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Study on the Reduction Behavior of Zirconia Supported Iron Oxide Catalysts by Temperature-Programmed Reduction Combined with *in Situ* Mössbauer Spectroscopy

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The reduction properties of Fe_2O_3/ZrO_2 catalysts with various Fe_2O_3 loading and the interactions between iron oxide and zirconia have been studied by using temperature-programmed reduction combined with *in situ* Mössbauer spectroscopy. This is shown that the intermediates formed during reduction depend strongly not only on the reduction temperature but also on the iron loading. Several iron species such as bulk phase α-Fe_2O_3, small α-Fe_2O_3 particles, and surface iron oxide species are found in the zirconia supported iron oxide catalysts. Reduction of the small α-Fe_2O_3 particles is easier than that of the bulk phase α-Fe_2O_3. In contrast, the surface iron oxide species are much more difficult to reduce because of their strong interactions with the support. The phenomena of partial oxidation of Fe^{2+} cations and Fe_3O_4 to Fe^{3+} cations in the reduction processes are observed.

INTRODUCTION

The interactions between metal oxide and support have gained growing interest in the past two decades, much attention has been given to the study of the reduction properties of supported metal oxide catalysts. Among these, supported iron oxide catalysts are of particular importance because of their extensive applications in many catalytic processes (1, 2). Tang Ren-Yuan *et al.* (3) were the first to use an *in situ* combined temperature-programmed reduction–Mössbauer spectroscopic technique to study the reduction of alumina supported iron catalysts, and they confirmed that the technique is very effective in studying the reduction process and intermediates of supported iron catalysts. Lund *et al.* (4–7) reported that the activity of magnetite particles for the water–gas shift reaction was greatly depressed when the particles were supported on silica. By using NO chemisorption and Mössbauer spectroscopy, they found that by substituting for Si^{4+} cations from the support, the Fe^{3+} cations in the surface tetrahedral sites of the magnetite could migrate to adjacent octahedral sites. XingTao Gao *et al.* (8) studied the reduction properties of Fe_2O_3/TiO_2 and Fe_2O_3/Al_2O_3 systems. They found that the properties of the support play an important role in determining the reduction intermediates of supported iron oxides, due to the different interactions between iron oxide and the supports. Different surface species can be formed by the interactions between metal oxide and various supports (9, 10), which in turn will affect the surface states and related properties of the catalysts.

Besides the nature of the support, the preparation conditions, especially the loading of metal oxide and calcination temperature and duration, can have a strong impact on the nature of the interactions between metal oxides and supports (11–14), hence influence the reduction behavior of the sample. For example, in a silica supported iron oxide sample with a loading of 1 wt% Fe, the high-coordination Fe^{2+} cations can be converted into low-coordination Fe^{2+} cations under severe reduction conditions (10). In another study, Fe^{3+} cations were found to transfer from octahedral to tetrahedral sites when the Fe_2O_3/SiO_2 sample was treated in oxygen at 773 K for 16 hr (13).

Zirconia is currently attracting considerable scientific interest for its potential use as a catalyst support or promoter for a variety of catalyst systems (15). F. J. Berry *et al.* (16) prepared iron–zirconia catalysts by the coprecipitation method and studied their catalytic properties for hydrogenation of CO. In our recent work, we also found that Fe_2O_3/ZrO_2 catalysts prepared by the impregnation method could markedly suppress the formation of methane when they were used in CO hydrogenation. The aim of this work is to study the reduction properties of Fe_2O_3/ZrO_2 catalysts with various iron oxide loading and the interactions between iron oxide and zirconia.

Temperature-programmed reduction combined with *in situ* Mössbauer spectroscopy is used in this work to study the formation of various intermediates during the successive steps of reduction of iron oxide deposited on zirconia. Along these lines, the interactions between iron oxide and zirconia is discussed.

