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# The Adjustment of Product Distribution of CO<sub>2</sub> Hydrogenation over Cu-Fe-Zn Catalyst while Maintaining its Activity *via* Potassium Addition

LI Bo<sup>1,2</sup>, ZHEN Wen-long<sup>1,2</sup>, LV Gong-xuan<sup>2,\*</sup>, MA Jian-tai<sup>1</sup>

(1. State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China;

2. State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics,

Chinese Academy of Science, Lanzhou 730000, China)

Abstract: The impact of potassium promoter on product distribution for  $CO_2$  hydrogenation over Cu-Fe-Zn catalyst was investigated. A series of transition metal  $K_x/Cu$ -Fe-Zn catalysts were prepared by a combination co-precipitation and impregnation method. The physiochemical characterizations of these catalysts were performed by BET, H<sub>2</sub>-TPR, XRD, TEM and XPS techniques to study the effect of potassium on the textural properties, reduction behaviour, structural and morphological change. The effects of addition of potassium promoter on  $CO_2$ -conversion, product distribution and deactivation were study for  $CO_2$  hydrogenation in a fixed bed reactor. The maximum catalytic activity was obtained from  $K_{0.1}/Cu$ -Fe-Zn catalyst and its catalytic activity decreased slightly thereafter. The  $CO_2$  conversion reached the highest value of 68.7% over  $K_{0.1}/Cu$ -Fe-Zn at 350 °C. In addition, the results revealed that addition of potassium promoter shifted selectivity to high molecular weight compounds and led to the formation of higher alcohols and oxygen containing compounds in the products. The possible mechanism in the presence of potassium was discussed.

Key words: adjustment of product distribution; CO<sub>2</sub> hydrogenation; Cu-Fe-Zn catalyst; potassium addition CLC number: 0643.32 Document code: A

With the extensive use of fossil fuels, a plenty of carbon dioxide has been released into the atmosphere, leading to severe greenhouse effect. Recently, the research of carbon dioxide capture and conversion has become a hot topic in energy and environmental science and technology<sup>[1-3]</sup>. The chemical conversion of carbon dioxide can produce chemicals, such as hydrocarbons and oxygen-containing compounds<sup>[4-8]</sup>. However, there are 16 electrons in a carbon dioxide molecule, which is a linear and non-polar central symmetry molecule containing two polar C = O bond under the ground state. In addition, carbon dioxide is a final product of the combustion of carbon-containing compounds, therefore, it is very stable.

Carbon dioxide molecules can be activated only o-

ver special catalysts, for example, and be converted into hydrocarbons or other chemicals through the hydrogenation or methanation<sup>[4,9-14]</sup>. Generally, catalytic system for hydrogenation of carbon dioxide was based on VIII metals supported on various oxides. In these catalysts, supported nickel catalysts were studied extensively<sup>[15-16]</sup>. One of major problems of nickel based catalysts is the deactivation due to formation of mobile nickel sub-carbonyls and segregation of nickel particles<sup>[17]</sup>. For other catalysts, Park *et al.* reported bifunctional catalyst Pd-Mg/SiO<sub>2</sub> for CO<sub>2</sub> methanation<sup>[18]</sup>. At 723K, that catalyst shows a high selectivity (>95%) to CH<sub>4</sub> with 59% of CO<sub>2</sub> conversion. Adding appropriate additives such as alkali metal can effectively modulate the nature of catalyst. Chen et al. reported

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First author: LI Bo(1988-), Master, Male, bli2012@lzu.edu.cn.

<sup>\*</sup> Corresponding author: 0931-4968178, E-mail: gxlu@ lzb. ac. cn.

