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Influence of Addition of ZnO on Property of Fe_2O_3-K_2O System Catalyst for Ethylbenzene Dehydrogenation to Styrene

Chang Xi MIAO*, Ming SHAN

Shanghai Research Institute of Petrochemical Technology, Shanghai 201208

Abstract: The incorporation of ZnO into Fe_2O_3-K_2O system increases its activity, enhances its moisture stability and mechanical strength. The origin of the enhancement in activity and moisture stability is discussed in the light of experimental results obtained by BET, XRD, XPS. It was found that the addition of ZnO to Fe_2O_3-K_2O system strengthens the interaction between Fe_2O_3 and K_2O, reduces the formation temperature of $KFe_{11}O_{17}$ at least by 50 ^oC, and promotes the transformation of Fe^{3+} to Fe^{2+} further.

Keywords: Fe_2O_3-K_2O system, ethylbenzene dehydrogenation, crush strength, moisture stability.

The industrial process for the dehydrogenation of ethylbenzene to styrene is used to make valuable commodity chemicals such as polystyrene and synthetic rubber such as ABS and SB latex, as much as 20 MM tons/yr of styrene monomer are made. Although this process was already commercialized in the 1930's, research and development have continued to improve it, including the development of new catalysts, reactor designs and process routes[1,2]. The catalytic dehydrogenation is carried out over potassium promoted iron-oxide-based catalyst at temperatures around 600 ^oC in the presence of steam. For improvement of the activity or selectivity[3,4], the Fe-K oxide catalyst has been further modified by addition of other promoters such as Cr, Ce, Mo, Mg. Muhler *et al*[5] have conducted a detailed study of the nature of the active phase in the styrene catalyst under real process conditions. They proposed that an equilibrium exists in the solid catalyst, $KFe_{11}O_{17} \rightleftharpoons KFeO_2$, in which $KFeO_2$ is the catalytically active phase. $KFe_{11}O_{17}$ phase acts as storage medium from which the active surface is continuously supplied with potassium ions. In the meantime, $KFe_{11}O_{17}$ is regarded as a very important phase to the moisture stability of Fe_2O_3-K_2O system catalyst[6]. In a recent study, Huerta and Meyer[7] synthesized an iron pillared clay and characterized it with several methods. It indicated that the clay was thermally stable and catalytically active in dehydrogenation of ethylbenzene to styrene. Benzene as byproduct of the process was also observed, due to the solid's higher cracking activity. We extended the previous work to improve activity and stability by adding a small amount of ZnO to the Fe_2O_3-K_2O system catalyst.

Fe_2O_3-K_2O oxide catalysts modified with ZnO were prepared by dry blending

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* E-mail: miaochx@sript.com.cn

appropriate amounts of Fe_2O_3, K_2CO_3 with ZnO, mixed with water to form an extrudable paste, then calcined at different temperatures for 5 h. The contents of K, Zn were fixed at 10 wt.% and 2 wt.% in the form of K_2O and ZnO, respectively.

The ethylbenzene dehydrogenation activity of Fe-K-Zn catalysts was listed in **Table 1**. The weight ratio of the steam to ethylbenzene is 2.0, LHSV is 1.0 h^{-1} and the pressure is maintained at atmosphere. The reaction temperatures are adjusted until the conversion of the ethylbenzene is 70%. The temperature is indicated as "T_{70}". The selectivity to styrene at 70% conversion is indicated as "S_{70}". The reaction temperatures needed for pure Fe_2O_3-K_2O samples are all above 630 ^{o}C, while for the samples contained Zn are only 625 ^{o}C. There is 7～11 ^{o}C difference between samples calcined at the same temperature before and after the addition of ZnO. It indicates the incorporation of ZnO into Fe_2O_3-K_2O system can reduce the dehydrogenation temperature, then affecting its activity and selectivity. In addition, because large amounts of steam are used in styrene production, there is significant potential for exposing the catalyst to moisture at low temperature during start-ups, shutdowns, and upsets. This exposure causes physical degradation of the catalyst, resulting in decrease in catalyst life. We can also find in **Table 1** that crush strength decreases only slightly after water immersion for the sample contains ZnO or pure Fe_2O_3-K_2O calcined at very high temperature such as 900 ^{o}C, otherwise it decreases greatly.

Table 1 Dehydrogenation results and crush strength of samples

Composition	Calcination temperature (^{o}C)	T_{70} (^{o}C)	S_{70} (%)	Crush strength/(N/mm)	
				B*	A*
Fe-K-Zn	750	629	92.1	18. 2	18.0
Fe-K-Zn	800	627	92.3	19.4	19.3
Fe-K-Zn	850	626	92.4	19.6	19.6
Fe-K-Zn	900	624	92.7	20.0	19.8
Fe-K	850	637	89.1	18.0	10.3
Fe-K	900	631	90.2	19.3	19.2

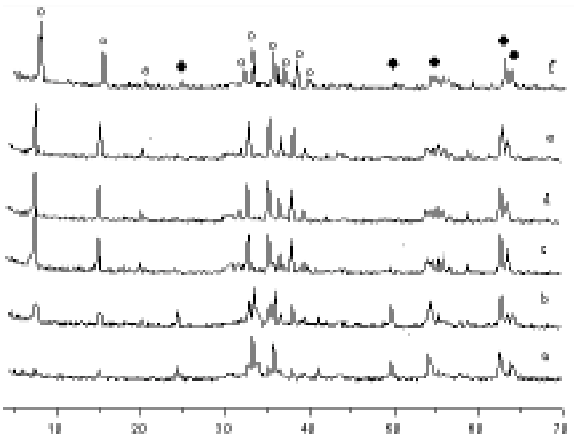
B*-Before water immersion, A*-After water immersion

In order to elucidate the reasons for the enhancement of the catalytic property and the moisture stability through the addition of Zn oxide to Fe_2O_3-K_2O system, some of the typical samples in **Table 1** were characterized using a wide variety of techniques.

