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On the Reduction of Supported Iron Catalysts Studied by Mössbauer Spectroscopy

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The reducibility of ferrous ions exchanged onto the surface of zeolite Y, amorphous aluminosilicate, and silica gel has been studied by Mössbauer spectroscopy. The iron content in these catalysts ranged from 0.17 to 13.8 wt%. Reduction was in general carried out in about 10–20 kPa of hydrogen at 673 K for several hours. Ferric ions were also introduced, but at the expense of some loss of zeolite crystallinity. Although such ferric ions could be reduced to ferrous, further reduction to metallic iron was, except possibly in the special circumstances indicated below, not observed. This lack of reducibility included a Fe^{2+}-Y zeolite sample in which 0.8 wt% of platinum had been incorporated by ion-exchange. By heating in oxygen at 673 K, ferrous ions were oxidized to the ferric state; the oxidation–reduction process was reversible. Under similar reducing conditions, bulk iron oxides could easily be reduced to metallic α-iron. When an amorphous Fe^{3+}-Y sample was heated in air at 1273 K, the Mössbauer spectrum showed, in addition to a central doublet, a six-line pattern due to α-Fe_2O_3. The magnetic hyperfine pattern due to α-Fe was, however, not observed when this sample was reduced: it is concluded that the iron was probably in the metallic state with particle size smaller than the ferromagnetic domain size. Thermodynamic considerations suggest that while both bulk iron oxides and nickel ions in zeolites can be reduced to the metallic state by hydrogen at 673 K, much severer conditions would be needed to reduce ferrous ions on the catalyst support, in agreement with observation.

INTRODUCTION

Mössbauer spectroscopy has recently become an important method for studying the surfaces of solids. It is particularly valuable in that it is applicable to highly porous solids with very large surface areas which are often of considerable industrial importance. Iron-57 has most widely been employed for Mössbauer studies.

Metallic catalysts are very often of the form in which the metal is dispersed on a support: as a probe, iron-57 can be alloyed with other metals such as platinum or palladium (*1,2*), thus allowing a study of the structure of dispersed catalysts containing these metals. Iron itself is a catalyst for a number of important reactions. However, the most important iron catalysts (e.g., for ammonia or for Fischer-Tropsch synthesis) are not highly dispersed on a support; rather they consist of stabilized porous iron prepared by reduction of some form of massive iron oxide. Although dispersed supported metallic iron catalysts have had occasional use in the laboratory, for instance recently in hydrocarbon hydrogenolysis reactions (*3*), there is evidence that when an iron compound is impregnated or adsorbed onto a support, reduction to yield dispersed metallic iron can be difficult or impossible. This difficulty of reduction was the motivation for the present work, inasmuch as supported dispersed iron catalysts would be of interest as process catalysts.

The reducibility of supported iron catalysts is subject to uncertainty. Although Morice and Rees (*4*) have reported that a Ca-X Linde sieve could, after exchange with Fe^{3+}, be reduced in hydrogen at 633 K to give particles of metallic iron, Garten *et al.* (*5*) have reported that the exchange of Fe^{2+} into a Na-Y Linde sieve gave a product that was resistant to hydrogen reduction. In the case of catalysts prepared by impregnation of a silica support, although at least partial reduction to dispersed metallic iron can certainly occur [cf. Ref. (*3*)], the extent to which this reduction is applicable to adsorbed iron as opposed to occluded iron, does not appear to have been resolved.

To clarify the status of iron on the support in relation to its reducibility, we have prepared various supported iron catalysts by ion-exchange methods, using both Linde sieve and silica gel supports, and studied their reduction and oxidation behavior by means of Mössbauer spectroscopy. For comparison, the behavior of some bulk iron oxides was also investigated.

EXPERIMENTAL METHODS

Iron Catalysts

The Fe^{2+}-Y sample was prepared from Na-Y zeolite (Linde SK-40, Lot No. 3606–468) by repeated ion-exchange with oxygen-free 0.5 *M* ferrous sulfate solution under a nitrogen atmosphere. Another Fe^{2+}-Y sample, similarly prepared and about 10 g, was then exchanged once with a solution of tetrammine platinous chloride (1 g salt dissolved in 250 cm^3 distilled water) to give a product containing both iron and platinum. Both exchanged samples were thoroughly washed with oxygen-free distilled water to remove excess salts. Throughout the preparation, the samples as well as the distilled water were kept under a nitrogen atmosphere. Both samples Fe^{2+}-Y and [Fe^{2+},Pt]-Y remained highly crystalline as indicated by X-ray diffraction patterns. Results of chemical analysis for all samples are shown in Table 1.

