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Mössbauer and X-Ray Photoelectron Spectroscopic Evidence for the Structure of Supported Bimetallic Catalysts: FeRu, FeRh, FePd, FeIr, and FePt on SiO_2

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Silica-supported bimetallic catalysts, consisting of iron and a more noble Group VIII metal M (Ru, Rh, Pd, Ir, Pt) with metal loading 5 wt% and molar ratio Fe : M = 1 : 1, have been investigated with *in situ* Mössbauer spectroscopy and X-ray photoelectron spectroscopy. Reduced FeRu, FeRh, FeIr, and FePt on SiO_2 contain the noble metal M in the zero-valent state, whereas iron is only partially reduced to Fe^0, the latter being present in an FeM alloy. Between 50 and 80% of the iron is present as Fe^{3+} in iron(III) oxide, which is resistant to reduction by H_2 up to at least 875 K. The Mössbauer parameters of the ferric iron change upon chemisorption of CO at 295 K, indicating that the iron(III) oxide is highly dispersed. In contrast to the other FeM/SiO_2 catalysts, reduced FePd/SiO_2 contains all Pd and almost all Fe in the zero-valent state. The presence of both bcc FePd alloy and α-Fe metal indicates that phase segregation has occurred. Passivation of the FeM/SiO_2 catalysts in air at 295 K results in oxidation of Fe^0 to Fe^{3+}, while the metal M remains reduced. An exception is FeRu/SiO_2, in which about half of the Ru is oxidized by air at 295 K. All passivated FeM/SiO_2 catalysts show reduction of Fe^{3+} to Fe^{2+} or Fe^0 by H_2 and by CO at 295 K, which is promoted by the noble metal. Implications of the results on models for the structure of a supported bimetallic catalyst are discussed.

INTRODUCTION

Supported bimetallic catalysts consisting of iron and one of the more noble Group VIII metals Ru, Rh, Pd, Ir, and Pt, have raised considerable interest as CO hydrogenation catalysts during the last decade. Several of these catalysts have been characterized by means of Mössbauer spectroscopy. Garten and co-workers have reported on alumina-supported FePd, FeRu, FePt, and on silica-supported FeRu catalysts (*1–7*), Bartholomew and Boudart on carbon-supported FePt (*8*), Guczi and co-workers on silica-supported FeRu and FePt (*9–13*), and our group on silica-supported FeRh catalysts (*14–16*). A review of Mössbauer studies on supported iron and iron alloy catalysts has been given by Topsøe *et al.* (*17*). These studies concentrated primarily on the reduction and oxidation of iron in the bimetallic catalysts. The general conclusion is that in bimetallic catalysts consisting of iron and a more noble Group VIII metal the two metals are intimately mixed and that in many cases the noble component promotes the reduction of the less noble component, iron, such that iron reduction by H_2 starts already at relatively low temperatures.

This does not necessarily imply that the degree of iron reduction in supported bimetallic catalysts is higher than in monometallic iron catalysts of comparable loading as was shown for FeRu/SiO_2 by Guczi *et al.* (*11*). Bartholomew and Boudart (*8*) and Garten (*3*), on the other hand, found a reduction degree close to 100% for iron in FePt/C and FePd/Al_2O_3, respectively.

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Although the studies of the different bimetallic combinations reported in the literature (*1–19*) suggest many similarities, comparison between the different catalysts is difficult, since different authors have used different supports, methods of preparations, and metal loadings. The main objective of this paper is to compare systematically the chemical state of the metals in a series of identically prepared FeM/SiO_2 catalysts (M = Ru, Rh, Pd, Ir, Pt), as a function of reduction, oxidation, and chemisorption of CO, by means of Mössbauer spectroscopy and X-ray photoelectron spectroscopy (XPS).

The choice of catalyst treatments prior to spectroscopic measurements has been based on two types of experiments reported in the literature. First, many authors have shown that when a reduced supported FeM catalyst is oxidized by exposing it to the air at room temperature, reexposure of the passivated catalyst to H_2 at room temperature leads to partial or sometimes even complete reduction of the iron in the catalyst (*1–8, 12, 14, 19*). Rereduction of iron oxide by H_2 at room temperature has not been observed in monometallic iron catalysts. Second, we have recently shown that *in situ* Mössbauer spectra of FeRu/SiO_2 and FeRh/SiO_2 change upon chemisorption of strongly adsorbing gases such as NH_3 and CO (*18*). As spectral changes induced by chemisorption at room temperature are in general associated with iron species located at the surface of the catalyst, such experiments yield information on the surface phases present in the bimetallic catalysts.

Our results show that the FeM/SiO_2 catalysts display many similarities with respect to reduction, oxidation, and chemisorption. Differences between the catalysts can be correlated with the position of the more noble Group VIII metal M in the periodic table. The results support certain models for the structure of an FeM/SiO_2 catalyst, whereas certain other models can be excluded.

EXPERIMENTAL

The bimetallic catalysts were prepared by pore volume impregnation. An aqueous solution containing the desired amounts of the two metals was added dropwise to the SiO_2 support (Cab-O-Sil, EH-5, 310 m^2/g) under frequent stirring until the incipient wetness point was reached. Starting materials were $RuCl_3 \cdot xH_2O$ (37 wt% Ru), $RhCl_3 \cdot xH_2O$ (38 wt% Rh), $PdCl_2$, $H_2IrCl_6 \cdot 6H_2O$, $H_2PtCl_6 \cdot 6H_2O$ (all Merck, P.A.), $Fe(NO_3)_3 \cdot 9H_2O$ (Baker, J.T.), and Fe_2O_3 (90% enriched in ^{57}Fe, Oak Ridge). The latter was reduced in flowing H_2 at 775 K for 16 h and next dissolved in 2 N HNO_3. All impregnating solutions had pH 1. Concentrations of the constituents were chosen such that the bimetallic catalysts contained equal molar amounts of the two metals, with a total metal loading of 5 wt%, whereas about 10% of the iron in the catalysts was ^{57}Fe.

Impregnated catalysts were dried in air at room temperature for several days, at 325 K for 24 h, and finally at 400 K for 72 h. Quantities of about 300 mg of catalyst were pressed into wafers with a diameter of 20 mm, using a pressure of 100 atm. All further treatments of the catalysts took place in the Mössbauer *in situ* reactor which has been described elsewhere (*19, 20*). The gases H_2 (Hoekloos, purity >99.9%) and CO (Hoekloos, >99.5%) were each purified over a reduced copper catalyst (BASF, R3-11) and a molecular sieve (Union Carbide, 5A).

Mössbauer spectra were measured *in situ* with a constant acceleration spectrometer equipped with a ^{57}Co-in-Rh source. Spectra were not corrected for the varying distance between source and detector. Isomer shifts are reported with respect to sodium nitroprusside (SNP) at 295 K. Magnetic fields were calibrated with the 515 kOe field of α-Fe_2O_3 at 295 K. Mössbauer spectra were fitted by computer with calculated subspectra consisting of Lorentzian-shaped lines, by varying the Mössbauer parameters in a nonlinear, iterative minimization routine. In the case of quadrupole doublets the linewidths and the absorption areas of the constituent peaks were constrained to be equal.