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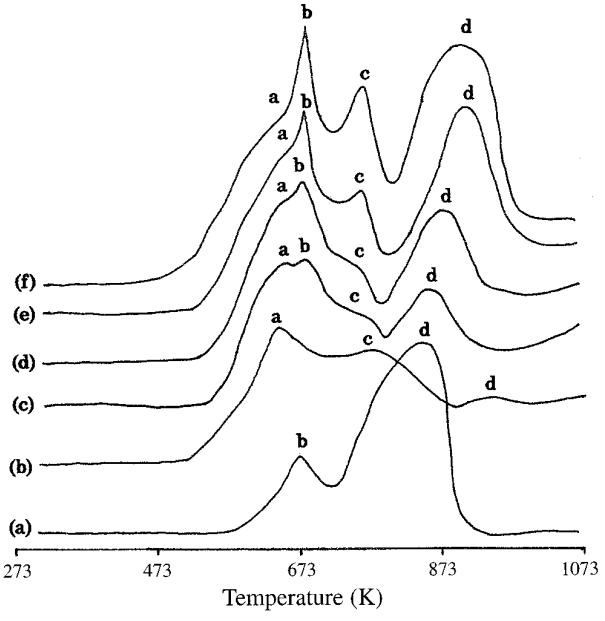

FIG. 1. TPR profiles of Fe_2O_3/ZrO_2 catalysts with various Fe_2O_3 loading. (a) Bulk α-Fe_2O_3, (b) 1.6 wt%, (c) 3 wt%, (d) 4 wt%, (e) 5 wt%, and (f) 7 wt%.

EXPERIMENTAL

Fe_2O_3/ZrO_2 catalysts with various Fe_2O_3 loading were prepared by impregnating zirconia (surface area 39 m^2/g, C. P. Shanghai) with an aqueous solution of iron nitrate, and then dried at 393 K and calcined at 773 K for 5 hr. X-ray diffraction measurements were performed on a Rigaku D/max-rA diffractometer using Cu$K\alpha$ radiation. The TPR experiments were carried out in a U-type quartz reactor with a heating rate of 16 K/min and a flow rate of H_2–Ar

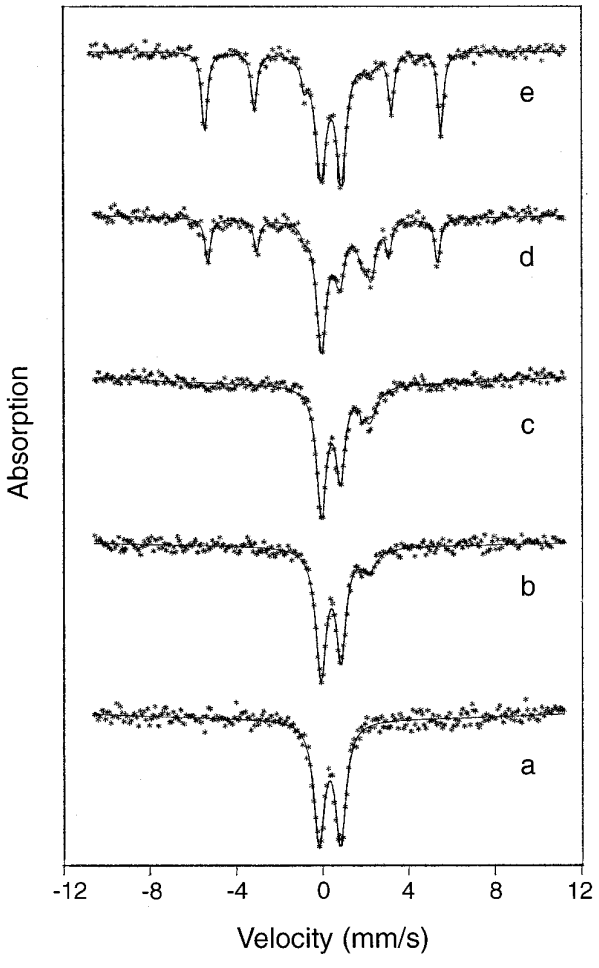

FIG. 2. Mössbauer spectra of 1.6 wt% Fe_2O_3/ZrO_2 catalyst treated at various conditions. (a) As-prepared, (b) TPR to 643 K, (c) TPR to 753 K, (d) TPR to 973 K, (e) TPR to 1073 K.

