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An *in Situ* Combined Temperature-Programmed Reduction–Mössbauer Spectroscopy of Alumina-Supported Iron Catalysts

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Two 10% Fe/Al_2O_3 catalysts with supports of different surface areas were studied by means of an *in situ* combined temperature-programmed reduction (TPR)–Mössbauer spectroscopy technique, which enabled a Mössbauer measurement to be obtained *in situ* after temperature-programmed reduction to any temperature. Various reactions occurring during the TPR process of the catalysts were revealed. It was found that, although the iron concentration was high, considerably strong metal (oxide)–support interactions occurred in the catalyst with higher surface area, and the TPR of the sample consisted of three consecutive stages, namely, at around 460°C, 790°C, and above 850°C. In the first stage from 300 to 600°C mainly the reduction of Fe(III) to Fe_3O_4 and then Fe_3O_4 to Fe(II) aluminate took place. It was amazing to find that over the temperature range of 470–600°C Fe_3O_4 was converted into Fe(II) and Fe(III) aluminates without the consumption of hydrogen, and thereby an increase in the amount of Fe(III) was observed when increasing the TPR temperature from 470 to 600°C. In the meantime, the Fe(III) species which remained unreduced were also transformed to Fe(III) aluminate at these temperatures. In the second stage from 600 to 850°C, Fe(III) aluminate was reduced, giving rise to the formation of Fe(II) aluminate and Fe(0). In the final stage, above 850°C, Fe(II) aluminate was reduced to Fe(0). It was found that the reduction of Fe(II) aluminate was accompanied by a migration of the Fe(II) ions from the octahedral sites to the less stable tetrahedral ones, and thus facilitated the reduction. Chemical control of the reduction was present during the TPR over the temperature range of 470–700°C. The catalyst with lower surface area gave a similar pattern of reduction, but with some varied features due to different extent of metal–support interactions. © 1987 Academic Press, Inc.

INTRODUCTION

Temperature-programmed reduction (TPR) (*1, 2*) has in recent years become one of the most widely used physicochemical techniques for the characterization of heterogeneous catalysts. The main feature of the method is its capability of continuously monitoring the consecutive reactions of reducible species at increasing temperatures. It can thus provide information about the dispersion states of the metallic components as well as the metal–support and metal–metal interactions in catalysts, since all of these influence reduction behavior. However, the reduction steps are sometimes so complicated, as represented by many reduction peaks in a TPR profile, that it is not easy to identify each of them. In this regard, Mössbauer spectroscopy becomes a powerful technique which can not only determine the chemical states of various species in catalysts, but also work under *in situ* conditions (*3, 4*). An *in situ* combination of TPR and Mössbauer spectroscopy, therefore, would be an ideal means for the characterization of heterogeneous catalysts.

We have recently developed a novel *in situ* combined TPR–Mössbauer spectroscopy technique, which proves to be very informative and effective in our applications to several kinds of supported iron catalysts. In the present paper the results obtained from two 10% Fe/Al_2O_3 catalysts are reported.

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EXPERIMENTAL

Preparation of the catalysts. The main 10% Fe/Al$_2$O$_3$ catalyst studied in the present work was prepared by the impregnation of a γ-Al$_2$O$_3$ (surface area 209 m^2/g and particle sizes 0.45–1.00 mm) with aqueous Fe(NO$_3$)$_3 \cdot 9$H$_2$O, followed by drying and calcination in air at 120°C overnight and at 480°C for 4 h, respectively.

Another 10% Fe/Al$_2$O$_3$ catalyst, used for comparison, was prepared by the same method but with a γ-Al$_2$O$_3$ of lower surface area (140 m^2/g). It is designated as 10% Fe/Al$_2$O$_3$-LSA.

