JOURNAL OF CATALYSIS **89**, 138–149 (1984)

Characterization of Surface Phases in Bimetallic FeRh/SiO$_2$ Catalysts by *in Situ* Mössbauer Spectroscopy at Cryogenic Temperatures

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Received November 29, 1983

Mössbauer spectra of FeRh/SiO$_2$ catalysts (5 wt% metal, Fe/Rh atomic ratio = 1) have been recorded *in situ* at liquid-helium, liquid-nitrogen, and room temperatures. After reduction in H$_2$ at 725 K, 80% of the iron in the catalyst is still in an Fe^{3+} surface phase, while 20% of the iron is Fe^0 alloyed with at least 1.5 times as much Rh. Fischer–Tropsch synthesis in CO + 3.3 H$_2$ at 525 K converts a part of the surface Fe^{3+} into an Fe^{2+} compound. Exposure of this catalyst to air at room temperature results in oxidation of all Fe^{2+} and nearly all of the Fe^0 to an Fe^{3+} state. The results illustrate the information contained in the temperature dependence of the resonant absorption areas of the Mössbauer spectra and the need for low-temperature spectra in quantitative analysis.

INTRODUCTION

Mössbauer spectroscopy has been successfully applied to ascertain alloying of iron with more noble Group VIII metals in supported bimetallic cluster catalysts. For reviews of investigations on supported FeRu, FePd, FeIr, and FePt catalysts we refer to the papers by Garten (*1*), Guczi (*2*), and Topsøe *et al.* (*3*). Characterizations of FeRh/SiO$_2$ catalysts with Mössbauer spectroscopy at 295 K and with Temperature-Programmed Reduction (TPR) have been reported recently (*4, 5*).

The general conclusion from all these studies is that clustering occurs between the metals in supported bimetallic catalysts consisting of iron and a more-noble group VIII metal, and that the noble metal greatly enhances the reducibility of the less noble component, iron. Bimetallic catalysts which have been reduced and reoxidized show reduction of Fe^{3+} to Fe^{2+} on exposure to H$_2$ at room temperature, whereas monometallic Fe/SiO$_2$ catalysts do not reduce under these conditions. The enhanced reducibility of iron in bimetallic catalysts provides direct evidence of the noble metal proximity and influence.

The shape of the Mössbauer spectra of reduced bimetallic catalysts at 295 K can vary with composition, particle size, and pretreatment. In general, the spectrum consists of a single peak with an isomer shift corresponding to the bulk alloy and a shoulder or resolved peak at higher velocity. Strong evidence exists that the high-velocity peak corresponds to an iron species at the surface. First, the relative intensity of this peak in the Mössbauer spectra of reduced FeRu/SiO$_2$ catalysts increases with increasing metal dispersion (*6–8*). Second, chemisorption of NH$_3$ or CO at room temperature changes the Mössbauer parameters of the high-velocity peak in the spectra of reduced FeRu/SiO$_2$ and FeRh/SiO$_2$ catalysts, confirming the accessibility of the corresponding iron species to the gas phase (*8*).

Assignment of the surface subspectrum to iron in a certain chemical state has been a matter of controversy in the literature. Garten and Garten and Lam (*1, 6*) favor the interpretation that the surface peak is part

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0021-9517/84 $3.00

of a doublet due to zero-valent iron atoms at sites of low symmetry on the surface of the bimetallic clusters. In the case of FeRu/SiO_2 catalysts, they explain the unusually high isomer shift for zero-valent iron by invoking a lower electron density at these sites which, they believe, could be the result of a higher effective atomic volume for iron at the surface (*6*). In contrast with this interpretation, we have proposed that, at least in the case of supported FeRu and FeRh catalysts, the surface doublet is due to an irreducible iron(III) oxide, as the Mössbauer parameters are characteristic of high-spin Fe^{3+} compounds (*8*). Guczi *et al.* (*9*) give a similar interpretation for spectra of FeRu/SiO_2 catalysts with metal loadings below 1 wt%. Yet another interpretation, although not mentioned in the literature up to now, is that the high-velocity peak represents an unresolved doublet of Fe^{2+} ions, as encountered in partially reduced carbon-supported iron catalysts (*10*). We show below that the temperature dependence of the spectrum makes this assignment unlikely.

From the viewpoint of chemistry, the presence of Fe^{3+} is unexpected. Fe^{2+} species, on the other hand, are commonly encountered in reduced supported iron catalysts (*3*) and it is not readily apparent why an Fe^{3+} surface phase would be stabilized under the influence of a noble metal which is expected to facilitate the reduction of iron. To improve our understanding of the origin of the high velocity or surface peak, we turn to Mössbauer spectroscopy at cryogenic temperatures at which spectra generally yield more detailed information. In particular, when the spectra become magnetically split at low temperature, assignment to Fe^{2+}, Fe^{3+}, or Fe^0 may be facilitated. Moreover, the recoilless fraction, as measured by the resonant absorption area, is low at room temperature due to the low effective Debye temperatures prevailing for well-dispersed particles, but is substantially increased at cryogenic temperatures. One must, of course, cool the sample and measure spectra *in situ* or at least under controlled atmosphere so as to preserve the chemical state of the highly reactive catalyst surface.