XPS spectra were measured with an AEI ES 200 spectrometer, equipped with Mg*Kα* and Al*Kα* X-ray sources. Catalysts were reduced, or heated to remove adsorbed H_2O, in a pretreatment chamber. After evacuating the latter to a pressure of about 10^{-7} Torr, the sample was transferred to the measurement chamber. Typical pressures in this section were between 10^{-10} and 10^{-11} Torr, obtained with turbomolecular and Ti-sublimation pumps.

RESULTS

Reduced Catalysts

Figure 1 shows the ^{57}Fe Mössbauer spectra of the reduced bimetallic catalysts, measured *in situ* at room temperature. We note that reduction at higher temperatures up to 875 K or for longer periods did not lead to different Mössbauer spectra, and hence the spectra in Fig. 1 refer to the maximum stage of iron reduction obtainable in the temperature range up to about 875 K. It is seen that the spectra of SiO_2-supported FeRu, FeRh, FeIr, and FePt catalysts are rather similar and consist of Mössbauer singlets and quadrupole doublets, whereas the spectrum of reduced FePd/SiO_2 exhibits magnetic splitting. We will now discuss the computer fits to these spectra; the corresponding Mössbauer parameters are given in Table 1.

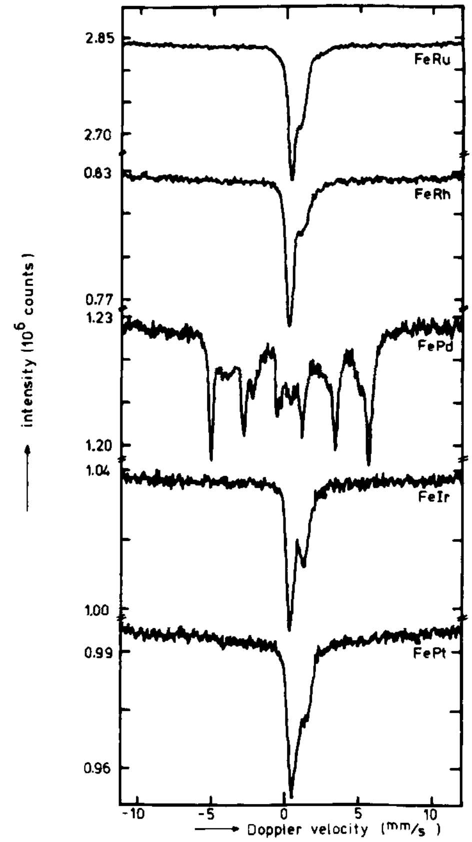

FIG. 1. Mössbauer spectra of reduced 1 : 1 Fe*M*/SiO_2 (*M* = Ru, Rh, Pd, Ir, Pt) catalysts measured *in situ* under H_2 at room temperature.

The spectrum of 1 : 1 FeRu/SiO_2 has been analyzed as a combination of two doublets, one with the Mössbauer parameters of hcp FeRu bulk alloy, as reported by Rush *et al.* (*21*) and by Williams and Pearson (*22*), and the other with the parameters of a high-spin Fe^{3+} compound. The small contribution (<5%) from an Fe^{2+} compound, visible at 2 to 2.5 mm/s, has been ignored in the fit. The inclusion of a doublet of hcp FeRu alloy is in agreement with the FeRu phase diagram, which indicates that FeRu alloys containing between 0 and about 76 at.% of iron have the hcp structure (*23*). In principle, the spectrum of FeRu/SiO_2 may also be interpreted as the combination of a broad singlet due to superparamagnetic metallic iron and a doublet of Fe^{3+}. However, a Mössbauer spectrum of the reduced FeRu/SiO_2 catalyst at 4 K showed that magnetically split patterns of zero-valent iron were absent (*24*). Hexagonal FeRu alloys, on the other hand, do not exhibit magnetic splitting at 4 K (*21*), and hence the 4 K spectrum of FeRu/SiO_2 confirms the presence of an hcp FeRu alloy phase.

The spectrum of 1 : 1 FeRh/SiO_2 has been analyzed as a singlet corresponding to fcc FeRh bulk alloy, in agreement with Chao *et al.* (*25*), and a doublet of high-spin Fe^{3+}. Isolated metallic iron is not observed. A previous investigation of the FeRh/SiO_2 system with *in situ* Mössbauer spectros-

TABLE 1

Mössbauer Parameters of Reduced 1 : 1 Fe*M*/SiO_2 Catalysts

Catalyst	Iron state	IS (mm/s)	QS (mm/s)	H (kOe)	LW (mm/s)	Percentage of area
FeRu/SiO_2	Fe^0	0.27	0.19		0.25	18
	Fe^{3+}	0.64	0.59		0.74	82
FeRh/SiO_2	Fe^0	0.31	—		0.51	47
	Fe^{3+}	0.76	0.94		0.71	53
FePd/SiO_2	Fe^0	0.29		334	0.45	45
	Fe^0	0.47		280	0.95^a	50
	Fe^{2+}	1.24	1.50		0.72	5
FeIr/SiO_2	Fe^0	0.33			0.49	26
	Fe^{3+}	0.76	0.96		0.64	74
FePt/SiO_2	Fe^0	0.54	0.46		0.55	45
	Fe^{3+}	0.86	1.10		0.61	55

Note. Accuracies: IS = 0.03 mm/s; QS = 0.06 mm/s; LW = 0.10 mm/s; area = 5–10%.

[a] Linewidth outer lines sextuplets.

copy at cryogenic temperatures (*16*) showed that the single peak in the spectrum at 295 K corresponds to a singlet at 77 K and a broad and poorly resolved sextet at 4 K. The sextet of metallic iron could not be detected. These results support the assignment of the singlet at 295 K to fcc FeRh alloy and exclude the presence of superparamagnetic metallic iron.

The spectrum of reduced 1 : 1 FePd/SiO_2 consists mainly of two magnetically split contributions, one with the Mössbauer parameters of metallic iron, and the other with a magnetic hyperfine splitting characteristic of bcc FePd bulk alloy (*26*, *27*). The latter sextet consists of broadened lines typical for a distribution in magnetic fields, which reflects a distribution in magnetic environments of the iron atoms in the FePd alloy. In order to obtain a good fit to the central part of the spectrum, an additional doublet with the parameters of Fe^{2+} ions had to be included in the fit. Evidence for the presence of significant amounts of Fe^{3+} as in FeRh/SiO_2 and FeRu/SiO_2 could not be found. The interpretation of the FePd/SiO_2 will be discussed in more detail elsewhere (*28*), but we note here that the degree of iron reduction is very high. About 95% of the spectrum of reduced FePd/SiO_2 is due to Fe^0 in either metallic iron or FePd alloy.

The Mössbauer spectrum of reduced 1 : 1 FeIr/SiO_2 was fitted with a singlet corresponding to fcc FeIr alloy as reported by Mössbauer *et al.* (*29*), and a doublet of high-spin Fe^{3+} ions. Significant contributions of metallic iron are not observed. As the isomer shift of the singlet, 0.33 ± 0.03 mm/s, is significantly higher than that of metallic iron, 0.26 mm/s, and as, to the best of our knowledge, the isomer shift of superparamagnetic metallic iron is equal to that of the bulk phase (*36*), we believe that the assignment of the singlet in the spectrum of reduced FeIr/SiO_2 to superparamagnetic metallic iron instead of fcc FeIr can be excluded. As only 26% of the Mössbauer spectrum of 1 : 1 FeIr/SiO_2 corresponds to zero-valent iron, the assignment of the Fe^0 subspectrum to fcc FeIr alloy can be reconciled with the FeIr phase diagram, which predicts the fcc structure for alloys with iron contents between 0 and about 45% (*23*).

