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Investigations of Fe-Ru bimetallic catalysts by in situ Mössbauer and EXAFS studies *

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In situ Mössbauer and EXAFS investigations have shown that the reduction of iron in the monometallic Fe/SiO_2 catalyst is only partial, the reduction being mostly to a ferrous silicate phase. In the bimetallic $Fe\text{-}Ru/SiO_2$ catalysts, the proportion of the FeRu alloy formed on reduction increases markedly with the increase in Ru content; clearly, Ru significantly enhances the reduction of iron on SiO_2. In the Ru-rich compositions (Ru/Fe 1.0), most of the iron is present in the alloy phase and there is no segregation of α-Fe. A comparative study of the different supports has shown that γ-Al_2O_3 and SiO_2 interact with iron strongly at low reduction temperatures while the TiO_2 support interacts at higher temperatures. The presence of traces of Fe^{3+} often found in reduced Fe-Ru catalysts is shown to arise from the oxidation of fine segregated iron particles on the support.

Keywords: Bimetallic catalysts; hydrogenation catalysts; $Fe\text{-}Ru/SiO_2$; supported Fe-Ru catalysts; Fe/SiO_2

1. Introduction

Increasing use of bimetallic catalysts for catalytic reforming has stimulated a great deal of interest in catalysis by alloy systems [1–3]. It is generally found that the structure and performance of bimetallic catalysts differ significantly from those of the corresponding monometallic catalysts [4–7]. Among the various bimetallic catalysts investigated, those of iron with a nobel metal such as Ru have drawn considerable attention because of their importance in Fischer–Tropsch synthesis [8]. Thus, in the case of Fe-Pt catalysts, methanol activity and selectivity is known to increase with the increasing proportion of the alloy phase [9]. Addition of Fe up to 20% maximizes the rate of methanol formation in silica- and zeolite-supported Pd catalysts [10]. The hydrocarbon product distri-

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bution in CO hydrogenation with the Fe-Ru bimetallic catalysts has been found to vary dramatically with the relative proportion of the two component metals [11].

A few characterization studies of Fe-containing bimetallic catalysts have been reported in the literature [11–15]. Based on Mössbauer and X-ray photoemission measurements Niemantsverdriet et al. [12,13] have reported promotion of the reduction of iron in silica-supported Fe-noble metal catalysts due to the hydrogen spillover process; these workers found iron to be only partially reduced to Fe^0. Berry et al. [11] have found that metal–support interaction in silica-supported Fe-Ru catalysts is less than in those supported on alumina. Berry et al. [16,17] have carried out extensive studies on Fe-Ru catalysts supported on TiO_2. They have found that some proportion of iron in 0.2%Fe-2%Ru/TiO_2 when treated in hydrogen above 720 K was different in that partial oxidation of Fe^{2+} to Fe^{3+} occurred under reducing conditions. The Fe K edge-EXAFS shows that Fe^{3+} is formed by reoxidation of Fe^{2+} and does not get incorporated in α-Fe_2O_3 but instead gets segregated at the interface with titania. We have carried out a detailed investigation of bimetallic Fe-Ru/SiO_2 catalysts employing ^{57}Fe Mössbauer spectroscopy and extended X-ray absorption fine structure (EXAFS) measurements. Besides studying the catalysts over a wide range of compositions under different reduction conditions, we have examined the effect of the support on the reducibility of iron in the bimetallic catalysts.

2. Experimental

The SiO_2 support was obtained commercially (Cab-O-Sil). The γ-Al_2O_3 and TiO_2 supports were prepared in the laboratory by the hydrolysis of $Al(NO_3)_3$ and $TiCl_4$ respectively using dilute ammonia solution; the resulting gels were vacuum-dried. The Al_2O_3 gel was calcined at 770 K and the TiO_2 gel at 670 K. Al_2O_3 and TiO_2 so prepared were in the γ- and anatase forms respectively as identified by X-ray diffraction. The surface areas of SiO_2, γ-Al_2O_3 and TiO_2 supports were 220, 110 and 90 m^2/g, respectively as measured with a Micromeritics AccuSorp 2100E instrument using nitrogen adsorption.

The catalyst samples were prepared by slow injection at the required quantity of ruthenium(III) chloride and iron(III) nitrate aqueous solutions (100 ml) into a suspension of the support in 400 ml of water at room temperature. During the injection the pH was maintained at 7 by simultaneous injection of CO_2-free KOH solution under constant stirring. Typical injection rates were 0.5 ml/min. After filtration and subsequent washing with distilled water, the catalyst precursors were dried in air at 350 K overnight. By such a coimpregnation method, bimetallic Fe-Ru/SiO_2 catalysts with a 1:1 molar ratio of Fe and Ru (total metal loadings, 5 and 10 wt%) were prepared. Catalysts with a total metal loading of 20 wt% and Fe : Ru molar ratios of 5 : 1, 2 : 1, 1 : 1 and 0.5 : 1 were also prepared in order to examine the effect of composition. The monometallic Fe/SiO_2 catalyst with 20 wt% metal loading was prepared at 6 pH. For the purpose of studying the support interactions in this bimetallic system, Fe-Ru catalysts supported on γ-Al_2O_3 and TiO_2 were prepared with a total metal loading of 10 wt% and with a 1 : 1 ratio of Fe : Ru.