In this paper we describe an investigation on the state of iron in FeRh/SiO_2 catalysts by means of *in situ* ^{57}Fe Mössbauer spectroscopy at temperatures of 4, 77, and 295 K. Mössbauer investigations on unsupported FeRh bulk alloys of different compositions at 295 K have been reported by Chao *et al.* (*11*), and at 4 K by Window *et al.* (*12*). Our results strongly suggest that the surface component in reduced FeRh/SiO_2 catalysts is an Fe^{3+} species, whereas the alloy occurs in particles of lower dispersion. The Theory section shows how information on the dispersion of the iron phases can be derived from the temperature dependence of the resonant absorption areas in the Mössbauer spectra.

THEORY

For catalysts consisting of well-dispersed particles on a support, a considerable fraction of the atoms will be at the surface of the particles. Since surface atoms are subject to vibrational modes that are softer, and hence to mean-square displacements that are higher than for atoms in the bulk, one may wonder whether surface atoms can be observed with Mössbauer spectroscopy. In general the intensity or resonant absorption area of a certain component in a spectrum is determined by its recoilless fraction, f, a number between 0 and 1 equal to the probability that a γ quantum will be absorbed resonantly. The quantity f is related to the mean-square atomic displacement $\langle x^2 \rangle$ by the equation

$$f = \exp(-k^2\langle x^2 \rangle), \qquad (1)$$

where k is the wavenumber of the γ quantum (*13*). By using the Debye model for the vibrational modes of the lattice, $\langle x^2 \rangle$ and hence f can be related to the temperature, T, and a parameter called the Debye temperature, θ_D. The latter characterizes the lattice vibration and can be considered as a measure of the binding strength of the

Mössbauer atom to its surroundings. The θ_D is high for a rigid lattice and low for a lattice exhibiting soft vibrational modes. Figure 1 shows the relation between f and T as θ_D varies. The Debye temperature of metallic iron is 470 K (*14*) whereas for α-Fe_2O_3 and α-FeOOH it is about 500 K (*15*). As Fig. 1 indicates, the corresponding recoilless fractions for these materials are not very temperature-dependent between 4 and 295 K.

In order to obtain the recoilless fraction of surface atoms, one needs to know the Debye temperature associated with the surface. Somorjai (*16*) has collected a table of Debye temperatures, as determined by low-energy electron diffraction (LEED), for the surfaces of various metals. The general conclusion is that the surface Debye temperature is roughly equal to half that of the bulk. A LEED study on the ZnO (1010) surface showed that this simple rule for the Debye temperature can also hold for a metal oxide surface (*17*). This means that the surface Debye temperature for iron compounds found in catalysts should be of the order of 250 K. Since the corresponding recoilless fraction is about 0.5 at room temperature (see Fig. 1), we conclude that surface atoms can indeed be observed with Mössbauer spectroscopy at room temperature. We note, however, that the temperature dependence of the recoilless fraction is much stronger for surface atoms than for bulk atoms. This suggests that analyzing the resonant absorption as a function of temperature may be a way to recognize iron compounds that are located at the surface.

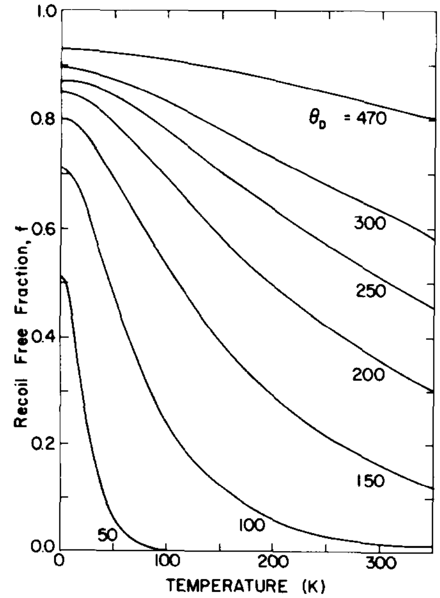

FIG. 1. The recoilless fraction as a function of temperature for different values of the Debye temperature θ_D (in K).

A few warnings may be appropriate. First, the Debye model is an approximation to the phonon spectrum in elemental bulk materials. Its validity for small particles, which, moreover, consist of more than one element, or for surface phases, may be questioned. Thus, values of θ_D derived from Mössbauer spectra of typical catalytic materials should best be taken as relative indicators of lattice stiffness. Trends in θ_D have real significance, however, as can be concluded from the following. Maradudin and Melngailis (*18*) have calculated the recoilless fraction of atoms in surface layers of simple cubic crystals using a Hamiltonian based on nearest- and next-nearest-neighbor central force interactions between the atoms. Their conclusions with regard to the observability of surface atoms by means of Mössbauer spectroscopy remain qualitatively the same as those based on the Debye model. Iron atoms at the surface can be observed at room temperature, and the temperature dependence of their recoilless fraction is considerably stronger than that of atoms in the bulk.

