Mössbauer study of function of magnesium in iron oxide catalysts*

Yang Jie-Xin[1], Jiang Ke-Yu[1], Hu Bing-Yuan[1], Yang Xie-Long[1]
Mao Lian-Sheng[2], Yuan Yi-Ting[2] and Zhang Gui-Lin[3]
[1] *Department of Physics, East China Normal University, Shanghai 200062*;
[2] *Shanghai Research Institute of Petrochemical Technology, Shanghai 201208*;
[3] *Shanghai Institute of Nuclear Research, the Chinese Academy of Sciences, Shanghai 201800*

Abstract Mössbauer spectroscopy has been utilized for studying the action of Mg element in iron oxide catalysts used for the dehydrogenation of ethylbenzene to styrene. The experimental results show that the presence of opportune amount of Mg can enhance the stability and dispersion of catalysts, i.e. Mg is an useful structure promoter in this kind of catalysts.

Keywords Mössbauer effect, Catalyst, Magnesium, Dehydrogenation, Iron oxides

1 Introduction

The catalytic dehydrogenation of ethylbenzene is of important in manufacture of styrene, which is applied to various process such as the production of synthetic rubber and resins by polymerization. It has recently been discovered that a potassium-promoted iron oxide catalysts containing minor but effective amounts of magnesium oxide exhibits a high selectivity and catalytic activity. However, the study of the action of magnesium in iron oxide catalysts for ethylbenzene dehydrogenation has rarely been reported.

In this work two series of the samples Mg-[Fe-K] and Mg-[Fe-K-Ce] have been measured systematically by using Mössbauer spectroscopy. The results show that the presence of opportune amount of Mg can increase the stabilization and dispersion, in result, delay the losing of activity. Therefore, Mg is considered as a kind of useful structure promoter in such catalysts.

2 Experimental

The experiments were performed using the samples of industrial catalysts in GS series. There are two series of A (Mg-[Fe-K]) and B (Mg-[Fe-K-Ce]). Each series has four samples containing different contents of magnesium for each sample.

The ^{57}Fe Mössbauer spectra were recorded in transmission geometry model at room temperature with a source of 74 MBq (20mCi) ^{57}Co(Pd). All Mössbauer parameters were obtained from computer-fitting and the isomer shift data were calculated relative to metallic iron.

3 Results and discussion

Fig.1 shows the Mössbauer spectra of series A (Mg-[Fe-K]) samples at room temperature. The experimental data were fitted with several sextets and one doublet (see Table 1). The doublet is designated to the paramagnetic component produced by γ-Fe_2O_3 small particles[1], the area of which decreases with the increase in Mg content. The sextet with the largest magnetic hyperfine field H=51.6 T and small line width is characteristic of α-Fe_2O_3. Another two sextets are considered the contribution from the potassium ferrite with spinel structure $KFe_{11}O_{17}$, one of which with magnetic splitting 47.5~48.6 T is attributed to Fe^{3+} on the tetrahedral sites and other with 43.4~43.8 is to Fe^{3+} on the octahedral sites.[2] The linewidth of sextet on the octahedral sites gradually broadens with the increase in Mg content.