The surface areas of samples after calcination at different temperatures were measured. After the incorporation of ZnO into Fe_2O_3-K_2O system the surface areas of the samples do not change very much. The differences between them and that of Fe_2O_3-K_2O sample are smaller than 25%. Therefore, the change in surface area is probably not the main cause leading to the variation in catalytic property and crush strength.

Fe_2O_3-K_2O system may mainly exist in two crystal phases after calcination at high temperatures: a α-Fe_2O_3 phase and a $KFe_{11}O_{17}$ phase which formed by interaction between Fe_2O_3 and K_2O. XRD patters of Fe_2O_3-K_2O samples before and after the incorporation of ZnO were recorded in **Figure 1**. For pure Fe_2O_3-K_2O sample, the formation temperature of $KFe_{11}O_{17}$ phase should be above 800 ^{o}C, and the diffraction peaks of the phase are still rather weak after calcination at 900 °C. After incorporation of Zn the formation temperature decreases by about 50 °C, many $KFe_{11}O_{17}$ phase presents even at 750 °C. As calcination temperature increasing further, the diffraction peaks of the $KFe_{11}O_{17}$ phase become stronger. It means the incorporation of ZnO promotes the formation $KFe_{11}O_{17}$ phase, which is favorable to an increase in the moisture stability and crush strength. The possible reason for the enhancement of stability is that $KFe_{11}O_{17}$ possesses the structure similar to that of K-β-Fe_2O_3, K^+ is hidden in a special spinel structure formed by Fe-O frames. When samples exposed to moisture, K^+ can not be attacked by water molecule, so the existence of $KFe_{11}O_{17}$ phase prevents K^+ loss from frames of catalyst.

Figure 1 XRD patterns of samples



2θ (°)

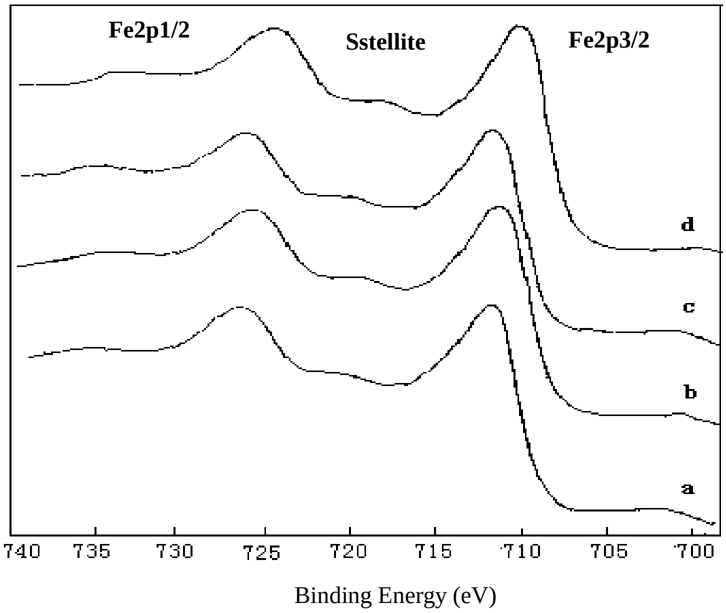
(a) Fe-K-850 (b) Fe-K-900 (c) Fe-K-Zn-750 (d) Fe-K-Zn-800 (e) Fe-K-Zn-850 (f) Fe-K-Zn-900
o $KFe_{11}O_{17}$ phase ♦ Fe_2O_3 phase

Figure 2 shows the Fe_{2p} XPS spectra observed from fresh and used samples. All the spectra of fresh samples show an intense peak at BE of 712 eV due to $2p_{3/2}$ accompanied by a satellite line visible at BE of 720 eV. This spectral feature is similar to that of α-Fe_2O_3. After ethylbenzene dehydrogenation at 620 °C for 48 h, the peaks of $Fe2p_{3/2}$ and their satellites lines shift to lower BE, and the width of satellite line becomes broad, see **Figure 2b,d**. It also can be seen that the shift of the sample with Zn is bigger than that of pure Fe_2O_3-K_2O. This BE shift corresponds to a decrease of Fe^{3+} and an increase of Fe^{2+} of the sample. Hence, the greater the BE shift, the more transformation of Fe^{3+} to Fe^{2+}. It has been reported in the previous work[8] that the dehydrogenation is through the mechanism of Fe^{3+} conversion to Fe^{2+}. This may imply that the incorporation of Zn increases the dehydrogenation rate *via* the conversion of Fe^{3+} to Fe^{2+}.

Conclusion

We used ethylbenzene dehydrogenation, BET, XRD, XPS methods to study the influence

Figure 2 Fe2p XPS spectra of samples



(a) Fresh Fe-K-900 （b）Used Fe-K-900 (c) Fresh Fe-K-Zn-900 （d）Used Fe-K-Zn-900

of addition of ZnO to Fe_2O_3-K_2O system on its properties in details. The addition of ZnO strengthens the interaction between Fe_2O_3 and K_2O, reduces the formation temperature of $KFe_{11}O_{17}$ at least by 50 ^{o}C, and promotes the transformation of Fe^{3+} to Fe^{2+} further. The results may be useful to improve the traditional industry catalyst.

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