Second, the observation that the surface Debye temperature is about half that of the bulk value (*16*) has been derived from LEED data obtained with well-defined flat surfaces of single crystals. The surface of small supported particles is certainly more complex, having more corner and edge atoms with greater freedom of vibration. It is conceivable, therefore, that the effective surface Debye temperature of small supported particles will be lower than that of a well-defined crystal surface. In fact, it has recently been shown that iron oxides on air-passivated Fischer–Tropsch catalysts appear in Mössbauer spectra only at temperatures below that of liquid nitrogen (*19, 20*) and that these oxides can be characterized by Debye temperatures as low as 50 K (*20*).

Third, we note that a relatively high recoilless fraction does not necessarily imply that the corresponding component is a bulk component. Highly dispersed atoms that are tightly bound to a support can also have high effective Debye temperatures, as has been demonstrated for Eu on Al_2O_3 (*21*).

Fourth, the theory given above is restricted to particles that are not in motion themselves. Hence, they must be either anchored to a support or embedded in a stiff matrix. Particle motion reduces the resonant absorption area by an additional factor, f_p, which also decreases with increasing temperature. This effect has been demonstrated for 10-nm α-Fe particles (*22*) and 20-nm α-FeOOH and 50-nm α-Fe_2O_3 particles (*15*).

Finally, it should be stressed that the linear relationship between the recoilless fraction and the resonant absorption area in the Mössbauer spectrum is only valid for thin absorbers in which saturation effects are absent at all temperatures used. For an excellent treatment of saturation effects we refer to a paper by Mørup and Both (*23*).

EXPERIMENTAL

The $FeRh/SiO_2$ catalyst was prepared by means of pore volume impregnation. An aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Mallinckrodt) and $RhCl_3 \cdot xH_2O$ (42.3 wt% Rh, Strem Chemicals) was added dropwise to the silica support (Cab-O-Sil, EH-5, 310 m^2/g) under frequent stirring until the incipient wetness point was reached. The catalyst contained 1.76 wt% iron and 3.24 wt% rhodium, which results in an atomic ratio Fe : Rh = 1 : 1. The impregnated samples were dried in air at room temperature for a few days and next under vacuum at room temperature for 1 h and at 425 K for several hours.

Experiments were carried out on 300 mg of catalyst pressed into a pellet with a diameter of 17 mm using a pressure of 100 atm. The catalyst was reduced in flowing H_2 (3 liters/h) at 400 K for 1 h and at 725 K for 5 h. The reduced catalyst was treated with synthesis gas ($CO : H_2$ = 1 : 3.3) at 525 K and 1 atm for 2 h. The gases, H_2 (Hoekloos, purity > 99.9%) and CO (Hoekloos, purity > 99.5%), were each purified over a reduced copper catalyst (BASF, R3-11) and a molecular sieve (Union Carbide, 5A) at room temperature.

In order to be able to measure Mössbauer spectra of the catalysts *in situ* at cryogenic temperatures, an absorber holder was used that can be closed vacuum-tight under the gas atmosphere inside the chemical reactor. The sealed absorber holder was then mounted in a cryostat which permits measurements of Mössbauer spectra at room, liquid-nitrogen, and liquid-helium temperatures without changing the configuration of the absorber with respect to the γ-ray beam. The latter is required when resonant absorption areas of the spectra at the three temperatures mentioned are to be compared. A detailed description of the apparatus has been given elsewhere (*20*).

A note of caution concerning the use of *in situ* cells at cryogenic temperatures may be appropriate. In an early stage of this work, we obtained *in situ* spectra at 4 K which seemed to contradict the conclusions from the spectra at 77 and 295 K. We then discovered that an *in situ* cell which is vacuum-tight at room temperature can leak at cryogenic temperatures. The traces of oxygen in the 10^{-5}-Torr vacuum of the cryostat were sufficient to oxidize the reduced catalyst. An additional spectrum at room temperature after completion of the low-temperature experiments provides an easy check on whether or not leaking has influenced the results at cryogenic temperatures.

Mössbauer spectra were obtained by using a constant acceleration spectrometer with a ^{57}Co in Rh source. The spectra were not corrected for the varying distance between source and detector, and hence the origin of the curved background in the spectra is instrumental. Isomer shifts (IS) are reported relative to the NBS standard sodium nitroprusside (SNP) at room temperature, while hyperfine fields (H) are calibrated against the 515-kOe field of α-Fe_2O_3 at room temperature.

Mössbauer spectra were fitted by computer with calculated subspectra consisting of Lorentzian-shaped lines and a parabola which accounts for the curved background, by varying the Mössbauer parameters (isomer shift, quadrupole splitting, magnetic hyperfine splitting, linewidth, and spectral area) and the parabola coefficients in a nonlinear, iterative minimization routine. This procedure differs from the generally applied Lorentzian fitting in which the Lorentzian parameters (position, width, and intensity) of each peak are varied separately. A detailed description of this method is given in Ref. (*24*). In the case of spectral doublets, the linewidths and the absorption areas of the two peaks were constrained to be equal. When analyzing spectra that consist of combinations of one or two doublets and a single line, the fitting routine generally finds more than one solution acceptable from a mathematical point of view. In this case a spectrum of the same absorber at a different temperature is of great value, since additional constraints can be imposed on the fits. The temperature dependence of the lattice dynamics requires that the isomer shift and the resonant absorption area decrease with increasing temperature for each component in the spectra (*13*). In practice, these additional constraints are usually sufficient to ensure a unique solution.