The precursors were pressed into self-supporting wafers after mixing with a fine powder of boron nitride (Merck) and a drop of polyvinylacetate. The thickness of the wafer was adjusted to about 15 mg/cm^2 of Fe. The wafers were mounted in a locally fabricated all-quartz in situ cell. Reduction was carried out in pure dry purified hydrogen (passed through BASF R-3-11) at atmospheric pressure. During the reduction, the temperature was increased to the desired value (523 or 723 K) at a rate of 6 K/min and was kept constant at that temperature for 2 h. Unless otherwise mentioned, the reduction conditions are the same for all catalysts. After reduction, the samples were cooled to room temperature under flowing hydrogen.

^{57}Fe Mössbauer spectra of the samples were recorded under in situ conditions by using a constant acceleration spectrometer using a 25 mCi ^{57}Co source in Pd matrix (Amersham Corporation, UK). Absolute velocity calibration was done with a Fe foil of 25 μm thickness and the isomer shifts are reported with respect to the same. The spectra were computer fitted using a general Lorentzian routine on a Vax88 system.

EXAFS spectra were recorded with the in situ cell using a Rigaku spectrometer with a rotating anode X-ray generator (Ru-200B, Rigaku, Japan). A Ge(220) crystal was used as the monochromator with a 0.1 mm slit for X-rays from a Mo-target. The spectral resolution was about 5 eV at 9 keV incident energy. The pre-edge data were collected in steps of 5 eV for 100 eV and data up to 700 eV after the edge were collected in steps of 1 eV. The Fourier transforms (FT) were carried out with $k_{\min} \approx 3.5$ and $k_{\max} \approx 12.5$ Å^{-1} after weighting the data by k^3.

3. Results and discussion

3.1. Fe/SiO_2 CATALYST

We shall first discuss our results with the monometallic Fe/SiO_2 catalyst since they are relevant to the study of Fe-Ru bimetallic catalysts. In fig. 1a, we show the Mössbauer spectrum of the dried Fe(20)/SiO_2 catalyst precursor before reduction. The spectrum shows a doublet with an isomer shift (IS) and quadrupole splitting (QS) of 0.45 and 0.80 mm s^{-1} respectively (see table 1) characteristic of the dispersed α-FeOOH phase [18]. The Fourier transform (FT) of the Fe K edge-EXAFS of this precursor shows the main peak at 1.64 Å.

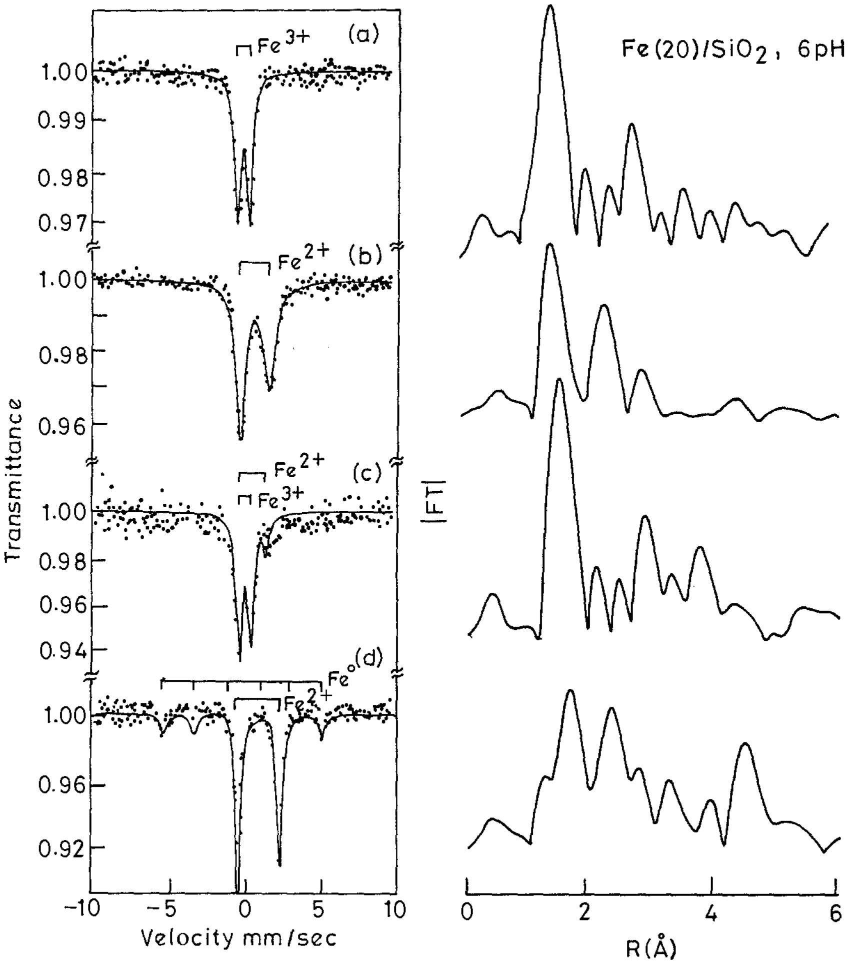

Fig. 1. Mössbauer spectra and Fourier transforms of the Fe K edge-EXAFS of monometallic Fe(20)/SiO_2 catalyst: (a) precursor dried at 350 K; (b) after reduction of the precursor at 723 K; (c) after exposing the reduced catalyst to air for a few hours; (d) after reduction of (c) at 1023 K. Asymmetry in the spectrum of the silicate (b) has been documented in the literature [18,19].