Another sample was prepared by ion-exchanging the Na-Y zeolite twice with 0.07 *M* ferric nitrate solution. The solution, which had a pH value of 1.53, contained twice the initial stoichiometric amount of ferric iron required for complete replacement of the sodium ions in the zeolite. The exchanged sample was then

TABLE 1

Composition of Exchanged Samples

Sample	% Ion-exchange	Composition (wt %)	Si/Al ratio
Fe^{2+}-Y	73 (Fe^{2+})	9.2, Fe 2.8, Na	2.34
[Fe^{2+}, Pt]-Y	66 (Fe^{2+})	6.6, Fe 0.82, Pt 2.61, Na	2.43
Amorphous Fe^{3+}-Y	—	13.8, Fe <0.07, Na	28.5
Partially amorphous [Fe^{3+}, Ca]-Y	—	6.5, Fe 0.7, Ca	2.81
Fe^{3+}-SiO_2	—	0.17, Fe	—

washed with copious amounts of distilled water and dried in air at room temperature. X-Ray diffraction study revealed a complete breakdown of the zeolite framework, and the sample had become amorphous. Chemical analysis also showed a major loss of aluminum and sodium (Table 1). The sample will be referred to as "amorphous Fe^{3+}-Y." A ferric iron-exchanged sample was also prepared by exchanging a Ca-Y zeolite with ferric nitrate solution, thus following the technique used by Morice and Rees (*4*). A sample of Na-Y zeolite was first exchanged with 0.27 *M* calcium chloride solution to give about 80% exchange; after washing, this was exchanged with a 0.05 *M* ferric nitrate solution for about 30 min, followed by washing. X-Ray diffraction study revealed partial breakdown of the zeolite framework, and the sample had become partially amorphous. Chemical analysis showed the loss of some aluminum. The composition details are given in Table 1, and the sample will be referred to as "partially amorphous [Fe^{3+},Ca]-Y."

Iron was exchanged onto the surface of silica gel using the following procedure. Two samples were prepared, one containing ^{57}Fe, the second containing unenriched iron. Both samples were prepared under identical conditions, the second (unenriched) being used for analysis to determine the iron content. The enriched sample was used for Mössbauer spectroscopy. Iron(III) oxide was dissolved in concentrated hydrochloric acid to prepare the exchange solution (Fe_2O_3 containing 90% ^{57}Fe from New England Nuclear, and α-Fe_2O_3 from Merck). In each case about 8 mg of the iron oxide were made up in a solution with a ferric ion concentration of 5×10^{-4} *M*, the pH being adjusted to 2.40 using aqueous ammonia, and each solution was exchanged at room temperature with 0.5 g silica gel (Grace SP-2). After exchange, the solution was decanted from the gel which was rinsed once with 100 ml of distilled water, and then dried in an oven at 373 K. Chemical analysis showed that the iron content was 0.17 wt%. The pH of 2.40 and concentration of 10^{-4} *M* for the exchange solution were chosen to avoid the formation of polynuclear iron species (*6*), but at the same time to be satisfactory for exchange onto a silica surface (*7*).

The α-Fe_2O_3 was examined by pressing the powder into a pellet along with Na-Y zeolite powder to act as a binder. Various samples used between 25 and 50 wt% α-Fe_2O_3.

Gases

High purity hydrogen, 99.995%; B.P. grade medical oxygen, 99.5%; CP grade carbon monoxide, 99.5%; were supplied from Commonwealth Industrial Gases Ltd: anhydrous ammonia, 99.7% from I.C.I. Australia Ltd. The purification and storage of these gases followed the usual procedure. Gases with boiling points above liquid nitrogen temperature were condensed in cold traps at this temperature, and in each case the middle portion was then distilled into a glass storage bulb. Hydrogen was slowly flowed through a liquid nitrogen cold trap and into a glass storage bulb.

Mössbauer Spectrometer

A constant acceleration Mössbauer spectrometer of standard design was used. The γ-ray detection and count storage devices included: a sodium iodide (thallium) scintillation detector, Model 802-11; a high voltage power supply, Model 3002; a preamplifier, Model 1405; a linear amplifier, Model 1418; and a single channel analyzer, Model 1430, all from Canberra Industries, Inc.; and a multichannel analyzer, RIDL Model 24-3, from Nuclear-Chicago. The γ-ray counts were stored in 400 locations and the output was obtained by paper tape in BCD form from a tape perforator, Tally Model 420, through a punch/type matrix, RIDL Model 99-24. The Mössbauer source was 10 mCi ^{57}Co in palladium, supplied from the Radiochemical Centre, Amersham, England.

Mossbauer Cell and Sample Pretreatment

The sample, about 0.2 g, was pressed into a 20 mm diameter pellet and was held in a stainless steel ring welded to the inside of a rectangular stainless steel frame. The sample block was then placed in a Pyrex tube with thinned glass windows on both sides of the sample pellet. There was a sidearm on the tube into which the sample block could be moved and around which a furnace could be placed. During the sample treatment, the Mössbauer cell was attached to a conventional high-vacuum gas handling apparatus, and after treatment was transferred to the Mössbauer spectrometer for measurement. The details of the sample treatment will be indicated when the results are discussed. For an average run, more than 50,000 counts were accumulated in each of the 400 channels.

