



Higher alcohols synthesis via CO hydrogenation on Cu/Zn/Al/Zr catalysts without alkalis and F–T elements



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ABSTRACT

A series of Cu/Zn/Al/Zr catalysts without alkalis and F–T elements, were prepared with various atomic ratios of Al/Zr by complete liquid-phase technology and tested for higher alcohols synthesis from CO hydrogenation. The results showed that the Cu/Zn/Al catalyst exhibited excellent higher alcohols selectivity, reaching approximately 58.8%. With the increase of Zr/Al atomic ratio, the catalytic activity and stability increased, but methanol became the dominant product in the liquid products over Cu/Zn/Zr catalyst. It was concluded that Al favored the formation of higher alcohols and Zr was beneficial to improve the stability of catalysts. Characterization results showed that the addition of Zr improved the dispersion of Cu and made the catalyst easier to be reduced. It also favored the stability of pore structure and decreased the amount of weak acidic sites. It was also found that the amount of the weak acidic sites played a key role in the higher alcohols formation and the amount of weak acidic sites decrease might lead to the deactivation of catalysts.

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1. Introduction

Higher alcohols synthesis from syngas produced by coal or renewable biomasses has attracted researchers' interest due to their nontoxicity and high chemical energy corresponding to that of gasoline [1]. Currently, there are four types of catalysts for higher alcohols synthesis from CO hydrogenation: Rh-based catalysts [2–4], modified methanol synthesis catalysts [5–7], modified Fischer–Tropsch (F–T) synthesis catalysts [8–10], Mo-based catalysts [11–13]. Of all these types, only Rh-based catalysts show relatively high selectivity for the synthesis of C_2+ oxygenates due to their unique CO adsorption behavior [14]. However, the high price of Rh restricts its industrial application. Among these non-precious metal catalysts, F–T synthesis catalysts which are modified to synthesize higher alcohols are regarded as the most promising candidates for higher alcohols synthesis [15–17].

It is well known that Cu/Zn/Al or Cu/Zn/Al/Zr catalysts are usually used to synthesize methanol from CO or CO_2 hydrogenation [18–20]. Over Cu-based catalysts, low content of higher alcohols are detected in the liquid products, which led almost all researchers to explore the addition of alkalis or some of F–T elements (Fe, Co, Ni) to the catalysts to increase the yield of higher alcohols. It is concluded that the formation of higher alcohols requires the dual active centers, which require the synergism between Cu species and F–T elements. The loss of synergism would destroy the active centers and lead to lower higher alcohols selectivity. Nonetheless, in our previous study, it was found that the ethanol selectivity of Cu/Zn/Al catalysts without promoters could reach an

unexpected point [21]. However, it was difficult to reproduce the former results, even if some catalysts exhibited excellent ethanol selectivity, which came up to approximately 40% at the initial stage of reaction, but the ethanol selectivity sharply decreased to 5% after 120 h reaction [22]. In addition, in our previous studies, we paid much attention to the synergism of Cu^0 and Cu^+ as well as high Cu/Zn ratio of the catalysts, whereas we did not notice the effect and variation of Al species.

Therefore, in the present work, a series of Cu/Zn/Al/Zr catalysts were prepared with various atomic ratios of Al/Zr. The influence of Al and Zr on the catalytic performance was investigated and the catalysts were characterized by X-ray diffraction (XRD), H_2 temperature-programmed reduction (H_2 -TPR), temperature-programmed desorption of ammonia (NH_3 -TPD-MS), N_2 adsorption, and X-ray photoelectron spectrometry (XPS).