Table 1

Mössbauer parameters (mm s^{-1}, ±0.03) of the oxidic iron species in the monometallic Fe/SiO_2 catalyst

Iron species	IS	QS
Fe^{3+} in the dried precursor	0.47	0.80
Fe^{2+} in the reduced catalyst (723 K)	1.16	1.93
Fe^{3+} formed after exposure to air	0.40	0.87
Fe^{2+} in the reduced catalyst (1023 K)	1.28	2.87

Table 2
Structural parameters from Fe K edge-EXAFS of monometallic Fe/SiO_2 catalysts [a]

Catalyst	Atom pair	N	R (Å)	$\Delta\sigma^2$ (Å^2)
Fe(20)/SiO_2 (6 pH)				
dried	Fe–O	5.0	2.01	0.0015
reduced (723 K)	Fe–O	3.5	1.99	0.0015
		5.2	2.74	0.0018

[a] N, R and $\Delta\sigma^2$ stand for the coordination number, the interatomic distance and the disorder term of the nearest neighbours. The errors involved are N, 20%; R, 0.03 Å, $\Delta\sigma^2$, 0.0001 Å^2.

Curve-fitting of the inverse transformed data (r-window: 1.44–1.84 Å) employing the phase and amplitude parameters of Ni–O in NiO gave a Fe–O coordination number of 5 at a distance of 2.01 Å with a high Debye–Waller factor (0.0015 Å^2). This is expected since the first coordination polyhedron of α-FeOOH is distorted. Best-fit parameters to the EXAFS data along with the Debye–Waller factors are listed in table 2.

After reduction at 723 K, the Fe(20)/SiO_2 catalyst shows an asymmetric doublet in the Mössbauer spectrum (fig. 1b) with an IS of 1.16 mm s^{-1} and QS of 1.93 mm s^{-1} due to the formation of a silicate phase [18]. The FT of Fe K edge-EXAFS of the reduced sample shows three distinct peaks at 1.52, 2.38 and 2.96 Å. The inverse transformed data of the first peak gave a good fit with one Fe–O distance of 1.99 Å and that of the second peak with a distance of 2.74 Å (table 2). The presence of two distinct Fe sites with oxygen coordination indicates that the silicate phase may be a highly dispersed $FeSiO_3$ [19]. However, it did not show any characteristic feature in the X-ray diffraction pattern under in situ conditions. When the reduced Fe/SiO_2 catalyst was exposed to air at room temperature, it almost completely converted back to Fe^{3+} as in the dried precursor as can be seen from the Mössbauer and EXAFS data shown in fig. 1c. This is an example of the Fe^{3+}–Fe^{2+} oxidation–reduction process involving metal–support interaction.

The ferrous silicate phase formed during reduction at 723 K cannot be further reduced up to very high temperatures. The Mössbauer spectrum of the catalyst reduced at 1023 K (fig. 1d) shows only a weak six-finger pattern due to α-Fe(BCC) superimposed on a strong doublet due to unreduced Fe^{2+} in the form of bulk silicate (IS, 1.28 mm s^{-1}; QS, 2.87 mm s^{-1}); the %Fe is estimated to be 20. The FT of the Fe K edge-EXAFS shows peaks similar to those of the catalyst reduced at 723 K (fig. 1b), but there is a noticeable increase in the magnitudes of the second and the third peaks. It appears therefore that the ferrous silicate phase gets well sintered at 1023 K under reduction conditions; the Fe(20)/SiO_2 catalyst is therefore hardly reducible.

3.2. BIMETALLIC Fe-Ru CATALYSTS

We have examined the reducibility of iron on SiO_2 after the addition of a small amount of Ru. The Mössbauer spectrum of the dried Fe(5)-Ru(1)/SiO_2 precursor (total metal loading, 20 wt%) given in fig. 2, shows a doublet characteristic of Fe^{3+} similar to that obtained with the precursor of Fe/SiO_2 (fig. 1a). However, the reduction behaviour of this catalyst is strikingly different due to the hydrogen spill-over process [13]. Fe^{3+} gets reduced almost completely to Fe^{2+} at a relatively low temperature of 523 K (fig. 2b). In the case of the monometallic iron catalyst, this conversion was above 670 K. More interestingly, the Fe^{3+} species formed when the reduced sample (523 K) is exposed to air (fig. 2c), is easily reduced to the Fe^{2+} state by hydrogen even at room temperature (fig. 2d). There is, however, no FeRu alloy formation possibly due to the different reduction rates of the Ru and Fe cations, the reduction of Ru occurring at a much lower temperature than that of iron. The Ru metal clusters, thus formed, provide atomic hydrogen by dissociative chemisorption which in turn reduces Fe^{3+} at a relatively low temperature. The temperature being insufficient for alloy formation, the reduction of Fe^{3+} stops at the Fe^{2+} state with the formation of the stable silicate phase. When the reduction is carried out at 723 K, however, Fe^{3+} gets reduced almost completely to α-Fe. We shall discuss this aspect in detail later on.

