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Influence of zirconia promoter on catalytic properties of Cu–Cr–Si catalysts for methanol synthesis at high CO conversion in slurry phase

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The low-temperature methanol synthesis was studied using novel Cu–Cr–Si catalysts promoted by zirconia at 115 °C and 3.0 MPa in slurry phase. Zirconia addition improved significantly the catalytic performance. From the characteristic results, copper and chromium were enriched on the catalyst surface and more Cu^+ cations were stabilized by the zirconia promotion.

KEY WORDS: low-temperature methanol synthesis; high CO conversion; copper–chromium catalyst; zirconia promotion; silica; hydrogenolysis; slurry.

1. Introduction

Methanol is an important chemical product in C1 chemistry for its annual production of 30 million tons and wide uses as a fundamental chemical and a fuel resource for vehicles [1, 2]. Low-temperature methanol synthesis (LTMS) in slurry phase is a promising route from syngas (a mixture of carbon monoxide and hydrogen, issued from natural gas or carbon).There are several advantages for LTMS: higher CO conversion at single-pass, high methanol purity with trace of water, and lower reaction temperature and lower energy consummation, etc. [3–5]. The two-step methanol synthesis at high CO conversion, different from the ICI process, comprises carbonylation of methanol to methyl formate (MF) followed by hydrogenolysis of MF, as follows:

$$(1)\ CH_3OH + CO = HCOOCH_3$$

$$(2)\ HCOOCH_3 + 2H_2 = 2CH_3OH$$

net reaction:

$$(3)\ CO + 2H_2 = CH_3OH.$$

It is generally accepted that the hydrogenolysis of MF is the rate-determined step because the rate of carbonylation is higher than that of hydrogenolysis by two magnitudes [2, 3]. Lower temperature is favorable to higher equilibrium conversion in thermodynamics while the hydrogenolysis and the net reaction rates are at lower level contrarily in dynamics. The copper-based oxide acts as the hydrogenolysis catalyst as well as carbonylation assistant, and sodium methoxie acts mainly as carbonylation catalyst [3, 4, 6–8]. In this reaction system, the deactivation mechanism of those catalysts was reported: sodium methoxide reacted with MF, and then the by-product sodium formate was produced and deposited on the copper-based catalyst surface; thus, the hydrogenolysis rate decreased and would be out of proportion to that of carbonylation, which in turn leads to accumulation of MF and acceleration of by-reaction rate; finally, the copper-based catalyst would be coated with sodium formate and the match-equilibrium of carbonylation–hydrogenolysis was destroyed completely [7, 8]. It can be induced that the activity of hydrogenolysis catalysts at lower temperature is the key factor for the net reaction of LTMS process.

Copper–chromium oxide and the co-catalyst sodium methoxide exhibited a higher initial activity in LTMS, but the catalyst system demonstrated poor stability. In our previous works, novel Cu–Cr–Al–O catalysts and Cu–Cr–Si–O catalysts have been developed [9], which improved the reaction activity and stability, and an optimized composition ratio was obtained like 1:1:0.5 for Cu:Cr:Al in molar ratio. However, the catalytic stability needed to be improved further and the catalysts had a relative higher content of chromium, which had a potential risk of pollution and was an imperative element for a high activity in the LTMS process.

As a metallic oxide, zirconia possesses both acid and basic sites, as well as oxidable–reducible properties. Zirconia, as catalyst support or promoter, has been attracting much interest in catalytic application [10–12].

On the basis of previous achievements in our group, this work investigated the effects of zirconia incorporation on catalytic performance and properties of copper-based catalysts with lower chromium oxide content (22 wt% compared with 42 wt%) for LTMS. The novel catalyst samples were characterized using several techniques like TPR, H_2-TPD, CO-TPD, XRD, ESR and

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XPS analysis, for better understanding the promoting effects of zirconia incorporation.