The computer analysis of the 1 : 1 FePt/SiO_2 spectrum was less straightforward. Investigations of FePt bulk alloys with iron contents between 24 and 34.5% by Palaith *et al.* (*30*) show that the corresponding ^{57}Fe

Mössbauer spectra consist of a single line with isomer shift between 0.55 and 0.58 mm/s with respect to SNP. Bartholomew and Boudart (*8*) reported that the Mössbauer spectrum of an ordered tetragonal FePt alloy consists of a doublet with an isomer shift of about 0.56 mm/s and a quadrupole splitting of 0.42 mm/s. Computer analysis of our 1 : 1 FePt/SiO_2 spectrum in terms of an FePt singlet and an Fe^{3+} doublet yielded unrealistic values of the Mössbauer parameters, but a fit with two doublets results in parameters for the FePt alloy in agreement with those reported by Bartholomew and Boudart (*8*), whereas the second doublet corresponds to high-spin Fe^{3+} ions. The isomer shift of the Fe^{3+} doublet, however, is significantly higher than that of the Fe^{3+} doublets of the FeRu, FeRh, and FeIr/SiO_2 catalysts.

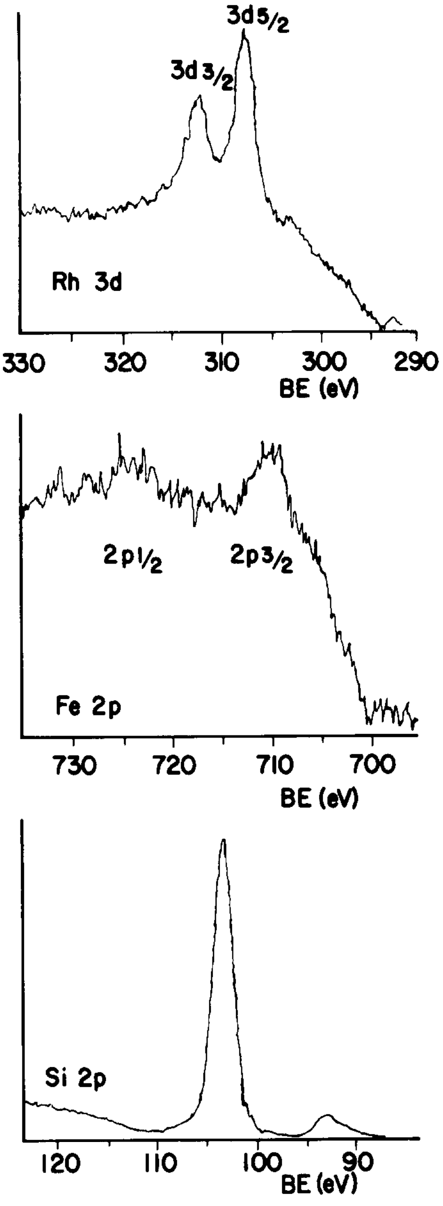

FIG. 2. XPS spectra of reduced 1 : 1 FeRh/SiO_2 catalyst. The BE scale has been corrected for electrical charging of the sample by means of the Si 2*p* signal.

XPS was used to determine the oxidation state of the noble metal in the reduced Fe*M*/SiO_2 catalysts. The experiments were done with the same samples that had been used before for the Mössbauer experiments. The catalysts were rereduced in the XPS pretreatment chamber under H_2 at about 700 K. It was checked with Mössbauer spectroscopy that this rereduction treatment brings the iron in the Fe*M*/SiO_2 catalysts back to the same state as after reduction of the fresh catalyst.

As a representative example of the XPS experiments we show the spectra of reduced 1 : 1 FeRh/SiO_2 in Fig. 2. The binding energy scale has been corrected for electrical charging of the nonconductive SiO_2 support by using the Si 2*p* signal as an internal reference. The binding energy of Si 2*p* photoelectrons in SiO_2 is 103.4 eV (*31*). However, differences in charging may be present between the alloy and the support, leading to systematic errors in the binding energies of the order of a few tenths of an electron volt. Figure 2 shows that the Rh 3*d* spectrum is of satisfactory quality, whereas the signal to noise ratio in the Fe 2*p* spectrum is rather poor. This is also the case in the XPS spectra of the other 1 : 1 Fe*M*/SiO_2 catalysts. Therefore, the XPS spectra have only been used to draw conclusions on the state of the noble metal *M*. We note, however, that the Fe 2*p* spectrum in Fig. 2 is in qualitative agreement with the conclusions derived from the FeRh/SiO_2 Mössbauer spectrum in Fig. 1, as the Fe $2p_{3/2}$ signal in Fig. 2 does show contributions at binding energies characteristic of iron metal (706.8 eV) and of oxidic iron (710–711 eV) (*31*).

The binding energies of the photoelectrons from the noble metals in the reduced 1 : 1 Fe*M*/SiO_2 catalysts are given in Table 2, along with the literature values for these metals in the zero-valent state. For Pt $4f_{7/2}$ electrons we found a binding energy of 71.4 eV, whereas in Pt metal it is 70.9 eV (*31*). As the binding energies of Pt $4f_{7/2}$ electrons in chlorides and oxides of Pt are 73.4 eV and higher (*31*), we assign the 71.4-eV peak in the spectrum of reduced FePt/SiO_2 to zero-valent Pt. The binding energy of Pd $3d_{5/2}$ electrons in FePd/SiO_2 was 335.7 eV, which is somewhat higher than the values reported for Pd metal, between 334.9 and 335.4 eV (*31*). The binding energies of Pd $3d_{5/2}$ electrons in PdO and $PdCl_2$ are 336.2 and 337.5 eV, respectively (*31*). As the Pd $3d_{5/2}$ peak in the spectrum of reduced FePd/SiO_2 is not broadened with respect to the Si $2p$ reference peak, there is no indication that the Pd peak should be attributed to a mixture of Pd metal and oxide or chloride. Therefore, we assign the Pd $3d_{5/2}$ peak at 335.7 eV to zero-valent Pd. The binding energies of Ru and Rh $3d_{5/2}$ electrons in reduced FeRu/SiO_2 and FeRh/SiO_2 are equal to the values reported for the metals. We conclude that in reduced Fe*M*/SiO_2 (M = Ru, Rh, Pd, Pt) the noble metal M is in the zero-valent state and we will assume that this conclusion holds for Ir in FeIr/SiO_2 as well.