TABLE 1
Mössbauer Parameters of 1.6 wt% Fe_2O_3/ZrO_2 Catalyst Treated under Various Conditions

Treatment condition	Mössbauer parameter			Iron species	Relative area (%)
	IS (mm/sec)	QS (mm/sec)	*H* (KOe)		
As-prepared	0.38	1.01	0	Fe^{3+}	100
TPR to 643 K	0.39	0.94	0	Fe^{3+}	76
	1.03	2.23	0	Fe^{2+}	24
TPR to 753 K	0.38	0.92	0	Fe^{3+}	61
	1.06	2.14	0	Fe^{2+}	39
TPR to 973 K	0.04	0.00	331	Fe^{0}	26
	0.37	0.89	0	Fe^{3+}	31
	1.08	2.25	0	Fe^{2+}	43
TPR to 1073 K	0.01	0.00	338	Fe^{0}	41
	0.38	0.93	0	Fe^{3+}	50
	0.99	2.24	0	Fe^{2+}	9

TABLE 2
Mössbauer Parameters of 7 wt% Fe_2O_3/ZrO_2 Catalyst Treated under Various Conditions

Treatment condition	Mössbauer parameter			Iron species	Relative area (%)
	IS (mm/sec)	QS (mm/sec)	H (KOe)		
As-prepared	0.43	−0.12	511	Fe^{3+}	53
	0.35	1.03	0	Fe^{3+}	47
TPR to 673 K	0.32	−0.07	490	Fe^{3+}	13
	0.77	0.00	467	Fe^{3+}, Fe^{2+}	40
	0.38	1.04	0	Fe^{3+}	47
TPR to 753 K	1.06	0.00	0	Fe^{2+}	38
	0.46	1.01	0	Fe^{3+}	62
TPR to 973 K	0.02	0.02	334	Fe^{0}	72
	0.38	0.99	0	Fe^{3+}	28
TPR to 1073 K	0.00	0.01	338	Fe^{0}	83
	0.42	0.99	0	Fe^{3+}	17

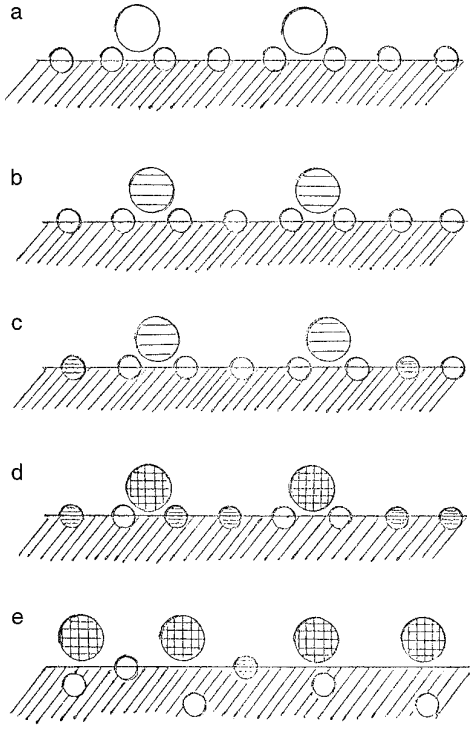

FIG. 3. Pictorial models for the reduction of the 1.6 wt% Fe_2O_3/ZrO_2 catalyst. (a) As-prepared, (b) TPR to 643 K, (c) TPR to 753 K, (d) TPR to 973 K, (e) TPR to 1073 K. ○ Fe^{3+} cations from the surface iron oxides; ○ Small Fe_2O_3 particles; ◍ Fe^{2+} cations from the reduction of the surface Fe^{3+} cations; ◍ FeO from the reduction of the small Fe_2O_3 particles; ● Metallic iron particles; //// Surface of the zirconia support.

