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Ferric Iron in Reduced SiO_2-Supported FeRu and FePt Catalysts: Evidence from Mössbauer Spectroscopy and Electron Spin Resonance

Supported bimetallic catalysts consisting of iron and one of the more noble Group VIII metals M (M = Ru, Rh, Pd, Ir, and Pt) have been studied extensively by Mössbauer spectroscopy (*1–11*). In general, the Mössbauer spectra of reduced FeM/SiO_2 catalysts contain two contributions, one due to an FeM alloy and the other to a doublet with an isomer shift (IS) of about 0.65 mm s^{-1} relative to sodium nitroprusside and a quadrupole splitting (QS) in the range 0.6–1.0 mm s^{-1}. These parameters are entirely characteristic of high-spin Fe^{3+}, and several authors (*5–11*) have made this assignment. Garten (*1*), Lam and Garten (*2*), Vannice *et al.* (*3*), and Garten and Sinfelt (*4*), on the other hand, favor the interpretation that the doublet in the Mössbauer spectra of reduced FeM/SiO_2 and FeM/Al_2O_3 catalysts corresponds to zero-valent iron atoms in the surface of the FeM alloy particles. The high isomer shift is explained by the assumption that the electron density for surface iron atoms is lower than that for bulk iron atoms (*2*). The Mössbauer spectra of reduced $FeRh/SiO_2$ and $FeIr/SiO_2$ catalysts, measured *in situ* at 4 K, however, do not support the interpretation in terms of zero-valent surface iron but are in agreement with the assignment of the doublet to Fe^{3+} (*9, 11*).

From the viewpoint of Mössbauer spectroscopy the assignment of the doublet with the parameters as given above to zero-valent iron seems unlikely and interpretation in terms of Fe^{3+} would be preferred. From a chemical point of view, however, it is not readily apparent why substantial amounts of ferric iron should be stabilized in the presence of a noble metal, which in general facilitates the reduction of the less noble component, iron. In most Fe/SiO_2 and Fe/Al_2O_3 catalysts, iron can be reduced to at least the Fe^{2+} state (*1, 15*), although in some cases, such as for the promoted ammonia or Fischer–Tropsch synthesis catalysts, small amounts of Fe^{3+} are also observed (*10, 15*). In conclusion, the presence of ferric iron in reduced FeM/SiO_2 catalysts, as deduced from Mössbauer spectroscopy, seems somewhat unexpected and confirmation by another *in situ* technique would be highly desirable.

Electron spin resonance (ESR) is very sensitive in detecting Fe^{3+} ions and can be applied *in situ*. Fe^{3+} ions have a very characteristic ESR signal centered at $g = 4.2$ whenever the site symmetry deviates slightly from the perfectly octahedral or tetrahedral symmetry (*12–14*). Trivalent iron has been the subject of many ESR studies and the corresponding $g = 4.2$ ESR signal cannot be mistaken for divalent or zero-valent iron.

In this note we report ESR and Mössbauer results of reduced SiO_2-supported FeRu and FePt. These catalysts represent the combination of iron with the least noble and the most noble metal in the FeM/SiO_2 series. The ESR experiments confirm that both catalysts contain ferric iron, in amounts comparable to those determined by Mössbauer spectroscopy.

Catalysts were prepared by impregnating the SiO_2 support (Cab-O-Sil, EH-5, 310 m^2 g^{-1}) with aqueous solutions of $Fe(NO_3)_3$ ·

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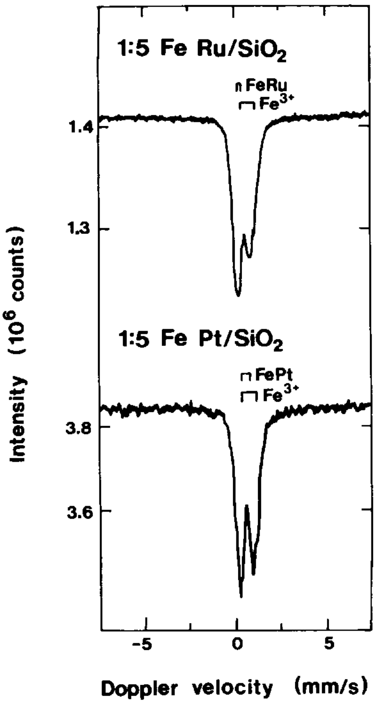

FIG. 1. Mössbauer spectra of reduced FeRu and FePt/SiO_2 catalysts, measured *in situ* under H_2 at 295 K.

