Effects of precipitation aging time on the performance of CuO/ZnO/CeO₂-ZrO₂ for methanol steam reforming

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Abstract：CuO/ZnO/CeO₂-ZrO₂ catalysts for methanol steam reforming（MSR）were prepared by a co-precipitation procedure, and the effects of precipitation aging time on the catalytic performance were investigated. It was found that the prolonged precipitation aging time increased the surface Cu atoms and improved the reducibility of catalyst, but decreased the oxygen storage capacity. A nearly linear increase between the surface Cu atoms and H₂ production rate was obtained in prepared CuO/ZnO/CeO₂-ZrO₂ catalysts with prolonged precipitation aging time. However, CO concentration increased with the decrease of the oxygen storage capacity. Considering the H₂ production rate and CO level, the optimal precipitation aging time was 2 h. CuO/ZnO/CeO₂-ZrO₂ prepared using this aging time exhibited the best activity with suppressed CO formation.

Keywords：methanol steam reforming；aging time；hydrogen；CuO/ZnO/CeO₂-ZrO₂；CO concentration

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The Cu-based catalysts has been used for hydrogen production through methanol steam reforming（MSR）[1~7]. Among the Cu-based catalysts, the commercial CuO/ZnO/Al₂O₃ catalyst has been most widely used. ZnO is added to improve the dispersion and redox properties of the copper phases and Al₂O₃ is added to increase the surface area and prevent Cu sintering. Only a small amounts of Al₂O₃ is usually used, because high concentrations may have negative effects on the catalytic activity[8]. Due to the negative effects of Al₂O₃ support in methanol reforming catalysts, the trend in recent years has been the addition of another component to the CuO/ZnO/Al₂O₃ catalysts or simply use other supports rather than alumina. Compared with the conventional Al₂O₃-surpported Cu catalysts, ZrO₂- or CeO₂-containing catalysts have shown increased activities and reduced CO levels in the MSR reaction[9~11]. The promoting effects of ZrO₂ have been attributed to improvement of Cu dispersion[12] and prevention of CuAl₂O₄ spinel formation[13]. Likewise, the application of CeO₂, as either a carrier or a promoter, has been found to improve the activity of Cu-based catalysts and minimize the CO content in the reforming gas[14].

In previous work of our team[15,16], we found that the formation of Ce$_x$Zr$_{1-x}$O₂ solid solution had high oxygen storage capacity which enhanced the catalytic activity toward water gas shift（WGS）and methanol steam reforming（MRS）reaction. The optimal composition of Ce$_{0.5}$Zr$_{0.5}$O₂ in terms of O mobility was obtained by Fornasiero et al[17]. Therefore, the Ce$_{0.5}$Zr$_{0.5}$O₂ solid solution was used as support in our experiment instead of conventional Al₂O₃ carrier in order to decrease the CO level in the reforming gas.

The co-precipitation is the most common preparation method for these kinds of catalysts. Shen et al[18] found that the catalyst prepared by co-precipitation can present higher surface area and methanol conversion than other methods. The co-precipitation method is a complicated process. Many factors can affect the catalyst activity, such as the precursor and precipitator concentration, the aging temperature and time, etc. The aging time is one of the most important factors in determining the catalytic performances in co-precipitation. Increasing catalytic activity as a result of prolonged precipitation aging time has been demonstrated for methanol synthesis, reverse water-gas shift reaction[19] and CO oxidation[20]. In present work, the relationships

between the preparation aging time and the catalyst performance for MSR reaction were investigated.

