

Short Communication

Influences of K and Cu on coprecipitated FeZn catalysts for Fischer–Tropsch reaction

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ABSTRACT

Catalyst KC/FZ25, promoted by K and Cu simultaneously, has stable CO conversion when it was used for Fischer–Tropsch reaction. The reasons are given based on the results of N₂ physisorption, XRD and XPS. Combined with the understanding from our previous works, the assembly of Zn, K and Cu is responsible for the improvement which is independent of the program used to prepare catalysts.

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1. Introduction

Fischer–Tropsch (FT) reaction refers to producing hydrocarbons from syngas (mixture of CO and H₂) with catalysts. The product of FT reaction on iron-based catalysts can be adjusted by changing reaction parameters [1–10], such as CO/H₂ ratio in syngas, the property and quantity of promoters, reaction temperature and reactor type, etc. As a result, FT reaction using iron-based catalysts is able to supply products desired by the market. However, the activity of iron catalysts is easily decreased by carbon deposition [5,11–13], oxidation of active sites [14,15], poisoning from sulfur [5,10–12] and so on. This makes it difficult to keep constant commercial FT reaction because the product selectivity changes with syngas conversion [16].

We studied the effects of Zn, K and Cu on the reactive performance of precipitated iron-based catalysts [17–21]. The deactivation of precipitated iron-based catalysts is related to the oxidation of active sites by water (a byproduct of FT reaction) rather than carbon deposition on catalysts [17,18]. It is found that the assembly of Zn, K and Cu can improve the reactive stability of studied catalysts in spite of the promoters are impregnated to or mechanically mixed with iron-based catalyst. In order to verify if the improvement is independent of the method used to prepare iron catalysts, it is worthy of to prepare the catalysts in new program. Recently, Zn was firstly introduced into iron-based catalyst by co-precipitation, then K and Cu were impregnated to the FeZn precursor. The structure and performance of the coprecipitated FeZn catalysts are given in the following parts.

2. Experimental

2.1. Catalyst preparation

The precursor of catalyst was prepared by precipitating mixed solution of Fe(NO₃)₃ and Zn(NO₃)₂ with (NH₄)₂CO₃ solution. Then, the precipitate was irradiated by ultrasound. The precipitate is called as FZ25 (the atomic ratio of Zn/Fe is 1/4) after it was dried and calcined. Catalyst Fe was prepared in the same program. Then, FZ25 was successively impregnated with one of K₂CO₃ (K) or Cu(NO₃)₂ (C) solution and endured the same drying and calcination used for FZ25. They are expressed as K/FZ25, C/FZ25 and KC/FZ25. The mass ratios of impregnated K and Cu are 2 wt.%, and 4 wt.%, respectively.

Some of the oxidized catalysts were reduced by CO and then passivated by O₂ (1%)/He. They are referred to as reduced catalyst and marked with R in the beginning. The catalysts after FT reaction are named as used catalysts and indicated with U in the beginning.

2.2. Activity test and product analysis

The activity of catalysts was tested in a stainless steel fixed bed reactor. The program and parameter for both of activity test and product analysis have been described in [17,18].

2.3. Characterization

The BET surface area was measured by Autosorb 1 (Quantachrome Inc.) using N₂ as adsorbate under temperature of liquid nitrogen. XPS analysis was done by ESCA 750 (Shimadzu LTD.) using Mg K α radiation. The working volt was 7 kV and electric current was 30 mA. The

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binding energy of C 1s (285.0 eV) was used to calibrate the peak position of other elements. XRD pattern was obtained from MiniFlex (Rigaku Co.). Cu K α radiation was used as X-ray source. The working electric current was 15 mA and volt was 30 kV.

3. Results and discussion

3.1. Catalyst structure

The BET surface area and pore structure of some oxidized catalysts are listed in Table 1. FZ25 has bigger surface area than catalyst Fe. This is consistent with the results of Li et al. [22]. They found that Fe₂O₃–Zn–K–Cu surface areas increased monotonically with raised Zn/Fe ratio.