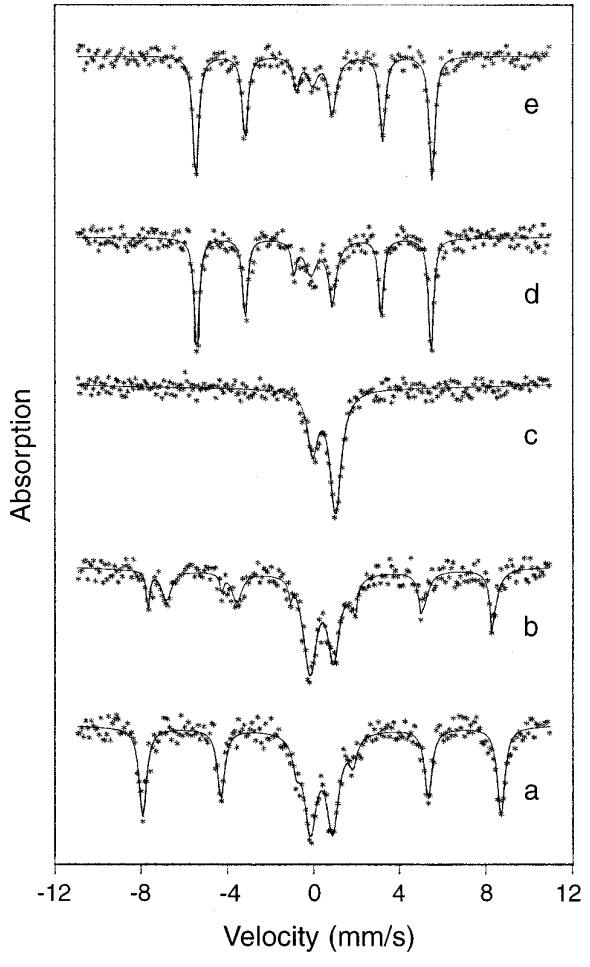

FIG. 4. Mössbauer spectra of 7 wt% Fe_2O_3/ZrO_2 catalyst treated at various conditions. (a) As-prepared, (b) TPR to 673 K, (c) TPR to 753 K, (d) TPR to 973 K, (e) TPR to 1073 K.

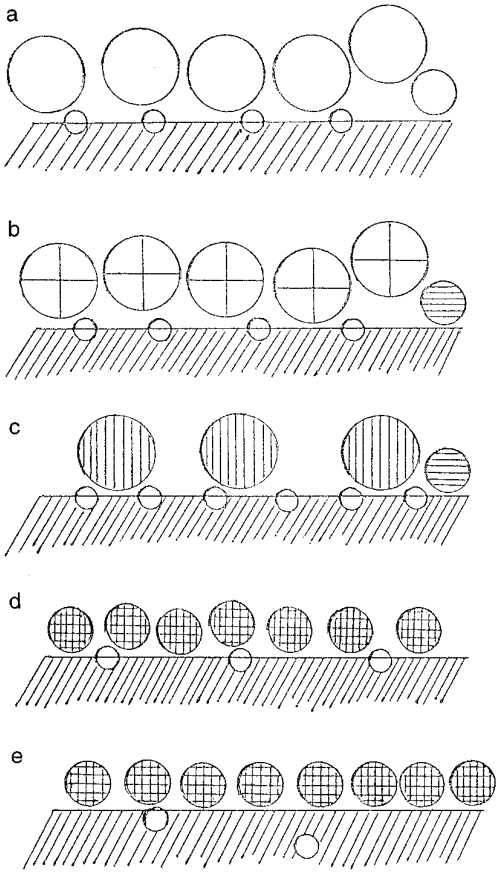

FIG. 5. Pictorial models for the reduction of the 7 wt% Fe_2O_3/ZrO_2 catalyst. (a) As-prepared, (b) TPR to 673 K, (c) TPR to 753 K, (d) TPR to 973 K, (e) TPR to 1073 K. ○ Fe^{3+} cations from the surface iron oxides; ○ Small Fe_2O_3 particles; ◯ Bulk phase Fe_2O_3 particles; ⊜ Fe^{2+} cations from the reduction of the surface Fe^{3+} cations; ⊜ FeO from the reduction of the small Fe_2O_3 particles; ◍ FeO from the reduction of the Fe_3O_4 particles; ⊕ Fe_3O_4 particles; ◍ Metallic iron particles; ////// Surface of the zirconia support.