The Fe(1)-Ru(1)/SiO_2 (with 5 wt% metal loading) catalyst after reduction at 723 K gives a Mössbauer spectrum (fig. 3a) composed of a singlet (IS, 0.044 mm s^{-1}) due to the FeRu alloy, superimposed on a small doublet due to Fe^{3+}. We have examined the structure of this catalyst by Fe and Ru K edge-EXAFS measurements. The FT of the Fe K edge-EXAFS (fig. 3b) shows two prominent peaks at 1.68 and 2.62 Å. Curve-fitting analysis of the first peak showed that it originates from a Fe–O coordination as in the case of Fe/SiO_2. Curve-fitting of the inverse transformed data of the 2.62 Å peak employing phase and amplitude parameters of Fe–Fe from Fe metal (fig. 3c) shows that it is due to metal–metal coordination ($N = 3$, $R = 2.95$ Å). The higher amplitude of the experimental data (in the high k-region) arises from the presence of a heavy scatterer (Ru) resulting from FeRu alloy formation; Ru K edge-EXAFS also showed oscillations characteristic of metal–metal coordination.

We have examined the effect of the composition of the catalyst on the proportion of the different surface species in the Fe-Ru/SiO_2 catalyst. In fig. 4a, we show the Mössbauer spectra of the Fe-Ru/SiO_2 catalysts with Fe : Ru ratios of 5 : 1, 2 : 1, 1 : 1 and 0.5 : 1 (total metal loading, 20 wt%) after reduction at 523 K. In the Fe-rich catalysts, iron exists mainly in the Fe^{2+} state. With increase in the Ru content, the proportion of the FeRu alloy increases with a simultaneous decrease in the proportion of Fe^{2+}; the Fe^{3+} phase increases only marginally. On the other hand, catalyst samples reduced at 723 K (fig. 4b) show an enhanced reducibility with only a small proportion of iron in the Fe^{2+} and

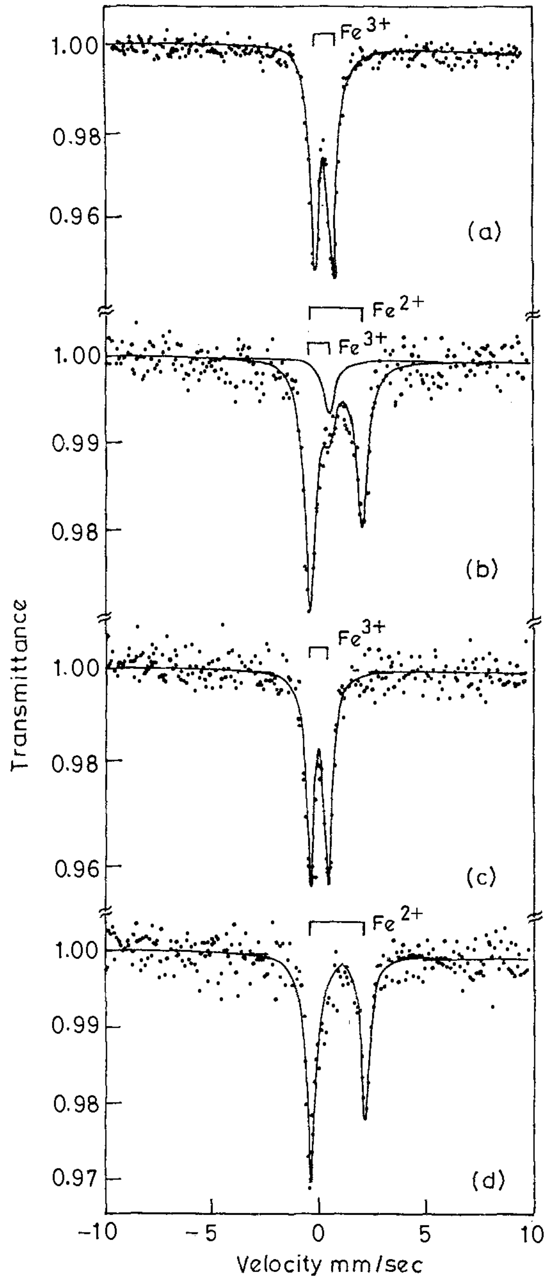

Fig. 2. Mössbauer spectra of bimetallic Fe(5)-Ru(1)/SiO_2 catalyst (total metal loading, 20%): (a) precursor after drying at 350 K; (b) after reducing the precursor at 523 K; (c) after exposing the reduced catalyst to air for a few minutes; (d) after exposing (c) to hydrogen at room temperature.

Fe^{3+} states; in the Fe-rich compositions, a high proportion of iron is in the α-Fe form; as the Ru content increases, especially when Ru/Fe $\geqslant$ 1, the proportion of the FeRu alloy increases. These variations are depicted in fig. 5.