RESULTS

Unreduced catalyst. The Mössbauer spectra of the unreduced FeRh/SiO_2 catalyst recorded at 295, 77, and 4 K all consist of a symmetrical quadrupole doublet (Fig. 2). The Mössbauer parameters, given in Table 1, are characteristic of Fe^{3+} in an iron oxide or oxyhydroxide in a paramagnetic or superparamagnetic state. The width of the lines suggests a distribution in the local environments of the Fe^{3+} ions. The values in Table 1 are the average values representative of a simple two-line fit. The average quadrupole splittings of the Fe^{3+} ions are high in comparison to bulk iron(III) oxides. As the quadrupole splitting of Fe^{3+} compounds is entirely determined by the electric field gradient of the lattice, this indicates that the environment of the Fe^{3+} ions is highly asymmetric. The values are consistent with those reported for well-dispersed iron oxide (*25*). The strong increase in the total resonant absorption of the spectra with decreasing temperature, in particular between 77 and 4 K, indicates, as discussed above, that a large portion of the iron ions are on the surface.

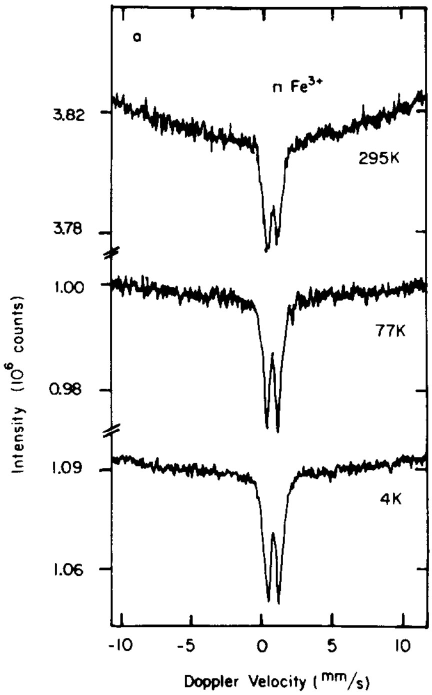

FIG. 2. Mössbauer spectra of the unreduced FeRh/SiO_2 catalyst, measured at the temperatures indicated.

Reduced catalyst. In situ Mössbauer

TABLE 1

Mössbauer Parameters of $FeRh/SiO_2$ at 295, 77, and 4 K

T (K)	Iron state	δ (mm/s)	ΔE_Q (mm/s)	A (a.u.)
		Before reduction		
295	Fe^{3+}	0.68	0.77	0.30 ± 0.03
77	Fe^{3+}	0.73	0.80	0.48 ± 0.05
4	Fe^{3+}	0.82	0.84	1.00
		After reduction		
295	Fe^0	0.38	—	0.21 ± 0.03
	Fe^{3+}	0.69	0.97	0.26 ± 0.04
77	Fe^0	0.47	—	0.24 ± 0.03
	Fe^{3+}	0.88	1.04	0.64 ± 0.08
		After exposure to air		
295	Fe^0	0.38	—	0.06 ± 0.01
	Fe^{3+}	0.63	0.90	0.46 ± 0.04
		After Fischer–Tropsch synthesis		
295	Fe^0	0.38	—	0.19 ± 0.04
	Fe^{2+}	1.31	2.30	0.10 ± 0.02
	Fe^{3+}	0.62	0.86	0.16 ± 0.03
77	Fe^0	0.47	—	0.26 ± 0.05
	Fe^{2+}	1.46	2.52	0.21 ± 0.04
	Fe^{3+}	0.77	1.00	0.34 ± 0.06
		After exposure to air		
295	Fe^0	0.38	—	0.08 ± 0.01
	Fe^{3+}	0.65	1.00	0.42 ± 0.04

Note. Uncertainties in δ: 0.04 mm/s, ΔE_Q: 0.06 mm/s. A: normalized such that the total area at 4 K is 1.

spectra of the reduced $FeRh/SiO_2$ catalyst at 295, 77, and 4 K are shown in Fig. 3. The spectrum at 295 K consists of a large central peak and a somewhat broadened peak at higher velocity, near 1 mm/s. The spectrum at 77 K shows a similar pattern, but the intensity of the high-velocity peak is substantially enhanced. Both spectra were analyzed by computer as a combination of a singlet and a doublet. We note that the room-temperature spectrum can also be analyzed as a combination of two single lines, one for zero-valent iron and one for high-spin divalent iron. As we mentioned in the Introduction, singlets or unresolved doublets of Fe^{2+} phases have recently been observed in carbon-supported iron catalysts in intermediate stages of reduction (*10*). At 77 K, however, this Fe^{2+} phase showed a well-resolved doublet (*26*), due to the electron contribution to the electric field gradient, which, in high-spin Fe^{2+} compounds, depends on temperature (*27*). Figure 3 shows that with $FeRh/SiO_2$ splitting of the peak near 1 mm/s has not occurred at 77 K. Hence, interpretation of the spectra at 295 and 77 K in terms of a singlet and a resolved doublet is preferred.