After FZ25 was promoted, the surface area and pore volume of K/FZ25, C/FZ25 and KC/FZ25 are decreased. There are two possible factors responsible for the changes. The first one is that water is used as solvent in the process of impregnation. Because water has high surface tension, pore structure, especially in smaller diameter, is destroyed when intrapore water is removed by drying [23]. It makes the loss of catalyst surface area. The second one is the distribution of promoter K and Cu in the catalysts. According to Table 1, K is stronger than Cu to diminish the surface area and pore volume of corresponding catalysts. This phenomenon is related to the atomic size of K and Cu. The radius of K¹⁺ (1.33 Å) is much larger than that of Fe²⁺/Fe³⁺ (0.76/0.64 Å), Zn²⁺ (0.74 Å) and Cu²⁺ (0.72 Å). The impregnated K mainly distributes on the surface of catalyst FZ25. It is easy to shrink pore diameter, even block off minor pores in catalyst. Thus, N₂ molecule is prevented to enter the inner of these pores in the experiment of N₂ adsorption at low temperature. It results in small measured surface area and pore volume.

The surface area of Fe₂O₃–Zn promoted with K and/or Cu [22] is higher than that of FZ25-based catalysts. This is the result of different methods to prepare catalyst. The Fe–Zn precipitate was obtained at constant pH of 7.0 \pm 0.1 [22], while we prepared FeZn precipitate by adding (NH₄)₂CO₃ solution quickly into the Fe(NO₃)₃ and Zn(NO₃)₂ solutions and the precipitate was irradiated by ultrasound. Ultrasonic irradiation brings forth the phenomena of “acoustic cavitation” that involves the formation, growth and collapse of bubbles in the liquid medium. This violent collapse of bubbles generates high temperature (several thousands of degrees) and high pressure (hundreds of atmospheres) [24]. The temperature and pressure influence precipitate's texture. The vestige of ultrasonic irradiation may be kept in catalyst calcined from the precipitate. We have compared the influence of ultrasonic irradiation on catalyst structure. The catalyst irradiated by ultrasound has bigger average pore diameter and smaller BET surface area than catalyst from unirradiated precipitate which can be seen from the values of catalyst Fe and Fe^a in Table 1.

Different surface areas mean different dispersive degrees of iron atoms. It also influences the dispersing state of promoters. As a result, the interaction among iron and promoters is changed.

3.2. XRD analysis

The XRD pattern of some reduced and used catalysts is shown in Figs. 1 and 2, respectively. The appeared crystal phases include χ -Fe₂C,

χ -Fe_{2.5}C, FeC, Fe₅C₂, Fe₃C, C, Fe₃O₄ and ZnFe₂O₄. Identification of exact iron carbide forms is usually difficult because of the overlapping of their diffraction peaks [25]. So, FeC_x is used to represent various iron carbides in Figs. 1 and 2. The same difficulty happened for the definite assignment of Fe₃O₄ and ZnFe₂O₄ phases. Because the H₂-TPR profile (not shown) clearly verified the coexistence of Fe₃O₄ and ZnFe₂O₄ in catalyst FZ25, the Fe₃O₄ and ZnFe₂O₄ phases are marked by the help of JCPDS card #19-629 and #22-1012, respectively.

In Fig. 1, most peaks are assigned to iron carbides for all the four catalysts, but the iron carbides in these catalysts have different crystalline structures which are reflected from the inconsistent peak position. Crystal carbon is found in catalysts RFe, RFZ25 and RK/FZ25. It is probably formed by the Boudouard reaction in CO reduction. On the contrary, Fe₃O₄ and ZnFe₂O₄ phases are detected in RKC/FZ25. We had reported the reduction process in CO of precipitated iron-based catalysts [18]. The carburization of Fe₃O₄ is evidently inhibited for the catalysts promoted by Zn, K and Cu simultaneously. It may result that some Fe₃O₄ and ZnFe₂O₄ phases remained in RKC/FZ25.

