

# A Mössbauer spectroscopic study on the action of Ce in the catalyst for dehydrogenation of ethylbenzene to styrene

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**Abstract** Two series of Fe-K catalysts for dehydrogenation of ethylbenzene to styrene were prepared with different amounts and different compounds of the additional element Ce. Mössbauer spectroscopy has been used to determine the Fe compound in the catalyst and to investigate the effect of Ce. The catalytic properties of the catalysts have also been measured. The results show that the element Ce in the catalyst is favorable to form the predecessor of the catalytic active phase, the compound  $\text{KFe}_{11}\text{O}_{17}$  and that the optimal percentage of  $\text{CeO}_2$  is 8%~15% in the catalyst which is favorable to the formation of  $\text{KFe}_{11}\text{O}_{17}$  and to get better catalytic properties.

**Keywords** Dehydrogenation of ethylbenzene · Mössbauer spectroscopy · Catalyst · Ce

## 1 Introduction

The most important catalyst used for dehydrogenation of ethylbenzene to styrene, is an iron-based catalyst. The main original material of the catalyst is ferric oxide ( $\text{Fe}_2\text{O}_3$  or  $\alpha\text{-FeOOH}$ ) and potassium carbonate ( $\text{K}_2\text{CO}_3$ ), in addition to other compounds of elements (Ce, Mg, Ti, Ca, et al). The amount of Ce compounds is more important than that of the compounds of other additional elements. In this work the present form of the Ce element in the catalyst and its catalytic function are investigated. On the other hand, in traditional catalysts the original compound of Ce is cerium nitrate. But this compound will be decomposed into nitrogen-oxides that

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could pollute our environment. So looking for a new substitute of cerium nitrate is also a focus of this work.

In our previous investigation using Mössbauer spectroscopy, it was determined that the fresh catalyst of potassium-promoted iron oxide contains a certain amount of potassium ferrite  $\text{KFe}_{11}\text{O}_{17}$  with the spinel structure, which can be considered as the predecessor of the catalytic active phase [1]. It is also mentioned in other patents [2, 3]. In this work, Mössbauer spectroscopy was used to study the components of the products, especially to study the dependence between the formation of  $\text{KFe}_{11}\text{O}_{17}$  and the amount of  $\text{CeO}_2$  in the catalyst. Combining the Mössbauer spectroscopic results and the catalytic properties of the samples, the optimal amount of Ce could be determined and the best substitute of cerium nitrate could also be selected. This is useful information for manufacturing the industrial catalyst.

## 2 Experimental

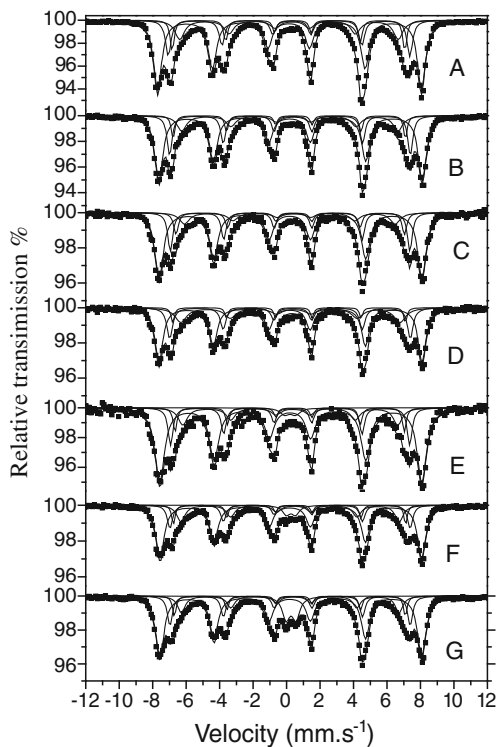
To simplify the investigation, only 4 kinds of original materials,  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{MgO}$  and Ce compounds were used for preparing samples. All raw materials are mixed together and shaped up, then calcinated at a certain temperature. Two series of samples with different amounts of Ce and different precursors of cerium (such as cerium oxalate, cerium nitrate and so on) were prepared.