The Mössbauer parameters are given in Table 1. Since the peak near 1 mm/s is broadened and deviates from the Lorentzian shape, the uncertainties in the Mössbauer parameters are relatively high. Within their accuracies, the parameters satisfy the requirements which follow from the theory of lattice dynamics, that the isomer shift and the resonant absorption area increase with decreasing temperature.

The single line in the spectra of the reduced $FeRh/SiO_2$ catalyst has an isomer shift at room temperature of 0.38 mm/s, which is a value characteristic of zero-valent iron, Fe^0. We attribute this to iron

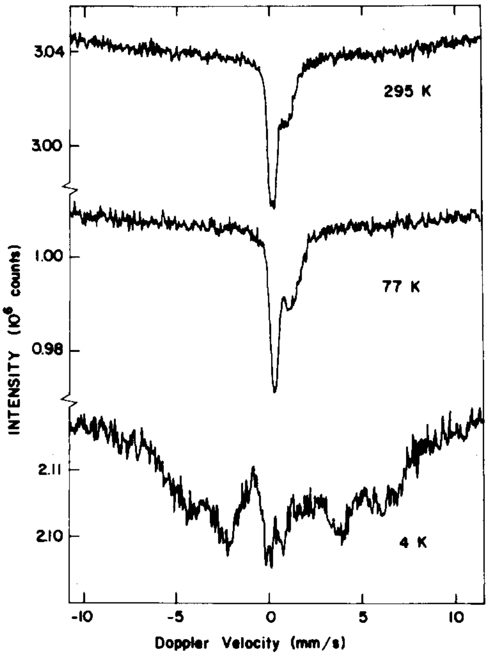

FIG. 3. *In situ* Mössbauer spectra at 295, 77, and 4 K of the $FeRh/SiO_2$ catalyst after reduction in H_2 at 725 K.

which has been alloyed with rhodium, and not to isolated particles of metallic iron, for the following reasons. First, the isomer shift of the Fe^0 0.38 mm/s, is significantly higher than that of metallic iron (0.26 mm/s). Second, no contribution of an Fe^{2+} component, which is always present in reduced highly dispersed silica-supported iron catalysts (*3*), is observed in the spectra of Fig. 3. We conclude, therefore, that isolated iron particles are absent and that the single line in the spectra of the reduced catalyst belongs to bimetallic particles of FeRh. The isomer shift of the FeRh alloy particles (0.38 ± 0.04 mm/s at 295 K) corresponds to rhodium-rich alloys with a Rh and Fe atomic ratio of at least 1.5, according to the results of Chao *et al.* (*11*). The increase in the resonant absorption area of the singlet between 295 and 77 K is characteristic for iron bulk compounds with a Debye temperature in the order of 400–500 K.

The isomer shift and quadrupole splitting of the doublet fall entirely in the range of high spin Fe(III) compounds and we assign the doublet to an iron(III) oxide. The quadrupole splitting of the Fe^{3+} doublet is higher than that for the unreduced catalyst. The increase in the resonant absorption area of the Fe^{3+} subspectrum between 295 and 77 K is large, significantly larger than for the unreduced catalyst. This result, together with the high value of the quadrupole splitting, is consistent with the assignment of the Fe^{3+} doublet to a surface phase.

The spectrum of the reduced $FeRh/SiO_2$ catalyst at 4 K shows a broad magnetically split pattern, in which a distribution of magnetic hyperfine fields occurs. Such patterns, which are frequently observed with amorphous materials, indicate the presence of a number of different iron environments in the absorber. The relatively high statistical errors in this poorly resolved spectrum do not allow computer fitting. Nevertheless, the total resonant absorption can be calculated. This parameter has increased from 0.88 to 1.00 between 77 and 4 K, which is not enough to suggest that a new very-low-Debye-temperature phase appears below 77 K, as, for example, in Ref. (*20*). Thus, the spectra at 77 and 4 K both represent the same phases in the catalyst.

In the 77 K spectrum, the iron(III) oxide accounts for 70% of the spectral area; hence it will also dominate the 4 K spectrum. Window *et al.* (*12*) reported that fcc FeRh bulk alloys exhibit magnetic splitting at 4 K and that all resonant absorption occurs in the velocity range −4 to +4 mm/s. If we assume that the FeRh alloy particles in the catalyst follow the behavior of fcc bulk alloys, then the absorption outside the −4 to +4 mm/s range is caused by the iron (III) oxide alone. The maximum splitting is about 450 kOe. Unfortunately, more details, such as an isomer shift, cannot be derived from this spectrum.