Sample holder. The sample holder for the *in situ* combined TPR–Mössbauer spectroscopy technique used in the present study is shown in Fig. 1. It consisted mainly of two parts, i.e., the TPR reactor and the Mössbauer absorber cell, joined by a connecting tube and a four-way stopcock. The left part was the TPR reactor made of quartz, at the bottom of which was a small gap between the outer and the inner tubes for the reducing gas to pass through. When TPR was conducted, the reducing gas was admitted from the right-hand entrance of the four-way stopcock and, after passing the sample bed at the bottom of the TPR reactor, let out from the left-hand exit to the thermal conductivity cell. The Mössbauer absorber cell on the right was made of glass, with two Mylar windows (0.1 mm thick) glued to both its upper and lower ends. In the front of the cell was a sample entrance and it was sealed with a rubber cork which was further fastened with a copper wire. The most outstanding feature of the sample holder described above is its capability to conduct Mössbauer measurements *in situ* after TPR of the sample to any temperature. This can be readily manipulated after the holder system is cut off by the four-way stopcock and the sample transferred from the TPR reactor to the absorber cell through the connecting tube. During operation the sample lay in the cell as a thin layer over the base with the cell placed in a vertical γ-ray beam.

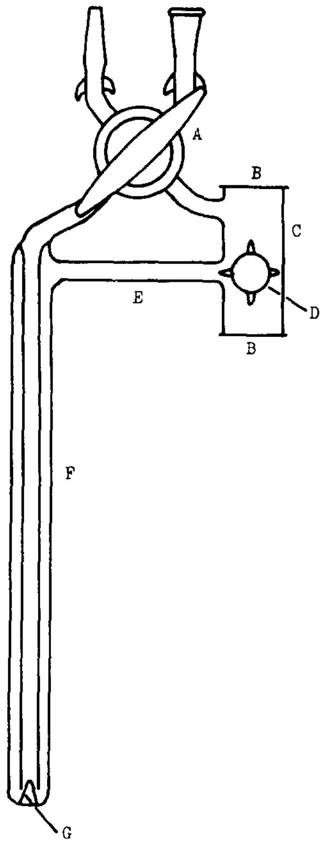

FIG. 1. Sample holder for *in situ* combined TPR–Mössbauer spectroscopy. (A) Four-way stopcock, (B) Mylar window, (C) Mössbauer absorber cell, (D) sample entrance (sealed with a rubber cork), (E) connecting tube, (F) TPR reactor, (G) thermal-couple well.

Experimental procedure. TPR was performed as previously described (5) on 0.15-g sample, in a Ar–H$_2$ (95:5) gas mixture flowing at 30 ml/min and at a constant heating rate of 16°C/min. Mössbauer spectroscopy were conducted with an AME-50 microprocessor-controlled Mössbauer spectrometer at room temperature using a 50 mCi ^{57}Co/Rh source. All spectra were computer-fitted to a Lorentzian line shape with the help of a least-squares fitting procedure, and the isomer shifts (IS) were given with respect to the centroid of α-Fe at room temperature.

The experimental procedure for the *in situ* combined TPR–Mössbauer spectros-

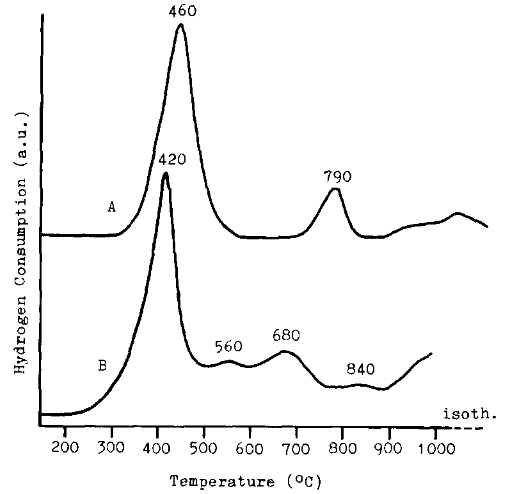

FIG. 2. TPR profiles of (A) 10% Fe/Al_2O_3 and (B) 10% Fe/Al_2O_3-LSA.

copy was as follows. First, a TPR run was performed to a temperature as high as possible to obtain an integrated profile, and then the sample was cooled in argon–hydrogen to room temperature for the corresponding *in situ* Mössbauer measurement. According to the range of temperatures over which each reduction peak appeared in the integrated TPR profile, at least two temperatures were selected for each of the peaks in the subsequent *in situ* combined TPR–Mössbauer experiments. When TPR proceeded to a given temperature it was held at that temperature for a time (e.g., ca. 10 min for low temperatures or ca. 5 min for high temperatures) to allow the hydrogen consumption for the whole or part of a peak. A fresh sample of the same amount was used for each of the runs.

