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Reduction of Supported Iron Catalysts Studied by Mössbauer Spectroscopy

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The reduction of ferrous ions exchanged into Y-zeolite by sodium vapor and sodium borohydride is described. Sodium vapor is able to reduce ferrous ions in the zeolite to α-Fe with particle sizes ca. 3.5 nm, and provides a method for production of highly dispersed supported iron metal. Reduction by sodium borohydride in solution appears to be a solute reaction and leads to leaching of iron from the zeolite.

INTRODUCTION

In an earlier paper (*1*) attempts to reduce zeolites exchanged with iron ions using hydrogen, hydrogen–ammonia mixtures, and hydrogen spillover from platinum metal were reported. In none of these experiments was it possible to reduce the iron below the ferrous state, whereas reduction of any of the bulk oxides of iron by hydrogen proceeds readily under the conditions used. There has been one previous report of reduction of a ferric-exchanged zeolite by hydrogen to metallic iron (*2*). However, this has not been confirmed by later work (*1, 3*) and it is likely that the reduction in this case was of an oxide rather than exchanged ions. There have recently been two detailed studies, using Mössbauer spectroscopy, of the formation of small iron particles by reduction of oxide, and of their catalytic properties (*4, 5*). In this paper we report two further attempts to reduce ferrous ions exchanged into Y-zeolite, by sodium vapor, and sodium borohydride.

EXPERIMENTAL

1. Mössbauer Spectrometer

A conventional Mössbauer spectrometer operating in the constant acceleration mode was used. Velocities were calibrated using a 6-μm α-Fe foil and are reported, referred to sodium introprusside (SNP), assuming the isomer shift (IS) of the ^{57}Co in copper source to be 0.48 mm s^{-1} (*6*).

Spectra are corrected for the varying source–absorber distance and least-squares fitted with Lorentzian lineshapes. The position, width, and intensity of each peak were allowed to vary in the fitting process and the goodness of fit was monitored by a χ^2 test (512 degrees of freedom). The linewidths were constrained to be greater than those for an absorber of zero thickness, and the intensities of the lines to be positive. Additional constraints on groups of peaks arising from a single iron species are mentioned below.

2. Sample Preparation

Ferrous-exchanged Y-zeolite (Fe^{2+}–Y) was prepared by repeated ion exchange of sodium Y-zeolite (Linde SK-40) with 0.5 *M* ferrous sulfate under a nitrogen atmosphere. Care was taken to deoxygenate all solutions used in the preparation. The ion exchange product was thoroughly washed with distilled water and dried by heating to 530 K in flowing nitrogen for 20 hr. The composition of the product was determined by atomic absorption spectroscopy to be 29% exchanged.

3. Sodium Reaction

A stainless-steel vacuum cell with 10-μm aluminum windows was constructed which

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allowed Mössbauer spectra of catalyst specimens to be taken under vacuum. The cell was connected to a glass, diffusion pumped vacuum system and attained pressures of 10^{-6} mbar.

The absorber was in the form of a self-supporting compressed disk of powder, 22 mm in diameter and ca. 0.5 mm thick. This was held centrally in a stainless-steel tube within the vacuum cell. The outside of the tube was wound with nichrome heating wire, which allowed heating of the holder to 1100 K. A thermocouple was attached to the specimen holder adjacent to the adsorber.

The reaction with sodium was performed by introducing a piece of sodium metal (0.2 g), which had been prepared by washing in *n*-hexane and cutting to remove oxidized surface, into the sample holder beside the adsorber. The open end of the sample holder tube was loosely capped with aluminum foil to ensure sufficient contact between the sodium vapor, distilling from the heated holder, and the absorber. The temperature of the evacuated sample holder was then raised to progressively higher temperatures from 500 K for ca. 10 min and allowed to cool to room temperature before a Mössbauer spectrum was obtained.

4. *Sodium Borohydride Reaction*

A portion of the ferrous-exchanged zeolite was suspended in 100 ml of deoxygenated distilled water and a 0.5 *M* solution of sodium borohydride added gradually. The reaction mixture was adjusted to pH 7 by addition of dilute sulfuric acid. The resulting suspension was washed with distilled water and dried before a Mössbauer spectrum was taken. The specimens were also examined by electron microscopy and diffraction.