2. Experimental

2.1. Preparation of novel Cu–Cr–Si–Zr–O catalysts

Catalysts were prepared by complex-coprecipitation [6, 9]. The copper–ammonia complex solution was prepared by adding the ammonia into the $Cu(NO_3)_2$ solution, and then the mixed solution of Na_2SiO_3, $(NH_4)_2Cr_2O_7$, and $Zr(NO_3)_4$ was added dropwise into the former complex solution. The pH value of mixtures was adjusted to 6.0 with 1:1 (V/V) nitric acid solution, and the precipitate was gained. The precipitate was stirred vigorously for 45 min and aged for 5 h, and then filtered and washed with distilled water, followed by drying at 110 °C for 16 h. After the precursor was calcined in nitrogen at 350 °C for 3 h, the catalyst sample was obtained. The compositions of these samples were shown in table 1.

2.2. The catalytic evaluation of catalysts in LTMS at high CO conversion

The catalytic tests were conducted in slurry phase in a 500 ml stainless-steel autoclave with a magnetic stirrer at 115 °C and 3.0 MPa. The mixtures of the copper-based catalyst, CH_3ONa solution in methanol, and the solvent xylene were added into the autoclave, then the autoclave was purged with nitrogen for three times to ensure the autoclave purified thoroughly. When heating to the reaction temperature, syngas ($V(H_2)/V(CO) = 2.0$) was introduced to a pressure of 3.0 MPa, and the flux was kept at a rate of 150 ml/min by a mass flow controller. The inlet and outlet gas were analyzed by a gas chromatograph equipped with thermal conduction detector (TCD) and TDX01 column, while the liquid products were analyzed using a GDX 103 column.

2.3. Catalyst characterization

The BET specific surface area of the calcined sample was estimated by nitrogen adsorption experiments on a NOVA 1000e automatic adsorption instrument.

The temperature-programmed reduction (TPR) experiments were carried out using a fixed-bed quartz reactor. Calcined sample was stabilized to a stream of 7.86% H_2 in H_2/N_2 mixture at 30 ml/min and the temperature was increased at a rate of 10 °C/min up to 480 °C. The outlet gas was analyzed by a TCD.

The temperature-programmed desorption (TPD) experiments were conducted at the same equipments as those of TPR. The sample was reduced by a mixture of 7.86% H_2 in H_2/N_2 at 350 °C for 60 min, then was cooled down in flowing N_2 to room temperature, and adsorbed H_2 or CO for 30 min, respectively. After the sample was purged by N_2, H_2-TPD or CO-TPD was conducted at a heating rate of 10 °C/min. The outlet gas was analyzed by the same method of TPR.

X-ray diffraction (XRD) analyses were carried out by an X-ray diffraction (Philips X'pert pro MPD) equipped with a graphite monochromator for Cu K_α radiation (40 kV, 40 mA).

Electron spin resonance (ESR) spectra were obtained using a Bruker EMX-10/12 spectrometer with a rectangular cavity operated at a microwave frequency of 9.78 GHz and 110 °C.

X-ray photoelectron spectroscopy (XPS) experiments were measured by a VG Escalab MK2 spectrometer with an Al K_α (1486.6 eV) X-ray source. The binding energies were calibrated relative to C_{1s} peak from carbon contamination of the samples at 284.6 eV.

3. Results and discussion

3.1. Effects of zirconia promoter on the catalytic performance of Cu–Cr–Si–O samples for LTMS process

The experiment results in figure 1 indicated that zirconia promoted Cu–Cr–Si–O effectively for LTMS in slurry phase. With the content of zirconia increasing from 0% to 2% and 6%, the catalyst activity and methanol selectivity increased remarkably. The reaction turnover frequency (TOF) was gained by 26.77% and 32.25%, respectively, and the methanol selectivity was enhanced from 91.75% to 95.63% and 96.21%. As the zirconia content increased further to 10%, the TOF and methanol selectivity decreased slightly though their values were still higher than those of the zirconia-free sample. The reaction results showed that the promoter zirconia could improve efficiently the activity and methanol yield.