RESULTS AND DISCUSSION

Figure 2A shows the integrated TPR profile to 1025°C of the 10% Fe/Al_2O_3 catalyst. Although with high iron concentration, a strong metal (oxide)–support interaction can be readily visualized by the much higher temperatures of the reduction peaks and the remarkably less reduction taking place following the initial reduction, as compared with those of the bulk α-Fe_2O_3 (*6*). The Mössbauer spectrum recorded from the calcined oxide sample showed a pure doublet (Fig. 3A, IS 0.33 mm/s and quadrupole splitting (QS) 0.78 mm/s), indicating consistently that Fe(III) was well dispersed on the support. The TPR profile indicated a three-stage reduction, at around 460, 790, and above 850°C, respectively, and it is of significance to find out what was going on in each of the stages.

The results showed that the first peak of the TPR profile at 460°C not only was the largest but also represented a very complicated reduction stage. Therefore we paid most attention to this stage, and traced it at quite a few temperatures, namely, 420, 450, 460, 470, and 600°C, respectively. Four

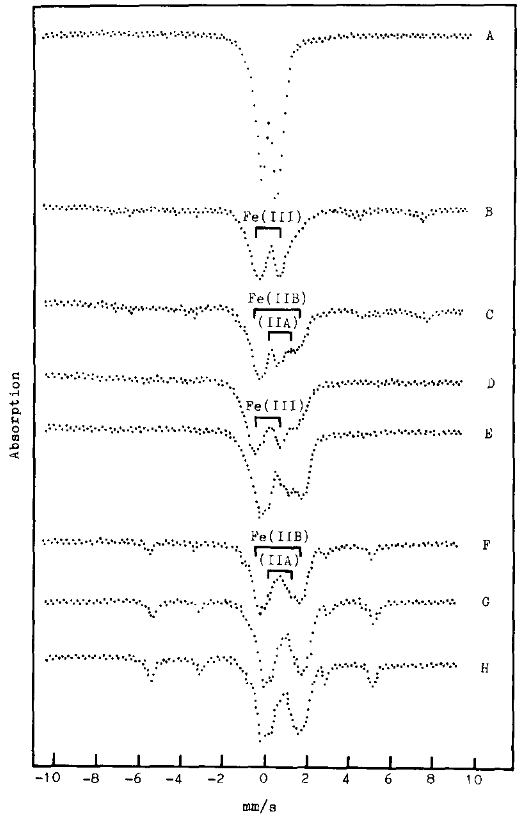

FIG. 3. *In situ* Mössbauer spectra for the 10% Fe/Al_2O_3 following (A) air calcination (not *in situ*), (B) TPR to 420°C, (C) TPR to 470°C, (D) TPR to 600°C, (E) TPR to 700°C, (F) TPR to 800°C, (G) TPR to 985°C, and (H) TPR to 1025°C.

TABLE 1

Mössbauer Parameters for the 10% Fe/Al_2O_3 following TPR to Various Temperatures

Temperature of TPR (°C)	Fe(III)		Fe_3O_4 (A)			Fe_3O_4 (B)			Fe(IIA)		Fe(IIB)		Fe(0)	
	IS[a]	QS[b]	IS	QS	H(KOe)	IS	QS	H(KOe)	IS	QS	IS	QS	IS	H(KOe)
420	0.37	1.11	0.46	0.22	481	0.73	−0.12	423						
470	0.38	0.91	0.28	−0.25	447	0.89	−0.01	437	0.79	1.11	0.73	2.27		
600	0.37	1.12							0.83	1.17	0.73	2.46		
700	0.34	0.97							0.79	1.01	0.82	2.21		
800									0.77	0.99	0.88	2.05	−0.02	329.5
985									0.86	1.19	0.90	2.04	−0.01	331.6
1025									0.90	1.19	0.93	2.03	−0.01	330.4

[a] Isomer shift values ±0.02 mm/s.