TABLE 2

Binding Energies of the Metal M in Reduced 1 : 1 Fe*M*/SiO_2 Catalysts, along with the Literature Values for Zero-Valent M (*31*)

Catalyst	Photoelectrons	BE (eV)	
		Measured	Literature
FeRu/SiO_2	Ru $3d_{5/2}$	279.6	279.7–280.0
FeRh/SiO_2	Rh $3d_{5/2}$	307.1	307.0
	Rh $3d_{3/2}$	311.7	311.8
FePd/SiO_2	Pd $3d_{5/2}$	335.7	334.9–335.4
	Pd $3d_{3/2}$	341.0	340.2–340.7
FePt/SiO_2	Pt $4f_{7/2}$	71.4	70.9
	$4f_{5/2}$	74.4	74.2

TABLE 3

Composition of the Mössbauer Spectra of Fe*M*/SiO_2 Catalysts after a Series of Different Treatments, as Given in Fig. 3

Treatment	Iron state	FeRu (%)	FeRh (%)	FeIr (%)	FePt (%)
Fresh	Fe^{3+}	100	100	100	100
Reduced	Fe^0	18	47	26	45
	Fe^{3+}	82	53	74	55
CO	Fe^0	18	52	38	44
	Fe^{2+}	17	30	19	25
	Fe^{3+}	65	18	43	31
Air	Fe^0	0	6	7	10
	Fe^{3+}	100	94	93	90
CO	Fe^0	0	17	20	32
	Fe^{2+}	6	42	53	51
	Fe^{3+}	94	41	27	17
H_2[a]	Fe^0	0	22	11	42
	Fe^{2+}	20	47	10	0
	Fe^{3+}	80	31	79	58

[a] After exposure of the catalysts to air.

Catalysts under CO, O_2, and H_2

In this section we will report systematic investigations of the sensitivity of the Fe*M*/SiO_2 catalysts toward chemisorption of CO, exposure to air and rereduction by H_2, all at room temperature. The Mössbauer spectra of SiO_2-supported FeRu, FeRh, FeIr, and FePt are presented together in Fig. 3, and spectral compositions are listed in Table 3. The spectra of FePd/SiO_2 will be discussed separately. We note that the total resonant absorption areas of all spectra belonging to one Fe*M*/SiO_2 sample were equal within 10%. Hence, comparison of spectral contributions expressed as percentages as in Table 3 is justified.

The spectra of the fresh catalysts all consist of a doublet with IS = 0.63 ± 0.03 mm/s and QS = 0.84 ± 0.06 mm/s, characteristic of Fe^{3+} ions in highly dispersed iron(III) oxides or oxyhydroxides (*16, 32*). The spectra of the reduced catalysts have been discussed in the previous section. We repeat here that all spectra of the reduced catalysts in Fig. 3 consist of a singlet, or a doublet with a small splitting, of Fe^0 in the Fe*M*

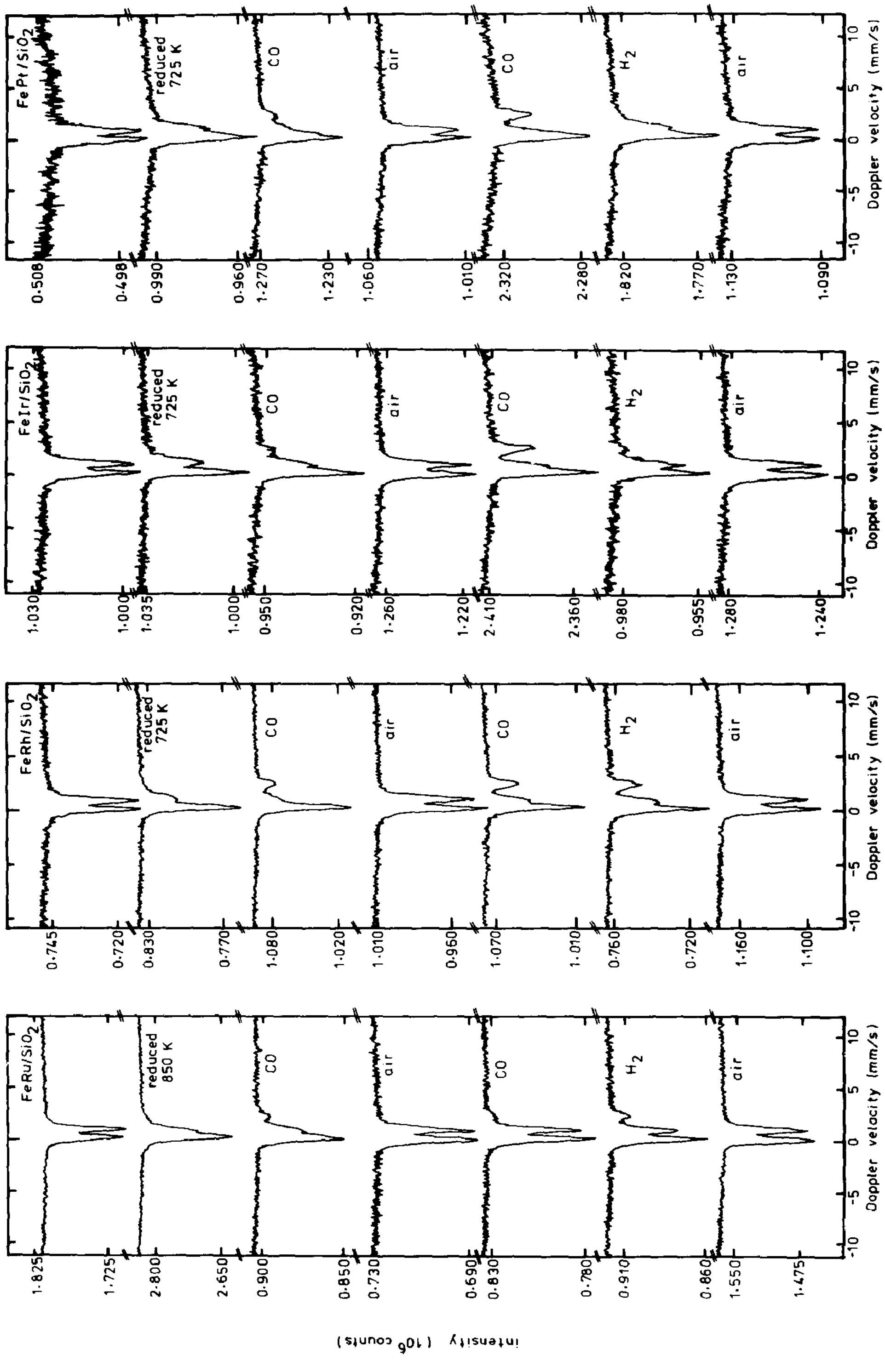

FIG. 3. Mössbauer spectra at 295 K of initially unreduced 1 : 1 Fe*M*/SiO$_2$ catalysts after a series of subsequent treatments as indicated. Exposure to CO, air, and H$_2$ occurred at room temperature. Note that the spectrum marked H$_2$ refers to H$_2$ chemisorption on the air-exposed catalyst.

alloy and a symmetrical doublet of Fe^{3+} ions which are resistant to reduction by H_2 at temperatures up to 875 K.

Exposure of the reduced catalysts to CO at 295 K leads to the formation of an Fe^{2+} phase, which is easily recognized in the spectra by the peak at about 2–2.5 mm/s. Such peaks represent the right half of a quadrupole doublet with its low-velocity counterpart in the 0 mm/s region of the spectrum. The average Mössbauer parameters of this doublet are IS = 1.45 ± 0.05 mm/s and QS = 2.15 ± 0.25 mm/s, and indicate that the coordination of the Fe^{2+} ions is octahedral or distorted octahedral (*16, 33*). The Fe^{2+} doublets have been formed at the expense of the Fe^{3+} doublets in the spectra of the reduced catalyst (Table 3). The percentage of Fe^{3+} in reduced Fe*M*/SiO_2 converted to Fe^{2+} by CO at 295 K is 20% for FeRu/SiO_2, 60% for FeRh/SiO_2, 30% for FeIr/SiO_2, and 45% for FePt/SiO_2. These results show that considerable fractions of the iron(III) oxide in the reduced Fe*M*/SiO_2 catalysts are accessible to and affected by CO chemisorption at room temperature. Implications of these results for the structure of the catalysts will be discussed later.