As disclosed in Fig. 2, there are evident Fe₃O₄ and ZnFe₂O₄ phases in UFe and UFZ25. They are from the oxidation of some iron carbides during FT reaction by H₂O [14,17,18]. However, the Fe₃O₄ and ZnFe₂O₄ in RKC/FZ25 disappeared after FT reaction as illustrated by UKC/FZ25. Such phase shift can increase active sites for FT reaction. Crystal carbon appears in UKC/FZ25. It may be the deposited carbon and the carbon containing in the wax remained in the used catalysts (referred by JCPDS card #26-1081). Based on the results in Fig. 4, it can be concluded that the deposited carbon has not arrived at the degree to impair the reactive performance of catalyst KC/FZ25 [18].

3.3. XPS characterization

Some oxidized and reduced catalysts are analyzed by XPS. Fig. 3 is the spectra of Fe 2P of these catalysts. Referencing to the binding energy of element iron in catalysts Fe and FZ25, surface iron atom exists in two states, i.e. metallic and oxidized in the reduced catalysts. The coexistence of iron species in different states was also found by other studies. Iron carbides and Fe₃O₄ were observed after 100Fe/5Cu/4.2K/11SiO₂ catalyst was activated by CO [26]. In the case of H₂ reduction and CO pretreatment, a fraction of the surface iron remained in the form of unreduced Fe²⁺/Fe³⁺ species [14]. Li et al. [22] studied the effects of Cu and K promoters on the structure, reduction and carburization. They found that Cu and K increased the rates of reduction and carburization of Fe–Zn oxide precursors, and of nucleation of reduced Fe-containing phases (Fe₃O₄ or FeC_x) when CO was used as the

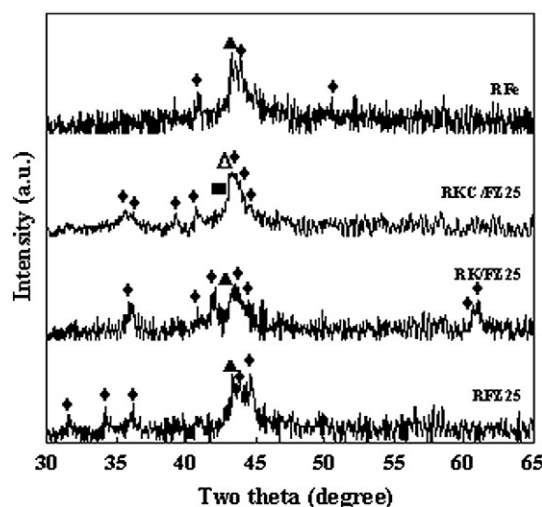


Fig. 1. XRD pattern of reduced catalysts ◆: FeC_x, ▲: Fe₃O₄, ■: ZnFe₂O₄.

Table 1
BET surface area and pore size.

Catalyst	FZ25	K/FZ25	C/FZ25	KC/FZ25	Fe	Fe ^a
Surface area (m ² /g)	51.7	43.3	46.8	29.3	43.5	61.2
Pore volume ^b (cm ³ /g)	0.175	0.118	0.153	0.117	0.216	0.22
Pore diameter ^b (nm)	11.5	8.1	9.9	10	19.9	9.1

^a The precipitate was not irradiated by ultrasound.

^b It is calculated by BJH method from the desorption branch.

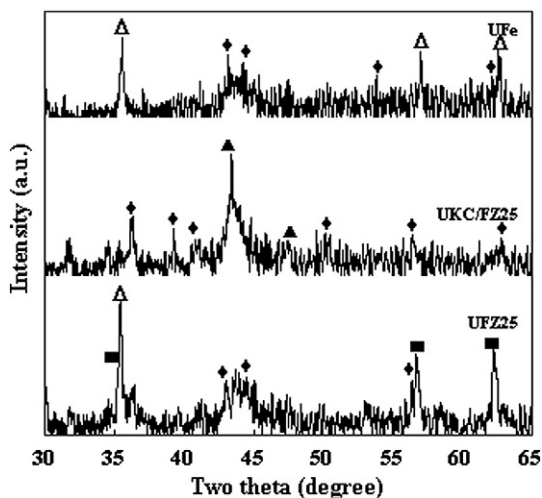


Fig. 2. XRD pattern of used catalysts ♦: FeC_x , ▲: C, △: Fe_3O_4 , and ■: ZnFe_2O_4 .

reactant. The oxidized iron in the reduced catalysts may result from passivation by O_2 [27], too.