[b] Quadrupole splitting values ±0.02 mm/s.

(630, 700, 800, and 850°C) and two (985 and 1025°C) temperatures were selected for the second and the third reduction stages, respectively. The representative Mössbauer spectra are shown in Fig. 3, and the corresponding parameters and spectral contribution of various iron species are listed in Tables 1 and 2. For the spectral contribution it has been assumed that the recoil-free fraction is the same for all the iron species. The data of spectral contribution are more explicitly depicted in Fig. 4.

The First Reduction Stage (from 300 to 600°C)

The *in situ* Mössbauer spectrum recorded following TPR to 420°C showed only the initial reduction of Fe(III) to Fe_3O_4 (Fig. 3B), as was the case for the first reduction stage of the bulk α-Fe_2O_3. A Fe(II) species, however, was also recorded following TPR to 450, 460, and 470°C, and it increased in amount with increasing TPR temperatures. The simultaneous decrease in the amount of Fe_3O_4 indicates that Fe(II) was produced from the reduction of Fe_3O_4. All Fe(II) species were well fitted to a Fe(II) aluminate, with its ferrous ions in both the tetrahedral (A site) and octahedral (B site) vacancies (Table 1). Vaishnava *et al.* (*7*) have reported the formation of Fe(II) aluminate for a 14% Fe/Al_2O_3 catalyst reduced in hydrogen at 400°C and our Mössbauer parameters are close to theirs. A comparison of the result from TPR to 470°C with that from an isothermal reduc-

TABLE 2

Spectral Contribution of Various Iron Species in the 10% Fe/Al_2O_3[a] (%)

Temperature of TPR (°C)	Fe(III)	Fe_3O_4 (A)	Fe_3O_4 (B)	Fe(IIA)	Fe(IIB)	Fe(0)
420	83.0	3.8	13.2			
470	36.8	4.2	7.9	21.5	29.6	
600	45.2			25.0	29.8	
700	9.3			35.5	55.2	
800				35.8	58.0	6.2
985				45.9	42.4	11.7
1025				47.2	38.9	13.9

[a] Assuming that the recoil-free fraction is the same for all the species. All the spectral contribution values ±0.9%.

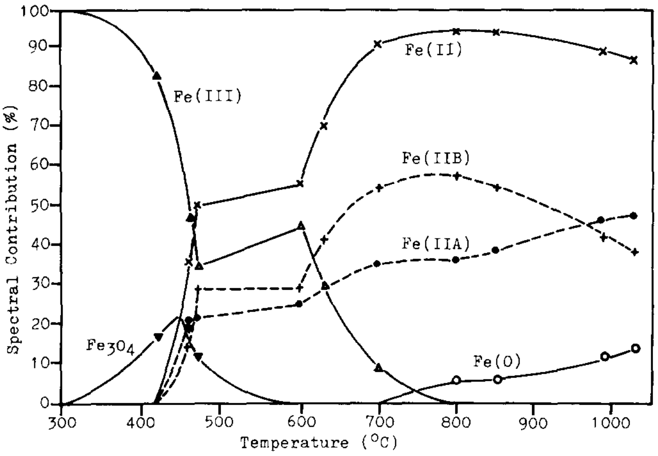

FIG. 4. Spectral contribution of various iron species in the 10% Fe/Al_2O_3 as a function of TPR temperature.

tion in hydrogen at 470°C for 4 h further revealed that under argon–hydrogen conditions Fe(II) aluminate was preferably formed to Fe(0). It is also noted that upon TPR of the oxide sample in argon–hydrogen to 420°C the quadrupole splitting increased markedly from 0.78 to 1.11 mm/s, indicating a decrease in particle sizes of Fe(III) species (*8*). The reactions which occurred during TPR to 470°C may be formulated by Eqs. (1) and (2) in Table 3, where Fe(III) is assumed to be in the form of α-Fe_2O_3 of small particle sizes.