$^{57}\text{Fe}$  Mössbauer spectra were recorded at room temperature using a constant acceleration spectrometer with a  $9.2 \times 10^8 \text{Bq } ^{57}\text{Co(Pd)}$  source in transmission geometry. Spectral parameters were obtained from computer fitting and the isomer shift was calculated with respect to an  $\alpha\text{-Fe}$  foil of 25  $\mu\text{m}$  thickness.

An isothermal stainless steel reactor with 2.5 cm inner diameter was used for measuring the catalytic activities in the laboratory. An amount of 100 ml of catalyst was placed in the reactor. The catalyst reacted under the following conditions: temperature 620°C, atmospheric pressure, liquid hourly space velocity (LHSV)  $1.0 \text{ h}^{-1}$  and steam to ethylbenzene ratio by weight 2:1. The reactive products were analyzed by gas spectrography.

## 3 Results and discussions

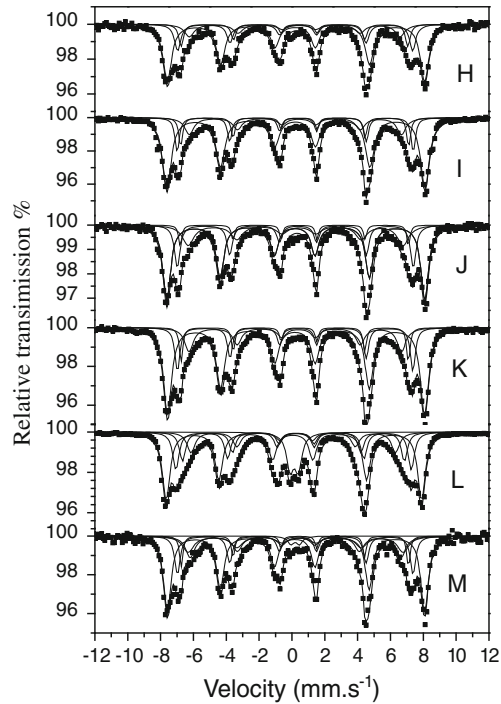
The presence of different iron compounds can be distinguished by their Mössbauer spectrum. We can see that in calcinated fresh catalyst the main compound of Fe-K is potassium ferrite  $\text{KFe}_{11}\text{O}_{17}$ , which has the spinel structure. It can be considered as the predecessor of the catalytic active phase [1, 4], which plays the important role in the dehydrogenation reaction of ethylbenzene. In the lattice of stoichiometric  $\text{KFe}_{11}\text{O}_{17}$ , there are four crystallographically identifiable Fe sites, namely, two octahedral sites (12k and 2a) and two tetrahedral sites. So the Mössbauer spectrum of the  $\text{KFe}_{11}\text{O}_{17}$  can be resolved into four six-line hyperfine patterns assigned to these four sites. But in fact the sub-spectrum of the 2a octahedral site has a very small area and the hyperfine magnetic field  $H$  assigned to two tetrahedral sites is quite close. So we often fit the Mössbauer spectrum of potassium ferrite with four (or three) sub-spectra:  $H = 48.4 \sim 48.9 \text{ T}$  is the contribution of  $\text{Fe}^{+3}$  on both tetrahedral sites,  $H = 44.1 \sim 44.6 \text{ T}$  is that on an octahedral site, and other two (or one) smaller  $H$

**Fig. 1** Mössbauer spectra of sample A, B, C, D, E, F, G**Table 1** The parameters of Mössbauer spectra and catalytic activity of sample A~G

Sample	A	B	C	D	E	F	G
Amount of Ce/%	0	2.5	8	10	15	20	30
Average width of peaks/mm·s <sup>-1</sup>	0.263	0.266	0.275	0.281	0.270	0.255	0.244
Styrene yield/%	61.52	68.07	68.54	69.23	69.10	68.77	68.95

is that on the octahedral site with imperfect crystal lattice. Normally, the widths of Mössbauer peaks are noticeably broadened by interactions with the nearby excess potassium ions or other non-magnetic ions. It is found that the broader the peaks, the more disperse the catalyst. It is favorable to enhance the activity of catalyst [5].