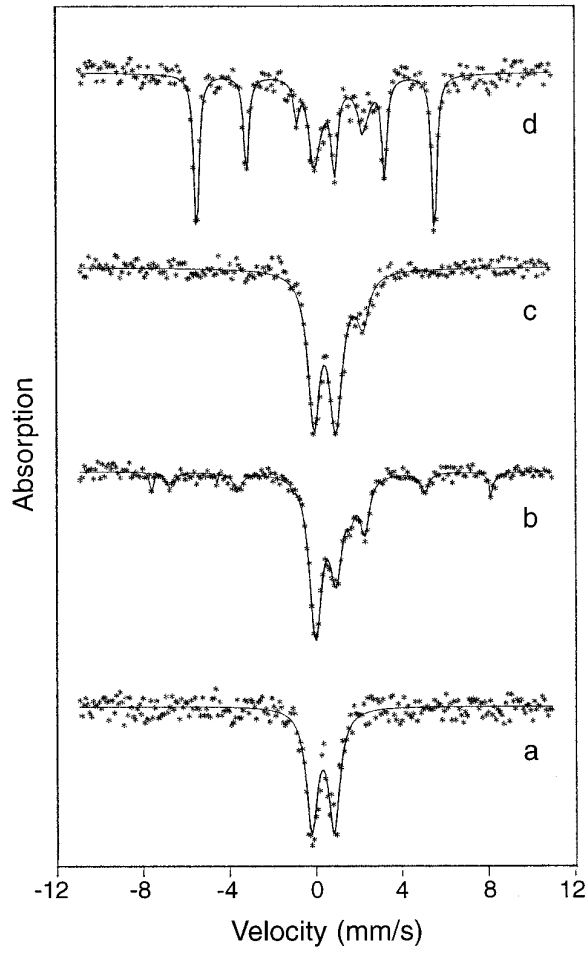

FIG. 6. Mössbauer spectra of 4 wt% Fe_2O_3/ZrO_2 catalyst treated at various conditions. (a) As-prepared, (b) TPR to 673 K, (c) TPR to 753 K, (d) TPR to 973 K.

mixture (5.0 vol% hydrogen) ca. 30 ml/min. Hydrogen consumption was monitored by a thermal conductivity detector. Before each TPR run, the as-prepared sample was heated *in situ* with dry air at 393 K for 1 hr. Mössbauer spectroscopy experiments were conducted with a constant acceleration spectrometer using a 10 mCi $^{57}Co/Pd$ source. All spectra were computer fitted to a Lorentzian line shape with a least-squares fitting procedure, and the isomer shifts (IS) were given with respect to the centroid of α-Fe at room temperature. For the Mössbauer tests of the samples with iron oxide loading less than 4 wt%, ^{57}Fe enriched iron containing 83% ^{57}Fe was used.

The experimental procedure for the combined *in situ* TPR–Mössbauer spectroscopy was as follows. First, a TPR run was performed to a temperature as high as possible to obtain an integrated reduction profile. According to the integrated profile, new TPR runs were carried out to a given temperature corresponding to different reduction stages and held for several minutes to allow for the hydrogen consumption of the whole peak. Then the sample was cooled under an argon–hydrogen flow to room temperature and transferred into the Mössbauer cell under the protection of nitrogen for the corresponding Mössbauer measurement. A fresh sample with the same amount was used for each of the runs.

RESULTS AND DISCUSSION

TPR

TPR profiles of the Fe_2O_3/ZrO_2 catalysts are shown in Fig. 1. For unsupported bulk α-Fe_2O_3, two peaks corresponding to the reduction of α-Fe_2O_3 to Fe_3O_4 and of Fe_3O_4 to α-Fe, respectively (17), are observed. For the Fe_2O_3/ZrO_2 catalysts, the TPR profiles are quite different from that of the unsupported α-Fe_2O_3 and change with the loading of iron oxide. Apparently, the interactions between