Further increase in the temperature of TPR from 470 to 600°C led to a dramatic alteration of the catalyst, which is shown by Fig. 3D and, more explicitly, by Table 2 and Fig. 4. Along with the reduction of Fe_3O_4 to Fe(II) aluminate, an amazing increase in the amount of Fe(III) was observed within this temperature range. The *in situ* combined TPR–Mössbauer experiments on this phenomenon were repeated many times for the present catalyst and, previously, for the 10% Fe/Al_2O_3-LSA, and the observation was definitely reproducible. It should be pointed out that the same amount of hydrogen was consumed during TPR to 600°C as to 470°C, which implied that the alteration occurred

TABLE 3

Possible Reactions in Each TPR Stage of the 10% Fe/Al_2O_3

TPR stage (°C)	Eq.	Possible reactions	Temperature (°C)
460	1	$3FeO_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$	300–470
	2	$Fe_3O_4 + 3Al_2O_3 + H_2 \rightarrow 3FeAl_2O_4 + H_2O$	450–470
	3	$Fe_3O_4 + 2Al_2O_3 \rightarrow FeAl_2O_4 + 2FeAlO_3$	470–600
	4	$Fe_2O_3 + Al_2O_3 \rightarrow 2FeAlO_3$	420–600
790	5	$2FeAlO_3 + Al_2O_3 + H_2 \rightarrow 2FeAl_2O_4 + H_2O$	600–790
	6	$2FeAlO_3 + 3H_2 \rightarrow 2Fe + 3H_2O$	790–850
>850	7	$FeAl_2O_4 + (4 - x)H_2 \rightarrow Fe + Al_2O_x + (4 - x)H_2O$ $(0 < x < 3)$	>850

actually without consumption of hydrogen. It was also noted that ca. 8% Fe(III) (in the A and B sites of Fe_3O_4, respectively) and ca. 4% Fe(II) (in the B sites of Fe_3O_4) were converted while the same amount of Fe(III) and Fe(II) species were newly formed (Table 2) and that the quadrupole splitting of Fe(III) increased again notably to a value of 1.12 mm/s at 600°C (Table 1). We therefore suggest a transformation of Fe_3O_4 into Fe(III) and Fe(II) aluminates as shown by Eq. (3) in Table 3. In the meantime, it is reasonable to expect that the Fe(III) species still not reduced was in the form of aluminate, on account of its high resistance to reduction. This part of Fe(III) aluminate may be formed through Eq. (4) during TPR to 420°C and higher temperatures, as suggested by the marked increase in the quadrupole splitting.

The Second Reduction Stage (*from 600 to 850°C*)

Both TPR to 630 and 700°C indicated the reduction of Fe(III) aluminate to Fe(II) aluminate, as shown by Fig. 4 for both, and Fig. 3E and Tables 1 and 2 for the latter. The reaction may be formulated by Eq. (5) in Table 3. It was interesting, however, that actually no hydrogen was consumed within this temperature range (Fig. 2A). This, together with some of the results in the preceding section, provided interesting information about the reduction rates of Fe(III) aluminate as well as Fe_3O_4.