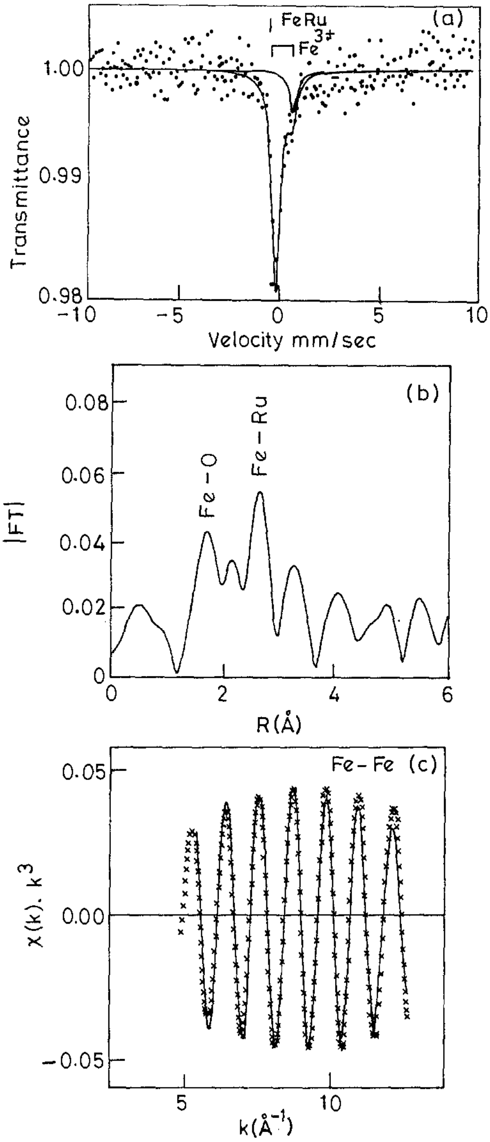

Fig. 3. (a) Mössbauer spectrum of Fe(1)-Ru(1)/SiO_2 catalyst (total metal loading, 5 wt%) after reduction at 723 K; (b) Fourier transform of the Fe K edge-EXAFS of the catalyst; (c) curve-fitting of the inverse transformed data employing Fe–Fe parameters of Fe metal.

We were interested in examining the effect of the oxide support on the formation of different phases in the bimetallic Fe-Ru catalysts. For this purpose, we have studied Fe(1)-Ru(1) catalysts (total metal loading, 10 wt%) supported on γ-Al_2O_3 and TiO_2 apart from those supported on SiO_2. In fig. 6a, we show the Mössbauer spectra of the catalysts reduced at 523 K. The reduction behaviour of the catalyst is different on the different supports. As pointed out

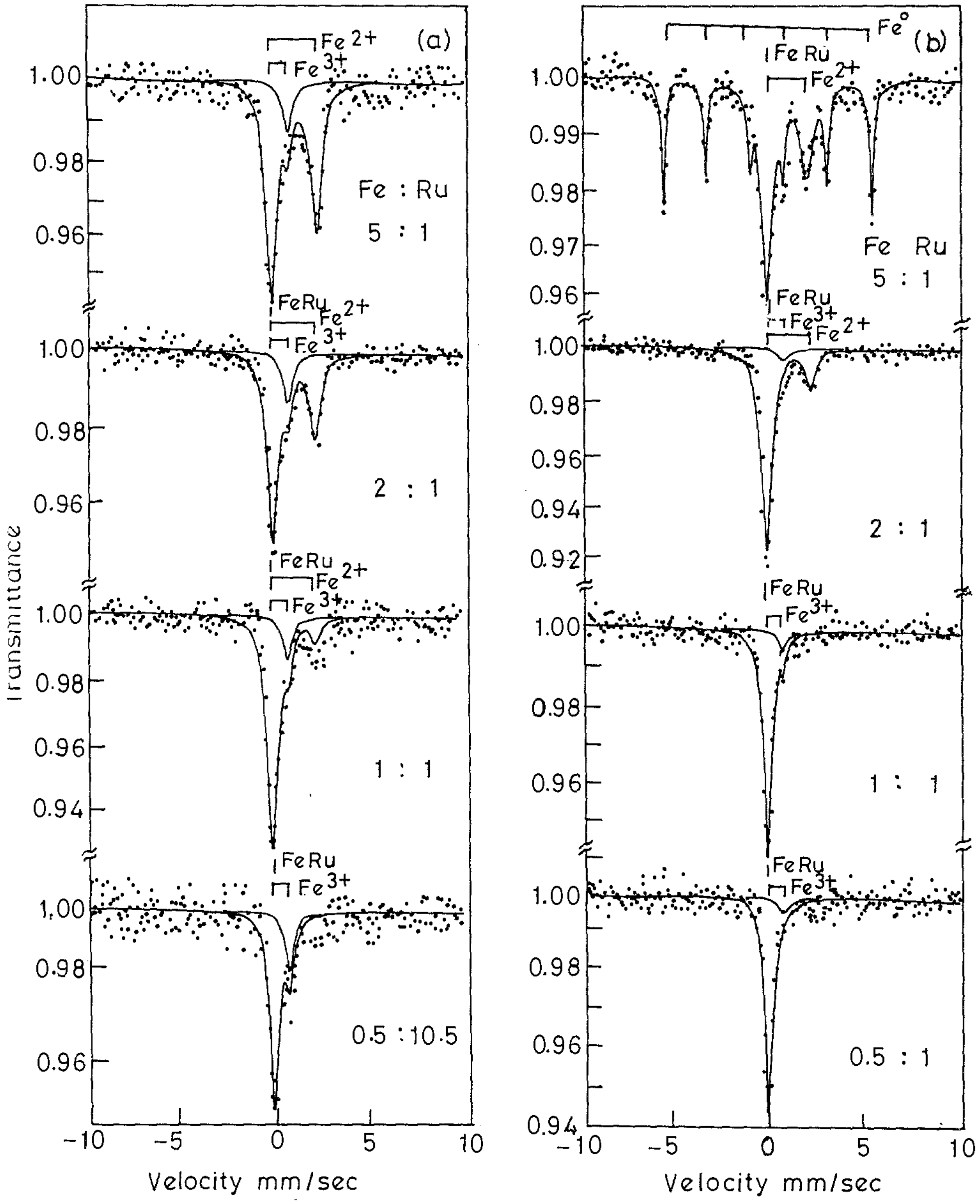

Fig. 4. Mössbauer spectra of bimetallic Fe-Ru/SiO_2 catalysts with different Fe:Ru ratios (total metal loading, 20 wt%) (a) reduced at 523 K; (b) reduced at 723 K.

earlier, the catalyst supported on SiO_2 shows features due to the FeRu alloy, a Fe^{2+} phase and unreduced Fe^{3+} (see table 3). The catalyst supported on γ-Al_2O_3 behaves somewhat similarly, but with a negligible proportion of Fe^{3+}. On the other hand, the catalyst supported on TiO_2 shows almost complete reduction to the alloy phase.