1 Experimental

1.1 Catalyst preparation

CuO/ZnO/CeO$_2$-ZrO$_2$ (CuZnCeZr) catalysts with a weight ratio of 45/25/30 were prepared by co-precipitation technique in aqueous solution. In short, the solution of Cu(NO$_3$)$_2$·3H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, Ce(NO$_3$)$_3$·6H$_2$O, and Zr(NO$_3$)$_4$·5H$_2$O (0.1 mol/L metal nitrate solution) were prepared in distilled water and then mixed in a volume proportion. The resulting solution was stirred and heated to 60 °C. Then a 0.5 mol/L Na$_2$CO$_3$ aqueous solution was added to the nitrate solution under vigorous stirring until pH = 8 was reached. The achieved precipitates were aged at 60 ℃ for 0 h (CP-0), 1 h (CP-1), 2 h (CP-2), 4 h (CP-4) and 8 h (CP-8) under stirring and then deposited at room temperature for 12 h without stirring. The excess solution was removed by filtering. The precipitates were thoroughly washed with deionized water. After washing, the precipitates were dried at 110 ℃ for 12 h. Finally, the precipitates were calcined at 400 ℃ for 2 h. The obtained powders were pelletized, crushed and sieved to a particle size of 0.28 ~ 0.45 mm, that was then used as catalysts for methanol steam reforming. The commercial CuO/ZnO/Al$_2$O$_3$ catalyst (CB-7) with a weight ratio of 60/25/15 was used as a reference.

1.2 Characterizations

The specific surface areas of the calcined samples were calculated from N$_2$ adsorption-desorption isotherms acquired at liquid N$_2$ temperature with a Quantachrome NOVA 2200E instrument.

Powder X-ray diffraction (XRD) patterns were collected on a Ru-200B with monochromatic Cu $K\alpha$ radiation operating at 40 kV and 200 mA, with 2θ from 20° to 70° and a scanning speed of 5°/min. Average particle sizes were calculated from the line-broadening of the XRD peaks by the Scherrer equation.

TPR was performed on a Quantachrome ChemBET Pulsar instrument. 50.0 mg catalyst was heated in an Ar flow to 300 ℃ with a heating rate of 10 ℃/min and kept at 300 ℃ for 30 min. H$_2$-TPR measurement was performed by heating the sample in a stream of 10% H$_2$/Ar (30 mL/min) from room temperature to 500 ℃ with 10 ℃/min heating rate. The hydrogen consumption was continuously monitored by means of a thermal-conductivity detector during the reduction.

The surface Cu atoms was measured in the same unit used for TPR runs using the N$_2$O titration method, as is typically done for copper based catalysts[21,22]. 50.0 mg catalyst was placed in a quartz tube reactor and held in place by quartz cotton. Prior to measurement, the samples were pre-reduced at 500 ℃ with 10% H$_2$ in Ar for 30 min, in order to reduce the copper species to Cu^0. After the reduction, the gas flow was switch to Ar and the samples were cooled down to room temperature. In the measurement, Ar flow was replaced by a mixture of 7.56% N$_2$O in Ar at 90 ℃ for 1 h, during which Cu^0 on the surface was transformed to Cu$_2$O. The nitrous oxide molecule was assumed to react selectively with the reduced surface copper atom with an O/Cu$_{(s)}$ stoichiometric ratio of 0.5, without oxidizing of the bulk copper. The surface Cu atoms was estimated by the amount of chemisorbed oxygen (Cu$_2$O$_{(s)}$).

OSC measurements were performed in the same unit used for TPR runs. The sample (0.1 g) was previously dried at 300 ℃ for 1 h under He flow, followed by reduction under 10% H$_2$ in Ar at 800 ℃ for 1 h. After the reduction, the gas flow was switch to He and the sample was cooled down to room temperature. Then, the sample was exposed to a 3% O$_2$ in He flow from room temperature to 550 ℃ with 20 ℃/min heating rate and kept for 1 h.

1.3 Catalytic performance

Catalytic activity in MSR was evaluated in a fixed-bed quartz tube reactor (internal diameter: 8 mm). 2.0 mL catalyst was packed between two quartz wool plugs to keep the catalyst bed in place. Prior to each run, the catalyst was reduced in situ in a stream of 5% H$_2$/N$_2$ (flow rate 100 mL/min) at 280 ℃ for 2 h. When the temperature had been stabilized at the reaction temperature, the methanol/water mixture was fed in. The gas products were analyzed on-line by a Agilent-4890D gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

2 Results and discussion

2.1 Analysis of surface characteristics

The data of the surface area, pore volume, and surface Cu atoms of catalysts are presented in Table 1. For the CuZnCeZr catalysts, the longer aging time resulted in the larger specific surface area. The larger specific surface area was beneficial to the dispersion of active components and improvement of the utilization rate of catalysts. But the commercial catalyst (CB-7) was an exception with lower surface Cu atoms compared to CuZnCeZr catalysts, even though it had the higher specific surface area. It was due to the fact that the composition of commercial

CuZnAl catalyst was not the same as our prepared　　catalysts.