In fact, we have obtained four different sets of data with the same amount of hydrogen consumption during TPR, namely, to (a) 470°C (held for 10 min), (b) 600°C (for 15 min), (c) 630°C (for 10 min), and (d) 700°C (for 5 min). In addition, we obtained *in situ* Mössbauer data from another sample (e) quenched immediately after the TPR temperature reached 600°C where the recorder returned to the baseline when obtaining the first peak. The data for the last case still indicated the existence of ca. 14.9% Fe_3O_4, in addition to 48.5% Fe(II) aluminate and 36.6% Fe(III). So, although consuming the same amount of hydrogen, the degree of reduction of the catalyst increased in the order e < a < b < c < d, which suggested chemical control during the reduction of Fe_3O_4 and Fe(III) aluminate over the corresponding temperature ranges. It is evident that the accomplishment of a TPR peak with a given amount of hydrogen does not necessarily mean the completion of reduction in the corresponding stage, and both the duration and temperature of reduction are of great importance. A general pattern for the hydrogen reduction of metal oxide is given in the literature (*9*). The $O^{2-}_{(s)}$ ions at the oxide surface react with hydrogen and are converted to $OH^-_{(s)}$, and a corresponding number of electrons are trapped at sites in or near the surface. The reaction can be propagated if the temperature is such that water is eliminated from $OH^-_{(s)}$ groups and is desorbed. The electrons are immediately or eventually collected by cations, giving rise to the product of reduction. Now, with the same amount of hydrogen consumed, less Fe_3O_4 was reduced in case e (transient reduction at 600°C) than in case a (lower temperature but longer duration), and all Fe_3O_4 was reduced only when the time was prolonged to 15 min at the same 600°C (case b). Moreover, it took 8 min to raise the temperature from 470 to 600°C and therefore a significant amount of water could have been eliminated if the formation of $OH^-_{(s)}$ groups were sufficiently fast. We therefore suggest that the formation of $OH^-_{(s)}$ must be quite slow at the surface of Fe_3O_4 supported on alumina, apparently due to the absence of metallic iron sites to dissociate hydrogen when ferrous spinel was formed. However, the TPR process indicated at the same time that Fe_3O_4 was fast in consuming hydrogen (finishing consumption upon the recorder returning to the baseline), which suggests that hydrogen must associate with $O^-_{(s)}$ in Fe_3O_4 in some form of a surface complex prior to the formation of $OH^-_{(s)}$ groups. On the other hand, further reduction with no more hydrogen consumption over 600–700°C, where Fe(III) aluminate was reduced to Fe(II) aluminate, may suggest a propagation process of reduction through the desorption of water at higher temperatures. Calculation shows that the reductive reactions over 300–700°C need 1.22×10^{-4} mol hydrogen, which is in excellent accordance with the amount of 1.24×10^{-4} mol consumed within the first peak and thereby supports strongly our suggestion of chemical control during reduction over this temperature range.

After TPR was performed to 800°C and held for 5 min to accomplish the second peak at 790°C, the disappearance of Fe(III) aluminate was accompanied mainly by the appearance of Fe(0), in addition to the final increase in the amount of Fe(II) aluminate to its height (Fig. 3F, Tables 1 and 2). The formation of Fe(0) may occur largely on the higher temperature side of the peak and the reaction can be represented by Eq. (6) in Table 3. The reason Fe(III) aluminate was reduced directly to Fe(0), but not through Fe(II) aluminate, may be that the nearby active sites in the alumina were saturated to form more ferrous spinel, and, on the other hand, the temperature was not so high as to reduce the spinel. It is interesting to note that TPR to 850°C gave almost the same degree of reduction while consuming the same amount of hydrogen, which indicates a feature different from the reduction of Fe_3O_4 in the first stage, obviously due to the presence of metallic iron sites to dissociate hydrogen. It is also worth noting that at 850°C, Fe(II) in B sites decreased and that in A sites increased concomitantly in their amounts, while the reduction of Fe(II) aluminate began to occur (Fig. 4). This may not be a mere coincidence when considering the smaller stabilization energy for tetrahedral sites than for octahedral sites (*10, 11*). It is likely that at high temperatures above 800°C a transformation initiated in the structure of Fe(II) aluminate in which Fe(II) ions migrated from the octahedral sites to the less stable tetrahedral ones, and which facilitated the reduction of Fe(II) aluminate.

The Third Reduction Stage (above 850°C)

The third stage of reduction above 850°C was simply the reduction of Fe(II) aluminate to Fe(0), as shown in Figs. 3G and 3H as well as in Tables 1 and 2. The TPR profile near 1000°C appeared to be a small terrace at the onset of the final peak, and when TPR proceeded to 1020°C a large consumption of hydrogen was initiated, which would have been displayed more clearly if not stopped short by holding at 1025°C (Fig. 2A). The *in situ* Mössbauer spectra recorded following TPR to 985 and 1025°C showed the continuous increase of Fe(0) and decrease of Fe(II) aluminate and, in the meantime, the spectral contribution of Fe(II) in A sites became larger than that of Fe(II) in B sites, indicating an unstable state of the spinel ready for reduction (Fig. 4 and Table 2). The reaction which occurred in this stage may be formulated by Eq. (7) in Table 3, in which a possible reduction of alumina is also assumed because of the high temperatures. It should be pointed out that due to the strong metal–support interactions, only about 14% Fe(0) was obtained after TPR to 1025°C, with the rest of the iron in the form of ferrous spinel.

