+} is precipitated at low pH (7.5) to form superfine copper precipitation, subsequently, Zr4+ precipitated at higher pH (9) to form sol-gel, which can effectively adsorb and envelope the precipitate containing copper. After drying and calcinations, the large particles with loose structure are formed, which can be propitious to increase the specific area as well as the copper surface area of Cu/ZrO₂. At the same time, owing to high dispersed state of copper and zirconia, much amount of Cu⁺ are formed on the interface of CZ-8-3-f between copper and zirconia, which not only hinders aggregation copper and crystallization of zirconia²⁸, but also maintains the catalytic stability and suppress production of CO^{12,28}. Therefore, CZ-8-3-f shows much higher activity and stability than copper or CZ-8-3-c. When ZrO₂ loading reaching 50 %, in spite of much larger surface area of CZ8-8-f, its activity is lower than that of copper, but CZ-8-8-c showed much higher activity. It is not difficult to imagine that high content ZrO₂ can accumulate on the surface of Cu/ZrO₂, and then copper species is blocked from touching with reactants; illustrating copper is also crucial to catalytic activity.

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On the other hand, it is also believed that the interaction between copper and zirconia rather than the specific surface area should be accounted for the high activity of Cu/ZrO₂ because of unique role of ZrO₂ such as acidity and basicity as well as strong adsorption properties. Therefore, the copper and ZrO₂ species over the catalysts are proposed to behave in a bifunctional manner, with copper and ZrO₂ playing synergetic roles in methanol synthesis reaction or methanol decomposition^{36,45}. Among them, methanol interacts with the OH groups over ZrO₂ to form methoxide, which finally to decompose to CO and H₂ via the intermediate of formaldehyde from methoxide dehydrogenation, while copper is proposed to accept the hydrogen spilled from the surface species located on ZrO_2 to form molecular hydrogen³⁶. In addition, the spillover between copper and zirconia is also of importance to the catalytic activity⁴⁶. The results of TEM and Raman in the present work shows that, in Cu/ZrO₂ prepared by fractionated precipitation, the copper and zirconia components are well dispersed each other and the loose microstructure and morphography are formed, which not only increase the specific area of catalysts, but also strengthen the interaction between copper and zirconia. IR adsorption of CO adsorption over Cu/ZrO2 furthermore illustrate that CZ-8-3-f shows facile CO spillover from Cu^0 to Cu^+ due to much higher interface between copper and zirconia and richer stabilized Cu⁺ species. The methanol-TPD results reveals that, moreover, Cu/ZrO₂ gives the desorption peaks of CO and H₂ at much lower temperature than pure ZrO₂, apart from exhibiting the desorption peaks of CO₂, but C-1-c only shows weak desorption of formaldehyde, hydrogen, CO₂ and methanol. These results further evidence the synergistic effect between copper and zirconia, indicating that zirconia not only serves as the supporter of copper, but also plays the role of active sites to activate the water and methanol molecular to promote the decomposition of adsorbed methanol and water.

The fact the Cu/ZrO₂ catalyst reduced in hydrogen with the initially low activity for MSR showed the promoted activity with temporary exposition in oxygen²⁰ indicates that oxygen species is also the key factor to promote the catalytic activity for MSR. Oguchi et al.^{21,22} further confirmed this view through the evidence of the approximate linear relation between the H_2 production rate and surface oxygen content over Cu/ZrO₂. Raman results herein revealed that the surface of Cu hold rich Cu^{\dagger} species even reduced at 300 °C for 60 min, hence it displayed certain initial activity. The transient stability of copper catalyst for MSR seems to be ascribed to the depletion of oxygen species over copper with reaction time because of its low adsorption ability to water. Despite the majority of Cu species over Cu/ZrO₂ being reduced to Cu⁰ after reduction for 1 h, surface Cu⁺ species is enhanced after adsorption of water indicating that the interface between copper and zirconia can promote surface hydroxyl over ZrO₂ obtained from dissociative adsorption of water to spillover to the surface of copper, subsequently the hydroxyl over copper is further dehydrogenated to form the surface oxygen species, accordingly CZ-8-3-f shows the optimum catalytic activity and stability. When the water introduced over $Cu/CeO_2/Al_2O_3^{47}$ or

Co/ZrO₂, it is also found that Cu^0 is oxidized to Cu^+ or the content of Co^0 reduced⁴⁸.

In addition, the surface science experiments⁴⁹ also revealed that methanol on clean single-crystal Cu surfaces tends to show little or no reactivity and the surface oxygen must exist on the surface of Cu crystal surface in order to facilitate the adsorption of methanol. Based on physical properties of Cu, it is clear that low specific area and nonpolar surface of clean copper metal results in low adsorption activation to methanol or water molecular with polarity. Furthermore, the electron in 5s orbital of Cu⁰ presents the repulsive interaction to lone electron pair of oxygen in methanol or water, which further hinders dissociative adsorption of them on the surface of Cu. However, Cu⁺ species with vacant orbital of 5s not only interact with lone electron pair of oxygen in methanol, but also provide the occupied symmetry-adapted d orbital which can activated the methanol by feedbacking d electron to antibonding orbital of methanol to form the intermediate of methoxide as well as formaldehyde. In Cu/ZrO₂, bonded with oxygen ions over ZrO₂, copper atom highly dispersed in ZrO₂ tends to be oxidized to higher valence, and then showed the higher activity to methanol.

5. Conclusion

A series of binary Cu/ZrO_2 catalysts by choosing different composition ratios and different precipitation sequences have been prepared for the steam reforming of methanol (SRM), and it shows that Cu/ZrO_2 catalysts with 27.3 % ZrO_2 introduced by fractionated precipitation method shows the best activity and stability. The characterization results including N₂ adsorption, N₂O chemisorption, TEM illustrate that CZ-8-3-f has a large metallic copper surface area as well as high component dispersion. The results of TPD and Raman reveal the synergy effect between copper and zirconia illustrated by the fact that methanol adsorption and decomposition were accelerated and Cu⁺ formed by adsorption of water over ZrO_2 , which further illustrates the high activity and stability of CZ-8-3-f for the steam reforming of methanol.

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