Table 1　Physical characteristics and performances of the prepared catalysts for MSR at 240 ℃

Catalyst	$A_{BET}/$ ($m^2 \cdot g^{-1}$)	Pore volume $v/$ ($cm^3 \cdot g^{-1}$)	Crystallite size of CuO d/nm	Surface Cu atoms $/$ ($\mu mol \cdot g_{cat}^{-1}$)	OSC/ ($\mu mol \cdot g_{cat}^{-1}$)	TOF[a] ($10^3 s^{-1}$)	H_2 production rate ($mL \cdot kg_{cat}^{-1} \cdot s^{-1}$)	CO concentration $w/\%$
CP-0	74.7	0.11	21.6	190.5	501	102	435	0.25
CP-1	77.5	0.11	20.3	202.1	493	100	458	0.38
CP-2	90.8	0.12	15.6	232.2	486	98	510	0.46
CP-4	93.8	0.13	14.8	235.8	434	98	516	0.86
CP-8	95.6	0.15	14.1	249.5	419	95	535	1.04
CB-7	95.6	0.20	---	176.1	0	86	340	1.24

reaction conditions：$t=240$ ℃，S/M=1.2，GHSV=1 200 h^{-1}，no carrier gas

[a] TOF(s^{-1})：turnover frequency，defined as the molecules of hydrogen produced per surface copper atom per second

Furthermore，as expected，the lowest H_2 production rate was obtained on the commercial CB-7 catalyst with the lowest surface Cu atoms and the highest H_2 production rate was obtained on the CB-8 catalyst with the highest surface Cu atoms. The correlation between the surface Cu atoms and H_2 production rate is shown in Figure 1. A nearly linear correlation between the surface Cu atoms and H_2 production rate was obtained in CuZnCeZr catalyst. Thus，the surface Cu atoms may be one of important factors for structure-activity correlations of CuZnCeZr catalysts. But the CB-7 catalyst was an exception which was a significant jump in activity that was not due solely to an increase in surface Cu atoms. The different carriers were the reason for this phenomenon.
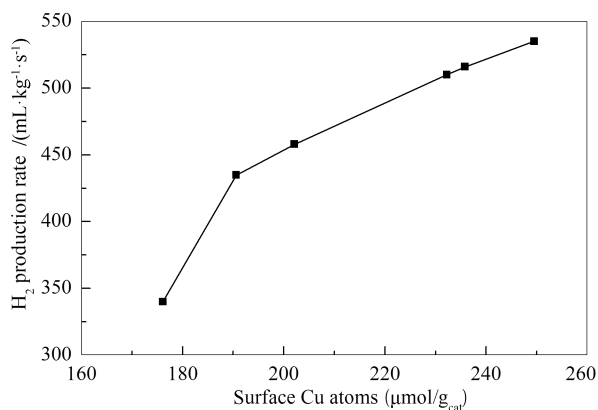
catalytic activity as a result of prolonged precipitation aging time was mainly due to the increase of the surface Cu atoms. Moreover，the CB-7 catalyst had the least TOF and the poorest Cu dispersion. It was the dominating reason for the fact that the CB-7 had the worst catalytic activity.