Table 1
Composition and textural properties of CCSZ catalysts

Catalyst	Composition/wt%				$S_{BET}/m^2\ g^{-1}$	$V/ml\ g^{-1}$	D/nm
	CuO	Cr_2O_3	SiO_2	ZrO_2			
CCSZ00	44.0	22.0	34.0	0.0	76.5	0.1182	86.80
CCSZ02	44.0	22.0	32.0	2.0	110.8	0.1601	84.99
CCSZ06	44.0	22.0	28.0	6.0	143.2	0.2551	88.53
CCSZ10	44.0	22.0	24.0	10.0	136.6	0.2355	88.91

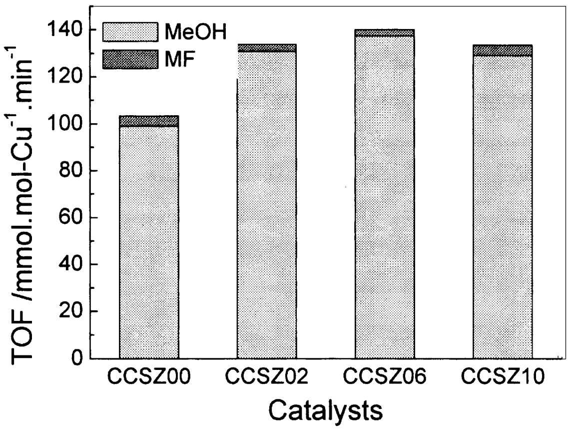

Figure 1. Effect of zirconia promoter content on the performance of Cu–Cr–Si catalysts for LTMS. Conditions: T = 115 °C, P = 3.0 MPa, reaction time = 480 min, [MeONa] = 0.5 mol/L, [Cat.] = 12.5 g/L, Syngas flow rate = 150 ml/min, V(H2):V(CO) = 2, space velocity = 45 h^{-1}.

The CO conversion, as shown in figure 2, kept at a high level during initial reaction time of 6 h. After the prolonged reaction time, CCSZ06 behaved best in reaction stability and CO conversion kept above 94% during the whole process. The stability of CCSZ10 was higher than that of CCSZ02. CCSZ00 demonstrated poor stability compared with other three samples, and the CO conversion decreased rapidly in an accelerated tendency. The results indicated that zirconia improved the reaction stability evidently.

3.2. *Texture analysis using the BET measurements*

From the data of BET (table 1), with the content of zirconia increasing from 0 to 2, 6, and 10 wt%, the specific surface area was enhanced by 44.84%, 87.19%, and 78.56%, respectively. The pore volume varied in a same way, while the mean pore size altered in a minor range. The results of BET measurements indicated that the zirconia incorporation improved the specific surface area remarkably, and the Cu–Cr–Si–Zr–O catalyst sample with 6 wt% zirconia gained a maximum surface area.

3.3. *Influence on the catalyst reducibility using TPR experiments*

It was shown in figure 3 that the catalysts promoted by zirconia kept two reduction peaks, but the total peaks area increased remarkably. As the zirconia content increased gradually, the area of lower-temperature peak increased rapidly while the area of higher-temperature peak ascended in the beginning and descended later. From the results of the quantitative calculation, the CCSZ06 sample showed the maximum of the total peak area and the lower-temperature peak area. The peak temperature varied with zirconia content: as the zirconia content increased, the lower-temperature peak temperature increased from 147 to 163 °C, while that of the higher-temperature peak decreased from 200 to 188 °C. Consequently, the two temperatures varied in a close-in tendency.

For the copper-based catalysts, the reduction peak area was in proportion to the reducible copper content. The variation of the reduction peak area indicated that the catalyst reducibility was modified by the addition of promoter. In these experiments, the reason of peak area variation could be that zirconia promoted the dispersion of the active copper component on the catalyst surface, where copper oxide reduced easily and the proportion of the reducible copper content increased [8, 9, 13]. When the content of zirconia increased to some degree, such as 10 wt% or more, the reducible copper content decreased for a decline in BET surface area and an intensified interaction among components in catalysts [14, 15].

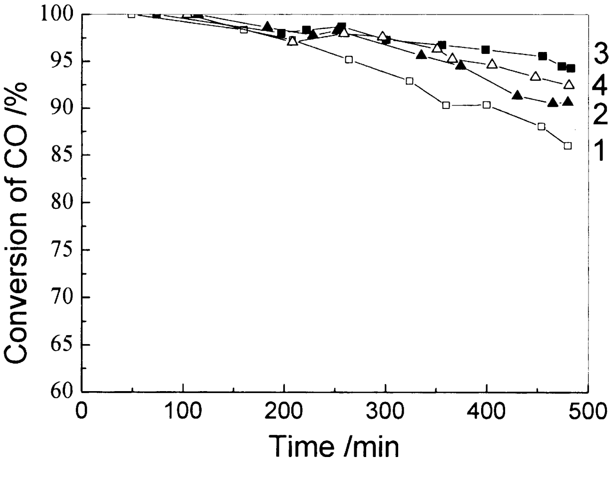

Figure 2. CO conversion versus reaction time on stream on zirconia promoted catalysts. Conditions: The same as those of figure 1. (1) CCSZ00, (2) CCSZ02, (3) CCSZ06, (4) CCSZ10.