2. Experiment

2.1. Catalyst preparation

The Cu/Zn/Al/Zr catalysts with Al/Zr atomic ratios of 4:1, 2:1 were prepared by complete liquid-phase technology, and the Cu: Zn: (Al + Zr) atomic ratio was kept at 2:1:0.8. Initially a certain amount of citric acid was dissolved in distilled water, following by addition of Aluminum isopropoxide [$(C_3H_7O)_3Al$] and $Zr(NO_3)_2 \cdot 5H_2O$, and the water bath temperature maintained at 323 K for 3 h, then the mixture temperature was raised to 368 K and kept for 1 h. Next, $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved in glycol and the resulting solution was slowly added to the Al/Zr solution. The resulting Cu/Zn/Al/Zr solution was stirred at 368 K until a homogeneous gel was obtained. The

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gel was aged at room temperature for 10 days and dispersed in liquid paraffin, heated under N₂ atmosphere from 333 K to 573 K at the rate of 5 K/min and maintained for 8 h at 573 K. A slurry catalyst was subsequently obtained. The two catalysts were denoted as CAT-AZ(4:1), CAT-AZ(2:1), respectively. Cu/Zn/Al catalyst omitted the addition of zirconium nitrate was named as CAT-Al and Cu/Zn/Zr catalysts omitted the addition of Aluminum isopropoxide was named as CAT-Zr.

2.2. Characterization of catalysts

Before catalyst characterization, the slurry catalysts were centrifuged, extracted with petroleum ether for 2 days, and dried at room temperature, and then the solid samples were obtained.

XRD patterns were recorded on a Rigaku D/MAX-2500 Diffractometer in a 2 θ range of 5–85° with Cu K α radiation (40 kV, 100 mA).

H₂-TPR tests were carried out in a fixed-bed reactor. For each TPR test, the sample (50 mg) was purged with He (40 mL/min) at 423 K to remove physically adsorbed water and other impurities, then it was reduced in a flow of 5 vol.% H₂ + N₂ (40 mL/min) at a heating rate of 10 K/min up to 773 K. A thermal conductivity detector (TCD) was used to record the reduction peaks.

The acidity of the samples was measured by NH₃-TPD-MS. The samples were first reduced at 553 K in a flow of 5 vol.% H₂ + N₂ (40 mL/min) for half an hour. After cooling to 323 K, the samples were saturated with pure NH₃ for 30 min and then flushed with He flow to remove all physical adsorbed molecules. After that, the TPD experiments were started with a heating rate of 10 K/min under He flow (40 mL/min), and the desorbed NH₃ were detected by an AMETEK mass spectrometer.

The pore size distribution of samples was carried out by N₂ adsorption at liquid nitrogen temperature 77 K, using a Micromeritics Quanta chrome instrument. Samples degassing were carried out at 473 K prior to acquisition of the adsorption isotherm.

X-ray photoelectron spectroscopy (XPS) measurements were conducted using an ESCALAB 250 spectrometer (VG Scientific Ltd., UK) equipped with monochromated Al K α ($h\nu = 1486.6$ eV, 150 W) under ultrahigh vacuum (7×10^{-8} Pa), The binding energies were calibrated by the C 1 s peak at 284.6 eV.

2.3. Catalytic activity test

CO hydrogenation was carried out in a continuous-flow, high-pressure, 0.5 L slurry reactor under continuous mechanical agitation. The catalyst was reduced with H₂/N₂ (75 mL/min, V(H₂)/V(N₂) = 1:4) under atmospheric pressure at 553 K for 8 h. After reduction, the synthesis gas (H₂/CO = 2) was introduced into the reactor under the reaction conditions of 523 K, 4.5 MPa with a feed flow rate of 150 mL/min. The steady-state activity measurements were taken after the reaction of 24 h. The gaseous products were analyzed online with a gas chromatograph equipped with a thermal conductivity detector (TCD) to detect H₂, CO, CH₄ and CO₂ and a flame ionization detector (FID) to detect ethanol, methanol, DME, and hydrocarbon, respectively. The liquid products were collected daily and analyzed offline using the gas chromatograph. The CO conversion and the carbon-based for higher alcohols, methanol, DME, CO₂ and hydrocarbon were calculated by an internal normalization method. Each data set was obtained from an average of three independent measurements.

3. Results and discussion

3.1. Catalytic performance

The catalytic performance of Cu/Zn/Al/Zr catalysts with different Al/Zr atomic ratio toward CO hydrogenation was summarized in Table 1. As shown in Table 1, the CAT-Al catalyst had lower CO conversion and total alcohols selectivity. However, the selectivity of higher alcohols (C₂₊OH) reached approximately 58.8%. With Zr content increasing,

Table 1

The catalytic performance of catalysts with different Al/Zr atomic ratio.

