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A MÖSSBAUER SPECTROSCOPIC STUDY ON THE STRUCTURE OF Fe–*M* ULTRAFINE PARTICLE CATALYSTS (*M*=Mn, Zn, Mg)*

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ABSTRACT

The structure of Fe–*M* ultrafine particle catalysts was investigated by in situ Mössbauer spectroscopy. Emphasis has particularly been put on the effect of the second metal component. It was found that the incorporation of second metal component hinders the reduction and carburization of iron-containing phase in the presence of H_2 and CO, and the degree of hindrance is in the order of Mg>Mn>Zn due to the interaction between iron and the second metal component. Consequently, the formation of light olefinic products is in the order of Fe–Mg>Fe–Mn>Fe–Zn catalysts consistent with the F–T synthesis performance.

Keywords: Mössbauer spectroscopy Fe–*M* catalysts Ultrafine particle

1 INTRODUCTION

Iron based catalysts have been used in commercial Fischer-Tropsch (F–T) synthesis. And many transition metals like Ti, V, Mo, W, Mn, *etc.* have been regarded as effective promoters for enhancing selectivity toward light olefins[1], whereas the effects of Zn and Mg have not been well-investigated.

The catalysts are conventionally prepared by coprecipitation (or impregnation) of the corresponding nitrates in alkali or by decarbonylation of the corresponding metal carbonyl compounds. In our laboratory, a novel method, the degradation of Fe–*M* complexes, has recently been used to obtain Fe–*M* UFP catalysts. This new type of catalyst is featured by its high conversion of CO, high space time yield and high selectivity to light olefins[2]. For example, a typical Fe–*M* UFP catalyst gives products of hydrocarbons with more than 90% below C_{11}, in which C_2 to C_4 fraction contains 84% olefins, and the total product contains 31.5% olefins[2].

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In this paper, attention is focused on the relation between the chemical state of iron in UFP Fe-*M* catalysts and the behavior of reduction and carburization in the presence of syngas and the catalytic performance. The results indicate that the second metal component has a strong influence on the chemical state catalysts, giving a different behavior of reduction, carburization as well as catalysis.

2 EXPERIMENTAL

All of the samples were prepared by a special degradation method[2] at 773 K from oxalate precursors. The ratio of Fe:*M* is 3 for all catalysts, and a "pure" Fe catalyst is used for reference.

Sample containing ca. 10mg Fe/cm^2 were stepwise treated at 573 K and 633 K in a Mössbauer in situ cell in which the syngas (H_2:CO = 2:1, 60cm^3/min) was flowing for 5 h and cooled to room temperature, and then the spectra were recorded at room temperature using a ^{57}Co soure on a Pd matrix. All spctra were fitted with computer and parameters are relative to α - Fe.

X-ray powder diffraction (XRD) and small angle X-ray scattering (SAXS) were performed on a Rigaku D/max-rA diffractometor using Cu K_{α} radiation in combination with a graphite monochrometor.

3 RESULTS AND DISCUSSION

The average particle sizes of principal phase measured by SAXS are 12.8, 9.9, 8.5, 11.3 nm for "pure" Fe, Fe-Mn, Fe-Zn, Fe-Mg catalysts, respectively.

Mössbauer spectra of the catalysts are shown in Figs.1-4 and Mössbauer parameters are summerized in Table 1.

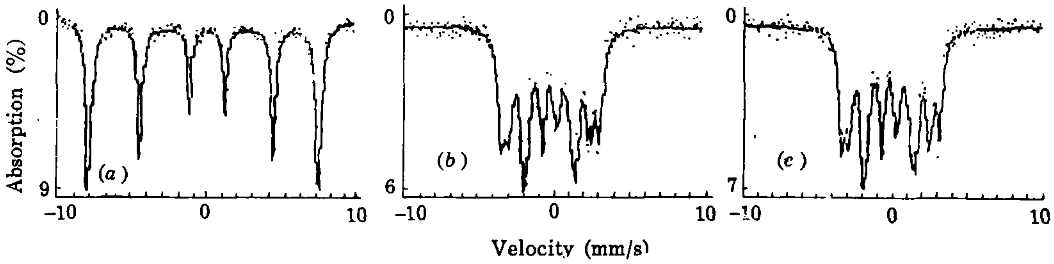

Fig.1 Mössbauer spectra of "Pure" iron UFP catalyst

(*a*) As-prepared (*b,c*) Treated in syngas at 573 K, 633 K sequentially

The spectrum of "pure" Fe catalyst is fitted to a sextet with hyperfine field (*H*) of 4.05× 10^{7}A/m which is typical characteristic of bulk antiferromagnetic α - Fe_2O_3[3], whereas the relative smaller *H* value suggests that the Fe(III) oxide is in a highly dispersed state[4]. XRD pattern indicates that this catalyst consist of α - Fe_2O_3 and a trace γ - Fe_2O_3.