On exposing the Fe*M*/SiO_2 catalysts to air at 295 K all Fe^{2+} and practically all Fe^0 present in the reduced catalysts under CO are oxidized to Fe^{3+}, as shown by the Mössbauer spectra of the passivated catalysts (Fig. 3 and Table 3). Garten and Ollis (*1*) have shown that the degree of iron oxidation of passivated FePd/Al_2O_3 catalysts can be taken as a qualitative measure of the dispersion. In this respect it is seen that the dispersion of the Fe*M*/SiO_2 catalysts is high.

Note that, in principle, two Fe^{3+} compounds are expected in the passivated Fe*M*/SiO_2 catalysts, one in the passivation layer on the alloy particles and the other corresponding to the irreducible iron oxide which was already present in the reduced catalysts. Unfortunately, these two Fe^{3+} species cannot be distinguished in the Mössbauer spectra.

When the passivated Fe*M*/SiO_2 catalysts are exposed to CO at 295 K, reduction of Fe^{3+} to Fe^{2+} occurs, to some extent in FeRu/SiO_2, but to a considerable degree in FeRh, FeIr, and FePt/SiO_2 (Fig. 3 and Table 3). Within the limits of accuracy, the Fe^{2+} Mössbauer parameters are identical to those of the Fe^{2+} in the reduced catalysts under CO, suggesting that the Fe^{2+}–CO geometries in the reduced and in the passivated catalysts under CO are similar. Note that in passivated FeRh, FeIr, and FePt/SiO_2 the amount of Fe^{2+} formed by CO is greater than in the reduced catalysts. In reduced and in passivated FeRu/SiO_2, however, the amount of Fe^{2+} formed by CO is roughly the same. Again we note that the CO-induced conversion of Fe^{3+} to Fe^{2+} can in principle occur on two different sites, namely, the passivated alloy and the irreducible iron oxide.

As the results in Fig. 3 and Table 3 show, passivated Fe*M*/SiO_2 catalysts can be reduced by H_2 at 295 K, to a variable degree. In FeRu/SiO_2 and FeRh/SiO_2 reduction of Fe^{3+} proceeds no further than Fe^{2+}, but in FeIr/SiO_2 and FePt/SiO_2 reduction occurs even to Fe^0. It appears that exposure of passivated FePt/SiO_2 to H_2 at 295 K is as effective as reduction by H_2 at 725 K. The extent of rereduction of passivated Fe*M*/SiO_2 by H_2 at 295 K increases in the order FeRu/SiO_2 < FeRh/SiO_2 < FeIr/SiO_2 < FePt/SiO_2, which correlates with the position of the noble metal in the periodic table.

Finally, when the Fe*M*/SiO_2 catalysts under H_2 are again exposed to air, the same Mössbauer spectrum is measured as for the reduced Fe*M*/SiO_2 catalysts after exposure to air.

The FePd/SiO_2 catalyst behaved differently. The Mössbauer spectrum of reduced FePd/SiO_2 (Fig. 4a) did not change significantly upon chemisorption of CO. This is not surprising when it is realized that CO-induced changes in the other Fe*M*/SiO_2 catalysts involved the Fe^{3+} ions only, and that Fe^{3+} contributions in the FePd/SiO_2 are hardly present. Exposure of the reduced

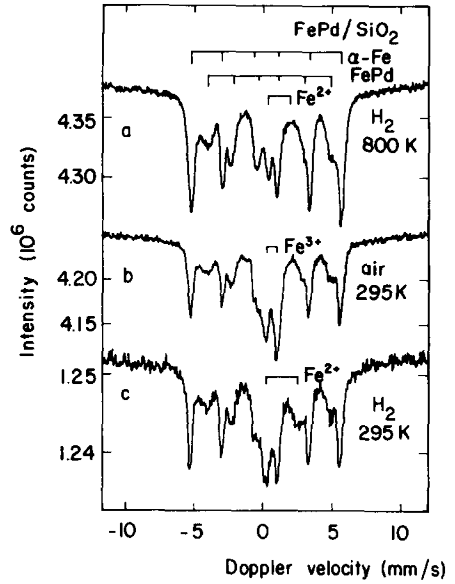

FIG. 4. Mössbauer spectra of a 1 : 1 FePd/SiO$_2$ catalyst, (a) reduced in H$_2$ at 800 K, (b) exposed to air at 295 K, and (c) rereduced in H$_2$ at 295 K. All spectra were measured in the *in situ* reactor at room temperature.

FePd/SiO$_2$ catalyst to air resulted in oxidation of some of the α-Fe and FePd alloy into Fe^{3+}, visible as a doublet in Fig. 4b. In comparison to the other Fe*M*/SiO$_2$ catalysts only a relatively small fraction of the Fe^0 is affected by air, suggesting that the dispersion of the FePd/SiO$_2$ is only low. Exposure of the passivated FePd/SiO$_2$ catalyst to H$_2$ at 295 K resulted mainly in the partial reduction of some of the Fe^{3+} ions to Fe^{2+}, as indicated by the increased Mössbauer absorption in the 2.5 mm/s range of the spectrum (Fig. 4c). Reduction of Fe^{3+} to Fe^0, however, was not observed. The Mössbauer parameters of the ferrous component in the rereduced FePd/SiO$_2$ catalyst are characteristic of coordinatively saturated Fe^{2+} ions, whereas the parameters of Fe^{2+} in reduced FePd/SiO$_2$ are indicative for a tetrahedral coordination. A similar situation has been observed in FeRh/SiO$_2$ catalysts in intermediate stages of reduction (*14*).

The remarkable reduction of Fe^{3+} ions in the passivated Fe*M*/SiO$_2$ catalysts by CO and by H$_2$ at room temperature has not been observed with monometallic Fe/SiO$_2$ catalysts. This suggests that the noble metal plays an important role in these processes. Therefore, XPS was applied to determine the oxidation state of the noble metal in the passivated catalysts.

The Fe*M*/SiO$_2$ catalysts, which have been used for Mössbauer experiments and kept under air, were heated in the XPS pretreatment chamber to remove adsorbed water. In the cases of FeRh, FePd, and FePt on SiO$_2$ the noble metal XPS spectrum was virtually identical to that of the reduced catalyst. Hence, we conclude that upon exposure of the reduced FeRh, FePd, and FePt on SiO$_2$ to the air at room temperature the noble metals remain in the reduced state. The Ru 3*d* spectrum of FeRu/SiO$_2$, however, did change upon exposing the catalyst to air at 295 K. As Fig. 5 shows, the Ru 3$d_{5/2}$ peak in the spectrum of reduced FeRu/SiO$_2$