By extrapolating the resonant absorption areas of the Fe^{3+} and Fe^0 contributions in the spectra of the reduced catalyst to $T = 0$ K, using Debye temperatures fitted to the 295 and 77 K data (Fe^{3+}: $\theta_D = 175 \pm 25$ K ad Fe^0: $\theta_D = 450 \pm 50$ K), one finds good agreement with the independently determined total resonant absorption area at 4 K. After correcting the extrapolated absorption areas for the difference in recoilless fraction at 0 K, one obtains the relative iron concentrations. It appears then that only about 20% of the iron has been reduced to the metallic state, and that the highly dispersed iron(III) oxide contains about 80% of the iron. Since the isomer shift of the FeRh alloy at 295 K indicates that the atomic ratio of Rh to Fe in the alloy particles is at least 1.5, it follows that between 30 and 100% of the rhodium in the catalyst is alloyed with iron. TPR results, obtained with $FeRh/SiO_2$ from a different batch, indicated that essentially all rhodium was affected by iron (*5*).

Exposure of the reduced $FeRh/SiO_2$ catalyst to air at room temperature caused the oxidation of most of the iron in the FeRh alloy to Fe^{3+}, as indicated by the Mössbauer spectrum at 295 K (not shown, parameters in Table 1). We regard this as direct evidence that the size of the alloy particles is very small.

Catalyst after Fischer–Tropsch reaction. Mössbauer spectra of the FeRh/SiO_2 catalyst after Fischer–Tropsch synthesis at 525 K in CO + 3.3 H_2 for 4 h are shown in Fig. 4. In comparison with the spectra of the reduced catalyst, a new, relatively small absorption peak appears in the spectra at 295 and 77 K at a Doppler velocity of about 2.5 mm/s. This peak is attributed to the quadrupole doublet of an Fe^{2+} compound, the low-velocity peak of which is hidden underneath the main spectral contribution near 0 mm/s. Analysis of the spectra at 295 and 77 K in terms of two doublets and a single line, corresponding to Fe^{3+}, Fe^{2+}, and Fe^0, respectively, yields Mössbauer parameters (Table 1) which satisfy the temperature requirements formulated in the experimental section. Within the limits of accuracy, the Mössbauer parameters of the Fe^{3+} and Fe^0 compounds are identical to those of the reduced catalyst (Table 1). The isomer shift and quadrupole splitting of the Fe^{2+} compound are characteristic of Fe^{2+} ions in a distorted octahedral coordination, which suggests that the Fe^{2+} ions have a coordinatively saturated or octahedral environment (*27*). By comparing the resonant absorption areas of the Fe^{3+} and Fe^0 subspectra in the reduced catalyst with those of the catalyst after Fischer–Tropsch synthesis, it appears that the Fe^{2+} compound has been formed at the expense of Fe^{3+} in the reduced catalyst. The resonant absorption area of the Fe^{2+} and Fe^{3+} doublets increase considerably on decreasing the temperature from 295 to 77 K, which suggests that both the Fe^{2+} and the Fe^{3+} compound are located in the surface region of the catalyst.

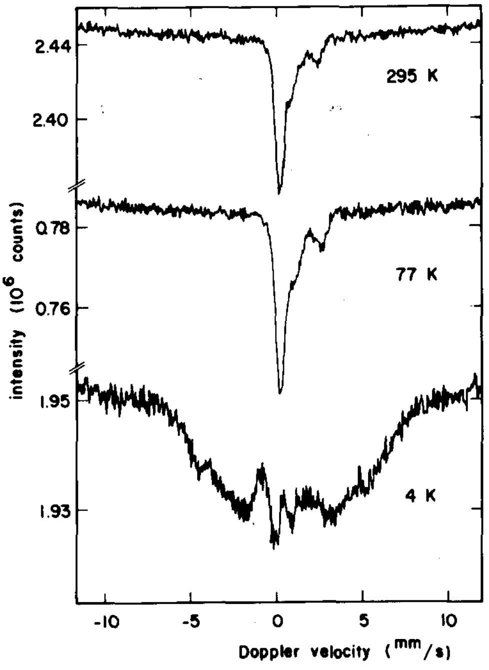

FIG. 4. *In situ* Mössbauer spectra at 295, 77, and 4 K of the FeRh/SiO_2 catalyst after Fischer–Tropsch synthesis in CO + 3.3 H_2 at 525 K and 1 atm for 2 h.

The liquid-helium spectrum of the FeRh/SiO_2 catalyst after Fischer–Tropsch reaction shows a broad pattern, in which peaks are even less resolved than in the corresponding spectrum of the reduced catalyst. Apparently, the Fe^{2+} compound exhibits magnetic splitting at 4 K. We note that the maximum hyperfine splittings, which are due to the Fe^{3+} subspectrum, are about equal for both spectra.

After the catalyst under CO and H_2 was exposed to air at room temperature, the Mössbauer spectrum at 295 K (not shown, parameters in Table 1) indicated that all Fe^{2+} and most of the Fe^0 were converted into iron(III) oxide.