Comparing the Fe $2\text{P}_{3/2}$ peak strength of oxidized and metallic iron in Fig. 3, it can be found that Zn promotes the reduction of surface iron species (RFZ25 vs. RFe). The BET surface area of FZ25 is bigger than that of Fe (Table 1). It means that the number of exposed iron atom of FZ25 is more than that of catalyst Fe. After the reduction by CO, more metallic iron atom appears on FZ25 than catalyst Fe. RK/FZ25 has lower reduction degree than RFZ25, but RC/FZ25 has a Fe 2P spectrum similar to that of RFZ25. Cu is thought as one promoter to make the reduction of oxidized iron easily [8,9,20].

3.4. Activity of promoted FZ25 catalysts

The activity of promoted FeZn catalysts is shown in Fig. 4. The CO conversion of FZ25 decreases with time on stream. The addition of Cu to FZ25 (catalyst C/FZ25) does not show any improvement. KC/FZ25 possesses more evident increasing CO conversion than K/FZ25 during activity test.

In contrast with FZ25, Cu increases the CH_4 selectivity, while K decreases it. The CH_4 selectivity of the four catalysts is varied in the order of $\text{C/FZ25} > \text{FZ25} > \text{KC/FZ25} \approx \text{K/FZ25}$. The sequence of

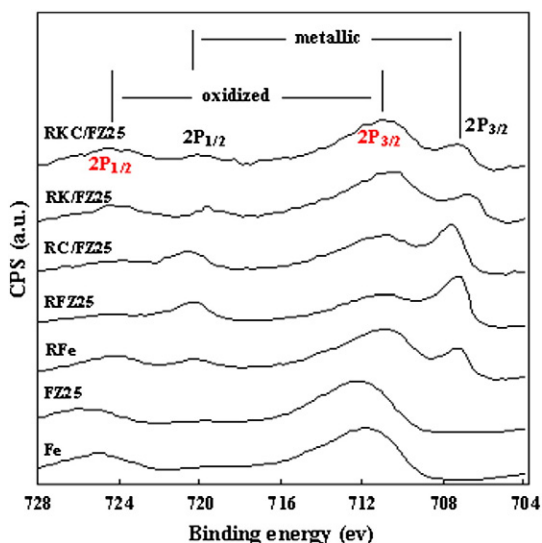


Fig. 3. XPS spectra of Fe 2P.