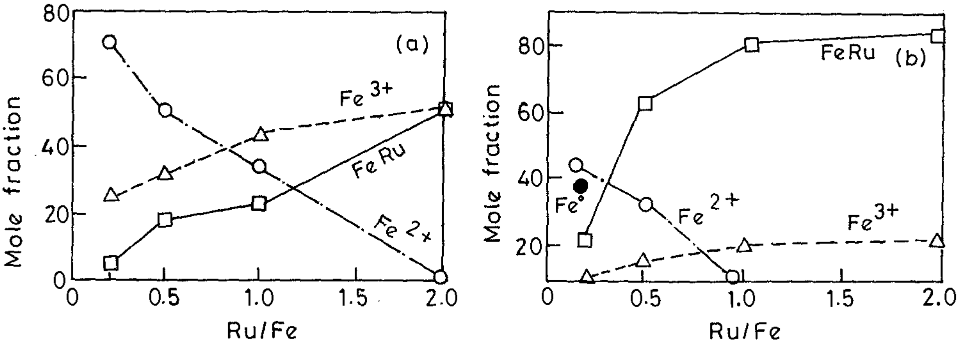

Fig. 5. (a) Variations in the proportions of the different phases in reduced Fe-Ru/SiO_2 catalysts with Ru content: FeRu alloy, squares; Fe^{2+}, circles; Fe^{3+}, triangles; – Fe solid circle. Reduction temperature (a) 523 K and (b) 723 K.

A higher reduction temperature of 723 K dramatically alters the nature of the support interaction (fig. 6b). In the case of SiO_2 and γ-Al_2O_3 supported catalysts there is an enhancement in the proportion of reduced iron as expected, while on the TiO_2 support we notice an oxidic iron species [16,17] which was absent in the reduction carried out at 523 K. The Mössbauer parameters (table 3) suggest that the oxidic phase could be $FeTiO_3$ [20]. Prolonged hydrogen reduction at 723 K of the catalysts already subjected to reduction at 523 K reduces the proportion of the Fe^{2+} phase on both SiO_2 and γ-Al_2O_3 supports (fig. 6c).

The presence of Fe^{3+} in reduced Fe-noble metal catalysts has been a matter of debate in the literature [11,13]. Niemantsverdriet et al. [13] have proposed that some proportion of Fe^{3+} gets trapped in between the FeRu alloy and the support, and that it is not amenable for reduction. It seems unlikely, however, that a noble metal alloy such as FeRu acts as a barrier in hydrogen reduction. We have carried out studies on this aspect by varying the rate of reduction. In fig. 7a, we show the Mössbauer spectrum, of the Fe(1)-Ru(1)/SiO_2 catalyst reduced at 723 K (employing a heating rate of 60 K/min to attain the temperature instead of 6 K/min generally employed by us for all the other catalyst samples). The spectrum has two well-separated singlets with IS values of -0.13 and $+0.16$ mm s^{-1}. Alternatively, one can consider the spectrum to be a quadrupole doublet with an IS of 0.03 and QS of 0.3 mm s^{-1}. A doublet with such a small QS is not expected with the type of iron phases encountered in this study. The singlet with a positive IS is instead assigned to the FeRu alloy particles and that with a negative IS to small Fe^0 particles [11,21]. The occurrence of superparamagnetic Fe^0 particles is not surprising since the rate of heating was high enough to cause such segregation. The iron particles being highly reactive, get oxidized to Fe^{3+} (fig. 7b) at room temperature, even under flowing hydrogen (possibly due to traces of oxygen present). Such segregation of iron is minimized when the reduction is carried out slowly. We suggest that the