Total resonant absorption. The total resonant absorption in the Mössbauer spectra of the FeRh/SiO_2 catalysts at the three different conditions and temperatures studied, is given in Fig. 5. Since the number of ^{57}Fe atoms in the absorbers was not the same for the different experiments, the data have been normalized to 1 at 4 K so the data in Fig. 5 reflect the temperature dependence of the average recoilless fraction of the catalyst as a function of catalyst treatment. The recoilless fraction, f, for each component is entirely determined by the mean-square atomic displacements of the ^{57}Fe atoms, $\langle x^2 \rangle$, as given in Eq. (1). When

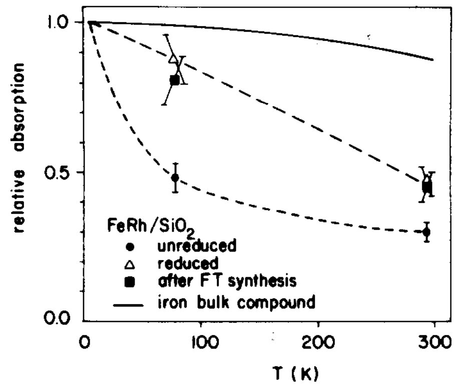

FIG. 5. Total resonant absorption areas of the FeRh/SiO_2 spectra in Figs. 2, 3, and 4, normalized to unity at 4 K. The full line corresponds to the temperature dependence of the resonant absorption in iron bulk compounds with a Debye temperature of 500 K. The dashed lines have been drawn as a guide to the eye only.

interpreted in these terms, Fig. 5 indicates that the weighted average of $\langle x^2 \rangle$ for the different iron components in the sample is rather high for the unreduced catalyst, whereas it is smaller for the reduced catalyst. However, the weighted average $\langle x^2 \rangle$ for the reduced catalyst is still considerably higher than the average atomic displacements which are usually encountered in iron bulk compounds, corresponding with Debye temperatures in the range of 400–500 K.

From the results in Fig. 5 we conclude that a relatively high fraction of the atoms in the unreduced catalyst is at the surface. The degree of dispersion decreases and/or the bond stiffness increases upon reduction in H_2 at 725 K, but remains the same on subjecting the catalyst to Fischer–Tropsch synthesis at 525 K.

DISCUSSION

The Mössbauer spectra at 295 and 77 K indicate that reduced bimetallic FeRh/SiO_2 catalysts contain iron in two states: Fe^0 in an FeRh alloy, and Fe^{3+} in a highly dispersed iron(III) oxide.

The FeRh subspectrum has an isomer shift in the range of rhodium-rich FeRh bulk alloys (*11*). The Debye temperature of the FeRh phase in the bimetallic catalyst is in the range of bulk materials; hence a relatively large fraction of the iron atoms is located in the interior of the alloy particles. On the other hand, exposure of the reduced catalyst to air at room temperature leads to oxidation of most of the Fe atoms in the alloy, indicating that the dimensions of the alloy particles cannot be very large. It seems reasonable to assume that the FeRh alloy occurs in particles with diameters in the order of magnitude of 4 nm.

Evidence for the high dispersion of the iron(III) oxide was found in the strong temperature dependence of its recoilless fraction, and the relatively high value of the quadrupole splitting. As has been reported elsewhere (*8*), *in situ* Mössbauer studies at 295 K with the same FeRh/SiO_2 sample as used here, showed that more than 50% of the Fe^{3+} in the reduced catalyst is affected by CO chemisorption at room temperature. This is consistent with the assignment of the Fe^{3+} subspectrum to a phase of high dispersion, i.e., with a large fraction of surface atoms.

The Fe^{3+} ions in the highly dispersed iron oxide are influenced by the presence of rhodium in some form, as follows from two considerations. First, Fe^{3+} ions in monometallic Fe/SiO_2 catalysts can always be reduced, at least to the ferrous state, when heated in H_2 (*3*). Second, the Fe^{3+} reduces readily to Fe^{2+} on exposure of reduced FeRh/SiO_2 to CO at room temperature (*8*). This conversion has not been observed in Fe/SiO_2 catalysts. Both points suggest some kind of Rh–Fe interaction.

In Ref. (*8*) we proposed a model for the structure of silica-supported FeRu and FeRh catalysts. This model was based on Mössbauer spectra of the catalysts after exposure to gases such as CO, NH_3, and O_2. Two assumptions were used in this model, namely (i) the iron(III) oxide forms a highly dispersed phase in which nucleation during the reduction is inhibited, and (ii) the alloy is present in particles of lower dispersion which are readily reduced. The present investigation confirms the validity of these assumptions on the dispersion of the two iron phases and provides, therefore, strong support for the model proposed in Ref. (*8*).

A significant fraction of the iron(III) oxide in the reduced FeRh/SiO_2 catalyst is converted into an Fe^{2+} compound during Fischer–Tropsch synthesis at 525 K. As the highly dispersed iron(III) oxide in the reduced FeRh/SiO_2 catalyst cannot be reduced by H_2 at 725 K, we conclude that the CO in the CO + H_2 mixture is responsible for the partial reduction of the iron(III) oxide under Fischer–Tropsch conditions. Carburization, as in monometallic iron catalysts, is not observed. Carburization was also absent in FeRu/SiO_2 under similar conditions (*28*). Clear conclusions on the nature of the Fe^{2+} compound cannot be drawn, but the Mössbauer parameters exclude assignment to FeO. The isomer shift suggests that the Fe^{2+} ions, although belonging to a surface compound, have a coordinatively saturated or octahedral environment. Therefore, we propose that this saturated coordination of the Fe^{2+} surface ions is due to adsorption of CO, or CO-derived species.