that Cu/SiO<sub>2</sub> with a K promoter offered better catalytic activity (12.8% of  $CO_2$  conversion) than the sample without K (5.3% of  $CO_2$  conversion) at 600 °C<sup>[19]</sup>. These created new active sites located at the interface between Cu and K favour the formation of formate species, which is a key intermediate for CO<sub>2</sub> hydrogenation, enhancing CO2 adsorption. Many modified Fischer-Tropsch synthesis catalysts were also reported for this reaction<sup>[20-26]</sup>. J. Erena<sup>[22]</sup> found CuO-ZnO-Al<sub>2</sub>O<sub>3</sub>/NaHZSM-5 catalyst for dimethyl ether (DME) synthesis at 275 °C with DME yield 80%. The selectivity of CO<sub>2</sub> hydrogenation was changed after addition of alkali metal. Kusam et al. found the main product distribution shift from methane to methanol and ethanol for CO<sub>2</sub> hydrogenation over Rh/SiO<sub>2</sub> catalyst after Li addition<sup>[27]</sup>. Here, alkali metal might lead to a strong electronic effect, which could enhance the chemical adsorption of CO<sub>2</sub> over catalysts and decreased the adsorption of H<sub>2</sub><sup>[25]</sup>. Therefore, alkali metal addition led to the decrease of selectivity to methanol and increase selectivity to higher alcohols<sup>[28]</sup>.

The interaction between K and Fe could also prevent the reduction of Fe species<sup>[29]</sup>, and decreased the numbers of active site for CO<sub>2</sub> hydrogenation reaction and thereby reduced the catalytic activity of the catalyst. Although many catalysts about hydrogenation of carbon dioxide have been reported, activity and selectivity of the transition metal catalyst are still relatively low, in addition, the reaction mechanism is not fully uncovered, especially the influence of additives on multi-component transition metal catalyst. In this paper, we synthesized multi-component transition metal Cu-Fe-Zn catalysts for CO2 hydrogenation, and studied the effect of K promoter on Cu-Fe-Zn for CO<sub>2</sub> hydrogenation. The results indicated that the addition of potassium promoter not only affected the catalytic activity of catalyst but also changed significantly product distribution of  $CO_2$  hydrogenation.

# **1** Experimental

#### 1.1 Preparation of the catalysts

K promoted Cu-Fe-Zn catalysts with different K-containing were prepared by a combination of both coprecipitation and wet impregnation technique. The catalyst precursor was precipitated from a mixed aqueous solution (total metal concentration of 0.5 mol/L) containing copper( $Cu(NO_3)_2 \cdot 3H_2O$ ), iron (Fe ( $NO_3$ )<sub>3</sub> ·  $9H_2O$ ), and zinc nitrates  $(\operatorname{Zn}(\operatorname{NO}_3)_2 \, \cdot \, 6\mathrm{H}_2\mathrm{O}\,)\,$  at  $1\, \div \, 3\, \div \, 1\,$  Cu/Fe/Zn ratio using an aqueous solution of NaOH (0.5 mol/L). Precipitation occurred continuously as the two solutions were added drop-wise to a vessel by parallel addition method at 80 °C and pH=8. The precipitates were aged for 1 h at 80 °C, then cooled to room temperature, filtered, and washed several times with distilled water to remove residual sodium. The precipitates were calcined at 350 °C for 6 h. Then, the obtained precursor was impregnated in an aqueous solution with calculated amount of K<sub>2</sub>CO<sub>3</sub> by wet impregnation method at room temperature. After 8 h impregnation, the samples were dried at 120 °C for 16 h, and then calcined at 350 ℃ for 6 h. The obtained powder was pressed, crushed and sieved into particles with diameter  $0.45 \sim$ 0.28 mm. The compositions of five catalysts were as follows: nK/nCu/nFe/nZn = x/1/3/1 (molar ratio, x=0, 0.05, 0.1, 0.15, and 0.2, which were marked as Cu-Fe-Zn, K<sub>0.05</sub>/Cu-Fe-Zn, K<sub>0.1</sub>/Cu-Fe-Zn, K<sub>0.15</sub>/Cu-Fe-Zn, K<sub>0.2</sub>/Cu-Fe-Zn, respectively.