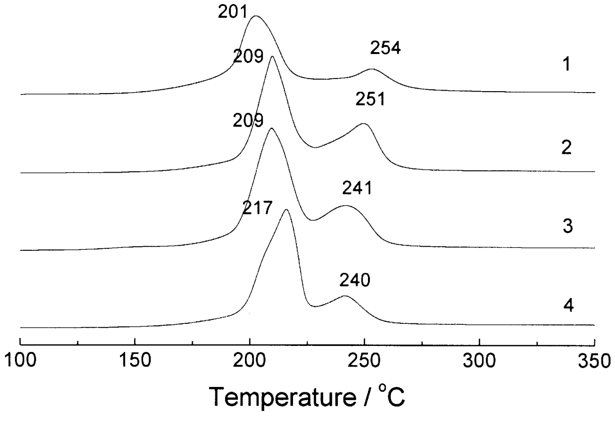

Figure 3. TPR patterns of copper-based catalysts with different Zr content. Conditions: Sample weight: 15 mg; Heating rate: 10 °C/min (1) CCSZ00, (2) CCSZ02, (3) CCSZ06, (4) CCSZ10.

3.4. Chemisorption properties of novel catalysts characterized by temperature-programmed desorption (TPD)

As illustrated in table 2, the peak temperature of hydrogen desorption rised with the increasing zirconia content. The peak area, or the hydrogen desorption amount, mounted rapidly while the zirconia increased, and the CCSZ06 with 6 wt% zirconia possessed the maximum desorption amount. As shown in table 3, the CO desorption peak temperature increased with the increasing zirconia content. The CO desorption amount decreased while the zirconia content increased, and CCSZ06 possessed the minimum desorption amount.

The desorption peak area corresponded to the amount of adsorption sites, which comprised copper and other components, on the catalyst surface. Meanwhile, the desorption temperature could indicate the adsorption intensity of adsorbed species on the active sites [8, 16]. The TPD data suggested that the zirconia promoter improved the adsorption intensity of H_2 and that of CO on the catalysts, enhanced the hydrogen adsorption amount, and reduced the CO adsorption amount. On the active component copper, the desorption temperatures of hydrogen closed to that of CO, thus the competitive adsorption between hydrogen and CO was obvious. The 10 °C higher of CO desorption than that of H_2 indicated that adsorption of CO was a bit more intense than that of H_2, and this was correlated with previous results [14, 16].

In the LTMS system, the main function of copper-based catalysts was hydrogenolysis. The higher H_2 adsorption intensity and amount were favorable to the H_2 dissociation adsorption; on the other hand, the appreciated adsorption of carbonyl in methyl formate by copper-based catalysts is helpful to methyl formate activation and hydrogenolysis [16]. At the same time, CO was poisonous to the copper-based catalyst in hydrogenolysis, thus the CO-poisoning resistant properties, which was related to the alkaline component, was a key factor for catalytic performance. The zirconia promoter, possessing alkaline and acidity properties concurrently, and higher appetency to methyl formate than to CO, could help the active sites for hydrogenolysis escaping from deactivation and being covered by CO [13]. Accordingly, zirconia was helpful to modify the adsorption properties of H_2 and CO, and it was also favorable for the carbonyl activation of methyl formate with a higher resistance to CO poison [10–12].

Table 2
The data of H_2-TPD experiments

Catalyst	T_p/ °C	Peak area /a.u.
CCSZ00	106.2	1.68
CCSZ02	114.8	2.62
CCSZ06	117.2	2.99
CCSZ10	121.7	2.94

Conditions: Sample weight: 150 mg; Heating rate: 10 °C/min.