2.2　Crystalline structure

The X-ray diffraction patterns of the catalysts prepared at different aging time are shown in Figure 2. All the prepared catalysts were composed of CuO，ZnO and $Ce_xZr_{1-x}O_2$ solid solution. Particle size presented in Table 1 was calculated using the (111) peak position of CuO from XRD patterns. It showed that，with the increase of the aging time，the particle size of CuO decreased gradually. These observations were consistent with the increase of specific surface area and surface Cu atoms measured.
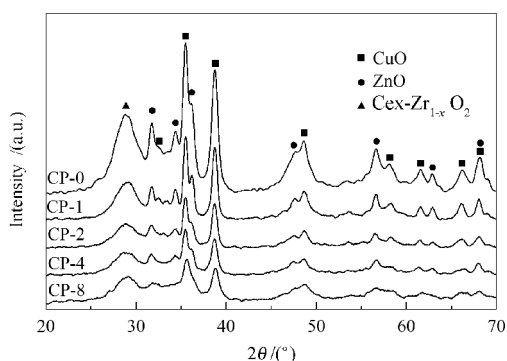

Figure 1　H_2 production rate as a function of specific Cu surface area

Figure 2　XRD patterns of prepared catalysts at different aging time

The turn-over frequencies (TOF) calculated from the hydrogen production rates using the metal surface area data. It can be seen that the TOF of catalysts aged at different time were almost the same. It implied that the molecules of hydrogen produced by per surface copper atom per second was almost the same. Higher dispersion of Cu atoms on the surface can produce more hydrogen. Thus，increasing

2.3　Temperature programmed reduction

In order to discover the relationship between the aging time and the catalyst reducibility，temperature programmed reduction (TPR) was performed on the prepared catalysts. The H_2-TPR profiles of the prepared catalysts are shown in Figure 3. For all the catalysts investigated，the catalysts prepared in

different aging time had two reduction peaks, one at lower temperature (the shoulder peak) was corresponding to the reduction process of the highly dispersed copper oxide species[23] and the other at higher temperature (the main peak) was ascribed to body phase of copper species or the reduction of the crystalline Cu(Ⅱ)O[24]. Combined with the catalytic activity, the most active catalysts, CP-2, CP-4 and CP-8, had the lowest temperature reduction peaks of all the catalysts. Therefore, the ease of reducibility was likely to be one of important factors in determining the catalytic activity. This result was confirmed by Takahashi etal[25]. The extend precipitation aging time can improve reducibility of catalysts.
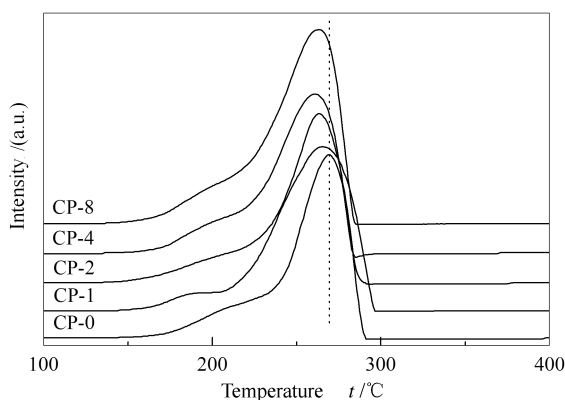

Figure 3 H_2-TPR profiles of the prepared catalysts at different aging time

2.4 Oxygen storage capacity (OSC)

The values obtained during OSC experiments are also listed in Table 1. As expected, the commercial CB-7 catalyst did not present any oxygen storage capacity. The total OSC of CuZnCeZr catalysts decreased with the prolonged precipitation aging time, especially from 2 to 8 h. The high oxygen storage capacity can enhance the catalytic activity toward water gas shift (WGS) reaction and suppress the CO formation[16]. This was the reason for the fact that CO concentration increased with the prolonged precipitation aging time as shown in Table 1.

2.5 Catalyst performance for MSR

The performance of catalysts was evaluated in terms of methanol conversion (mol%) and level of CO in the reforming gas. Figure 4 shows methanol conversion and CO concentration as a function of temperature for each catalyst tested. Compared with CB-7 commercial catalyst, the methanol conversion of prepared CuZnCeZr catalysts were much higher, but the CO mole concentration was much lower as shown in Figure 4. It was mainly due to the fact that the CuZnCeZr catalysts had the high surface Cu atoms