#### **1.2 Evaluation of catalytic activity**

The performance of CO<sub>2</sub> hydrogenation reaction was evaluated in a 10mm diameter stainless steel tubular, fixed-bed continuous-flowing reactor. The catalyst (particle diameter 0.45 ~ 0.28 mm, 5 g) sample diluted with quartz sand (particle diameter  $0.45 \sim 0.28$  mm, 5 mL) was loaded in the middle of the reactor. In order to ensure the reaction system run safely and stably, nitrogen was applied to flush all gas channels. Before reaction, the catalyst was in situ reduced at 400  $^{\circ}$ C for 6 h in H<sub>2</sub> atmosphere with gas hourly space velocity (GHSV) of 1 800 h<sup>-1</sup>. After reduction and cooling to room temperature, the reactant gas  $(H_2/CO_2 = 3/1)$ , molar ratio) flow was introduced into the reactor. The  $CO_2$  hydrogenation reaction was conducted at 200 ~ 500 °C, 2.0 MPa, and GHSV of 7 200 h<sup>-1</sup>. The liquid product was collected every 12 h at each reaction condition and analysed by a gas chromatograph-mass spectrometer (GC-MS) (Agilent 7890A-5975C), the GC part of GC-MS equipped with a flame ionization detector (FID). The gaseous product was analysed every 12 h online by a GC (Agilent 7890A) equipped with a TCD. The catalytic performance of  $CO_2$  hydrogenation reaction was evaluated by conversion of  $CO_2(C_{CO_2})$  and selectivity of major products (S<sub>P</sub>) according to Eqs. (1–2)

$$C_{CO_2}(\%) = \frac{Moles \ of \ CO_2(in) - moles \ of \ CO_2(out)}{Moles \ of \ CO_2(in)} \times 100\% \tag{1}$$

$$Sproduct(\%) = \frac{Carbon number of moles for product}{Moles of CO_2(in) - moles of CO_2(out)} \times 100\%$$
(2)

#### 1.3 Characterization of the catalysts

The Brunauer-Emmet-Teller (BET) surface area  $(S_{BET})$ , pore volume  $(V_P)$ , and average pore diameter (D<sub>p</sub>) of the catalysts were detected by the adsorption and desorption isotherms of nitrogen at 76 K using a ASAP 2020M analyzer (Micromeritics US). Powder X-ray diffraction (XRD) patterns of the catalysts were obtained using a X' Pert PRO X-ray diffractometer (PANnalytical US) with Cu K $\alpha$  radiation operated at 40 kV and 40 mA. H<sub>2</sub>-temperature program reduction (H<sub>2</sub>-TPR) was carried out in a quarts tube reactor with a 5.0%  $H_2$ /Ar as the reduction gas. The samples (50 mg) were reduced in a flow of 40 mL/min reduction especially gas at a rate of 10 °C/min from 25 °C to 700  $^{\circ}$ C with a programmable temperature controller. The consumed gas was monitored by a thermal conductivity detector (TCD). Transmission electron microscopy (TEM) and HRTEM images were taken with a Tecnai-G2-F30 field emission transmission electron microscope operating at accelerating voltage of 300 kV. X- ray photoelectron spectroscopy (XPS) analysis was obtained using a VG Scientific ESCALAB 250Xi photoelectron spectrometer with an Al  $K_{\alpha}$  X-ray resource. Binding energies were calibrated by the C1s binding energy of 284.7 eV.

# 2 Results and discussion

#### 2.1 Textural Properties

The summary of surface area and pore volume for all calcined and reduced catalysts are given in Table 1 and Table 2. Table 1 showed that the incorporation of K promoter significantly changed the textural properties of Cu-Fe-Zn catalyst. Incorporation of K results in the decreasing pore volume and BET surface area, whereas the increasing pore diameter. It indicated that low addition of K promoter decreased the surface area of the Cu-Fe-Zn composite catalyst. Subsequently, accompanied with a gradually increasing K content, the BET surface area of the samples presents a slowly increase, while the average pore diameter decreases slightly. Table 2 also showed the textural properties of catalysts after reduction. It indicated that the specific area and pore characteristics did not change significantly. The above results imply that the increasing of K content may improve anti-sintering properties of the catalyst precursor and promote the dispersion of catalyst particles, leading to a slight increase of surface area. The formation of ZnFe2O4 species (XRD, Fig. 1 and TEM (Fig. 2) also support this conclusion. The  $ZnFe_2O_4$ species can promote the dispersion of catalyst particles by inhibiting sintering during processes of thermal treatment and activation in H2/CO2 reactant mixtures<sup>[30]</sup>.