Table 3
The data of CO-TPD experiments

Catalyst	T_p/ °C	Peak area/a.u.
CCSZ00	116.2	9.12
CCSZ02	119.7	7.71
CCSZ06	130.8	7.52
CCSZ10	131.5	7.83

Conditions: The same as those of table 2.

3.5. Cystallite phase analysis of novel catalysts using XRD characterization

The powder XRD patterns of CCSZ series oxides were shown in figure 4. The catalyst prepared by copper–ammonia complex coprecipitation consisted of $CuCrO_2$, in which copper and chromium existed as Cu^+ and Cr^{3+}, respectively, when $n(Cu)/n(Cr)$ in catalyst was equal to 1 [17]. As shown in figure 4, when the ratio of $n(Cu)/n(Cr)$ was 1.9 in these CCSZ catalysts, the copper and chromium existed mainly as Cu_2O and $CuCr_2O_4$, which just displayed very weak diffraction peak, and no diffraction peaks of zirconia at lower angle were observed. The XRD patterns indicated that zirconia introduced in catalysts did not form the separated ZrO_2 crystallite but dissolved in Cu_2O and $CuCr_2O_4$ crystals, in which the crystal disorder intensified and the diffraction peaks were weakened [16–18].

3.6. Results of electron spin resonance (ESR) and those of X-ray photoelectron spectroscopy (XPS) measurements

The electron spin resonance (ESR) experiments of CCSZ00 and CCSZ06 were performed. As shown in figure 5, a significant ESR signal of CCSZ00 indicated

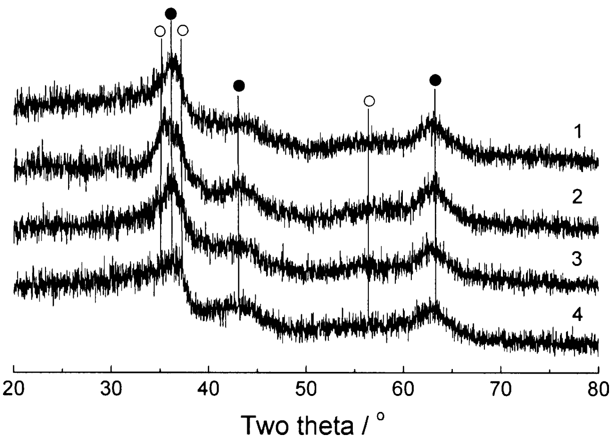

Figure 4. XRD patterns of CCSZ catalysts. (1) CCSZ00, (2) CCSZ02, (3) CCSZ06, (4) CCSZ10 •, Cu_2O; O-$CuCr_2O_4$.

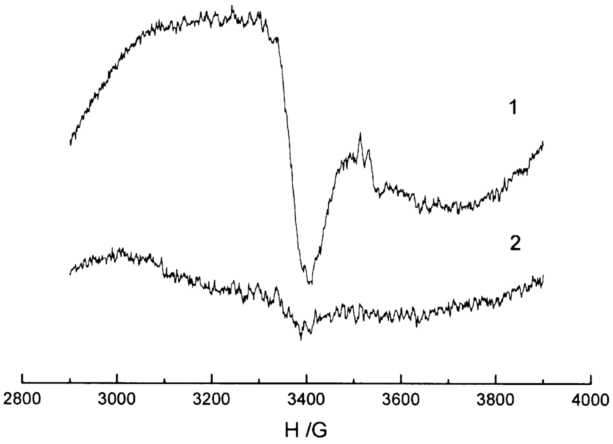

Figure 5. ESR spectra of CCSZ catalysts. (1) CCSZ00; (2) CCSZ06.

that much more copper existed in the form of Cu^{2+} in CCSZ00, while a small ESR signal suggested that copper existed mainly as Cu^0 or Cu^+ in CCSZ06 [19].

The XPS spectra of the Cu2p of CCSZ00 and CCSZ06 were shown in figure 6. As a paramagnetic oxide, copper oxide demonstrated a strong characteristic shake-up peak near 941.7 eV, which was the signal of Cu^{2+} in the binding energy spectra [20–21]. Compared with CCSZ00 sample, the $Cu2p_{3/2}$ binding energy near 932 eV in CCSZ06 shifted by −0.8 eV and the area of the characteristic shake-up peak near 941.7 eV decreased simultaneously. The XPS spectra suggested again that, on the catalysts surface, the copper content existing in form of Cu^{2+} cation decreased, and those of Cu^+ or Cu^0 increased. The XPS spectra of Cr and Zr (omitted here) did not change obviously.