In a first series of samples the amount of CeO<sub>2</sub> is 0%~30%, and the amount of K, Mg (2% only) does not change. Figure 1 shows the Mössbauer spectra of 7 samples A~G. In the Mössbauer spectra of all samples there are 4 sextets corresponding to KFe<sub>11</sub>O<sub>17</sub>. For sample E, F, G a doublet with small area (2%, 4%, 8%) also exists in the spectra. The doublet in the Mössbauer spectra assigned to Fe<sup>+3</sup> in the catalyst also has contribution to the activity of the catalyst, because the samples F and G show better catalytic activity while their average widths are smaller (The sample L in Table 2 also proves this point). But not any cerium–iron compound can be detected in the Mössbauer spectra. X-ray diffraction results also prove that CeO<sub>2</sub> and Fe-K compound exist in the catalyst. However, different amounts of Ce give a different effect to the Fe-K compound in the catalyst, as shown in its Mössbauer parameters.

**Fig. 2** Mössbauer spectra of sample H, I, J, K, L, M**Table 2** The parameters of Mössbauer spectra and catalytic activity of sample H~M

Sample	H	I	J	K	L	M
Compound of Ce	compound of Ce (new 1)	Cerium nitrate (condition a)	Cerium nitrate (condition b)	Compound of Ce (new 2)	Compound of Ce (new 3)	Compound of Ce (new 4)
Average width of peaks/ $\text{mm}\cdot\text{s}^{-1}$	0.291	0.285	0.281	0.267	0.260	0.255
Styrene yield/%	70.30	69.55	69.57	68.44	68.75	68.37

According to the percentage of each sub-spectrum area, the average width of the Mössbauer spectra peaks of the Fe-K compound was calculated and the result is shown in Table 1. From Table 1 the samples C, D and E have broader average width of Mössbauer spectra peaks and better catalytic and better catalytic property.

There are some reports [6, 7] about the study of the effect on the performance of this kind of Fe-K catalyst by different cerium salts. In our work, in order to look for a new substitute for cerium nitrate, a second series of samples H~M was prepared. Their original compound of Ce is different, but the real chemical formula of these Ce compounds cannot be disclosed because of commercial confidentiality. Samples I and J, which used the same raw material of cerium nitrate, were manufactured in different conditions.

The different original Ce compound also gives different effect to Fe-K compounds. Figure 2 shows the Mössbauer spectrum of 6 samples H~M. The calculated

average width of Mössbauer spectra peaks and their catalytic data are shown in Table 2. One kind of a new compound of Ce, sample H, that has broader average width of peaks and nice catalytic property, could become an optimal substitute of cerium nitrate in the future.

The Mössbauer parameters and the catalytic property of samples I and J, which use the same raw material of cerium nitrate, but different manufacturing conditions, show no obvious difference.

#### 4 Conclusions

In conclusion, the above results prove that adding Ce into the Fe based catalyst is effective to form the predecessor of the catalytic active phase, compound  $\text{KFe}_{11}\text{O}_{17}$ , and also to improve the catalytic properties. The catalytic properties of the catalyst are optimal when the content of  $\text{CeO}_2$  is 8%~15%. In those cases the styrene yield could increase about 7% relative to the catalyst without Ce.

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#### References

1. Jiang, K.Y., Yang, J.X., Hu, B.Y., Yang, X.L., Mao, L.S., Yuan, Y.T., Zhang, G.L.: *Hyperfine Interact.* **111**, 45–49 (1998)
2. Watson, J.M., Crabbe, D.: *Conrsen: JR.T.S.* US4963343, 16 Oct 1990
3. Watson, J.M., Crabbe, D.: *Conrsen: JR.T. S.* US4975267, 4 Dec 1990
4. Jiang, K.Y., Fan, Q., Zhao, Z.J., et al.: *Hyperfine Interact.* **167**, 825–831 (2006)
5. Jiang, K.Y., Yang, X.L., Yuan, Y.T., et al.: *Hyperfine Interact.* **139/140**, 97–105 (2002)
6. Liao, S.J., Fan, Q., Miao, C.X., et al.: *Chem. React. Eng. Tech.* **24**(6), 493–497 (2008)
7. Xin, G.P.: *Chem. Ind. Eng. Progr.* **26**(8), 1192–1194 (2007)