Catalysts	$S_{BET} / (m^2 \cdot g^{-1})^a$	$V_{P}/(cm^{3} \cdot g^{-1})^{b}$	$D_P/nm^c$	
Cu-Fe-Zn	38.76	5.3×10 <sup>-4</sup>	4.96	
K <sub>0.05</sub> ∕ Cu-Fe-Zn	33.83	4.2×10 <sup>-4</sup>	5.49	
K <sub>0.1</sub> ∕ Cu-Fe-Zn	63.09	7.7×10 <sup>-4</sup>	4.81	
K <sub>0.15</sub> ∕ Cu-Fe-Zn	67.10	8.9×10 <sup>-4</sup>	4.71	
K <sub>0.2</sub> / Cu-Fe-Zn	71.04	9.6×10 <sup>-4</sup>	4.63	

Table 1 Physical properties of the calcined catalysts

a. Obtained from BET method; b. Total pore volume taken from the nitrogen adsorption volume at a relative pressure  $(P/P_0)$  of 0.99; c. Average pore diameter determined from the adsorption data of the isotherms using BJH method.

Table 2 Physical properties of the reduced catalysts				
Catalysts	$S_{BET}/(m^2 \cdot g^{-1})^a$	$V_{p}/(cm^{3} \cdot g^{-1})^{b}$	$D_p/nm^c$	
Cu-Fe-Zn	39.75	5.4×10 <sup>-4</sup>	4.86	
$K_{0.05}$ / Cu-Fe-Zn	34.84	4.3×10 <sup>-4</sup>	5.39	
K <sub>0.1</sub> / Cu-Fe-Zn	64.11	$7.9 \times 10^{-4}$	4.71	

68.31

72.44

a. Obtained from BET method; b. Total pore volume taken from the nitrogen adsorption volume at a relative pressure  $(P/P_0)$  of 0.99; c. Average pore diameter determined from the adsorption data of the isotherms using BJH method.

 $9.2 \times 10^{-4}$ 

9.9×10<sup>-4</sup>



Fig. 1 XRD patterns of reduced  $K_{0.1}$ /Cu-Fe-Zn(a), reduced Cu-Fe-Zn(b), used  $K_{0.1}$ /Cu-Fe-Zn(c) and used Cu-Fe-Zn(d)

#### 2.2 XRD analysis

Bulk phases of K<sub>0.1</sub>/Cu-Fe-Zn and Cu-Fe-Zn catalysts after reduction and used Cu-Fe-Zn and K<sub>0.1</sub>/Cu-Fe-Zn catalysts were detected by XRD and were shown in Fig. 1. The reduced Cu-Fe-Zn catalyst showed the diffraction peaks at  $2\theta$  values of  $31.8^\circ$ ,  $34.4^\circ$ ,  $36.3^\circ$ and 47.5°, which belonged to ZnO (JFACDS NO.36-1451), the diffraction peaks appeared at  $2\theta$  values of 44.7°, 65.2°, 82.5° (JFACDS NO. 87-0722) and 43.3°, 50.5°, 74.1° (JFACDS NO.85-1326) were corresponded to Fe, and Cu species, respectively<sup>[31]</sup>. From the XRD spectrum of reduced K<sub>0.1</sub>/Cu-Fe-Zn (Fig. 1a), we can find that K addition does not change phase structures of metal species over the catalysts. However, according to the XRD spectra of spent Cu-Fe-Zn (Fig. 1d) after reaction at 350 °C, the new diffraction peaks at 18.3°, 35.5°, 62.5° and 30.0°,