The copper concentration on the catalyst surface, as shown in table 4, was influenced strongly by the modification of zirconia. The results of semi-quantitative calculation indicated that the copper atom concentration on the surface of CCSZ06, compared with CCSZ00, increased by a factor of 34%, and the chromium concentration increased by 45%.

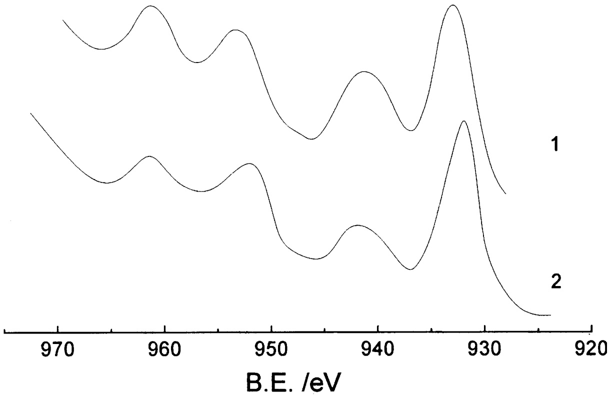

Figure 6. XPS spectra of Cu2p of CCSZ catalysts. (1) CCSZ00; (2) CCSZ06.

Table 4
Surface element molar ratio of Cu–Cr–Si catalyst from XPS measurements

Catalyst	Surface element molar ratio/%			
	Si	Cr	Cu	Zr
CCSZ00	8.52	1.86	2.77	0.00
CCSZ06	8.52	2.70	3.70	5.30

Based on the results of characterization and reaction, zirconia acted as a structural promoter in these copper-based catalysts. With the promotion of zirconia, the specific surface area of catalysts increased remarkably, and the enrichment of copper and chromium on surface was proved by the analysis results, which were related to the surface elements analysis with XPS and the increase of reduction peak area in TPR.

On the other hand, zirconia acted as an electronic promoter as well. The characterization suggested that zirconium dissolved into the crystallite lattices of these copper-based catalysts, and drew the electrons from other components. Consequently, the Cu^{2+} and Cu^+ on the catalysts surface could hardly reduced thoroughly to Cu^0 in a reducible atmosphere, but existed as Cu^0/Cu^+ or $Cu^{\delta+} (0 < \delta < 1)$, which could be stabilized by zirconium promoter [10–12].

It could be induced that abundant $Cu^+–O^{2-}–Cr^{3+}$ and $Cu^+–O^{2-}–Zr^{4+}$ complex active sites were formed on these catalysts surface, which consisted of Cu_2O and $CuCr_2O_4$ [17, 22]. And on these complex active sites, Cu^+ was not only the adsorption center for methyl formate, but also the H_2 adsorption and activation site, where both the homo-cracking via Cu^+ and the hetero-cracking via $Cu^+–O^{2-}$ ion couple happened. In addition, the Cr^{3+} and Zr^{4+} played important roles in not only offering the micro surroundings for the stabilization of Cu^+ valence, but also promoting the activation and hydrogenolysis of carbonyl in methyl formate and the cracking of intermediate C–O bond [18, 21].

4. Conclusion

Zirconia improved the catalytic activity, methanol selectivity and stability of Cu–Cr–Si catalysts for LTMS, and the optimal zirconia content was 6 wt%.

Zirconia acted as a structural promoter in copper-based catalysts; with the promotion of zirconia, the specific surface area of catalysts increased remarkably, copper and chromium were enriched on surface, and plenty of active sites consisted of copper, chromium and zirconium were formed.

Zirconia acted as an electronic promoter in copper-based catalysts as well; copper oxides could be hardly reduced thoroughly to Cu^0 in reducible atmosphere, but existed as Cu^0/Cu^+ or $Cu^{\delta+} (0 < \delta < 1)$ in active sites, which could be stabilized by zirconia promoter.

Acknowledgments

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