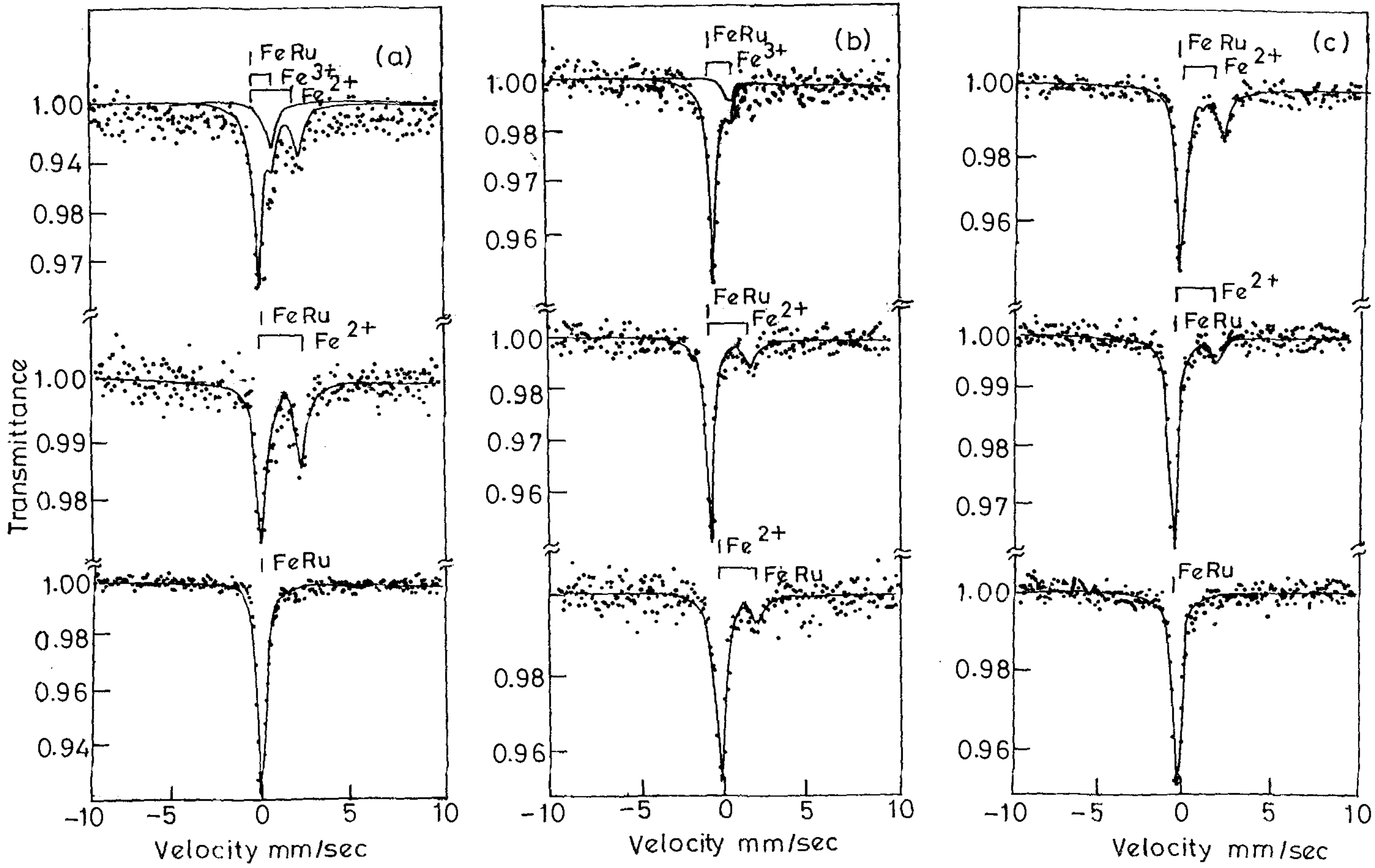

Fig. 6. Mössbauer spectra of Fe(1)-Ru(1) catalysts (total metal loading, 10 wt%) supported on SiO_2, γ-Al_2O_3 and TiO_2: (a) after reduction at 523 K; (b) after reduction at 723 K; (c) after further reduction of the 523 K reduced samples (a) at 723 K.