53. 3° were observed except for the previously mentioned diffraction peaks in XRD spectrum of used Cu-Fe-Zn catalyst, which corresponded to  $\mathrm{Fe}_3\mathrm{O}_4$  and Zn- $Fe_2O_4$ , respectively. Meanwhile, the XRD spectrum of used K<sub>0.1</sub>/Cu-Fe-Zn catalyst is similar to that of fresh K<sub>0.1</sub>/Cu-Fe-Zn catalyst. This result indicated that the moderate amount of potassium promoter could maintain the structure of catalyst. Although the  $ZnFe_2O_4$  signal was strong in the XRD spectrum of used Cu-Fe-Zn, the weak signals of ZnFe<sub>2</sub>O<sub>4</sub> were still appeared the K-contained samples, for examples around 50 degree in sample c, might due to the high dispersion of ZnFe<sub>2</sub>O<sub>4</sub> in K-contained samples. In addition, the diffraction peaks of Fe in used K<sub>0.1</sub>/Cu-Fe-Zn catalyst and Cu in used Cu-Fe-Zn catalyst were observed. These results are in accordance with the TEM results in Fig.2, activity test in Fig. 5 and stability tests in Fig. 6. No diffraction peak characteristic of potassium was observed because of low addition amount. Above results indicated that the incorporation of suitable potassium promoter could improve the stability and dispersion of catalyst particles.

#### 2.3 TEM analysis

According to the BET characterization (Table 1), addition of potassium significant changed the surface area and pore volume of the catalysts. XRD spectra of catalysts indicated that the appropriate addition of potassium promoter could improve the stability and dispersion of catalyst particles. In order to gain more insight on morphological changes, the TEM images of reduced prepared Cu-Fe-Zn, K<sub>0.1</sub>/Cu-Fe-Zn catalysts and used Cu-Fe-Zn, K<sub>0.1</sub>/Cu-Fe-Zn catalysts are

4.62

4.53

K<sub>0.15</sub>/ Cu-Fe-Zn

K<sub>0.2</sub>/ Cu-Fe-Zn



Fig. 2 TEM images of reduced Cu-Fe-Zn(a), used Cu-Fe-Zn(c), reduced K<sub>0.1</sub>/Cu-Fe-Zn (e) and used K<sub>0.1</sub>/Cu-Fe-Zn (g); HRTEM images of reduced Cu-Fe-Zn(b), used Cu-Fe-Zn (d), reduced K<sub>0.1</sub>/Cu-Fe-Zn (f) and used K<sub>0.1</sub>/Cu-Fe-Zn (h); EDX of image and peaks of reduced Cu-Fe-Zn (A) and reduced K<sub>0.1</sub>/Cu-Fe-Zn (B) catalyst.

shown in Fig. 2. TEM image shows the Cu-Fe-Zn catalyst particles is in small pieces (Fig. 2a), but slightly agglomerative phenomenon occurred. From the Fig. 2e of  $K_{0.1}$ /Cu-Fe-Zn catalyst, the problem of

catalyst aggregation has been effectively suppressed. Compared to the Cu-Fe-Zn catalyst, the catalyst of  $K_{0.\,1}/{\rm Cu-Fe-Zn}$  was higher dispersed with small particles about 10 nm.

For the used Cu-Fe-Zn catalyst, more  $Fe_3O_4$  species were exposed on the surface of the catalyst, which might lead to the decrease of catalytic activity. After addition of potassium promoter, the catalyst sintering problem was improved effectively and the catalyst particles were dispersed uniformly. Fig. 2A, Fig. 2B are the analysis for elemental composition of Cu-Fe-Zn and  $K_{0.1}/Cu$ -Fe-Zn catalysts. These results were in accordance with those results of XRD characterization.

#### 2.4 H<sub>2</sub>-TPR analysis

Fig. 3 depicts the  $H_2$ -TPR analysis of all five catalysts. Three overlapped peaks of  $H_2$  consumption were



Fig. 3 H<sub>2</sub>-TPR profiles of the catalysts
a. Cu-Fe-Zn; b. K<sub>0.05</sub>/Cu-Fe-Zn; c. K<sub>0.1</sub>/Cu-Fe-Zn;
d. K<sub>0.15</sub>/Cu-Fe-Zn; e. K<sub>0.2</sub>/Cu-Fe-Zn