$9H_2O$ and $RuCl_3 \cdot 3H_2O$ or $H_2PtCl_6 \cdot 6H_2O$ under frequent stirring, until the incipient wetness point was reached. The FeRu/SiO_2 catalyst contained 0.46 wt% iron and 4.15 wt% ruthenium; the FePt/SiO_2 catalyst 0.28 wt% iron and 4.72 wt% platinum. The iron was 10% enriched in the isotope ^{57}Fe. Catalysts were dried in air at 295 K for 1 week, at 330 K for 24 h and at 400 K for 72 h. The catalysts were reduced at 400 K for 0.5 h and subsequently at 725 K for 6 h in the Mössbauer *in situ* reactor.

Mössbauer spectra were measured at room temperature with a constant acceleration spectrometer. Doppler velocities are reported with respect to the isomer shift of sodium nitroprusside at 295 K. After measuring the Mössbauer spectra, the catalysts were passivated in air at 295 K and transferred to an *in situ* ESR sample holder, described in (*16*). The samples were reduced in flowing hydrogen at 725 K. It was checked that Mössbauer spectra of the catalysts after passivation and rereduction at 725 K are identical to those obtained after the first reduction treatment.

The *X*-band ESR spectra were recorded with a Varian E-15 spectrometer equipped with an Oxford Instruments ESR-9 continuous flow cryostat. In order to quantitatively determine Fe^{3+} concentrations we measured ESR spectrum intensities of the two reduced catalysts and of a reference compound with a known Fe^{3+} concentration (Al_2O_3 CK300, Ketjen: 0.03 wt% Fe^{3+}) at different temperatures between 4 and 80 K.

Mössbauer spectra of the reduced FeRu/SiO_2 and FePt/SiO_2 catalysts are shown in Fig. 1. The spectra have been analyzed by computer to determine the Mössbauer parameters of the iron compounds present and their spectral contributions; see Table 1 for the results. The spectrum of FeRu/SiO_2 consists of two quadrupole doublets, one characteristic of iron in hcp FeRu (*17, 18*) and the other of high-spin Fe^{3+}. The spectrum of FePt/SiO_2 has been fitted with two doublets as well. One is identical to the doublet reported for iron in an ordered tetragonal FePt alloy (*19*), the other doublet is characteristic for high-spin Fe^{3+}. As Table 1 shows, the contribution of Fe^{3+} to the Mössbauer spectra at 295 K of reduced FeRu/SiO_2 and FePt/SiO_2 is on the order of 80%. This number should be considered as a lower limit for the actual Fe^{3+} content, because a previous study of the FeRh/SiO_2 system has shown that the recoilless fraction of Fe^{3+} is considerably smaller than that of zero-valent iron in the FeRh alloy (*19*). Hence, the actual Fe^{3+} content of the

TABLE 1

Mössbauer Parameters of Fe in FeRu/SiO_2 and FePt/SiO_2 after Reduction in H_2 at 725 K

Catalyst	IS ($mm\ s^{-1}$)	QS ($mm\ s^{-1}$)	Percentage	Assigned to
FeRu	0.27	0.19	16	Fe^{3+} in FeRu
	0.69	0.71	84	Fe^{3+}
FePt	0.56	0.43	17	Fe^0 in FePt
	0.69	0.76	83	Fe^{3+}

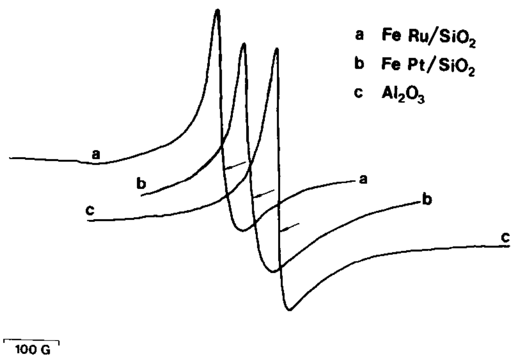

FIG. 2. ESR spectra of the reduced FeRu and FePt/SiO$_2$ catalysts measured *in situ* at 4 K. Spectrum (c) corresponds to the 0.03 wt% Fe^{3+}-in-Al$_2$O$_3$ reference. For clarity, the curves have been shifted; the arrows correspond to $g = 4.2$. The intensities are not to scale.

reduced FeRu and FePt catalysts may well exceed 80%.

Figure 2 shows the ESR spectra of reduced FeRu/SiO$_2$ and FePt/SiO$_2$ and of the Fe^{3+}-containing Al$_2$O$_3$ reference compound. All spectra show the characteristic Fe^{3+} spectrum at $g = 4.2$. The presence of ferric iron has thus been established. The amount of ferric iron in both catalysts has been obtained by measuring the ESR intensity at different temperatures. The spectral intensity follows from the formula

$$I = H(W_{\mathrm{pp}})^2$$

in which I is the intensity, H is the peak-to-peak height of the spectrum (corrected for receiver gain), and W_{pp} is the peak-to-peak line width of the spectrum in gauss.