iron oxide and zirconia lead to the formation of different iron-containing species with different reducibilities. When the amount of iron oxide was increased, the relative area of peak (a) at ca. 643 K decreased while those of peak (b), (c), and (d) at ca. 673, 753, and 903 K, respectively, increased. It is reasonable to consider that the supported Fe^{3+} species might exist in the following different states: (i) large particles or bulk phase α-Fe_2O_3 (X-ray diffraction lines for α-Fe_2O_3 can be observed in the XRD pattern), (ii) small α-Fe_2O_3 particles, and (iii) surface species formed by the strong interactions of iron oxide and zirconia. If there were no interactions between Fe^{3+} species and the support, the small α-Fe_2O_3 particles should be more easily reduced than the bulk phase α-Fe_2O_3 (18). Compared to the reduction profile of unsupported α-Fe_2O_3, peak (b) with a maximum at 673 K can be assigned to the reduction of bulk α-Fe_2O_3 to Fe_3O_4. Peak (a) may originate from the reduction of small α-Fe_2O_3 particles which have very weak interactions with the support. Peak (c) may correspond to the reduction of the surface iron oxide species and/or the intermediates formed in the first (peak a) and the second (peak b) reduction steps. During the fourth reduction stage with peak (d), iron oxides are reduced to α-Fe. This assignment is consistent with the result that the relative area of peak (b), (c), and (d) increases while that of peak (a) decreases with increasing iron oxide loading, since the increase of iron oxide loading would lead to the increase of large α-Fe_2O_3 particles.

Reduction of the Low Loading (1.6 wt% Fe_2O_3) Fe_2O_3/ZrO_2 Catalyst

The room-temperature Mössbauer spectra of the 1.6 wt% Fe_2O_3/ZrO_2 sample reduced at 643, 753, 973, and 1073 K, respectively, are shown in Fig. 2. The spectrum of the as-prepared sample can be fitted by a doublet with parameters typical of superparamagnetic Fe^{3+} cations (19). In the TPR profile of this sample, peak (b) which corresponds to the reduction of the bulk phase α-Fe_2O_3 does not appear, indicating that no large α-Fe_2O_3 particles exist in the sample. After the sample is reduced at 643 K, Mössbauer results (Table 1) reveal that 24% Fe^{3+} cations are reduced to Fe^{2+} cations, while most of the Fe^{3+} cations are not reduced due to the strong interaction with zirconia. Based on the above TPR and Mössbauer spectroscopic results, one can assume that there are two kinds of Fe^{3+} cations in the sample: (i) small α-Fe_2O_3 particles which have very weak interactions with the support and are easier to reduce than the bulk phase α-Fe_2O_3, and (ii) surface iron oxide species which have strong interactions with the support and are difficult to reduce. From Table 1 it can be seen that along with the increase in the reduction temperature from 643 to 973 K, more and more Fe^{3+} cations are reduced. After the sample is treated at 973 K, 26% Fe^{2+} cations which are thought to originate from the reduction of the small α-Fe_2O_3 particles are reduced to α-Fe. In contrast, the Fe^{2+} cations originating from the surface iron oxide species are not reduced due to their strong interactions with the support.

Further increase of the reduction temperature from 973 to 1073 K leads to a dramatic alternation of the catalyst. Along with the reduction of Fe^{2+} to α-Fe, an amazing increase in the amount of Fe^{3+} cations is observed. Similar results have been obtained by Tang Ren-Yuan *et al.* (3) and F. J. Berry *et al.* (20). They found the phonomena of partial oxidation of Fe^{2+} to Fe^{3+} and of Fe_3O_4 to Fe^{3+} in the reduction processes. According to the surface interaction "incorporation model" (11), surface vacant sites exist in the surface of zirconia support, and the supported iron

TABLE 3
Mössbauer Parameters of 4 wt% Fe_2O_3/ZrO_2 Catalyst Treated under Various Conditions

Treatment condition	Mössbauer parameter			Iron species	Relative area (%)
	IS (mm/sec)	QS (mm/sec)	H (KOe)		
As-prepared	0.35	1.04	0	Fe^{3+}	100
TPR to 673 K	0.40	0.87	0	Fe^{3+}	55
	1.05	2.30	0	Fe^{2+} (A)	22
	0.28	−0.04	485	Fe^{3+}	6
	0.66	0.03	459	Fe^{3+}, Fe^{2+}	17
TPR to 753 K	0.40	0.99	0	Fe^{3+}	52
	0.99	0.00	0	Fe^{2+} (B)	21
	1.07	2.26	0	Fe^{2+} (A)	27
TPR to 973 K	0.00	0.00	340	Fe^{0}	58
	0.37	1.00	0	Fe^{3+}	16
	1.15	2.13	0	Fe^{2+} (A)	26