and well oxygen storage capacity which can promote the MRS reaction and suppress the RWGS reaction.
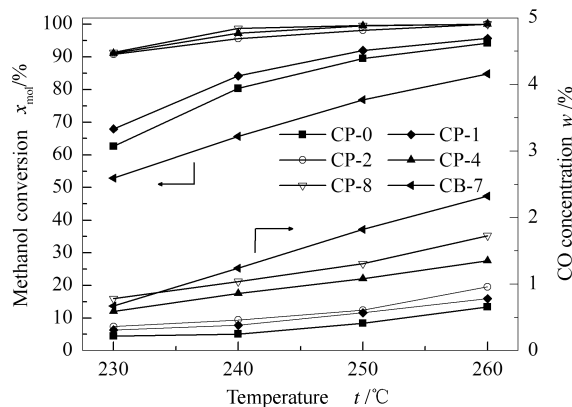

Figure 4 Profiles of the catalysts activity and CO concentration with the temperature

$n(H_2O)/n(MeOH) = 1.2$, GHSV = 1200 h^{-1}, no carrier gas

Moreover, as shown in Figure 4, the methanol conversion was promoted by the prolonged precipitation aging time. Yet the prolonged precipitation aging time also increased the CO concentration. It was the reason for the increase in CO concentration that the oxygen storage capacity decreased with the prolonged precipitation aging time. Furthermore, the increased methanol conversion produced more hydrogen and carbon dioxide, which promoted the RWGS reaction. This was another reason for the fact that the CO concentration increased.

Since the CO level was dependent greatly on the methanol conversion, it was useful to compare the CO selectivity of different catalysts at specific conversion. Table 2 shows the CO selectivity and the temperature of the catalysts at around 91% methanol conversion. The CP-2 catalyst exhibited considerably lower CO selectivity than the other catalysts. Thus, the appropriate aging time not only can promote the methanol conversion, but also can suppress CO formation. The aging time is one of significant factors in co-precipitation procedure. In our experiment, the optimal aging time was 2 h (CP-2).

Table 2 Comparison of CO selectivity at around 91% conversion

Catalyst	Conversion $x/\%$	Selectivity $s/\%$	Temperature $t/℃$
CP-0	90	1.6	250
CP-1	92	2.3	250
CP-2	91	1.4	230
CP-4	91	2.3	230
CP-8	91	3.1	230
CB-7	90	10.5	270

3 Conclusions

Optimizing the aging time during the preparation of the catalyst by co-precipitation can promote the catalytic activity and selectivity. In this paper, the characteristics of the $CuO/ZnO/CeO_2$-ZrO_2 catalysts prepared with different precipitation aging time during catalyst preparation were investigated. Combined with characterizations by XRD, TPR, OSC, BET surface area and N_2O titration, it suggested that the precipitation aging time was important for the catalytic performance through controlling surface Cu atoms and oxygen storage capacity. The optimal aging time was found to be 2 h considering the methanol conversion and the CO concentration. Especially at 240 ℃, the methanol conversion reached 95%, which is 30% higher than that of the commercial catalyst. The CO concentration was only 0.46%, which is one third of the CO concentration in the case of the commercial catalyst.

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陈化时间对 CuO/ZnO/CeO$_2$/ZrO$_2$ 甲醇水蒸气重整制氢催化剂性能的影响

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摘　要： 采用共沉淀法制备了 CuO/ZnO/CeO$_2$/ZrO$_2$ 甲醇水蒸气重整催化剂，探讨了陈化时间对催化剂性能的影响。结果发现，延长陈化时间能增加催化剂的表面铜原子数和改善催化剂的还原性能，但与此同时也降低了催化剂的储放氧性能。延长陈化时间，CuO/ZnO/CeO$_2$/ZrO$_2$ 催化剂的氢产率随表面铜原子数的增加而成线性增长。另一方面，重整尾气中的 CO 含量也随着储放氧能力的下降而增加。综合考虑产氢率和重整尾气中 CO 含量，最佳陈化时间为 2h，此时，CuO/ZnO/CeO$_2$/ZrO$_2$ 催化剂表现出了最佳性能。

关键词： 甲醇水蒸气重整；老化时间；H$_2$；CuO/ZnO/CeO$_2$-ZrO$_2$；CO 含量

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