For a series of runs having the same velocity range, the spectra were calibrated with those of the standard compounds: sodium nitroprusside for the narrow velocity range, and ^{57}Fe-enriched α-Fe_2O_3 for the wide range. All spectra were taken at room temperature. For easy identification of peaks, the results were printed in a large scale on computer output, with the ordinate being expressed in percentage of the difference between the maximum and the minimum number of counts, and the abscissa expressed in channel numbers. All the figures shown in this paper have the ordinate expressed similarly, but with the abscissa converted into the velocity unit of millimeters per second with reference to sodium nitroprusside. The spectra are reported after manual fitting to the data points.

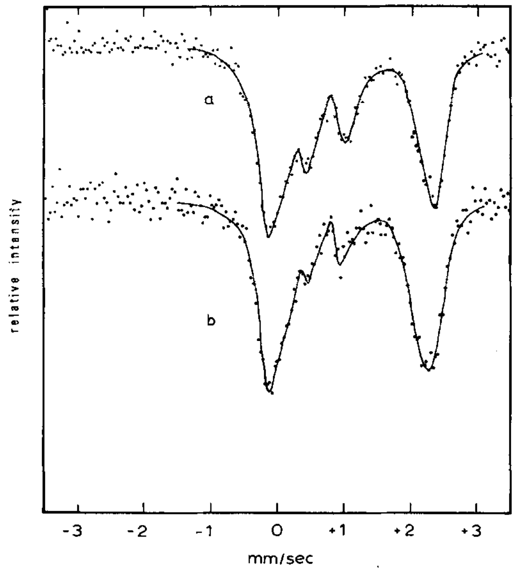

FIG. 1. Mössbauer spectra from Fe^{2+}-Y samples: (a) as prepared, then dehydrated at 673 K; (b) after heating (a) in hydrogen at 673 K.

RESULTS

Iron-Exchanged Zeolites

The dehydration of Fe^{2+}-Y zeolite at 673 K gave a Mössbauer spectrum consisting of two pairs of peaks (outer and inner, cf. Fig. 1a). The isomer shifts and the quadrupole splittings are listed in Table 2 and are in good agreement with those given by Delgass *et al.* (*8*). No significant change in the spectrum could be obtained by heating the exchanged zeolite in 13.3 kPa of hydrogen at temperatures up to 673 K for periods up to 40 hr. Furthermore, attempted reduction with carbon monoxide under conditions similar to those used with hydrogen, was also entirely fruitless. Figure 1b shows a spectrum taken after attempted reduction.

We made two further experiments to try to reduce Fe^{2+}-Y to yield metallic iron. The first was based on the formation of platinum particles to act as sites for hydrogen chemisorption, whereby it was hoped that iron reduction might be effected by hydrogen atoms diffusing from the chemisorption sites (hydrogen atom spillover). The reality of accelerated re-

TABLE 2
MÖSSBAUER PARAMETERS[a]

Sample	Treatment		δ (mm s^{-1})	QS (mm s^{-1})
Fe^{2+}-Y	Dehydrated (673 K)	(outer)	+1.54 (+1.53)[b]	2.42 (2.37)[b]
		(inner)	+1.17 (+1.14)[b]	0.58 (0.62)[b]
	Heated in H_2 (673 K)	(outer)	+1.52	2.38
		(inner)	+1.17	0.56
	Heated in CO (673 K)	(outer)	+1.50	2.35
		(inner)	+1.17	0.63
	Heated in NH_3 + H_2 (673 K)	(outer)	+1.53	2.42
		(inner)	+1.22	0.63
[Fe^{2+}, Pt]-Y	Heated (673 K) in H_2 or NH_3 + H_2 after dehydration	(outer)	+1.59	2.31
		(inner)	+1.22	0.63
Partially amorphous [Fe^{3+}, Ca]-Y	As prepared (air dried 298 K)		+0.64	0.86
	Dehydrated (623 K)		+0.61	1.61
	Heated in O_2 (673 K)		+0.59	1.51
	Heated in H_2 (673 K)		+1.40	2.14
Amorphous Fe^{3+}-Y	As prepared (air dried 298 K)		+0.78	0.69
	Heated (673 K) in H_2 after dehydration		+1.36	1.84
	Heated in O_2 (673 K)		+0.61	1.50
Fe^{3+}-SiO_2	As prepared (air dried 373 K)		+0.67	0.69
	Dehydrated (683 K)		+1.19	0.81
	Heated in H_2 (673 K)		+1.19	1.04
	Heated in O_2 (673 K)		+0.50	1.50
	Heated in H_2 (683 K)		+1.24	0.92

[a] Reference: sodium nitroprusside.
[b] From Ref. (*5*).

duction processes at surfaces by hydrogen atom spillover is sufficiently well known [e.g., Refs. (*2,9*)] for further comment here to be unnecessary. The [Fe^{2+},Pt]-Y zeolite sample was prepared with this end in view. Heating the [Fe^{2+},Pt]-Y sample in 13.3 kPa of hydrogen at 673 K for periods up to 40 hr gave a Mössbauer spectrum almost unchanged from that of a platinum-free specimen. The only difference was that the isomer shift was slightly more positive (cf. Table 2). However, the clear conclusion is that essentially no reduction occurred.