Hence, in summary, the reduction of the 10% Fe/Al_2O_3 exhibited a behavior quite different from the bulk α-Fe_2O_3 due to strong metal–support interactions. The Fe(III) species, presumably a superparamagnetic α-Fe_2O_3, was reduced or converted to Fe(II) and Fe(III) aluminates in the first reduction stage. Then Fe(III) aluminate was reduced to form Fe(II) aluminate and Fe(0) in the following stage. In the final stage the reduction of the most stable ferrous spinel occurred.

Comparison with the 10% Fe/Al₂O₃-LSA

A similar *in situ* combined TPR–Mössbauer study has also been conducted on the 10% Fe/Al_2O_3-LSA catalyst, which differed only in its lower surface area of the support, and the TPR profile is shown in Fig. 2B. It is apparent that the metal–support interactions in this sample were weaker than those in its counterpart with higher surface area (HSA), as demonstrated by its lower temperatures for initial reduction and the more reduction which occurred further over the higher temperature range. This is proved by the much higher amount of Fe(0) (ca. 40%) formed during the TPR of it to 1000°C. However, it is interesting that the results obtained on the two catalysts were quite similar, although with some varied features due to the extent of different metal–support interactions.

The first reduction stage for the LSA catalyst actually separated into two TPR peaks, at 420 and 560°C, respectively, due to a decrease in the reduction temperatures of the α-Fe_2O_3. The results showed that the first peak at 420°C corresponded to the reduction mainly from Fe(III) to Fe_3O_4, although TPR to 430°C also indicated the formation of some Fe(II) aluminate from Fe_3O_4, which must result from the intensive superposition between the peaks. The reduction of Fe_3O_4 to Fe(II) aluminate took place largely within the peak at 560°C, and in a run to 590°C the dramatic increase in the amount of Fe(III) species was also observed. The peak at around 680°C was found to correspond to the second stage of reduction for the HSA catalyst where Fe(III) aluminate was reduced to Fe(0) in addition to Fe(II) aluminate. The remarkable decrease in the temperatures can be attributed to a poor order of the Fe(III) aluminate due to relatively weak metal–support interaction. Because Fe(II) aluminate also became more amenable to reduction for the same reason, the major part of its reduction peak above 1000°C appeared below 1000°C, and the small terrace at the onset was made a broad peak at 840°C by overlapping. So it is apparent that the decrease in the reduction temperatures of α-Fe_2O_3 and Fe(II) aluminate in the LSA catalyst resulted in the formation of two more TPR peaks, and the formation of more reduction peaks during TPR, in turn, can usually be an indication of weaker metal–support interactions.

CONCLUSIONS

Our conclusions from the *in situ* combined TPR–Mössbauer spectroscopic study of the 10% Fe/Al_2O_3 catalysts and the prospects for the technique are as follows.

1. The reduction process of the 10% Fe/Al_2O_3 (HSA) under TPR conditions is quite different from that of bulk α-Fe_2O_3, and it comprises three consecutive reduction stages in which some five reductive reactions and two transformations without hydrogen consumption occur.
2. Two 10% Fe/Al_2O_3 catalysts with supports of different surface areas give similar patterns of reduction, but with some varied features due to the extent of different metal–support interactions.
3. With the sample holder described in the present paper, the *in situ* combined TPR–Mössbauer spectroscopy technique can readily be extended further to temperature-programmed oxidation (TPO), desorption (TPD), and even surface reaction (TPSR) combined *in situ* with Mössbauer spectroscopy.

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