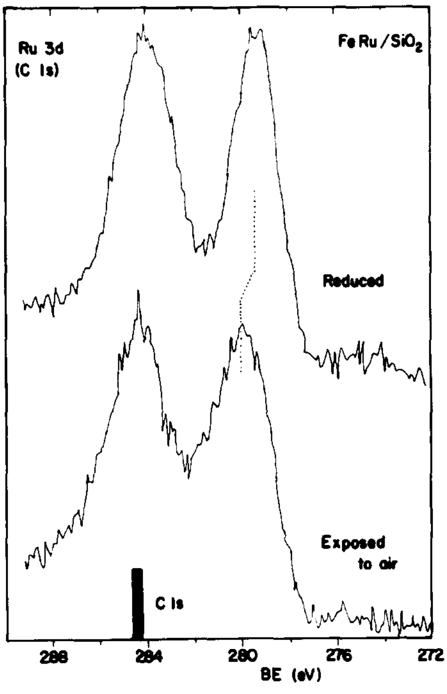

FIG. 5. XPS spectra of a 1 : 1 FeRu/SiO$_2$ catalyst after reduction in H$_2$ at 850 K and after exposure to air at room temperature. The BE scale has been corrected for electrical charging of the sample. The C 1*s* signal at about 285 eV is due to a carbon contamination on the catalyst.

is a rather sharp line at binding energy 279.7 eV. This peak has broadened and shifted to an average binding energy of 280.3 eV in the spectrum of the passivated FeRu/SiO_2 catalyst. We propose that the latter is due to the presence of both Ru metal (BE = 279.7 eV) and Ru oxide (BE = 281–283 eV) (*31*), which would explain why the peak has broadened and shifted to a binding energy intermediate between Ru metal and oxide. Note that in the spectrum of Fig. 5 the Ru $3d_{3/2}$ photoelectron peak is of little use, since it overlaps with the C 1*s* peak of a carbon contamination which was observed in all our samples at a binding energy of about 284.6 eV.

DISCUSSION

Reduced Catalysts

In reduced silica-supported Fe*M* catalysts (*M* = Ru, Rh, Pd, Ir, Pt) the noble metal *M* occurs entirely in the reduced state. Except in FePd/SiO_2, iron is only partially reduced. Between 50 and 80% of the iron is present as Fe^{3+}, which is resistant to reduction by H_2 at temperatures up to 875 K, the highest temperature obtainable in our *in situ* reactor. The zero-valent iron forms an Fe*M* alloy with an unknown amount of the noble metal *M*. The occurrence of the Fe*M* alloys as hcp FeRu, fcc FeRh, fcc FeIr, and tetragonal FePt indicates that the alloy particles are rich in the noble metal as follows from the phase diagrams (*23*). In reduced FePd/SiO_2 iron is to a large extent reduced and is present as α-Fe and as bcc FePd. Only about 5% of the iron in FePd/SiO_2 occurs as ionic iron.

The presence of substantial amounts of unreduced iron in reduced FeRu/SiO_2 has also been observed by Deszi *et al.* (*9, 10*), and by Guczi *et al.* (*11*). Lam and Garten (*5*) and Vannice *et al.* (*6*), on the other hand, measured similar Mössbauer spectra with FeRu/SiO_2 as reported in Refs. (*9–11*) and the present paper, but these authors proposed that the doublet, which we assign to Fe^{3+}, is due to Fe^0 atoms at the surface of the FeRu alloy. Garten and Sinfelt (*7*) favored the same interpretation for Mössbauer spectra of reduced FeIr and FePt on Al_2O_3. Also in this case they assigned a doublet to Fe^0 atoms at the surface of the alloy, in spite of the fact that the isomer shift of the doublet is characteristic of Fe^{3+} rather than Fe^0. Lam and Garten (*5*) attributed the difference of 0.4 mm/s in isomer shift to a difference in atomic volume between atoms in the interior and at the surface of the particles.

Increased values for the isomer shift of surface atoms have been reported in the literature. The effect, however, is usually rather small. Wiartalla *et al.* (*34*) reported that the isomer shift of iron atoms in the surface of γ-Fe was 0.02–0.03 mm/s higher than for atoms in the bulk. Clausen *et al.* (*35*) found an increase between 0.16 and 0.24 mm/s for the isomer shift of surface atoms in Fe/SiO_2 catalysts. Demonstration of this effect, however, required that spectra were measured at 78 K and in an applied magnetic field of about 12 kG. Distinct contributions of surface atoms could not be detected in Mössbauer spectra at 4, 77, and 295 K of 2-nm α-Fe particles in carbon-supported catalysts (*36*).

Furthermore, as we have discussed in detail elsewhere, assignment of the doublet in the spectra of FeIr/Al_2O_3 and FePt/Al_2O_3 to Fe^0 does not seem consistent with the spectra of these catalysts at liquid-helium temperature (*7*), which clearly show the presence of magnetic hyperfine splittings up to 450 kOe (*16*). Such values are much higher than the fields observed with FeIr and FePt bulk alloys, or with α-Fe; on the other hand, they are consistent with the presence of Fe^{3+} ions.

The experiments with the Fe*M*/SiO_2 catalysts under CO provide further support for the assignment of the doublet in the spectra of reduced catalysts to Fe^{3+}. As shown in Fig. 3 and Table 3, considerable amounts of Fe^{2+} are formed upon exposing either the reduced or the air-passivated catalysts to

CO. Similar results were obtained upon exposing FeRu/SiO_2 and FeRh/SiO_2 catalysts to NH_3 (*18, 37*). We note that CO-induced formation of Fe^{2+} from Fe^{3+} at 295 K has not been observed in monometallic Fe/SiO_2; hence it reflects the presence and influence of the noble metal. In our interpretation, the formation of Fe^{2+} in both reduced and passivated catalysts corresponds to the reduction of Fe^{3+} to Fe^{2+} by CO or NH_3, engendered by the presence of the noble metal. If we use the picture proposed by Garten and co-workers (*5–7*) and assign the surface doublet to Fe^0, then formation of Fe^{2+} in the reduced Fe*M*/SiO_2 catalyst under CO or NH_3 would correspond to *oxidation* of Fe^0 to Fe^{2+} under influence of the noble metal, whereas in passivated catalysts it would correspond to *reduction* of Fe^{3+} by CO or NH_3. Oxidation of Fe^0 by oxygen atoms originating from dissociated CO can perhaps not be excluded, but oxidation of Fe^0 by NH_3 seems unlikely.

The question remains why some of the iron in reduced Fe*M*/SiO_2 is so resistant to reduction by H_2 in the presence of a noble Group VIII metal, which is thought to catalyze the reduction of the less noble component, iron. We propose the following picture. It is well known that the behavior of small alloy particles depends on the state of its surroundings. Chemisorption-induced surface segregation of the component which forms the strongest bond with the chemisorbed gas is a good example (*38*). Likewise, we suggest that in supported alloy particles the alloy–support interface has a tendency to be enriched in the component which is most strongly bound to the support. The common experience with highly dispersed Fe/SiO_2 catalysts is that the degree of iron reduction is low, indicating that iron ions are stabilized by the oxidic support (*17*). SiO_2-supported noble metals, on the other hand, can easily be reduced to near 100%. We suggest that in bimetallic Fe*M*/SiO_2 catalysts the particle–support interface is enriched in iron, which is stabilized as Fe^{3+} by the SiO_2 support. As a substantial fraction of the Fe^{3+} is accessible to adsorbing gases such as CO and NH_3, it seems likely that these Fe^{3+} ions are preferentially located in the periphery of the alloy particles, on the support. This interpretation would be consistent with the earlier reported observation that the degree of iron reduction decreases with decreasing size of the FeRu alloy particles in FeRu/SiO_2 catalysts (*18*).