Figure 3 shows the calculated reciprocal intensity for the three samples as a function of temperature. At temperatures above 10 K the magnitude of $1/I$ depends linearly on T. Above 60 K saturation occurs, giving deviation from the linear dependence. Since the slope of the linear part of the $1/I$ curve is inversely proportional to the Fe^{3+} concentration, the latter follows from the formula

$$C_{\mathrm{s}} = \left(\frac{D_{\mathrm{s}}}{D_{\mathrm{r}}}\right)\left(\frac{S_{\mathrm{r}}}{S_{\mathrm{s}}}\right) C_{\mathrm{r}}$$

in which C is the concentration of Fe^{3+} in weight percent, D is the bulk density of the sample, and S is the slope of the linear part in the reciprocal-intensity versus temperature plot. The indices s and r denote sample (catalyst) and reference compound (the 0.03 wt% Fe^{3+}-in-Al$_2$O$_3$). Table 2 summarizes these results.

The ESR analyses confirm that FeRu/SiO$_2$ and FePt/SiO$_2$ catalysts contain substantial amounts of ferric iron which survives reduction in H$_2$ at 725 K, notwithstanding the presence of a noble metal. For the FeRu/SiO$_2$ catalyst, both Mössbauer spectroscopy and ESR indicate that at least 80% of the iron is in the ferric state. For FePt/SiO$_2$, on the other hand, the Fe^{3+} contents as determined by Mössbauer spectroscopy and ESR are 83 and 40%, respectively. It should be noted that ESR detects Fe^{3+} provided that these ions are not antiferromagnetically ordered as in the common bulk iron(III) oxides, Fe$_2$O$_3$ and FeOOH. Also, the intensity of the $g = 4.2$ signal may depend slightly on the deviation of the site symmetry from octahedral or tetrahedral. Therefore, the amounts of Fe^{3+} calculated from the ESR intensities should

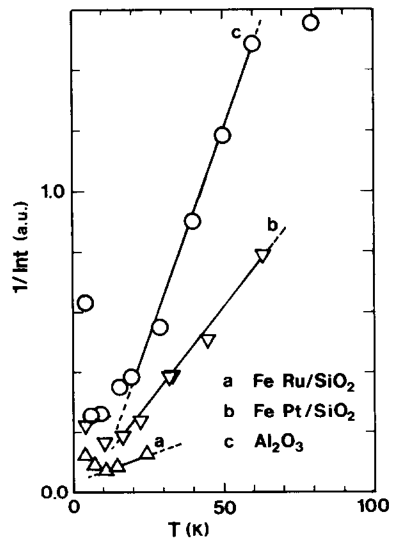

FIG. 3. Reciprocal intensities of the $g = 4.2$ ESR lines versus temperature for the reduced FeRu and FePt/SiO$_2$ catalysts and the 0.03 wt% Fe^{3+}-in-Al$_2$O$_3$.

TABLE 2

ESR Results and Comparison with Mössbauer Results

Sample	Bulk density (ml/g)	Slope ($\times 10^{-1}$)	Weight percent		
			1[a]	2[b]	3[c]
Al_2O_3	1.49	1.400	0.03		
FeRu	2.33	0.181	0.36	80	84
FePt	2.33	0.617	0.11	40	83

[a] 1, Weight percent Fe^{3+} for the catalyst as determined by ESR.

[b] 2, Percentage of iron present as Fe^{3+} as determined by ESR.

[c] 3, Contribution of Fe^{3+} to the Mössbauer spectra at 295 K.

be considered to be semiquantitative. Nevertheless, they prove that substantial amounts of Fe^{3+} are present in reduced FeRu and Fept/SiO_2 catalysts and that these amounts are of the same magnitude as those determined by Mössbauer spectroscopy.

The fact that relatively large amounts of Fe^{3+} can be detected by ESR is in agreement with the conclusion based on Mössbauer spectra that the ferric iron is present in a highly dispersed state, in close contact with the SiO_2 support (*8–10*). The reason why unreduced iron occurs predominantly as Fe^{3+} in bimetallic FeM/SiO_2 catalysts and as Fe^{2+} in most monometallic catalysts is probably due to differences in dispersion. According to Guczi (*5*), the iron and the noble metal impede each other's migration over the support during reduction and maintain each other in a state of high dispersion. In this view, the formation of ferrous iron in Fe/SiO_2 catalysts is accompanied by sintering of the iron to some extent. Experiments to test the validity of this explanation are in preparation.

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