Conversion of syngas to higher alcohols over Cu-Fe-Zr catalysts induced by ethanol

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Abstract

Ethanol induced method was applied to prepare Cu-Fe-Zr catalysts for conversion of syngas to higher alcohols. The catalytic performance of the catalysts induced by ethanol was superior to that of the catalyst prepared by the conventional precipitation method. Among various procedures for ethanol induced method, it was found that incorporation of ethanol in the precipitation process was the better. After incorporation of ethanol, the crystal size of CuO decreased and the reduction of copper species became easier. The better activity of Cu-Fe-Zr catalysts prepared by ethanol induced procedures was probably caused by the higher dispersion of Cu species.

1. Introduction

The production of liquid fuels and high-value added chemicals from coal has received significantly increasing interest due to the limited petroleum reserves [1,2]. Synthesis of alcohols from syngas is an important pathway to realize this process because syngas can be produced from relatively abundant coal resource. In recent years, various catalyst systems were developed to synthesize alcohols from syngas, such as Cu-Co, Cu-Fe and MoS_2 based catalysts [3−9].

Higher alcohols ($C_{2+}OH$) have potential applications as fuels, additives to increase the octane number of gasoline, and materials for synthesis of fine chemicals [10]. Although, the conversion of syngas to higher alcohols has been improved to some extent, the space-time yield of alcohols and/or the selectivity of C_{2+} alcohols is still unsatisfactory. Therefore, it is highly desirable to seek catalysts with high activity and selectivity for synthesis of higher alcohols from syngas. The pretreatment of solid catalysts can change their structure, such as Au/Al_2O_3 pretreated by H_2 for oxidation of CO [11], Sb-Mo-O catalyst pretreated by ethanol for the oxidative esterification of ethanol [12], and HY zeolite

pretreated by various gases for o-xylene isomerization [13], which improves their catalytic performance. It was reported that the selectivity of methanol was significantly improved using the catalyst prepared in the solvent of methanol [14]. Xu *et al.* has also reported that the Cu-Co-Fe catalysts obtained in ethanol medium or pretreated by ethanol showed higher activity and selectivity for synthesis of higher alcohols from syngas [15,16].

In the present work, we investigated in detail the preparation of Cu-Fe-Zr based catalysts by ethanol induced method and their catalytic performance in the conversion of syngas to higher alcohols. The nature of the catalyst was characterized by X-ray diffraction (XRD) and temperature-programmed reduction (TPR) by H_2.

2. Experimental

2.1. Catalyst preparation

$Cu(NO_3)_2 \cdot 3H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $ZrOCl_2 \cdot 8H_2O$ and K_2CO_3 were of A. R. grade and were used as the materials for preparation of Cu-Fe-Zr catalyst.

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2.1.1. Cu-Fe-Zr catalyst prepared by conventional method

Cu-Fe-Zr sample prepared by conventional method was named as S1. First, $Cu(NO_3)_2 \cdot 3H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $ZrOCl_2 \cdot 8H_2O$ were dissolved in water to form a solution. The molar ratio of Cu : Fe : Zr was 2 : 1 : 0.04. Then this solution and the aqueous solution of K_2CO_3 were simultaneously added drop-wise into a beaker containing water. The mixture was stirred at 343 K and its pH value was kept at 7.5. The precipitate was aged at 343 K for 1 h, then it was filtered and washed thoroughly with distilled water. After drying at 393 K for 12 h, the sample was calcined at 623 K in air for 5 h.

2.1.2. Cu-Fe-Zr catalyst prepared by different ethanol induced methods

Four catalysts (S2–S5) were prepared by ethanol induced method. Among them, catalyst S2 was prepared by adding ethanol into water in a beaker, catalyst S3 was prepared by washing the precipitate with ethanol-water solution, catalyst S4 was prepared by drying in the presence of ethanol vapor, and catalyst S5 was prepared by calcination in the ethanol vapor. All the other experimental conditions for S2–S5 were the same with catalyst S1.

2.2. Catalyst characterization

XRD patterns were recorded on a Philips PW3040/60 diffractometer fitted with Cu K_α radiation ($\lambda = 1.5404$ Å). H_2-TPR experiments were carried out with a homemade apparatus. All samples (20 mg) were first pretreated at 373 K in Ar (50 ml/min) for 1 h. For TPR measurements, the samples were heated from 373 K to 973 K at a rate of 10 K/min in an 8 vol% H_2/Ar flow (50 ml/min).