RESULTS AND DISCUSSION

1. *Reaction with Sodium*

The Mössbauer spectrum of the dehydrated Fe^{2+}–Y (Fig. 1a) is in agreement with earlier studies of this material (*1–3*). The spectrum comprises two pairs of quadrupole split lines (Table 1) which have been identified as ferrous ions in hexagonal prism sites (outer pair) and fourfold sites (inner pair) of the zeolite structure. The progressive reaction with sodium at temperatures up to 852 K leads to a reduction in the intensity of the high-velocity absorption peaks. The concurrent reduction in the low-velocity peaks is obscured by an increase in absorption in this region by the product of the reaction (Fig. 1). A constrained fitting of the spectrum of Fig. 1d with a symmetric doublet at the Fe^{2+}–Y (outer pair) positions and two unconstrained peaks shows that the new absorption consists of a doublet with isomer shift (IS) of 0.45 mm s^{-1} and quadrupole splitting (QS) of 0.72 mm s^{-1}.

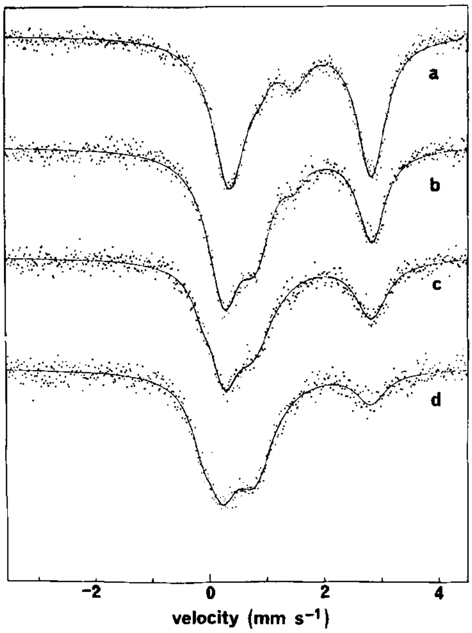

FIG. 1. Room temperature Mössbauer spectra of Fe^{2+}–Y. (a) Dehydrated Fe^{2+}–Y; (b) after heating with sodium to 688 K; (c) heated with sodium to 747 K; (d) heated with sodium to 852 K. Velocities are relative to SNP.

Heating the sample to 1066 K produced a quantitative change in the room temperature Mössbauer spectrum (Fig. 2). Three

TABLE 1

Parameters Found to Fit Mössbauer Spectra of Sodium Reduction Products

Figure	Maximum temperature (K)	Peaks		
		Position relative to SNP (mm s^{-1})	Width (mm s^{-1})	Thickness (arb. units)
1a	300	0.38	0.35	2.50
	$(\chi^2 = 610)$	0.49	0.20	0.21
		1.48	0.26	0.49
		2.80	0.29	2.11
1b	688	0.28	0.34	2.34
	$(\chi^2 = 495)$	0.82	0.31	1.36
		1.49	0.19	0.23
		2.81	0.28	1.39
1c	747	−0.09	0.20	0.28
	$(\chi^2 = 560)$	0.28	0.29	1.39
		0.78	0.45	1.52
		2.82	0.33	0.94
1d	852	Fe^{2+}-Y[a]	0.29	0.99
	$(\chi^2 = 567)$	0.09	0.36	1.55
		0.81	0.40	1.62
2	1066	α-Fe[a]	0.23	1.48
	$(\chi^2 = 570)$	Fe^{2+}-Y[a]	0.56	0.42
		0.24	0.57	1.10

[a] Peak positions constrained.