The second experiment was based on the use of an ammonia/hydrogen mixture (7:1) as the reductant. In this there were two considerations: (a) Fe^{2+} (but not Fe^{3+}) strongly coordinates ammonia ligands [cf. Ref. (*11*)], so it was thought possible that this might reduce the strength of Fe^{2+} interaction with the zeolite sites, and (b) we had observed ammonia decomposition on Fe^{2+}-Y zeolite at 673 K, and one would have expected hydrogen atoms to have been formed transiently. However, no reduction of the Fe^{2+}-Y or the [Fe^{2+},Pt]-Y specimens was observed at 673 K in periods up to 19 hr using a total gas pressure of 29.3 kPa.

The partially amorphous [Fe^{3+},Ca]-Y specimen gave an as-prepared (air dried) spectrum with $\delta = +0.64$ mm s^{-1} and $QS = 0.86$ mm s^{-1}, due to ferric iron. After vacuum outgassing (mainly dehydration) for 1 hr at 634 K the values were $\delta = +0.61$ mm s^{-1} and $QS = 1.61$ mm s^{-1}, indicating that the iron was still in the ferric state, but with the larger quadrupole splitting resulting from dehydration at the adsorption site. Apparently dehydration involves the removal of some hydroxyaquo ligands which, as a result of ferric iron coordination to zeolite oxide ions, leads to an increased field asymmetry at the iron nucleus. In comparison with this, it is known (*4,5*) that vacuum outgassing under more severe conditions leads to the conversion of ferric to ferrous (see also section on Iron-Exchanged Silica).

If our specimen at this stage of dehydration (ferric iron) was heated in 26.7 kPa of oxygen for 1.5 hr at 673 K, no change in the spectrum was observed. Heating in 21.3 kPa of hydrogen for 5 hr at 673 K resulted in reduction to the ferrous state, the spectrum containing a doublet with $\delta = 1.40$ mm s^{-1} and $QS = 2.14$ mm s^{-1}. No evidence for reduction to metallic iron was found. The spectra are recorded in Fig. 2, and the spectral parameters are summarized in Table 2.

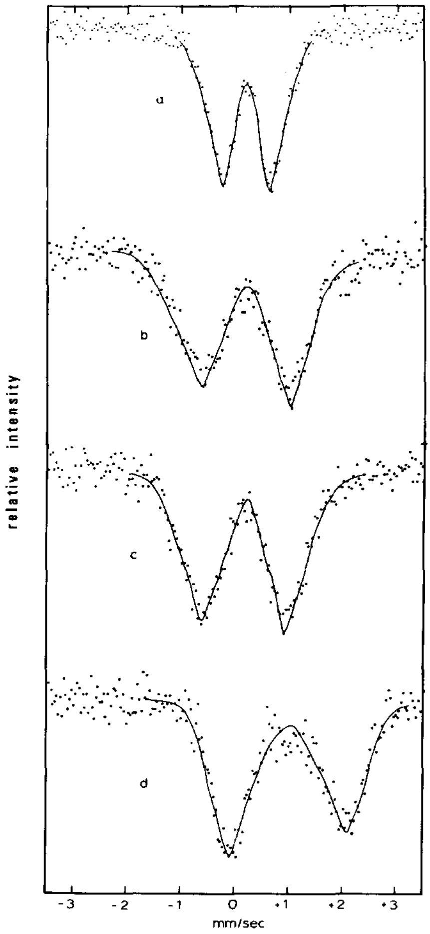

FIG. 2. Mössbauer spectra from partially amorphous [Fe^{3+},Ca]-Y samples: (a) as prepared (air dried 298 K); (b) after dehydration of (a) at 623 K; (c) after heating (b) in oxygen at 673 K; (d) after heating (c) in hydrogen at 673 K.

The amorphous Fe^{3+}-Y sample, as prepared, showed a doublet in the spectrum with $\delta = +0.78$ mm s^{-1} and $QS = 0.69$ mm s^{-1}, indicating that the iron was (as expected) in the ferric state. After dehydration at 1.33 mPa and 673 K, followed by heating in hydrogen at 673 K for 3 hr, the sample gave an asymmetrical doublet with $\delta = +1.36$ mm s^{-1} and $QS = 1.84$ mm s^{-1} (Fig. 3a and b), which we assign to ferrous iron. The ferrous and ferric states were readily interconvertable by treatment with oxygen or hydrogen at 673 K (Fig. 3b and c) in the same way as we [and others (*8*)] have observed for the crystalline Fe-Y zeolite. The asymmetry of the doublet from the ferrous state of the amorphous Fe-Y sample is reminiscent of the asymmetry of the doublet observed (*11*) for Fe^{3+} on η-Al_2O_3.