Mössbauer spectra of Fe-*M* catalysts (M = Mn, Zn, Mg) are quite different from that of "pure" Fe catalyst. All of them consist of a doublet. The spectra of Fe-Mn and Fe-Mg catalysts contain also a small contribution of a six line component with smaller H value (4.03×10^7A/m and 3.95×10^7A/m respectively). The Mössbauer parameters of both doublet and sextet are characteristic of high-spin Fe^{3+} ions in highly dispersed states[4]. For Fe-Zn (or Fe-Mg) catalyst, XRD shows that it is in the form of $ZnFe_2O_4$ ($MgFe_2O_4$) or γ-Fe_2O_3 with Zn (Mg) dissolved in its lattice. They cannot be differentiated by XRD, but the oxides are highly dispersed regardless of the form.

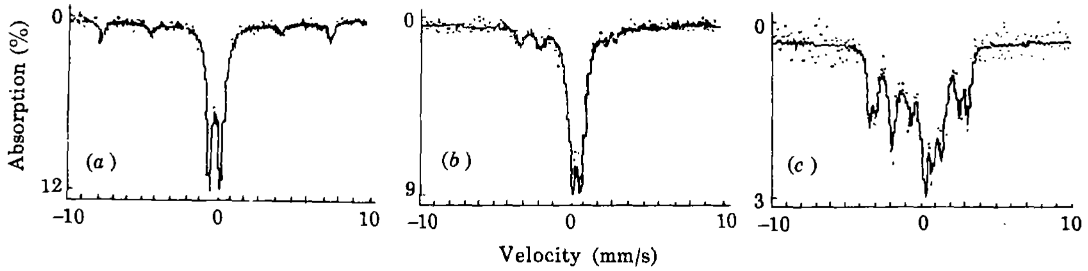

Fig.2 Mössbauer spectra of Fe-Mn UFP catalyst

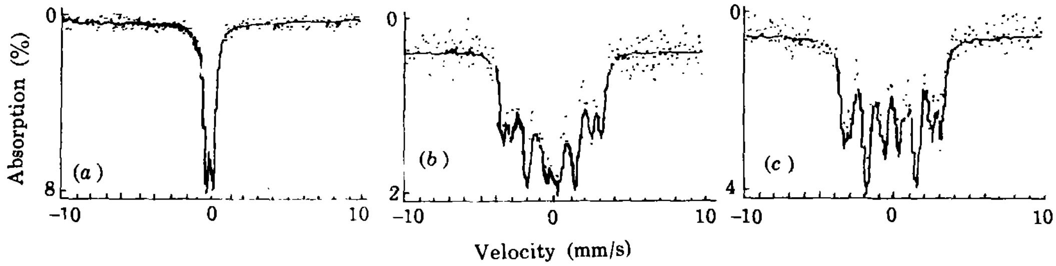

Fig.3 Mössbauer spectra of Fe-Zn UFP catalyst

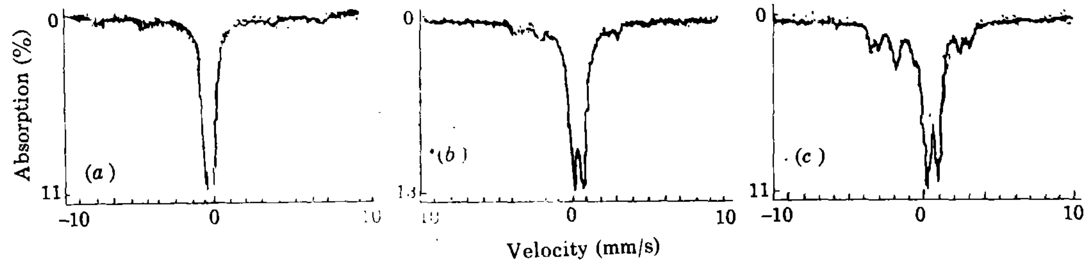

Fig.4 Mössbauer spectra of Fe-Mg UFP catalyst

In Fig.2-4, (*a*) As-prepared (*b,c*) Treated in syngas at 573 K, 633 K sequentially

The results indicate that the incorporation of a second metal component into iron based UFP catalyst will markedly modify its structural characteristics by the change of the chemical environment of iron atoms, as evidenced by the remarkable change of Mössbauer parameters. In "pure" Fe catalyst, iron atoms are magnetically ordered and the sites they occupied are slightly deviated from cubic symmetry, as indicated by a small QS value. As mentioned above, the particle size of "pure" iron catalyst is very small. The incorporation of manganese, zinc and magnesium makes the particle size even still smaller by segregating iron-containing crystallites, as is manifested by the decrease of H value of magnetic sextets and the emergence of superparamagnetic doublets. Iron atoms in these catalysts are in non-cubic symmetrical sites.