appeared on all samples. The reduction peak centered 250 ~ 350 °C is related to the reduction of CuO to Cu and  $\text{ZnFe}_2O_4$  to  $\text{Fe}_3O_4^{[32]}$ . In addition, a broad peak appeared at 300 ~ 500 °C on the reduction curves of different K-promoted catalysts was corresponding to the reduction of  $\text{Fe}_3O_4$  to Fe via FeO. FeO is not expected to appear in the TPR spectra as it has been shown that FeO is unstable compared to Fe and  $\text{Fe}_3O_4^{[33]}$ . From the Fig. 3, we could find that the hydrogen consumption increased significantly during the process of reduction of catalysts with the increased of potassium promoter, and the degree of reduction of the catalyst also increased. This was contrary to the report of Li, in which potassium inhibited reduction of iron catalyst when  $\text{H}_2$  was used as the reducing  $\text{agent}^{[34-37]}$ . This may be the

result of the strong interaction between potassium oxide and metal oxide, which suppresses the adsorption of hydrogen on catalyst surface, In general, potassium is considered as an electronic promoter, which may suppress the  $H_2$  chemisorption on the catalyst surface, therefore results in a higher reduction temperature<sup>[38-41]</sup>. From the point of view in hydrogen consumption and degree of reduction of the catalyst, the K promoter increased dispersion and surface area of catalysts.

#### 2.5 XPS analysis

In order to further understand the change of catalysts before and after reaction, XPS characterizations have been performed for Cu-Fe-Zn (reduced and used) and  $K_{0.1}/\mbox{Cu-Fe-Zn}$  (reduced and used) catalysts. Fig. 4A showed the Cu 2p XPS spectra of above four catalysts. The peaks with binding energies at 932.7, 952.5, 934.4 and 954.4 eV were assigned to Cu  $2p_{3/2}(Cu)$ , Cu  $2p_{1/2}(Cu)$ , Cu  $2p_{3/2}(CuO)$  and  $Cu 2p_{1/2}(CuO)$ , respectively. Fig. 4B showed the Fe 2p XPS spectra of above four catalysts. The peaks with binding energies at 707.1, 720.1, 708.2, 721.2 eV could be assigned to Fe  $2p_{3/2}(\,{\rm Fe})$  , Fe  $2p_{1/2}\,,$  Fe  $2p_{3/2}$ (  $\mathrm{Fe_3O_4}$  ) and Fe  $\mathrm{2p_{1/2}}$  (  $\mathrm{Fe_3O_4}$  ), respectively. The peaks with binding energies at 1 021.8, 1 044.2 eV were assigned to  $\text{Zn } 2p_{3/2}(\text{ZnO})$ ,  $\text{Zn } 2p_{1/2}(\text{ZnO})$ , and the peaks with energies at 292.9, 295.5 eV were assigned to  $K 2p_{3/2}(K_2O)$ ,  $K 2p_{1/2}(K_2O)$ . Those XPS results indicated that the addition of potassium did no significantly change the valence state over the catalyst surface before reaction, but corresponding signals varied remarkably after the reaction.

Metallic Cu and metallic Fe were presented on the surface of both Cu-Fe-Zn and  $K_{0.1}/Cu$ -Fe-Zn catalysts before reaction. However, CuO and Fe<sub>3</sub>O<sub>4</sub> have been observed on the surface of used Cu-Fe-Zn catalyst, meanwhile, metallic state of Cu and Fe were still existed largely on the surface of used K<sub>0.1</sub>/Cu-Fe-Zn catalyst. These results were strongly supported by XRD characterizations. The XPS spectra of Zn 2p indicated that Zn was in the +2 oxidation state on the surface of all catalysts. In ad-



Fig. 4 XPS spectra of the catalysts (A): Cu2p XPS spectra; (B): Fe2p XPS spectra; (C): Zn2p XPS spectra;
(D) K2p XPS spectra. a. reduced K<sub>0.1</sub>/Cu-Fe-Zn; b. reduced Cu-Fe-Zn; c. used K<sub>0.1</sub>/Cu-Fe-Zn; d. used Cu-Fe-Zn) Reaction conditions: H<sub>2</sub>/CO<sub>2</sub> = 3 : 1, GHSV = 7,200 h<sup>-1</sup>, 2.0 MPa, 350 °C.

dition, potassium promoter could depress the oxidation of Cu and Fe during the  $CO_2$  hydrogenation and it might be another reason of the change of product distribution over Cu-Fe-Zn and  $K_{0.1}/Cu$ -Fe-Zn catalysts.