Although the presence of Fe^{3+} in reduced Fe*M*/SiO_2 catalysts seems well established (*9–13, 16, 18, 19*), it is still not clear why unreduced iron is stabilized in the ferric and not in the ferrous state as in many supported iron catalysts (*17*). In this respect, factors such as size differences, covalency and crystal field stabilization effects, and the influence of hydroxyl groups on the support may be the reason that Fe^{3+} is favored over Fe^{2+} in bimetallic catalysts. It is interesting to note, however, that promoted iron catalysts for ammonia synthesis (*17*) and Fischer–Tropsch synthesis (*39*) also contained some Fe^{3+} after reduction.

Passivated Catalysts

When reduced Fe*M*/SiO_2 catalysts are passivated by exposing them to air at room temperature, most of the iron is oxidized to iron(III) oxide. For clarity, we note that the air-passivated catalysts most probably contain two different Fe^{3+} species, corresponding to the passivation layer on top of the alloy particles and to the unreduced iron which was already present in the reduced catalysts. In the least noble bimetallic combination, FeRu/SiO_2, about half of the ruthenium is oxidized. In all other Fe*M*/SiO_2 catalysts studied here the noble metal remains in the zero-valent state.

For FeRh/SiO_2, this result is in agreement with earlier conclusions from experiments in which TPO (temperature-programmed oxidation) was combined with Mössbauer spectroscopy (*15*). It was found that temperatures up to 775 K were necessary to oxidize the reduced FeRh/SiO_2 catalyst completely. Mössbauer spectra, on the other hand, showed that most of the iron was already oxidized at room temperature. Combination of the two results indicated that the oxidation state of Rh in air-passivated FeRh/SiO_2 is zero. This conclusion is by no means trivial, as various authors reported that TPO experiments of Rh^0 on SiO_2, Al_2O_3, or TiO_2 supports show considerable O_2-uptake at room temperature, indicating the formation of a rhodium oxide passivation layer (*15, 40–42*).

All passivated Fe*M*/SiO_2 catalysts show partial reduction of Fe^{3+} by H_2 at room temperature, in agreement with the literature (*1–8, 12, 14*). As we have argued before, the zero-valent noble metal provides the sites where molecular hydrogen can be adsorbed and dissociated to yield H atoms which are capable of reducing Fe^{3+} at relatively low temperatures (*15, 18*). This simple mechanism, which has been called intraparticle hydrogen spillover (*43*), does not, however, explain why Ru, Rh, and Pd promote reduction of Fe^{3+} to Fe^{2+}, whereas Ir and Pt promote reduction of Fe^{3+} to Fe^0. Apparently, the mechanism of reduction is more complex than simple hydrogen spillover from the noble metal to iron oxide only. Garten and Ollis (*1*) have suggested that Pd weakens Fe–O bonds in oxidized FePd/Al_2O_3 catalysts. In this respect, the present results suggest that the noble Group VIII metals weaken the Fe–O bonds to a variable extent and that this influence determines the degree of iron reduction in air-passivated Fe*M*/SiO_2 catalysts. Listing the noble metals in order of increasing promoter strength for the reduction of Fe^{3+} at 295 K, we obtain Ru < Rh = Pd < Ir < Pt, which happens to correlate with the position of those metals in the periodic table.

When passivated FeRh, FeIr, and FePt on SiO_2 are exposed to CO, more Fe^{2+} is formed than in the reduced catalysts under CO, illustrating that air-passivated catalysts have more Fe^{3+} exposed to the gas phase than reduced catalysts. Passivated FeRu/SiO_2, on the contrary, is less sensitive toward CO. The difference between FeRu/SiO_2 on the one hand, and FeRh, FeIr, and FePt on SiO_2 on the other, is that part of the ruthenium becomes oxidized upon exposure of the FeRu/SiO_2 catalyst to air, whereas Rh, Ir, and Pt remain reduced. As argued before (*18*), the Fe^{3+} to Fe^{2+} conversion by CO occurs under the influence of the zero-valent noble metal. Hence, the low amount of Fe^{2+} in passivated FeRu/SiO_2 under CO can be related to the fact that part of the Ru is oxidized.

Structure of the Catalysts

The present results have implications for the structure of the catalysts. The changes in the Mössbauer spectra observed when the catalysts are exposed to CO, are particularly useful, as these experiments reveal the presence of Fe^{3+} ions at the surface. Similar effects as reported here for CO have also been observed with chemisorption of NH_3 on FeRu/SiO_2 catalysts (*18*). Additional information, which will turn out to be relevant toward understanding the structure of the Fe*M*/SiO_2 catalysts, follows from spectra of passivated samples under CO. The latter experiments show that air-exposed FeRh, FeIr, and FePt on SiO_2 contain more surface Fe^{3+} than the reduced catalysts (Fig. 3 and Table 3).

The models in Figs. 6a–c are consistent with the present results. In all three models a substantial fraction of the Fe^{3+} ions is accessible for chemisorption of gases. Oxidation of the alloy particles leads to the formation of Fe^{3+} ions at the surface of the alloy particles and hence the passivated catalysts contain more surface Fe^{3+} than the reduced catalysts.

Two other structural arrangements of the iron phases in supported bimetallic catalysts, which have been suggested in the literature, are represented by Figs. 6d and e.

Garten and co-workers (*5–7*) suggested that the supported particles in FeRu/SiO_2 consist of an FeRu alloy core covered by an Fe^0-containing surface phase, which gives

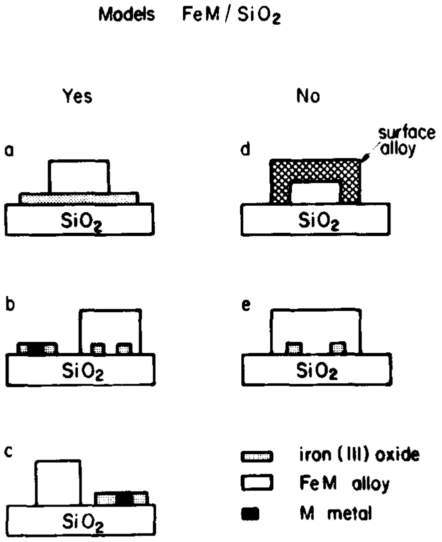

FIG. 6. Models for the structure of reduced SiO_2-supported FeRu, FeRh, FePd, FeIr, and FePt catalysts; see text for explanation.

rise to a doublet in the Mössbauer spectra. As discussed above, this doublet should be assigned to ferric iron and hence the model in Fig. 6d cannot be correct. We note that if one were to replace the surface alloy in Fig. 6d by iron oxide, the model would still be in disagreement with our results, as it would not explain why the air-exposed catalysts contain more Fe^{3+} which is accessible to CO than the reduced catalysts.

Yermakov and Kuznetsov (*44*) have suggested that supported alloy particles are bound to the support by means of metal ions, which serve as anchors (Fig. 6e). However, such anchors are covered by the alloy phase and are inaccessible to adsorbing gases. In order to explain the present results in terms of this model, one has to invoke the presence of accessible Fe^{3+} anchors on the support as in Fig. 6b. These Fe^{3+} ions, however, should be influenced by reduced noble metal, as the Fe^{3+} to Fe^{2+} conversion by CO at 295 K has never been observed with monometallic Fe/SiO_2 catalysts.