cations can incorporate into these surface vacant sites. The interactions between iron cations and the zirconia support are very strong, and hence the reduction of these iron cations becomes very difficult. At high temperature reduction conditions, the Fe^{2+} cations which incorporate into the surface vacant sites of zirconia might migrate to the bulk phase of the zirconia support, and the solid-state reaction between zirconia and these Fe^{2+} cations could occur; hence the Fe^{2+} cations were reoxidized to Fe^{3+} cations, and the reduction of these Fe^{3+} cations became very difficult.

In summary, the pictorial models for the reduction of the 1.6 wt% Fe_2O_3/ZrO_2 catalyst are shown in Fig. 3.

Reduction of the High Loading (7 wt% Fe_2O_3) Fe_2O_3/ZrO_2 Catalyst

The room-temperature Mössbauer spectra of the as-prepared 7 wt% Fe_2O_3/ZrO_2 catalyst reduced at 673, 753, 973, and 1073 K, respectively, are shown in Fig. 4. The spectrum of the as-prepared sample is composed of a doublet similar to that of the 1.6 wt% Fe_2O_3/ZrO_2 sample and a sextet due to large particles or bulk phase α-Fe_2O_3. The existence of the bulk phase α-Fe_2O_3 is confirmed by the appearance of peak (b) in the TPR profile and the X-ray diffraction lines for α-Fe_2O_3 in the XRD pattern of the sample. Upon reduction at 673 K, the bulk phase α-Fe_2O_3 is reduced to Fe_3O_4 (Table 2). It is pertinent to note that the ratio of Mössbauer spectra are contributed by the octahedral site to that of the tetrahedral site (S) is observed to increase to a value of 3 compared to a value of 2 for the pure Fe_3O_4, indicating there are more iron cations in B site than that for pure Fe_3O_4. A comparison of this behavior with that noted by Lund *et al.* (4–7) and XingTao Gao *et al.* (8) in their studies on silica supported magnetite and titania supported magnetite lead to the suggestion that the iron cations in tetrahedral sites in the zirconia supported Fe_3O_4 are substituted by zirconium cations from the support, resulting in the increase in S. A weak shoulder peak at 643 K is observed in the TPR profile, indicating that some small α-Fe_2O_3 particles are reduced to Fe^{2+} cations. But the Mössbauer parameters assigned to these Fe^{2+} cations are not obtained in the Mössbauer data, due to that the spectrum is very complex and the content of these Fe^{2+} cations is rather low.

After the sample is treated at 753 K, it is observed that the two sextets assigned to Fe_3O_4 are substituted by a singlet assigned to Fe^{2+} cations (21, 22). Moreover the amount of Fe^{3+} cations increase, indicating the partial oxidation of Fe_3O_4 to Fe^{3+} in the reduction process. It is also interesting to find that the chemical circumstance of these Fe^{2+} cations obtained by reduction of the Fe_3O_4 particles which are partly substituted by zirconium cations is different from that of the Fe^{2+} cations originated from the small