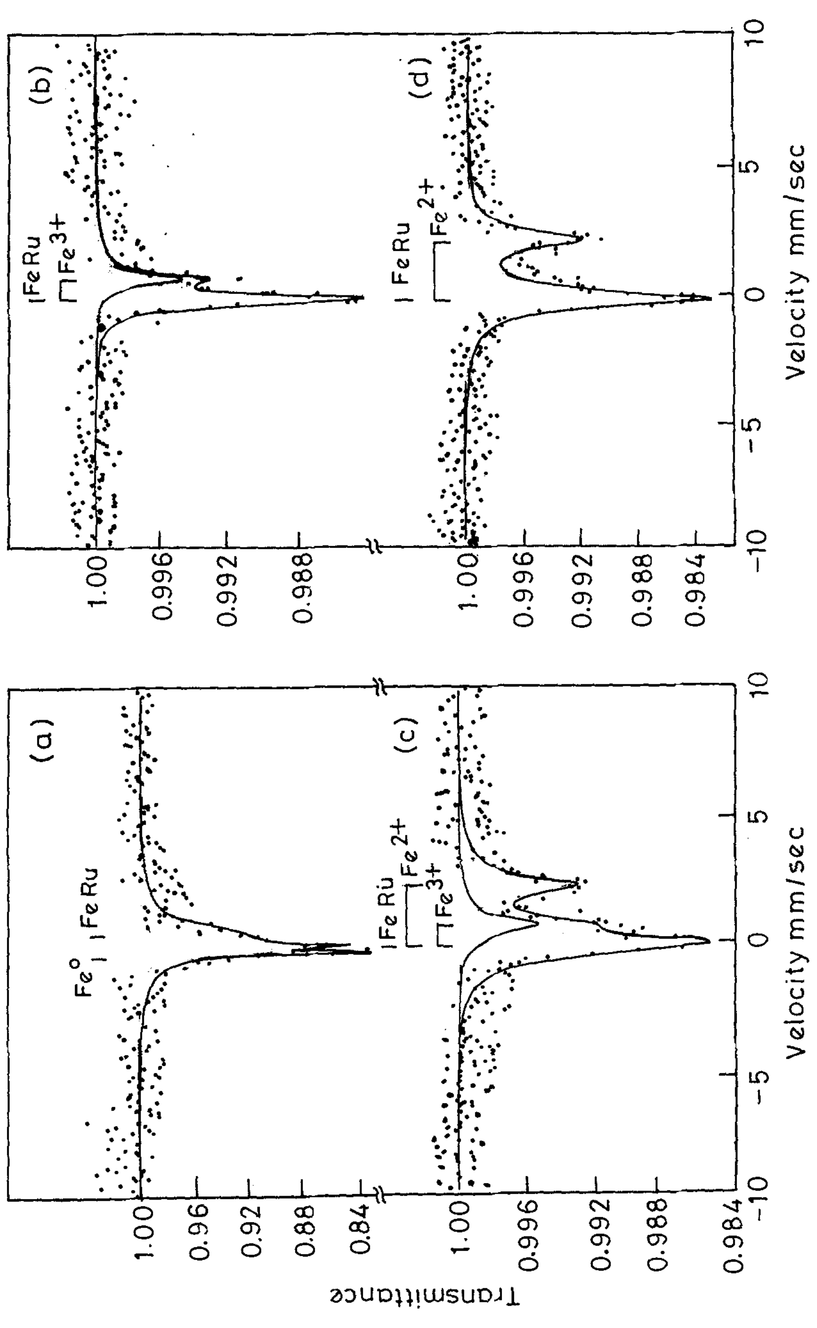

Fig. 7. Mössbauer spectra of the Fe(1)-Ru(1)/SiO_2 (total metal loading, 5 wt%) (a) after reduction at 723 K (with a heating rate of 60 K/min to reach the temperature; (b) after mild oxidation of the reduced catalyst; (c) after reduction at 523 K of the dried precursor; (d) after reduction of (c) at 723 K.

Table 3
Mössbauer parameters and the proportions of different iron species in the reduced Fe-Ru catalysts. IS and QS are with respect to α-Fe (in mm s^{-1})

	FeRu alloy singlet		Fe^{2+} doublet			Fe^{3+} doublet		
	%	IS	%	IS	QS	%	IS	QS
support SiO_2								
reduced at 523 K	22	0.10	35	1.22	2.24	43	0.46	0.7
further reduced at 723 K	55	0.09	45	1.27	2.30	–	–	–
directly reduced at 723 K	78	0.05	–	–	–	22	0.50	0.90
support TiO_2								
reduced at 523 K	100	0.08	–	–	–	–	–	–
further reduced at 723 K	100	0.06	–	–	–	–	–	–
directly reduced at 723 K	76	0.07	24	1.17	2.17	–	–	–
support Al_2O_3								
reduced at 523 K	30	0.12	70	1.30	2.38	–	–	–
further reduced at 723 K	90	0.07	10	1.22	2.37	–	–	–
directly reduced at 723 K	64	0.05	36	1.240	2.38	–	–	–

Fe^{3+} species observed in reduced Fe-Ru/SiO_2 catalysts arises predominantly from the oxidation of the segregated Fe^0 particles.

We have substantiated this conclusion by carrying out a two-step reduction of the catalyst to stabilize a proportion of iron as Fe^{2+}. The Mössbauer spectrum of the catalyst after the first stage reduction at 523 K is shown in fig. 7c. It comprises features due to FeRu alloy, Fe^{2+} and unreduced Fe^{3+}. When this catalyst was reduced at 723 K, there is practically no Fe^{3+} in the spectrum (fig. 7d). Instead, we see a singlet due to the FeRu alloy and a small doublet due to Fe^{2+}. This behaviour is different from that of Fe-Ru/TiO_2 catalysts reported by Berry et al. [16,17].

4. Conclusions

(1) In the monometallic Fe/SiO_2 catalyst, iron interacts strongly with the SiO_2 support forming a ferrous silicate phase, reduction to the metallic state not being more than 20% even after reduction at 1023 K.

(2) When the relative proportion of Ru in the Fe-Ru/SiO_2 catalysts is small, enhancement in the reduction of iron is mainly due to the hydrogen spill-over process. The reduction leads to the formation of Fe^{2+} or Fe^0 depending on the reduction temperature.

(3) Reduction of iron in Fe-Ru/SiO_2 catalysts to the metallic state is promoted by FeRu alloy formation. The alloy formation and the reducibility of iron increase with the increase in the Ru content. Reduction at 523 K of the Fe(5)-Ru(1)/SiO_2 catalyst shows the presence of Fe^{2+} ($\approx 25\%$), Fe^{3+} ($\approx 25\%$) and FeRu alloy ($\approx 5\%$). With increase in the Ru content, the proportion of Fe^{2+} decreases by a simultaneous increase in the FeRu alloy phase; the proportion of Fe^{3+} is nearly constant. However, when the reduction is carried out at 723 K, most of the iron in the Ru-rich compositions is present in the form of FeRu alloy. When Ru/Fe 1.0, there is neither any Fe^{2+} nor any segregated α-Fe and the proportion of Fe^{3+} is also low. A reduction temperature of 723 K is therefore preferred.

(4) A comparative study with different supports has shown that the SiO_2 and γ-Al_2O_3 supports interact with iron in the Fe-Ru catalyst during the reduction at 523 K and form silicate and aluminate phases respectively. A higher temperature of 723 K, however, reduces the Fe^{2+} phase to the FeRu alloy. On the other hand, the TiO_2 support remains inert at low temperatures of reduction and interacts only at higher temperatures (> 723 K) forming a titanate.

(5) The Fe^{3+} species often found in reduced Fe-Ru catalysts is probably due to the oxidation of fine Fe^0 particles formed on the support.

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