#### 2.6 Catalytic activity and selectivity

The tests of CO<sub>2</sub> hydrogenation reaction of all five catalysts were performed at 2. 0 MPa, 7 200 h<sup>-1</sup> and  $H_2/CO_2 = 3 \div 1$ . CO<sub>2</sub> conversion and selectivities towards major product are presented in Fig. 5. For Cu-Fe-Zn catalyst without adding potassium promoter (Fig. 5a), the conversion of CO<sub>2</sub> was around 5% when the reaction temperature was in the range of 200 to 250 °C. The conversion of CO<sub>2</sub> increased obviously as the increasing of reaction temperature, the conversion of  $CO_2$  reached the highest value of 58.9% at 350 °C. Beyond 350 °C, a gradually decrease of catalyst activity was observed with increasing reaction temperature. The conversion of  $CO_2$  declined to 51.1% at 500 °C.

As shown in Fig. 5a, the  $CO_2$  conversion increased to a maximum with the increase of potassium addition at  $K_{0.1}$ /Cu-Fe-Zn catalyst. Further increasing potassium content, the decrease of activity was observed.  $K_{0.1}$ /Cu-Fe-Zn showed the highest  $CO_2$  conversion (68.7%) at 350 °C among all five catalysts. The previous reference paper reported<sup>[42]</sup> that  $CO_2$  conversion was enhanced with the increased of K content, because K could enhance  $CO_2$  adsorption. However, other literatures reported that over-loading potassium in

catalyst led to the deposition of carbon on the surface, which resulted in the formation of immobile carbon on

the active surface sites and the decline in the hydrogenation  $activity^{[42-48]}$ .



Fig. 5 The CO<sub>2</sub> conversion (a), product distribution over different catalyst at 350  $^{\circ}$ C (b).

The impact of potassium promoter on the product distribution is presented in Fig. 5b. It can be found that the selectivity of ethanol decreased gradually, whereas that of total oxygen compounds and total alcohols presented a slowly increasing trend with increasing potassium concentration. Fig. 5b revealed that the selectivity to ethanol decreased and selectivity to higher alcohols and oxygen containing compounds increased with increase in potassium incorporation. The main products shift from ethanol to higher alcohols and oxygen containing compounds like acetone, acetic acid. The increase of potassium content may increase chain growth probability of product. This might due to the increased CO<sub>2</sub> and lowered H2 surface coverage caused by introduction of alkali metal promoter  $K^{[45, 49]}$ . In addition, the change of the product distribution might be caused by the changes in the structure of catalyst during the reaction process, which was further supported by XRD and XPS results of used catalysts.

#### 2.7 Stability tests of catalysts

Fig. 6 showed the stability tests of catalysts Cu-Fe-Zn and  $K_{0.1}$ /Cu-Fe-Zn under same reaction conditions. For the Cu-Fe-Zn catalyst, the CO<sub>2</sub> conversion reached the highest value of 58.9% in the early stage of stability test, and then declined slowly when the reaction time exceeded 50 h, the CO<sub>2</sub> conversion decreased to 55% when the reaction time over 100 h. However, correspondingly, for the  $K_{0.1}$ /Cu-Fe-Zn catalyst, the CO<sub>2</sub> conversion still maintained at high level around 68.7% after 100 h.



Fig. 6 Stability tests over Cu-Fe-Zn and  $K_{0.1}$ /Cu-Fe-Zn catalysts Reaction conditions:  $H_2$ /CO<sub>2</sub> = 3 : 1, GHSV = 7, 200 h<sup>-1</sup>, 2.0 MPa, 350 °C.