When the amorphous Fe-Y sample was

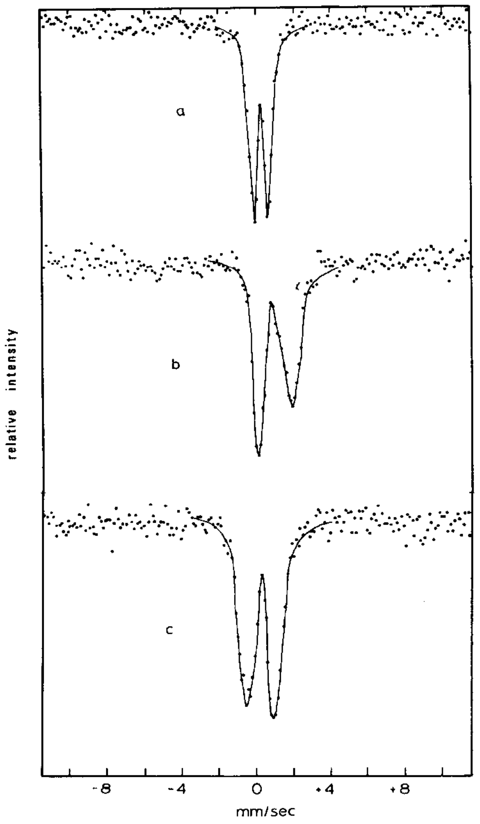

FIG. 3. Mössbauer spectra from amorphous Fe^{3+}-Y samples: (a) as prepared (air dried 298 K); (b) after dehydration of (a) and heating in hydrogen at 673 K; (c) after heating (b) in oxygen at 673 K.

calcined in air at 1273 K overnight, the spectrum shown in Fig. 4a was obtained. By comparison with the known spectrum of α-Fe_2O_3, the spectrum of Fig. 4a consists of that due to α-Fe_2O_3 superimposed on a central complex peak which is a part-doublet. Subtracting the contribution from the α-Fe_2O_3 gave for the central peak $\delta = +0.61$ mm s^{-1} and an estimate of QS of 0.8 mm s^{-1}. X-Ray diffraction readily confirmed the presence of α-Fe_2O_3. After heating in 22.6 kPa of hydrogen at 673 K for 16 hr, the α-Fe_2O_3 spectrum had largely, but not completely, disappeared, and there remained a central part-doublet (Fig. 4b) of total integrated intensity rather greater than that of the part-doublet for the unreduced sample: this peak

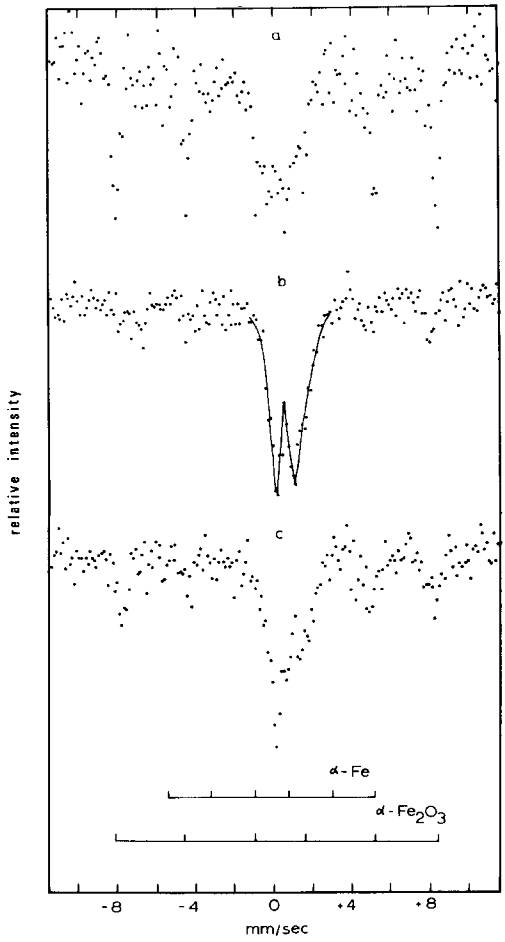

FIG. 4. Mössbauer spectra from amorphous Fe^{3+}-Y samples: (a) after heating sample of Fig. 3c to 1273 K in air; (b) after heating (a) in hydrogen at 673 K; (c) after heating (b) in oxygen at 673 K.

gave $\delta = +0.99$ mm s^{-1} and $QS = 0.87$ mm s^{-1}. The original spectrum of Fig. 4a was only incompletely recovered (Fig. 4c) by heating the hydrogen treated sample in 26.7 kPa of oxygen for 4 hr at 673 K.

Iron-Exchanged Silica

With this material the spectra were subject to a relatively poor signal-to-noise ratio because of the low iron content of the samples. Nevertheless, the data are quite adequate to show that in each case the spectrum is a doublet, and for the δ and QS parameters to be evaluated.

The spectrum for the as-prepared (air dried 373 K) sample (Fig. 5a) gave $\delta = +0.67$ mm s^{-1} and $QS = 0.69$ mm s^{-1}, clearly indicating the presence of ferric iron, as expected. This specimen was then carried through the following sequence of treatments: outgassing (mainly dehydration) in vacuum at 683 K for 3 hr; reduction in 14.6 kPa of hydrogen at 673 K for 15 hr; oxidation in 38.6 kPa of oxygen at 673 K for 17 hr; and reduction in 19.6 kPa of hydrogen at 683 K for 22 hr.