Table 1

Mössbauer parameters of Fe– *M* UFP catalysts

Sample	Treatment	Mössbauer parameters			Assignment	Spectral contribution
		IS (mm/s)	QS (mm/s)	H ($\times 10^6/4\pi$ A/m)		
"Pure" Fe	As-prepared	0.37	-0.23	509	$\alpha-Fe_2O_3$ (m)	100%
	573 K, 5 h (Syngas)	0.27		216	$\chi-Fe_5C_2$ (I)	100%
		0.19		178	$\chi-Fe_5C_2$ (II)	
		0.34		118	$\chi-Fe_5C_2$ (III)	
	633 K, 5 h (Syngas)	0.30		216	$\chi-Fe_5C_2$ (I)	100%
		0.20		178	$\chi-Fe_5C_2$ (II)	
		0.32		119	$\chi-Fe_5C_2$ (III)	
Fe-Mn	As-prepared	0.37	0	507	Fe^{3+} (m)	15%
		0.37	0.81	0	Fe^{3+} (s)	85%
	573 K, 5 h (Syngas)	–		210	$\chi-Fe_5C_2$	16%
		1.03	0.65	0	Fe^{2+}	84%
	633 K, 5 h (Syngas)	0.32		218	$\chi-Fe_5C_2$ (I)	82%
		0.24		186	$\chi-Fe_5C_2$ (II)	
		0.39		111	$\chi-Fe_5C_2$ (III)	
		1.05	0.52	0	Fe^{2+}	18%
Fe-Zn	As-prepared	0.35	0.51	0	Fe^{3+} (s)	100%
	573 K, 5 h (Syngas)	0.33		220	$\chi-Fe_5C_2$ (I)	93%
		0.29		177	$\chi-Fe_5C_2$ (II)	
		0.37		111	$\chi-Fe_5C_2$ (III)	
		1.02	0.69	0	Fe^{2+}	7%
	633 K, 5 h (Syngas)	0.32		216	$\chi-Fe_5C_2$ (I)	100%
		0.24		179	$\chi-Fe_5C_2$ (II)	
		0.30		115	$\chi-Fe_5C_2$ (III)	
Fe-Mg	As-prepared	0.38	-0.10	496	Fe^{3+} (m)	13%
		0.33	0.54	0	Fe^{3+} (s)	87%
	573 K, 5 h (Syngas)	–		221	$\chi-Fe_5C_2$	12%
		1.04	0.75	0	Fe^{2+}	88%
	633 K, 5 h (Syngas)	0.27		217	$\chi-Fe_5C_2$ (I)	39%
		0.18		179	$\chi-Fe_5C_2$ (II)	
		1.08	0.78	0	Fe^{2+}	61%

Under the treatment of syngas, all catalysts undergo reduction and carburization as metioned in the first part. At 573 K, "pure" Fe catalyst is reduced exclusively to zero-valent iron and then transformed to $\chi-Fe_5C_2$, whilst most of Fe^{3+} present in Fe-Mn and Fe-Mg catalysts is converted to Fe^{2+} by synthesis gas and only a small amount of Fe^{3+} is reduced to Fe^0. In Fe-Zn catalyst, exposure of the catalyst to synthesis gas at 573 K leads to the reduction of most of Fe^{3+} to Fe^0 which is transformed to $\chi-Fe_5C_2$ and a small amount of Fe^{3+} to Fe^{2+}. The Mössbauer parameters of the ferrous iron, IS = 1.05 ± 0.03 mm/s and QS = 0.60 ± 0.15 mm/s are characteristic of high-spin Fe^{2+}.[5]

The final treatment of the catalysts was carried out at 633 K in presence of syngas for 5 h. The spectrum of "pure" iron catalyst remains the same as that treated at 573 K, confirming the fact that the reduction and carburization of the catalyst are completed at 573 K. Treatment of Fe-Mn, Fe-Zn and Fe-Mg catalysts at this temperature leads to further reduction and carburization of the catalysts. It goes without saying that the extent of carburization is coincident with the reducibility of the catalysts, both of them are in the order of "pure"Fe > Fe-Zn > Fe-Mn > Fe-Mg.

It should be pointed out that the magnetic splitting spectra of Fe-Mn and Fe-Mg catalysts at 573 K treatment are difficult to fit reasonably. But from the temperature evolution of the spectra, it is assumed that they are spectra of χ-Fe_5C_2 which are difficult to fit just because their amount is very small.

The above results demonstrate clearly that the incorporation of Zn, Mn, Mg hinders the reduction and carburization of the iron-containing phases in the catalysts. This is an indication of the interaction between iron and the second metal component in the catalysts. For example, Fe and Mg exhibit the strongest interaction and thus the catalyst is most difficult to reduce and carburize. All iron-containing crystallites contain, or at least are in contact with, the second metal component as evidenced by the difference between the behavior of reduction and carburization of Fe-*M* catalysts and that of "pure" iron catalyst.

The F-T activity-selectivity patterns of the catalysts are in good agreement with the Mössbauer results. The formation of carbide is most difficult for Fe-Mg catalyst, thus a shift to lighter products is expected for this catalyst because the carbide is regarded to be responsible for the formation of heavier hydrocarbon products. Accordingly, the formation of light olefinic products is in the order of Fe-Mg > Fe-Mn > Fe-Zn catalysts. Among them Fe-Mg catalyst gives low selectivity to ethylene in the product.

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