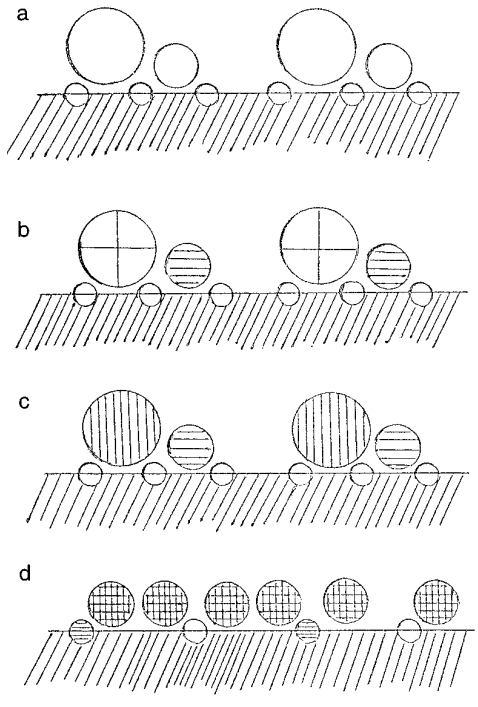

FIG. 7. Pictorial models for the reduction of the 4 wt% Fe_2O_3/ZrO_2 catalyst. (a) As-prepared, (b) TPR to 673 K, (c) TPR to 753 K, (d) TPR to 973 K. ○ Fe^{3+} cations from the surface iron oxides; ○ Small Fe_2O_3 particles; ◯ Bulk phase Fe_2O_3 particles; ⊜ Fe^{2+} cations from the reduction of the surface Fe^{3+} cations; ⊜ FeO from the reduction of the small Fe_2O_3 particles; ◍ FeO from the reduction of the Fe_3O_4 particles; ⊕ Fe_3O_4 particles; ◍ Metallic iron particles; ////// Surface of the zirconia support.

α-Fe_2O_3 particles and the surface iron oxide species, as the discrepancy in their QS is very large. Further increases in the reduction temperature from 753 to 1073 K lead to more and more Fe^{3+} cations and Fe^{2+} cations reduced to α-Fe. But some surface iron oxide species cannot be reduced due to their strong interactions with zirconia.

The pictorial models for the reduction of the 7 wt% Fe_2O_3/ZrO_2 catalyst are shown in Fig. 5.

Reduction of the Medium Loading (4 wt% Fe_2O_3) Fe_2O_3/ZrO_2 Catalyst

The room-temperature Mössbauer spectra of the as-prepared 4 wt% Fe_2O_3/ZrO_2 catalyst reduced at 673, 753, and 973 K, respectively, are shown in Fig. 6. For the sample with a medium iron oxide loading, peaks (a), (b), (c), and (d) can all be clearly observed in the TPR profile. We therefore assume that the large α-Fe_2O_3 particles, small α-Fe_2O_3 particles, and the surface iron oxide species coexist. This assumption is consistent with the results of the following Mössbauer spectroscopy (Table 3). After the sample is reduced at 673 K, three kinds of iron species are observed in the Mössbauer spectrum, namely, Fe_3O_4 originated from the reduction of the large α-Fe_2O_3 particles, Fe^{2+} (A)

cations from the reduction of the small α-Fe_2O_3 particles, and Fe^{3+} cations from the surface iron oxide species. After an increase in the reduction temperature to 753 K, the Fe_3O_4 particles are reduced to Fe^{2+} (B) cations, and a few of the Fe^{3+} cations from the surface iron oxide species are reduced to the Fe^{2+} (A). A further increase in the reduction temperature from 753 to 973 K results in the reduction of the Fe^{2+} (B) and part of the Fe^{2+} (A) to form α-Fe, while another part of the Fe^{2+} (A) and Fe^{3+} are not reduced due to their strong interactions with zirconia.

The pictorial models for the reduction of the 4 wt% Fe_2O_3/ZrO_2 catalyst are shown in Fig. 7.

According to the above results, we can find that the reduction behavior of zirconia supported iron catalysts is quite different from that of Fe_2O_3/Al_2O_3, Fe_2O_3/SiO_2, and Fe_2O_3/TiO_2 (3–8).

CONCLUSIONS

The interactions between iron oxide and the support depend not only on the support property but also on the iron oxide loading. For the Fe_2O_3/ZrO_2 catalysts with various Fe_2O_3 loading, the dispersion states of Fe_2O_3 are quite different. The average particle size of α-Fe_2O_3 increases with increasing Fe_2O_3 loading and hence influences the interactions between Fe_2O_3 and ZrO_2. It is considered that three kinds of Fe^{3+} species exist in the sample: (i) large particles or bulk phase α-Fe_2O_3, (ii) small α-Fe_2O_3 particles, and (iii) surface iron oxide species. Reduction of the small α-Fe_2O_3 particles which have very weak interactions with zirconia is easier than that of the bulk phase α-Fe_2O_3, but the reduction of the surface iron oxide species is much more difficult due to the strong interactions between iron oxide and zirconia.

ACKNOWLEDGMENT

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