

## THE CHARACTERIZATION OF IRON BASED Fe—M ULTRAFINE PARTICLE (UFP) CATALYSTS. II. EFFECT OF SECOND METAL COMPONENT (M=Mn, Zn, Mg)

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The effect of second metal component on the structural characteristic of Fe—M UFP catalysts was investigated by in situ Mossbauer spectroscopy. The incorporation of second metal component hinders the reduction and carburization of iron containing phase in the presence of H<sub>2</sub> 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.

### 1. Introduction

One of the recent trends in F-T synthesis is the development of new catalysts with higher light olefins selectivity. Many transition metals like Ti, V, Mo, W and Mn etc. have been shown to serve this purpose in certain extent [1], whereas the effects of Zn and Mg have not been well investigated. 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 of iron in the 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 773K from oxalate precursors. Fe:M is 3 for all catalysts, and a "pure" Fe catalyst is used for reference. The average particle sizes of principal phase as measured by small angle X ray scattering are 12.8, 9.9, 8.6, 11.3 nm for "pure" Fe, Fe—Mn, Fe—Zn, Fe—Mg catalysts, respectively. The use of Mossbauer spectroscopy and XRD has been described in the first part.

### 3. Results and discussion

Mossbauer spectra of the catalysts are shown in Figs. 1-4. The spectrum of "pure" Fe catalyst is fitted to a sextet with hyperfine field(H) of 509K Oe which is typical

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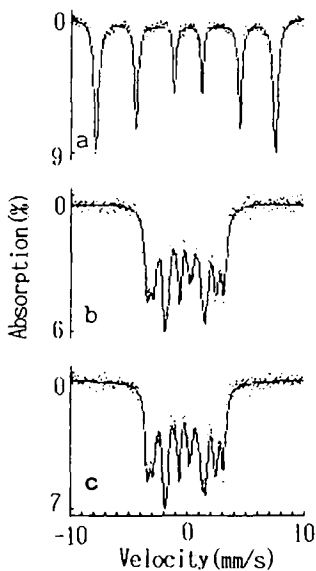


Fig. 1 Mossbauer spectra of "pure" iron UFP catalyst a) as-prepared; b, c) treated in syngas at 573K, 633K sequentially.

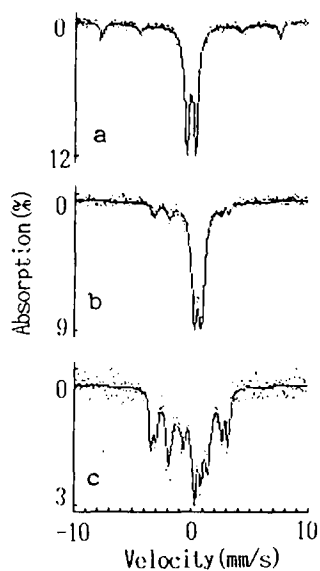


Fig. 2 Mossbauer spectra of Fe-Mn UFP catalyst a) as-prepared; b, c) treated in syngas at 573K, 633K sequentially.

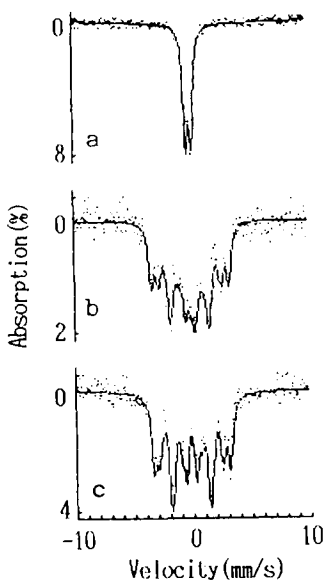


Fig. 3 Mossbauer spectra of Fe-Zn UFP catalyst a) as-prepared; b, c) treated in syngas at 573K, 633K sequentially.

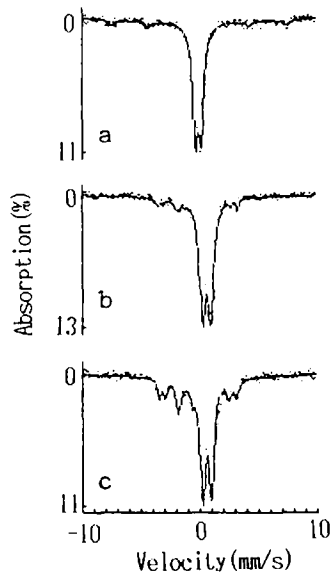


Fig. 4 Mossbauer spectra of Fe-Mg UFP catalyst a) as-prepared; b, c) treated in syngas at 573K, 633K sequentially.

characteristic of bulk antiferromagnetic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/3/, whereas the relative smaller  $\delta$  value suggests that the Fe(III) oxide is in a highly dispersed state/4/. XRD pattern indicates that this catalyst consist of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and a trace amount of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

Mossbauer 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  $\delta$  value (507 and 496 KOs respectively). The Mossbauer parameters of both doublet and sextet are characteristic of high spin Fe<sup>3+</sup> ions in highly dispersed states/4/. For Fe-Zn (or Fe-Mg) catalyst, XRD shows that it is in the form of ZnFe<sub>2</sub>O<sub>4</sub> (MgFe<sub>2</sub>O<sub>4</sub>) or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with Zn(Mg) dissolved in its lattice. They cannot be differentiated by XRD, but the oxides are highly dispersed regardless of the form.

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 Mossbauer 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  $\delta$  value of magnetic sextets and the emergence of superparamagnetic doublets. Iron atoms in these catalysts are in non-cubic symmetrical sites.

Under the treatment of syngas, all catalysts undergo reduction and carburization as mentioned in the first part. At 573K, "pure" Fe catalyst is reduced exclusively to zero valent iron and then transformed to  $\gamma$ -Fe<sub>5</sub>C<sub>2</sub>, whilst most of Fe<sup>3+</sup> present in Fe-Mn and Fe-Mg catalysts is converted to Fe<sup>2+</sup> by synthesis gas and only a small amount of Fe<sup>3+</sup> is reduced to Fe<sup>0</sup>. In Fe-Zn catalyst, exposure of the catalyst to synthesis gas at 573K leads to the reduction of most of Fe<sup>3+</sup> to Fe<sup>0</sup> which is transformed to  $\gamma$ -Fe<sub>5</sub>C<sub>2</sub> and a small amount of Fe<sup>3+</sup> to Fe<sup>2+</sup>. The Mossbauer parameters of the ferrous iron,  $\delta$ S=1.05±0.03mm/s and QS=0.89±0.15mm/s are characteristic of high spin Fe<sup>2+</sup>/5/.

The final treatment of the catalysts was carried out at 633K in presence of syngas for 5 hours. The spectrum of "pure" iron catalyst remains the same as that treated at 573K, confirming the fact that the reduction and carburization of the catalyst are completed at 573K. 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.

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 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 Mossbauer 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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