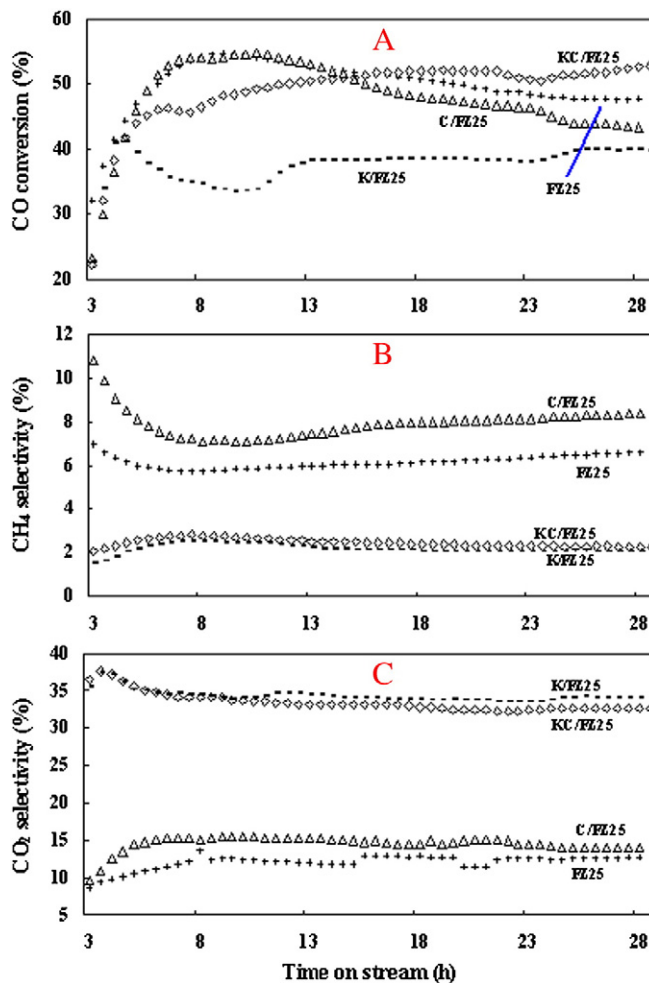


Fig. 4. The activity of catalyst FZ25 and promoted FZ25 catalyst $\text{H}_2/\text{CO} = 2$, $P = 1.6 \text{ MPa}$, $T = 503 \text{ K}$.

CO_2 selectivity is $\text{K/FZ25} \approx \text{KC/FZ25} > \text{C/FZ25} \approx \text{FZ25}$. The water-gas-shift (WGS) activity is increased if Cu is added onto pure iron catalyst [8], however, this effect does not appear for catalyst C/FZ25 containing Zn. It is well known that K increases CO_2 selectivity [2,8,19–21]. According to Fig. 4, only the effect of K is displayed on the selectivity of CH_4 and CO_2 when K and Cu are used simultaneously.

Thermodynamic data on the metallic iron/iron oxide system are cited that oxidizing condition exists at a $\text{H}_2\text{O}/\text{H}_2$ ratio > 0.03 or a CO_2/CO ratio > 2.8 , and Fe_3O_4 is the stable phase compared to metallic iron [28]. It is thought that water vapor formed during FT reaction is responsible for the oxidation of metallic iron and/or iron carbides to Fe_3O_4 [14]. Krishnamoorthy et al. [2] studied pathways for CO_2 formation during FT reaction on coprecipitated Fe–Zn catalyst promoted with Cu and K. There are two pathways. The primary route is that the adsorbed oxygen formed in the CO dissociation steps required for monomer formation during FT reaction is removed by adsorbed carbon monoxide to form CO_2 . The secondary route is WGS reaction. According to the two mechanisms of CO_2 formation, high CO_2 selectivity is also beneficial to inhibit the oxidation of active site during FT reaction. For FT reaction, high CO_2 selectivity usually corresponds to low H_2O yield [8].

The water content in the catalyst bed can be calculated using the equation given in our previous work [18]. The value of the four catalysts is $\text{FZ25} > \text{C/FZ25} > \text{KC/FZ25} > \text{K/FZ25}$. The water vapor in the catalyst bed of FZ25 and C/FZ25 is higher than the other two catalysts. The possibility of active site oxidation by water is high consequently. XRD results (Figs. 1 and 2) disclose that iron carbides in reduced FZ25

were oxidized into iron oxides during FT reaction. The reappearing of iron oxides is responsible for the activity decline of FZ25 [15].

As shown in Figs. 1 and 2, the remained Fe_3O_4 and ZnFe_2O_4 in reduced KC/FZ25 were transferred into FeC_x during FT reaction. It increases active sites. Correspondingly, increasing CO conversion is observed for KC/FZ25. K/FZ25 has higher surface area than KC/FZ25, but its CO conversion is lower than KC/FZ25. The different trends and levels of CO conversion of the two catalysts cannot be explained from their texture. The differences are decided by the chemical nature of active site related with the dispersing state of promoters. We are trying to understand them in the further works.

4. Conclusions

The zinc coprecipitated with iron increases the surface area and reducibility of catalyst FZ25. Although there are no iron oxides detected in RK/FZ25 by XRD, the XPS result shows oxidized iron existing on the catalyst surface. The addition of K inhibits catalyst surface reduction. There are Fe_3O_4 and ZnFe_2O_4 in reduced KC/FZ25.

Catalyst KC/FZ25 has increasing activity during FT reaction. There are two possible factors deciding the trend. Higher WGS activity is beneficial to prevent the oxidation of active sites by H_2O during FT reaction for KC/FZ25. The conversion of iron oxides into iron carbides can supply new active sites in the reaction.

Acknowledgments

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