2.3. Catalytic tests

The catalytic performance was evaluated in a fixed-bed stainless-steel micro-reactor with 6 mm inner diameter. Prior to reaction, the catalysts were reduced *in-situ* by the reactant gas ($n(H_2)/n(CO) = 2.0$) at atmospheric pressure, which contained 8.0 mol% CO_2 and 0.4 mol% CH_4. The following temperature-programmed procedure was employed:

(1) room temperature → 523 K for 1 h and keeping the temperature at 523 K for 0.5 h;

(2) 523 K → 573 K for 1 h and keeping at 573 K for 0.5 h;

(3) 573 K → 623 K for 1 h and keeping at 623 K for 2 h. After pretreatment, the temperature was decreased slowly to 593 K and the catalytic reaction was performed under the conditions of 6.0 MPa and GHSV of 20000 h^{-1}. The steady-state activity was measured using an on-line gas chromatograph with a 4 mm×2000 mm stainless-steel packed column and an FID detector.

3. Results and discussion

3.1. Crystal phase analysis of Cu-Fe-Zr based catalysts

Figure 1 shows the XRD patterns of Cu-Fe-Zr based catalysts before reduction. The phase of CuO (JCPDS card No. 48-1548) was detected in S1 and S2 samples, but no ZrO_2 and ferric oxide was detected. The result suggested that the experimental methods had no significant effect on the phase formation of the Cu-Fe-Zr catalysts. But the peak intensity of CuO in S2 was lower than that in S1. It indicated that the addition of ethanol probably decreased the crystal size of CuO.
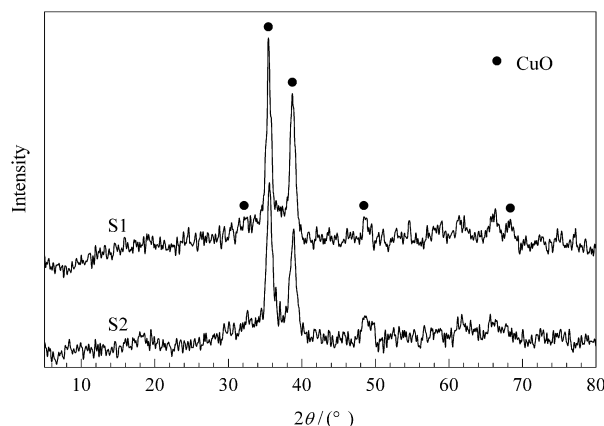

Figure 1. XRD patterns of the as-synthesized S1 and S2

3.2. H_2-TPR measurements

The H_2-TPR results of the Cu-Fe-Zr catalysts are presented in Figure 2. Every sample exhibited two reduction peaks in the range of 500−700 K and 700−900 K. The first peak was attributed to the reduction of copper species, and the second peak was related to the reduction of ferric species. The first reduction peak of S1, S2, S3, S4 and S5 samples centered at 630, 583, 610, 614 and 609 K, respectively. The reduction peak of copper species in S2–S5 samples shifted to lower
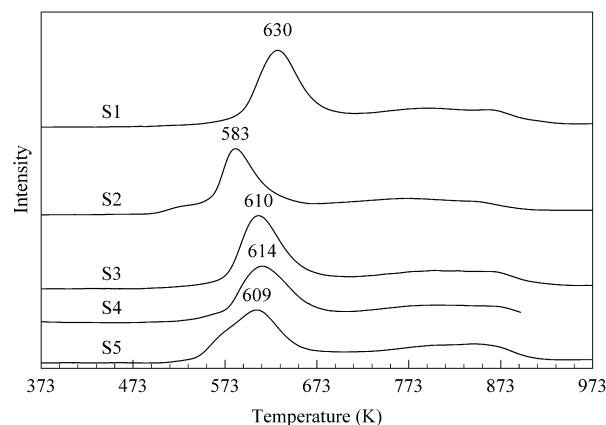

Figure 2. H_2-TPR curves of the as-synthesized S1–S5

temperature compared with that of S1, indicating that the reduction of copper species became easier because of its smaller crystal size. Additionally, the reduction of copper species in S2 sample was the easiest.