The models in Figs. 6a–c explain the results on SiO_2-supported FeRu, FeRh, FeIr, and FePt in this paper, and are also consistent with earlier TPR and TPO work on $FeRh/SiO_2$ (*15*). A detailed description of the model in Fig. 6c and the changes occurring upon exposing the catalysts to CO and air has been given in Ref. (*18*), and applies to Figs. 6a and b as well.

It is not clear to what extent these models are valid for the $FePd/SiO_2$ catalyst. Obviously, modifications to allow for the presence of separate α-Fe can easily be made. However, as, first, the dispersion of the $FePd/SiO_2$ catalyst is considerably smaller than that of the other Fe*M*/SiO_2 catalysts, and, second, the $FePd/SiO_2$ Mössbauer spectra are dominated by the magnetically split patterns of α-Fe and bcc FePd, it is difficult to observe the small contributions of Fe^{2+} and/or Fe^{3+} doublets characteristic of the metal–support interface. A more detailed investigation of 1:1 and 1:5 FePd/SiO_2 catalysts will be published elsewhere (*28*).

In view of the models for the 1:1 Fe*M*/SiO_2 catalysts several other interesting questions can be asked, such as the genesis of the bimetallic catalysts, the surface composition of the alloy particles, or the catalytic properties of ensembles which consist of noble metal atoms and iron ions. We hope to be able to answer some of these questions in the near future.

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REFERENCES

1. Garten, R. L., and Ollis, D. F., *J. Catal.* **35,** 232 (1974).
2. Vannice, M. A., and Garten, R. L., *J. Mol. Catal.* **1,** 201 (1975/76).
3. Garten, R. L., *J. Catal.* **43,** 18 (1976).
4. Garten, R. L., *in* "Mössbauer Effect Methodology" (I. J. Gruverman, Ed.), Vol. 10, p. 69. Plenum, New York, 1976.

5. Lam, Y. L., and Garten, R. L., "Proc., 6th Ibero-American Symposium on Catalysis" (Rio de Janeiro, 1978).

6. Vannice, M. A., Lam, Y. L., and Garten, R. L., *Adv. Chem.* **178,** 15 (1979).

7. Garten, R. L., and Sinfelt, J. H., *J. Catal.* **62,** 127 (1980).

8. Bartholomew, C. H., and Boudart, M., *J. Catal.* **29,** 278 (1973).

9. Deszi, I., Nagy, D. L., Eszterle, M., and Guczi, L., *React. Kinet. Catal. Lett.* **8,** 301 (1978).

10. Deszi, I., Nagy, D. L., Eszterle, M., and Guczi, L., *J. Phys. (Paris)* **40,** C2-76 (1979).

11. Guczi, L., Matusek, K., Manninger, I., Kiraly, J., and Eszterle, M., "Preparation of Catalysts," Vol. 2, p. 391. Elsevier, Amsterdam, 1979.

12. Guczi, L., *Catal. Rev.-Sci. Eng.* **23,** 329 (1981).

13. Guczi, L., *J. Mol. Catal.* **25,** 13 (1984).

14. Niemantsverdriet, J. W., van der Kraan, A. M., van Loef, J. J., and Delgass, W. N., *J. Phys. Chem.* **87,** 1292 (1983).

15. van't Blik, H. F. J., and Niemantsverdriet, J. W., *Appl. Catal.* **10,** 155 (1984).

16. Niemantsverdriet, J. W., van der Kraan, A. M., and Delgass, W. N., *J. Catal.* **89,** 138 (1984).

17. Topsøe, H., Dumesic, J. A., and Mørup, S., *in* "Applications of Mossbauer Spectroscopy" (R. L. Cohen, Ed.), Vol. 2, p. 55. Academic Press, New York, 1980.

18. Niemantsverdriet, J. W., Aschenbeck, D. P., Fortunato, F. A., and Delgass, W. N., *J. Mol. Catal.* **25,** 285 (1984).

19. Niemantsverdriet, J. W., thesis. University of Technology, Delft, 1983.

20. van der Kraan, A. M., and Niemantsverdriet, J. W., *in* "Proceedings, International Conference on the Applications of the Mössbauer Effect." Alma Ata, 1983, in press.

21. Rush, J. D., and Johnson, C. E., and Thomas, M. F., *J. Phys. F* **6,** 2017 (1976).

22. Williams, J. M., and Pearson, D. I. C., *J. Phys. (Paris)* **C6,** 401 (1976).

23. Kubaschevski, O., "Iron-Binary Phase Diagrams." Springer-Verlag, Berlin, 1982.

24. Nonnekens, R. C. H., M.Sc. thesis. Delft, 1984.

25. Chao, C. C., Duwez, P., and Chang, C. F., *J. Appl. Phys.* **42,** 4282 (1971).

26. van Deen, J. K., thesis. University of Groningen, 1980.

27. Nair, N. V., and Khan, D. C., *J. Phys. F* **13,** 1965 (1983).

28. Niemantsverdriet, J. W., van Grondelle, J., and van der Kraan, A. M., in preparation.

29. Mössbauer, R. L., Lengsfeld, M., von Lieres, W., Potzel, W., Teschner, P., Wagner, F. E., and Kaindl, G., *Z. Naturforsch.* **26,** 343 (1971).

30. Palaith, D., Kimball, C. W., Preston, R. S., and Crangle, J., *Phys. Rev.* **178,** 795 (1969).

31. Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., and Muilenberg, G. E., "Handbook of X-Ray Photoelectron Spectroscopy." Perkin–Elmer, Eden Prairie, Minn., 1978.

32. Gager, H. M., and Hobson, M. C., *Catal. Rev.-Sci. Eng.* **11,** 117 (1975).

33. Travis, J. C., *in* "An Introduction to Mössbauer Spectroscopy" (L. May, Ed.). Plenum, New York, 1971.

34. Wiartalla, W., Becker, W., Keune, W., and Pfannes, H.-D., *J. Phys. (Paris)* **45,** C5-461 (1984).

35. Clausen, B. S., Mørup, S., and Topsøe, H., *Surf. Sci.* **106,** 438 (1981).

36. Niemantsverdriet, J. W., van der Kraan, A. M., Delgass, W. N., and Vannice, M. A., *J. Phys. Chem.* **89,** 67 (1985).

37. Aschenbeck, D. P., Ph.D. thesis. Purdue University, 1979.

38. Somorjai, G. A., "Chemistry in Two Dimensions: Surfaces." Cornell Univ. Press, Ithaca, N.Y., 1981.

39. van Dijk, W. L., Niemantsverdriet, J. W., van der Kraan, A. M., and van der Baan, H. S., *Appl. Catal.* **2,** 273 (1982).

40. Vis, J. C., thesis. Eindhoven University of Technology, 1984.

41. van't Blik, H. F. J., thesis. Eindhoven University of Technology, 1984.

42. Vis, J. C., van't Blik, H. F. J., Huizinga, T., van Grondelle, J., and Prins, R., *J. Mol. Catal.* **25,** 367 (1984).

43. Hurst, N. W., Gentry, S. J., Jones, A., and McNicol, B. D., *Catal. Rev.-Sci. Eng.* **24,** 233 (1982).

44. Yermakov, Y. I., and Kuznetsov, B. N., *J. Mol. Catal.* **9,** 13 (1980).