The liquid-helium spectrum of the reduced FeRh/SiO_2 catalyst looks very similar to the spectra of alumina-supported FeIr and FePt catalysts at 18–23 K, as reported by Garten and Sinfelt (*29*). They propose that the low temperature spectra consist of one sextet only, associated with iron in FeIr or FePt alloys. However, as Fig. 4 of Garten and Sinfelt's paper shows, this simplified interpretation leads to a six-line fit with distances between the peaks which are in conflict with the energy level scheme of ^{57}Fe nuclei in a magnetic field. Consequently, no physical meaning can be attached to the results of this fit. Even if a correct analysis in terms of a distribution of magnetic hyperfine fields is made, the hyperfine field values are much higher than in FeIr and FePt reference alloys (*29, 30*). Garten and Sinfelt recognize this problem and suggest that the small size of the bimetallic particles is responsible for the increased value of the magnetic hyperfine field. This seems unlikely. In general, the effect of decreasing particle size is to lower the magnetic hyperfine field (*31*). Enhancement of the magnetic field in small, ferromagnetic single-domain particles can occur, due to the demagnetizing field (*32*), but the increase is relatively small. For example, in α-Fe the demagnetizing field is about 7 kOe for spherical particles, and it reaches a maximum value of 21 kOe in thin films (*33*). The distributions of magnetic hyperfine fields in the spectra of FeIr/Al_2O_3 and FePt/Al_2O_3 at 18–23 K, and of FeRh/SiO_2 at 4 K, extend to values well over 360 kOe, the maximum value conceivable for metallic iron in the absence of applied magnetic fields. Therefore, the distribution cannot be assigned to either iron in an FeIr, FePt or fcc FeRh alloy, or to isolated metallic iron.

In our interpretation the 4 K spectrum of the reduced FeRh/SiO_2 catalyst is dominated by the iron(III) oxide, which contains 80% of the iron in the catalyst. At 4 K this phase manifests itself in a distribution of magnetic hyperfine fields with values up to about 450 kOe. Such distributions have been observed before with surface layers of iron(III) oxide (*20, 34*), although in the cases cited the distribution extended to almost 544 kOe, the field of bulk α-Fe_2O_3 at 4 K. It is conceivable that the very high dispersion of the iron(III) oxide on the SiO_2 support and the presence of rhodium in this phase are responsible for the fact that the Fe^{3+} hyperfine fields are lower than in surface layers of α-Fe_2O_3.

We believe that the present investigation demonstrates that application of *in situ* Mössbauer spectroscopy at temperatures as low as 4 K is very useful in the study of supported bimetallic catalysts. Due to the low effective Debye temperatures of dispersed phases, the spectra at 77 K show higher resonance absorption and improved resolution compared to the room temperature spectra. Comparison of resonant absorption areas at different temperatures yields information on the recoilless fraction of the ^{57}Fe atoms and hence on their dispersion. These spectra at different temperatures also provide useful additional constraints on the fitting procedure and are often sufficient to yield unequivocally determined Mössbauer parameters.

Finally, we would like to stress that extrapolation of the resonant absorption areas for the different iron constituents in the Mössbauer spectra to a temperature of 0 K is the only reliable way to estimate the actual composition of a sample. The commonly made assumption that the recoilless fraction of the constituents will be equal at room temperature leads certainly to erroneous results in the case of well-dispersed particles, as follows directly from the strong temperature dependence of the Fe^{3+} contribution to the Mössbauer spectra of the reduced $FeRh/SiO_2$ catalyst.

CONCLUSIONS

The following conclusions on $FeRh/SiO_2$ can be drawn from this work.

(1) Iron in the unreduced catalyst is present as finely dispersed Fe^{3+} ions.

(2) Reduction of the catalyst in H_2 at 725 K forms FeRh alloy particles which contain about 20% of the total amount of iron and at least 1.5 times as much rhodium. Isolated metallic iron is absent. The remaining 80% of the iron is present in the form of highly dispersed iron(III) oxide. Most of the alloyed iron is oxidized to the Fe^{3+} state on exposing the catalyst to air.

(3) The FeRh alloy in the reduced catalyst appears as a single line in the Mössbauer spectra at 295 and 77 K, whereas at 4 K it is magnetically split. The iron(III) oxide shows a doublet at 295 and 77 K and a broad magnetically split pattern at 4 K, in which a distribution in magnetic hyperfine fields with values up to 450 kOe is present. The high quadrupole splitting at 295 and 77 K, and the strong increase in recoilless fraction between 295 and 77 K are indicative of a high dispersion.

(4) During Fischer–Tropsch synthesis at 525 K a considerable fraction of the highly dispersed iron(III) oxide is transformed into a ferrous compound. The Mössbauer parameters suggest that the coordination of the Fe^{2+} ions, although located at the surface, is octahedral. This Fe^{2+} species is unstable in oxygen at room temperature. Formation of bulk carbides, as in monometallic iron catalysts, is not observed.

(5) The resonant absorption areas of the Mössbauer spectra indicate that the dispersion is high in the unreduced catalyst. It decreases somewhat upon reduction at 725 K, but does not change further in the Fischer–Tropsch reaction at 525 K.

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