3.3. Effect of ethanol-incorporated method on the catalytic performance of Cu-Fe-Zr catalysts

The catalytic performance of Cu-Fe-Zr catalysts prepared by the conventional co-precipitation and ethanol induced co-precipitation method in the conversion of syngas to alcohols is shown in Table 1. The main products were alcohol, dimethyl ether, methane and ethene. It was obvious that the activity and selectivity of alcohol over Cu-Fe-Zr catalysts prepared

by ethanol induced method were higher than those of catalyst prepared by the conventional co-precipitation method. Additionally, the ethanol-incorporated method also affected the activity and selectivity of the catalysts. Among all the catalysts, the S2 and S3 samples exhibited higher time-space yield of alcohol (ROH) and selectivity of $C_{2+}OH$ than other catalysts. Over S2 catalyst, the time-space yield and selectivity of ROH were 1.25 $g \cdot ml^{-1} \cdot h^{-1}$ and 57.9 wt%, respectively. The percentage of $C_{2+}OH$ in products of alcohols was 69.7 wt%, which was higher than that over Cu-Fe-Co catalyst induced by ethanol [16], Cu-Co [5], or Cu-Co-Zn-Zr [17] catalyst described in literature. The better catalytic performance probably benefited from the small crystal size of copper species in S2 catalyst [17].

Table 1. Results of CO hydrogenation over Cu-Fe-Zr based catalysts prepared by the conventional co-precipitation and ethanol induced co-precipitation method

Catalyst	Selectivity (wt%)				Yield of ROH[a] ($g \cdot ml^{-1} \cdot h^{-1}$)	Conversion of CO (wt%)	Distribution of alcohols (wt%)				
	CH_4	Ethene	$(Me)_2O$	ROH[a]			MeOH	EtOH	PrOH	BuOH	$C_{2+}OH$
S1	15.4	8.4	21.7	54.5	1.04	43.2	39.9	27.3	23.0	9.8	60.1
S2	12.8	7.9	21.4	57.9	1.25	46.7	30.3	30.7	28.9	10.1	69.7
S3	13.5	8.5	23.0	55.0	1.22	46.5	30.1	30.4	28.2	11.3	69.9
S4	14.6	8.0	21.2	56.2	1.16	45.9	33.8	27.3	27.7	11.3	66.2
S5	15.4	8.4	21.7	54.5	1.09	44.8	31.4	29.2	28.3	11.1	68.6

Reaction conditions: $T = 593$ K, $P = 6.0$ MPa, GHSV = 20000 h^{-1}, $n(H_2)/n(CO) = 2.3$; [a] ROH represents alcohol

3.4. Catalytic performance of Cu-Fe-Zr catalysts prepared by the incorporation of ethanol in the course of precipitation

As discussed above, the catalyst prepared by the incorporation of ethanol in the course of precipitation showed better catalytic performance, so we further investigated this preparation method. The addition of ethanol into metal nitrate solution, precipitator K_2CO_3 solution and precipitation medium, and the adding amount of ethanol were investigated. The results of CO hydrogenation to alcohols over these catalysts are listed in Table 2, Table 3 and Table 4, respectively. Over all the catalysts, the main products of alcohol are MeOH, EtOH, PrOH and BuOH. But the space-time yield of ROH and the selectivity of $C_{2+}OH$ are influenced by the amount of ethanol added during the catalyst preparation. Over the catalysts prepared by adding ethanol into metal nitrate solution, the optimum amount of ethanol was 10 ml, where the highest space-time yield of ROH (1.36 $g \cdot ml^{-1} \cdot h^{-1}$) with $C_{2+}OH$ selectivity for 74.2 wt% was obtained as shown in Table 2. For the catalysts prepared by adding ethanol into precipita-

tor K_2CO_3 solution, the highest space-time yield of ROH reached 1.76 $g \cdot ml^{-1} \cdot h^{-1}$ with 73.7 wt% $C_{2+}OH$ selectivity when 20 ml ethanol was added as shown in Table 3. When we added ethanol (8 ml) into the precipitation medium, the selectivity of $C_{2+}OH$ was 71.6 wt% at the highest space-time yield of ROH (1.45 $g \cdot ml^{-1} \cdot h^{-1}$) as shown in Table 4. When making comparisons with all the preparation methods, this method was superior to the formers. It consumed the least amount of ethanol to obtain the higher space-time yield of ROH and selectivity for $C_{2+}OH$. In order to study why the amount of ethanol influenced the catalytic performance, we performed the H_2-TPR of the catalysts prepared by adding ethanol into the precipitation medium (Figure 3). It was found that the reduction temperature of Cu species decreased with increasing the amount of ethanol from 0 to 24 ml. But when the amount of ethanol was further increased, the reduction temperature increased. So it can be speculated that the amount of ethanol affected the state of the active copper species, which in turn influenced the catalytic performance of the Cu-Fe-Zr catalysts.