The isomer shift and quadrupole splitting parameters corresponding to these stages are recorded in Table 2, while Fig. 5b and c contain examples of the spectra. The data after this outgassing treatment clearly show the iron to be present in the ferrous state. This conversion of ferric to ferrous on vacuum outgassing is similar to that reported (*4*) with ferric iron-exchanged Ca-X and Na-Y zeolites, and for a ferrous iron-exchanged Na-Y zeolite (*5*) which had been previously oxidized to the ferric state and rehydrated (although in this latter case conversion to ferrous on outgassing was not complete). The most reasonable course for this conversion involves an aquoferric ion acting as a Brønsted acid, followed by reductive dehydroxylation (*4*)

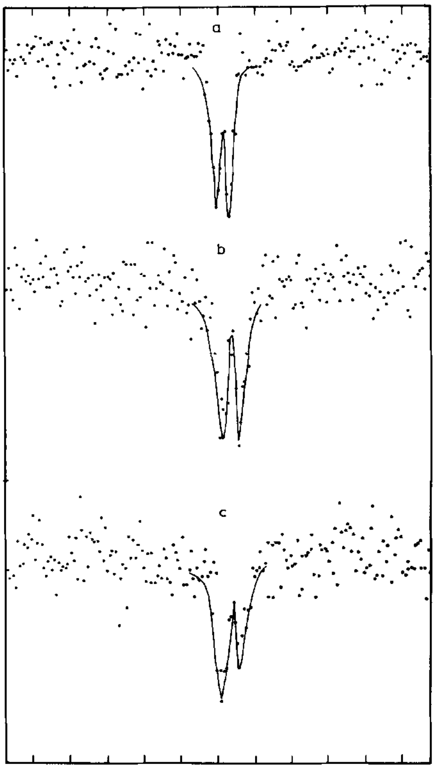

FIG. 5. Mössbauer spectra from Fe^{3+}–SiO_2 samples: (a) as prepared (air dried 373 K); (b) after dehydration of (a) at 683 K; (c) after heating (b) in hydrogen at 673 K.

$$O^{2-} + [Fe\text{-}H_2O]^{3+} \rightarrow OH^- + [Fe\text{-}OH]^{2+}, \quad (1)$$

$$2[Fe\text{-}OH]^{2+} \rightarrow 2Fe^{2+} + H_2O + \tfrac{1}{2}O_2. \quad (2)$$

Hydrogen reduction of our dehydrated iron exchanged silica left the iron in the ferrous state (cf. Table 2 and Fig. 4c), and there was no indication of the formation of any metallic iron. The subsequent oxygen and hydrogen treatments gave results which obviously showed that the adsorbed iron could be interconverted between the ferrous and ferric states.

Iron Oxide

Samples containing α-Fe_2O_3 gave the well-known six-line Mössbauer spectrum. Reduction in 40 kPa of hydrogen for 5 hr at temperatures in the range 523–573 K gave only Fe_3O_4, identified by its well-known six-line spectrum with doublet peaks. Reduction in 36 kPa of hydrogen for 5 hr at 673 K gave a spectrum indicating complete conversion to metallic α-Fe. Adsorption of oxygen on the α-Fe specimen, first at 77 K and then at 298 K at pressures ≤ 6.7 kPa gave a Mössbauer spectrum not significantly different from that of the α-Fe: heating to 673 K in oxygen, however, reconverted the specimen to α-Fe_2O_3.

DISCUSSION

Under none of the conditions used in this work were we able to effect the reduction of iron below the ferrous state when it was exchanged onto the surface of zeolite or silica gel. The systems studied included an iron-exchanged Ca-Y zeolite which was similar to the system studied by Morice and Rees (*4*) (an iron-exchanged Ca-X). Our results thus disagree with those of Morice and Rees, but confirm the observations of Garten *et al.* (*5*). Using hydrogen as a reducing agent, the only way we have found to reduce exchanged iron to the metallic state was if iron oxide was first formed by high temperature oxidation. The loss of zeolite crystallinity in ferric-exchange Y-zeolite has also been reported by Nesterov *et al.* (*21*), but whereas we observed this to begin immediately after exchange, these authors only observed it after dehydration at about 773 K.