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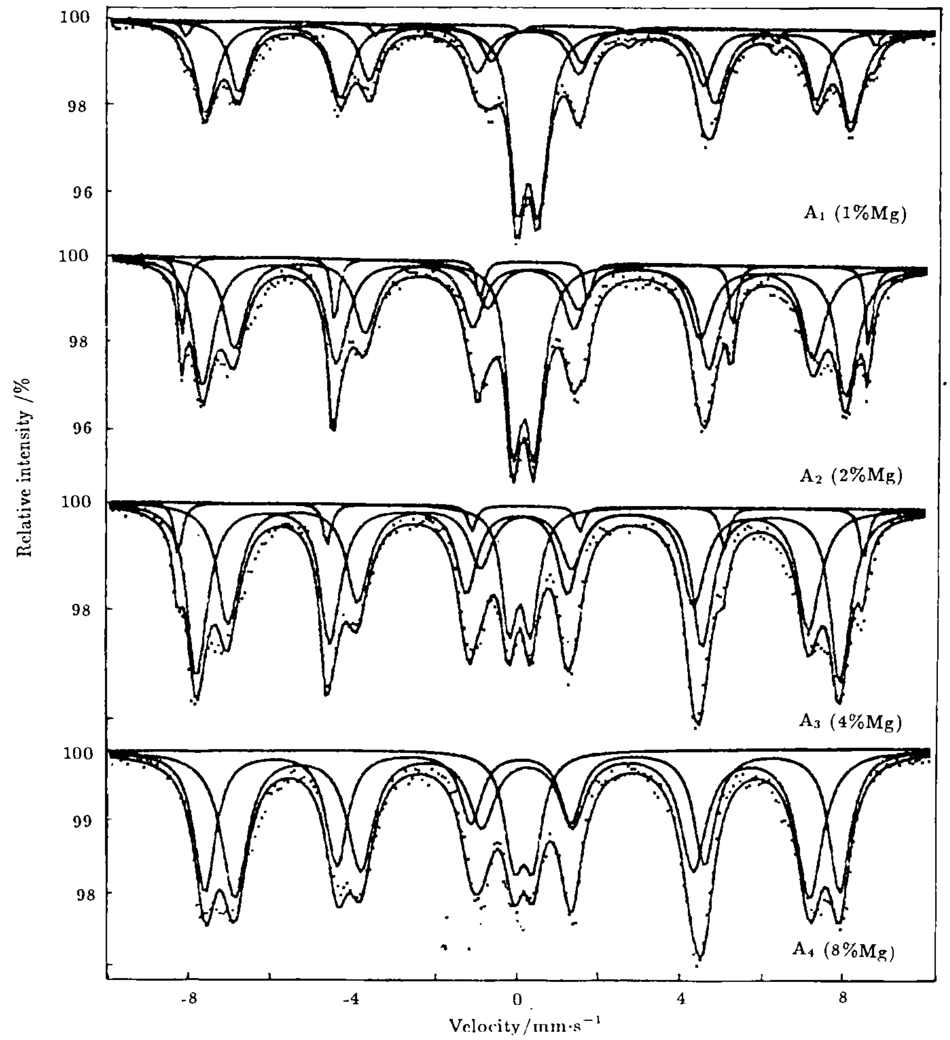

Fig.1 Mössbauer spectra of series A sample at room temperature

Table 1 Mössbauer parameters of series A sample at room temperature

Number of sample	Mass fraction of Mg	γ-Fe_2O_3			α-Fe_2O_3			$KFe_{11}O_{17}$					
								Site A			Site B		
		δ	Δ	S	H	$\Gamma/2$	S	H	$\Gamma/2$	S	H	$\Gamma/2$	S
A_1	1%	0.35	0.51	0.26	51.90	0.07	0.03	48.58	0.31	0.42	43.45	0.28	0.29
A_2	2%	0.31	0.51	0.19	51.69	0.10	0.09	48.45	0.31	0.42	43.56	0.32	0.30
A_3	4%	0.31	0.53	0.11	51.64	0.12	0.06	48.43	0.30	0.47	43.71	0.33	0.36
A_4	8%	0.31	0.46	0.11	–	–	–	47.93	0.31	0.40	43.41	0.37	0.49

In Tables 1,2: δ—isomer shift (mm/s); Δ—quadrupole splitting (mm/s); H—magnetic hyperfine field (T); Γ—linewidth (mm/s); S—area of subspectrum (%)

Fig.2 shows the Mössbauer spectra of series B (Mg-[Fe-K-Ce]). All spectra are composed of two or three sets of sextet and one doublet as mentioned above (see Table 2). The situation of one doublet and two spinel sextets is similar to the samples in series A. The lowest magnetic splitting appeared only in sample B_4 (16%Mg) is attributed to opportune additional Ce in comparison with series A. In addition, in all samples of series B, the sextet corresponding to α-Fe_2O_3 does not appear noticeably.