Table 2. Results of CO hydrogenation over Cu-Fe-Zr based catalysts prepared by adding different amount of ethanol into metal nitrate solution

Adding amount of ethanol (ml)	Space-time yield of ROH[a] ($g \cdot ml^{-1} \cdot h^{-1}$)	Distribution of alcohols (wt%)				
		MeOH	EtOH	PrOH	BuOH	$C_{2+}OH$
0	1.04	39.9	27.3	23.0	9.8	60.1
10	1.36	25.8	32.2	31.2	10.9	74.2
20	1.08	28.9	31.7	28.6	10.8	71.1
40	1.06	26.9	30.2	29.6	13.2	73.1

Reaction conditions: $T = 593$ K, $P = 6.0$ MPa, GHSV = 20000 h^{-1}, $n(H_2)/n(CO) = 2.3$; [a] ROH represents alcohol

Table 3. Results of CO hydrogenation over Cu-Fe-Zr based catalysts prepared by adding different amount
of ethanol into precipitator K_2CO_3 solution

Adding amount of ethanol	Space-time yield of ROH[a]	Distribution of alcohols (wt%)				
(ml)	(g·ml^{-1}·h^{-1})	MeOH	EtOH	PrOH	BuOH	C_{2+}OH
0	1.04	39.9	27.3	23.0	9.8	60.1
20	1.76	26.3	33.4	34.7	5.6	73.7
40	1.35	24.8	33.5	29.1	12.5	75.2

Reaction conditions: T = 593 K, P = 6.0 MPa, GHSV = 20000 h^{-1}, $n(H_2)/n(CO)$ = 2.3; [a] ROH represents alcohol

Table 4. Results of CO hydrogenation over Cu-Fe-Zr based catalysts prepared by adding different amount of ethanol into precipitation medium

Adding amount of ethanol	Space-time yield of ROH[a]	Distribution of alcohols (wt%)				
(ml)	(g·ml^{-1}·h^{-1})	MeOH	EtOH	PrOH	BuOH	C_{2+}OH
0	1.04	39.9	27.3	23.0	9.8	60.1
8	1.45	28.4	31.4	28.3	11.8	71.6
24	1.23	26.2	31.5	29.8	12.5	73.8
40	1.08	32.8	30.7	25.7	10.7	67.2
80	0.96	34.5	31.1	25.4	8.9	65.5

Reaction conditions: T = 593 K, P = 6.0 MPa, GHSV = 20000 h^{-1}, $n(H_2)/n(CO)$ = 2.3; [a] ROH represents alcohol
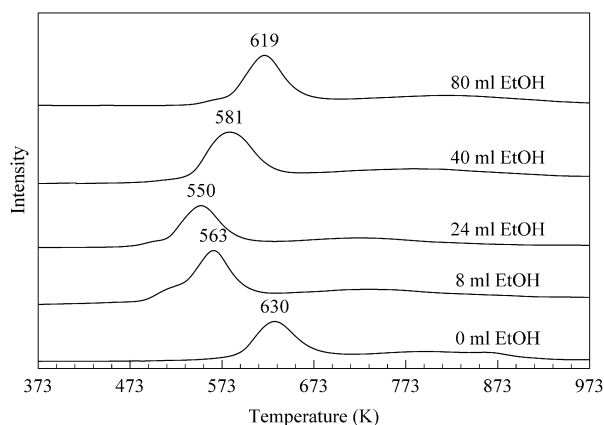

Figure 3. H$_2$-TPR curves of samples prepared by adding different amount of ethanol into the precipitation medium

4. Conclusions

In conclusion, in the synthesis of higher alcohols from syngas, the catalytic performance of Cu-Fe-Zr catalysts prepared by the ethanol induced method was better than that of catalyst prepared by the conventional precipitation method. The addition of ethanol decreased the crystal size of CuO and thus the reduction of copper species became easier. Moreover, incorporation of ethanol in the process of precipitation was better. Additionally, addition of ethanol into the precipitation medium was better than into the solution of metallic salt and the precipitator. This method could also be extended conveniently to other catalyst system for synthesis of higher alcohols from syngas.

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