Catalyst	CO conversion (%)	Selectivity (wt.%)				Methanol (%)	C ₂₊ OH (%)
		ROH	HC	DME	CO ₂		
CAT-Al	19.8	16.8	17.1	10.0	56.1	41.2	58.8
CAT-AZ(4:1)	25.5	19.4	8.5	23.7	48.3	55.9	44.1
CAT-AZ(2:1)	27.1	22.6	7.4	22.4	45.6	69.7	30.3
CAT-Zr	36.7	58.0	0.5	18.5	19.6	92.0	8.0

Notes: Reaction conditions: T = 523 K, P = 4.5 MPa, H₂/CO = 2, feed low rate = 150 mL/min, ROH for total alcohols and HC for hydrocarbon.

the CO conversion and total alcohols selectivity increased, whereas the selectivity of higher alcohols and CO₂ decreased notably, illustrating that the introduction of Zr restrained the water-gas shift reaction and lessened the formation of higher alcohols. The catalytic performance results showed that Al might favor the formation of higher alcohols. Fig. 1 showed the variation of higher alcohols selectivity of Cu/Zn/Al/Zr catalysts with time on stream (TOS). As seen in Fig. 1, the higher alcohols selectivity first increased and then decreased after 72 h except for CAT-Zr catalyst, illustrating that the catalysts had a process of induction and had different degrees of deactivation. Remarkably, with Zr content increasing, the deactivation rate of the catalysts decreased, illustrating that Zr was beneficial to improve the stability of the catalyst. Thus, a suitable Al/Zr atomic ratio for improving the stability of the catalysts and maintaining the selectivity of higher alcohols requires to be researched deeply in the future.

3.2. XRD characterization

The XRD patterns of the catalysts with different Al/Zr atomic ratio before and after reaction were presented in Fig. 2. As seen in Fig. 2, all catalysts exhibited similar diffraction lines of Cu⁰ and weakly ZnO, no CuO and Cu₂O were observed, which had been proved by our previous work [23,24]. Metallic Cu⁰ appeared in the un-reduced catalysts was due to the decomposition of liquid paraffin which led to the reduction of CuO species [25]. Moreover, it could be found that the diffraction peaks of Cu⁰ became weaker with the increase of Zr content, illustrating that Zr was beneficial to improve the dispersion of Cu species of the catalysts. In addition, the diffraction peaks of ZrO₂ could be detected only for the CAT-Zr since the strong Cu⁰ diffraction peaks, which suggested that Al and Zr species existed in an amorphous state. After reaction, compared with Zr-containing catalysts, the diffraction peaks of Cu⁰ and ZnO for CAT-Al had changed significantly, which further suggested that Zr was beneficial to the dispersion of Cu species.

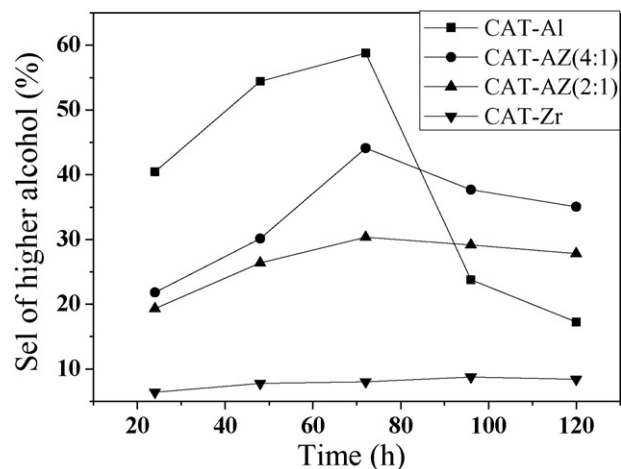


Fig. 1. The higher alcohols selectivity of catalysts with different Al/Zr atomic ratio. Reaction conditions: T = 523 K, P = 4.5 Mpa, H₂/CO = 2, Feed flow rate = 150 mL/min.

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