# 2.8 Proposed reaction paths of CO<sub>2</sub> hydrogenation over Cu-Fe-Zn and K<sub>x</sub>/Cu-Fe-Zn

The CO<sub>2</sub> hydrogenation reaction process over  $K_x/$ Cu-Fe-Zn catalytic system can be explained in terms of Scheme 1. Copper is known to be the major active element for catalytic hydrogenation reaction of CO<sub>2</sub>, which facilitates the associative adsorption of CO<sub>2</sub> and dissociative adsorption of H<sub>2</sub>. Iron can improve the stability of



Scheme 1 Proposed reaction mechanism of CO\_ hydrogenation over Cu-Fe-Zn and  $\rm K_{x}/\rm Cu-Fe-Zn$ 

active species of the catalysts, and zinc oxide can improve the dispersion and stabilization of copper<sup>[21, 50]</sup>. Under the reaction condition, the CO<sub>2</sub> molecule and H<sub>2</sub> molecule adsorbed on the catalyst surface, produce CO via reverse water gas shift (RWGS) reaction then form carbon species (COads). For the Cu-Fe-Zn catalyst without K promoter, the carbon species (COads) transferred over the catalyst surface and react with H<sub>2</sub> to produce ethanol through formate intermediate. For the K<sub>x</sub>/Cu-Fe-Zn catalyst, incorporated K may strengthen COads chemisorption and weaken H2 chemisorption on the catalyst surface, as a result, the amount of carbon species (COads) absorbed on the catalyst surface increases, which leads to a high concentration ratio of COads to H2<sup>[24]</sup>. In addition, alkali metal promoter K increased the basicity of the catalyst, which may enhance the adsorption of CO<sub>2</sub> over the surface of catalyst to produce higher alcohols and oxygen containing compounds. For the K-added catalysts, Fe was supposed to increase the carbon chain of products similar to F-T synthesis reaction. The main products shift from ethanol to higher alcohols and oxygen containing compounds was observed with the incorporation of potassium promoter.

## **3** Conclusions

In the present study,  $CO_2$  hydrogenation was carried out over Cu-Fe-Zn catalyst promoted by K. Results indicated that K affected the textural property of catalysts, as well catalytic activity and product distribution remarkably. The addition of K facilitated the better dispersion of metal oxide and increased the BET surface of catalysts. In the hydrogenation reaction, conversion of  $CO_2$  was mainly controlled by temperature while the product distribution and selectivity were largely influenced by the relative amount of K promoters and operating conditions. A maximum activity and stability was obtained over  $K_{0,1}$ /Cu-Fe-Zn catalyst at 350 °C, the conversion of  $CO_2$  reached 68.7%. Further increase K addition in Cu-Fe-Zn catalysts, the conversion of  $CO_2$  declined slightly and the product distribution shifted from ethanol to oxygen containing compounds and higher alcohols.

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# K助剂对催化剂 Cu-Fe-Zn 二氧化碳加氢 反应产物分布的调整

李 博<sup>1,2</sup>, 甄文龙<sup>1.2</sup>, 吕功煊<sup>2\*</sup>, 马建泰<sup>1</sup>

(1. 兰州大学 化学化工学院, 甘肃 兰州 730000;

2. 中国科学院兰州化学物理研究所 羰基合成与选择氧化国家重点实验室, 甘肃 兰州 730000)

**摘要:**用共沉淀法和浸渍法制备了一系列过渡金属复合物催化剂 K<sub>x</sub>/Cu-Fe-Zn,通过对催化剂进行了 BET, H<sub>2</sub>-TPR, XRD, XPS, TEM 等一系列物理化学性质的表征来探究了助剂 K 对催化剂的比表面积、还原行为、结构 特性以及形貌等方面的影响.在固定床反应器上研究了碱金属助剂 K 的浸渍量以及温度对 CO<sub>2</sub> 加氢反应的催化 活性,稳定性以及对产物分布的影响.研究发现,当温度为 350 ℃,助剂 K 的浸渍量为 K<sub>0.1</sub>/Cu-Fe-Zn 时,催化剂 的催化活性达到最高,CO<sub>2</sub> 的转化率可以达到 68.7%,进一步增加催化剂中 K 的含量时,催化剂的催化活性出现 缓慢下降趋势.研究还发现随着助剂 K 的浸渍量的增加,CO<sub>2</sub> 加氢反应中大分子量化合物增加,碳链增长,并且 有大量高级醇和含氧化合物的形成.我们还讨论了在助剂 K 存在下催化剂上 CO<sub>2</sub> 加氢反应机理. 关键词: K 助剂; CO<sub>2</sub>; 加氢; Cu-Fe-Zn 催化剂