The α-Fe_2O_3 particles, produced by 1273 K air-calcination of the amorphous Fe-Y sample (cf. Fig. 4), must have been larger than the lower limit to the ferromagnetic domain size (about 20 nm at room temperature) for the magnetically split six-line spectrum to have been retained. The removal of the α-Fe_2O_3 spectrum by hydrogen reduction at 673 K is open to two possible interpretations, bearing in mind that the spectrum of the reduction product gave a central doublet with $\delta = +0.99$ mm s^{-1} and $QS = 0.87$ mm s^{-1}, but no evidence for a magnetically split six-line spectrum of metallic α-Fe. Reduction might have proceeded to metallic iron particles which were below the ferromagnetic domain size (20–30 nm at room temperature). This process has $\Delta G^0_{700} = +7.0$ kJ (mol $Fe_2O_3)^{-1}$, that is, it is favorable at 700 K provided $p_{H_2O}/p_{H_2} < 0.67$, a condition easily achieved. Alternatively, reduction might have been intercepted at the Fe^{2+} stage by reaction of Fe^{2+} with the support and it is useful to note that Fe_2SiO_4 is relatively resistant to reduction, since the reaction,

$$Fe_2SiO_{4(c)} + 2H_{2(g)} \rightleftarrows 2Fe_{(c)} + SiO_{2(c)} + 2H_2O_{(g)}, \quad (3)$$

has $\Delta G^0_{700} = +64.1$ kJ (mol $Fe_2SiO_4)^{-1}$. We do not have the data to decide between these alternatives, but we consider the former to be the more probable.

The thermodynamics of reaction (3) are also in indicative agreement with our inability to reduce our exchanged Fe–SiO_2 specimen to metallic iron.

It is useful to compare the behavior of X- or Y-zeolites exchanged with Ni^{2+} and Fe^{2+}. In contrast to the behavior of Fe^{2+}, a number of workers (*12–14*) agree that X- and Y-zeolites which have been exchanged with Ni^{2+} yield particles of metallic nickel on hydrogen reduction at temperatures in the range 620–670 K.

The site location of Ni^{2+} and Fe^{2+} in X- and Y-zeolites has considerable similarity. The Ni^{2+} ions occur at S_I and S_{II} sites, with a modest preference for S_I (*16,17*). In S_I sites, the nickel is octahedrally coordinated. Ni^{2+} or Fe^{2+} ions exchanged into A-zeolite occupy sites which resemble S_{II}, and it has been concluded from optical absorption spectra in the case of Ni^{2+} (*18,19*), and from Mössbauer spectra in the case of Fe^{2+} (*20*) that these ions are trigonally coordinated to three zeolite oxygens. However, there is also Mössbauer evidence (*5*) in the case of Fe^{2+}, and evidence from optical spectra (*18,19*) in the case of Ni^{2+} that the coordination may be converted to tetrahedral by adsorption of a foreign species, in which are used three oxygens from a S_{II} site and (say) a hydroxyl or oxide ion originating from adsorbed water or adsorbed oxygen.

Thermodynamic data (*15*) indicate that, in general, Ni^{2+} compounds are more easily reduced than corresponding Fe^{2+} compounds of similar structure. For instance, in the reduction of $Ni(OH)_2$ and $Fe(OH)_2$ (both hexagonal with the CdI_2 structure) according to

$$M(OH)_{2(c)} + H_{2(g)} \rightleftarrows M_{(c)} + 2H_2O_{(g)}, \quad (4)$$

the values of ΔG^0_{298} are -3.8 and $+26.8$ kJ (mol $M(OH)_2)^{-1}$, respectively. In the reduction of NiO and "FeO"[1] (in both of which the metal ions are in octahedral coordination with nearest neighbor oxygens) according to

$$MO_{(c)} + H_{2(g)} \rightleftarrows M_{(c)} + H_2O_{(g)}, \quad (5)$$

the values of ΔG^0_{700} are -28.9 and -1.7 kJ (mol MO)$^{-1}$, respectively.

To consider Ni^{2+} and Fe^{2+} in octahedral coordination in X- or Y-zeolite, we propose to write the reduction formally as follows

$$[M^{2+},O_6^{2-}]_Z + H_{2(g)} \rightleftarrows M_{(c)} + [(OH^-)_2,O_4^{2-}]_Z, \quad (6)$$

where the formula $[M^{2+},O_6^{2-}]_Z$ represents octahedrally coordinated M^{2+} in the zeolite, and $[(OH^-)_2,O_4^{2-}]_Z$ represents this site after removal of M^{2+} and the protonation of two oxide ions. Data are not available from which to estimate standard free energy changes for this reaction for Ni^{2+} and Fe^{2+} individually, but one can reasonably estimate the difference. We may construct reaction (6) by the following series of partial reactions

$$[M^{2+},O_6^{2-}]_Z \rightleftarrows M_{(g)}^{2-} + [O_6^{2+}]_Z, \quad (7a)$$

$$M_{(g)}^{2+} + 2e \rightleftarrows M_{(g)}, \quad (7b)$$

$$M_{(g)} \rightleftarrows M_{(c)}, \quad (7c)$$

$$H_{2(g)} \rightleftarrows 2H_{(g)}^{+} + 2e, \quad (7d)$$

$$[O_6^{2-}]_Z + 2H_{(g)}^{+} \rightleftarrows [(OH^-)_2,O_4^{2-}]_Z. \quad (7e)$$