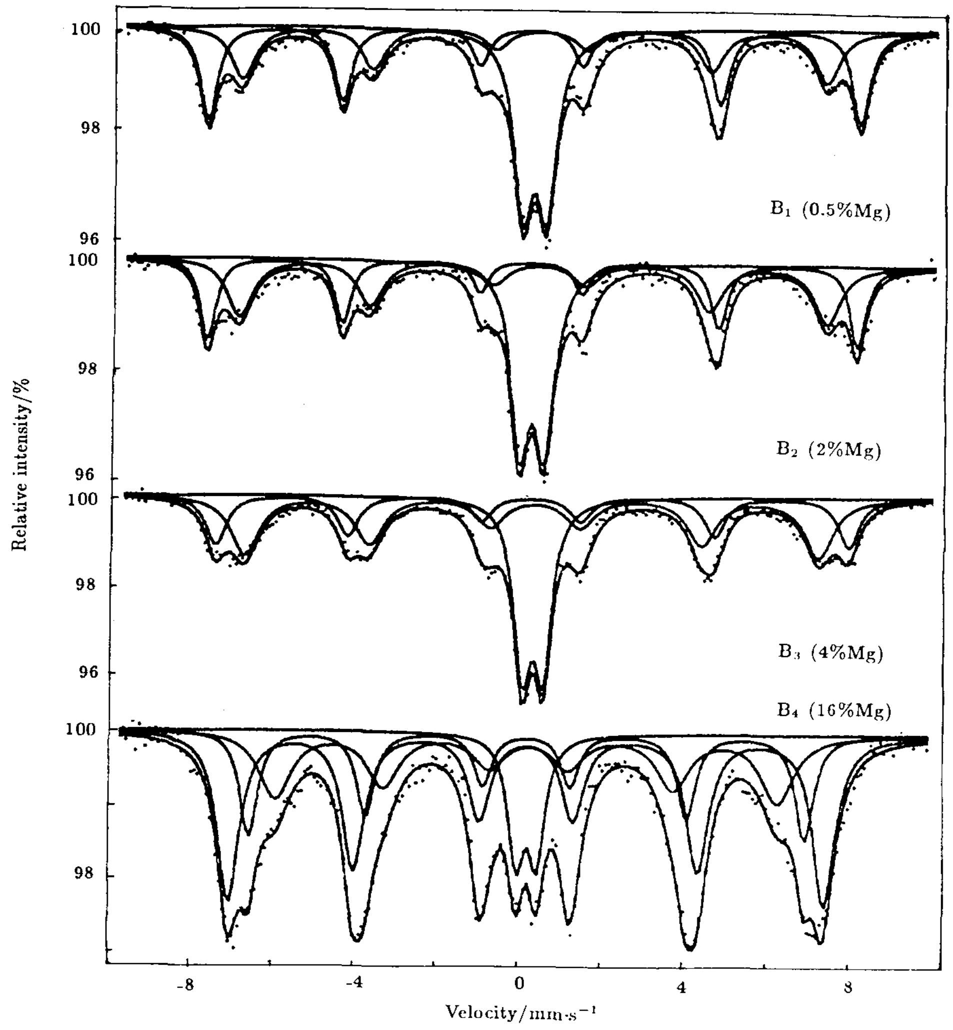

Fig.2 Mössbauer spectra of series B sample at room temperature

Table 2 Mössbauer parameters of series B sample at room temperature

Number of sample	Mass fraction of Mg	γ-Fe_2O_3			$KFe_{11}O_{17}$								
					Site A			Site B (1)			Site B (2)		
		δ	Δ	S	H	$\Gamma/2$	S	H	$\Gamma/2$	S	H	$\Gamma/2$	S
B_1	0.5%	0.28	0.58	0.34	49.15	0.25	0.37	44.02	0.36	0.29	–	–	–
B_2	2%	0.33	0.53	0.38	48.52	0.26	0.32	43.55	0.32	0.30	–	–	–
B_3	4%	0.35	0.51	0.31	47.73	0.30	0.26	43.27	0.42	0.43	–	–	–
B_4	16%	0.30	0.50	0.10	44.93	0.32	0.44	41.90	0.26	0.22	37.86	0.47	0.24

Previous works[3,4] show that the K ferrite is the precursor of the catalytic active phase, which can turn into $KFeO_2$ under certain temperature. However, $KFeO_2$ is unstable and can be decomposed into γ-Fe_2O_3 small particles and K_2O, especially if exposed to the atmosphere. According to our knowledge, the γ-Fe_2O_3 small particle appearing in this kind of catalyst is related to the decrease in K content in the catalyst and to the losing of the activity of the catalyst. Now, the area of γ-Fe_2O_3 doublet decreases with increasing Mg amount in both samples of series A and B. This fact indicates that the losing of the catalytic activity is delayed by the adding Mg to the catalyst, i.e., the presence of Mg enhances the stability of the active phase in Fe-K-Mg catalysts.

In all samples of series B, the spectrum of α-Fe_2O_3 is not found due to adding new element Ce relative to series A, while in series A the α-Fe_2O_3 spectrum appears in 3 samples (1%, 2%, 4% Mg). This result shows that the adding of Ce in catalyst is in favour of the formation of Fe-K spinel structure.

On the other hand, both in samples of series A and B, the magnetic splitting of K ferrite decreases but the linewidth of octahedral site increases with increase in Mg content (see Tables 1,2). The reason is that the nonmagnetic Mg^{2+} ions enter the crystal structure of K ferrite compound, and occupy partly the near neighbor and next near neighbor of Fe^{3+} irons, leading to the decrease in the exchange interaction between Fe^{3+} ions. It means that Mg^{2+} entering into the crystal structure plays the role of dispersion.

In conclusion, the adding of magnesium oxide to Fe-K and Fe-K-Ce systems delays the losing of the catalytic activity by increasing the stabilization and dispersion, therefore Mg is a kind of useful structure promoter in catalyst. The presence of Ce is favorable to produce the spinel structure relative to the active phase in catalysts for dehydrogenation of ethylbenzene.

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