Thus

$$(\Delta G^0_{Ni} - \Delta G^0_{Fe})_6 = (\Delta G^0_{Ni} - \Delta G^0_{Fe})_{7a} + (\Delta G^0_{Ni} - \Delta G^0_{Fe})_{7b} + (\Delta G^0_{Ni} - \Delta G^0_{Fe})_{7c} \quad (8)$$

where $(\Delta G^0_{Ni} - \Delta G^0_{Fe})_6$ represents for reaction (6) the standard free energy difference when $M^{2+} = Ni^{2+}$ and $M^{2+} = Fe^{2+}$, and the other terms have similar significance with respect to reactions (7a), (7b) and (7c). We find $(\Delta G^0_{Ni} - \Delta G^0_{Fe})_{7b} = -196.0$ kJ mol^{-1}, evaluated using the metal atom double ionization energies, 18.2 and 16.16 eV for nickel and iron, respectively; while for 298 K $(\Delta G^0_{Ni} - \Delta G^0_{Fe})_{7c} = -21.0$ kJ mol^{-1}, evaluated using the standard free energies of atomization for nickel and iron of 380.05 and 359.08 kJ mol^{-1}, respectively. The term $(\Delta G^0_{Ni} - \Delta G^0_{Fe})_{7a}$ we evaluate from the corresponding difference in the ion hydration, that is for the reaction,

$$M_{(g)}^{2+} + \infty H_2O \rightleftarrows M_{(aq)}^{2+}(\infty H_2O), \quad (9)$$

for which the enthalpy changes at 298 K are -2994 and -2826 kJ (mol M^{2+})$^{-1}$ for Ni^{2+} and Fe^{2+}, respectively (*10*). It is reasonable to believe that the difference in the standard entropy changes will be small, and thus we estimate for $(\Delta G^0_{Ni} - \Delta G^0_{Fe})_{7a}$ a value of 167 kJ (mol M^{2+})$^{-1}$, obtained from the enthalpy values. While it is true that the ion hydration enthalpies contain contributions from secondary ion solvation energies, it is reasonable to believe that these terms will not contribute significantly to the difference. Furthermore, a value of 167 kJ (mol M^{2+})$^{-1}$ is also obtained by using hexammine ion formation enthalpies (*10*) in place of hydration energies.

Using these values we obtain an estimate for $(\Delta G^0_{Ni} - \Delta G^0_{Fe})_6$ of -50 kJ (mol M^{2+})$^{-1}$. It is clear that in practice this standard free energy difference would be quite enough to differentiate the reducibilities of iron and nickel-exchanged zeolite, since at 700 K it would require the critical hydrogen pressure for reduction just to be possible according to reaction (6), to be higher by a factor of 5.2×10^3 with iron than with nickel.

If we are concerned with the reduction of tetrahedrally coordinated M^{2+}, the standard free energy difference $(\Delta G^0_{Ni} - \Delta G^0_{Fe})_{tetra}$ for the reduction reactions analogous to reaction (6) will be more

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[1] "FeO" refers to the nonstoichiometric compound $Fe_{0.95}O$ for which thermodynamic data are available.

favorable in the direction of Ni^{2+} relative to Fe^{2+} than in the octahedral case. If we use thermodynamic data (*10*) for the reaction,

$$[MCl_4]^{2-} + 6H_2O \rightleftarrows [M(H_2O)_6]^{2+} + 4Cl^-, \quad (10)$$

to estimate the energy differences between octahedral and tetrahedral coordination we find $(\Delta G^0_{Ni} - \Delta G^0_{Fe})_{tetra} \approx -85$ kJ (mol $M^{2+})^{-1}$.

In this discussion, we have tacitly ignored the possibility that reduction is kinetically limited, the point being that the formation of metallic crystals from an atomically dispersed precursor necessarily requires atom transport over considerable distances. With the exchanged zeolites, the fact that hydrogen reduction to metallic nickel is possible strongly suggests that the failure to reduce to metallic iron is not kinetic in origin. In any case, in the exchanged zeolites the metal ions were, on the average, not a great distance apart, about 0.8–0.9 nm. On the other hand, in our exchanged silica sample, the ions were, on the average, some 3 nm apart, and a kinetic limitation is perhaps more possible, although we have no evidence to confirm that it did in fact occur.

As an extension to the above discussion, it will be apparent that reduction to metallic iron would be thermodynamically favorable if hydrogen atoms rather than hydrogen molecules were the reducing agent, since this would make the standard free energy change for any reduction reaction more negative by some 364–440 kJ/mole of H_2 involved, depending on the temperature in the range 700–300 K. The failure of added platinum to bring about the hydrogen reduction of the Fe^{2+}-exchanged zeolite we attribute to the inability of spillover hydrogen atoms to travel sufficient distances across the zeolite to reach a significant number of Fe^{2+} ions. Thus, under the preparative conditions used, we would expect the dispersion of the metallic platinum to have been about 0.2, so that at a platinum loading of 0.82 wt%, the platinum particles would have been about 300–400 nm apart on the zeolite, compared with the exchanged Fe^{2+} ions which were 0.8–0.9 nm apart.

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