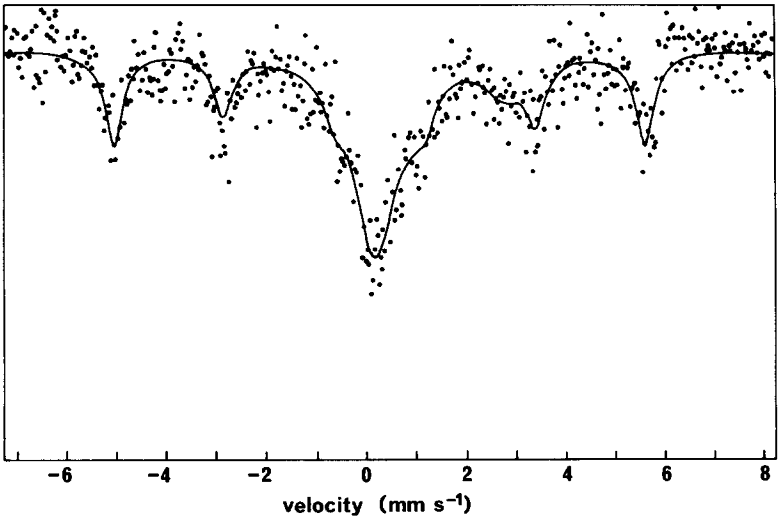

FIG. 2. Room temperature Mössbauer spectra of the product of sodium reaction with Fe^{2+}-Y heated to 1066 K. Velocities are relative to SNP.

FIG. 3. Electron micrograph of the product of sodium reaction with Fe^{2+}–Y heated to 1066 K.

additional peaks appeared at −4.99, −2.79, and 5.63 mm s^{-1}. These peaks are readily identified as three of the six lines of the magnetically split α-Fe spectrum. The remaining three peaks of this spectrum are at −0.59, 1.23, and 3.43 mm s^{-1} and are obscured by other absorptions. The peak observed at 3.24 mm s^{-1} is too broad to be only an α-Fe line, as well as being in the wrong position, and must include a contribution from the outer doublet of the Fe^{2+}–Y spectrum. A constrained fitting of the spectrum with the six-peak α-Fe pattern, a symmetric Fe^{2+}–Y doublet (outer pair), and a single unconstrained peak shows that the absorption in the central region has an isomer shift of 0.24 mm s^{-1}. Allowing two unconstrained peaks in this region did not significantly improve the fit.

The product from the reaction discussed above was also examined by electron microscopy and diffraction, which revealed the presence of particles of α-Fe on the

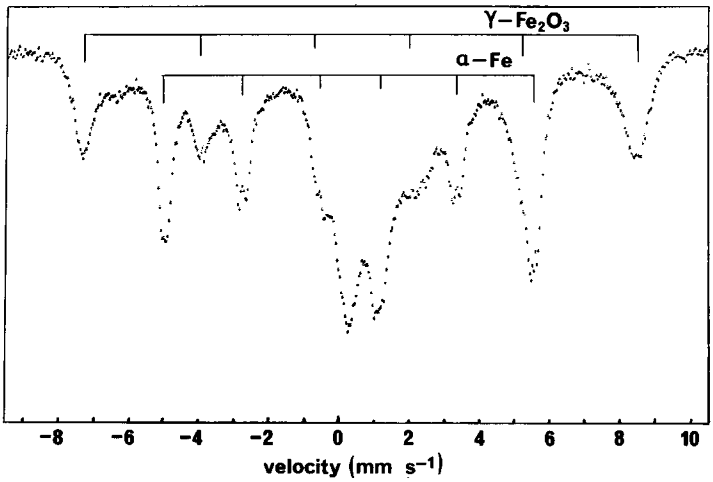

FIG. 4. Room temperature Mössbauer spectra of the product of the reaction of Fe^{2+}–Y with sodium borohydride. Velocities are relative to SNP.

TABLE 2

Mössbauer Parameters for the Product of $NaBH_4$ Reduction

	IS (mm s^{-1})	QS (mm s^{-1})	Hi (kOe)
1. (α-Fe)	0.37	0	324
2. (γ-Fe_2O_3)	0.66	-0.1	489
3. (Fe^{3+})	0.83	0.82	—

zeolite crystals (Fig. 3). The size distribution of the iron particles was estimated by measurement of the electron micrographs, and showed a narrow distribution of sizes with a mean diameter of 3.5 nm. The electron diffraction patterns also reveal that the zeolite has remained crystalline.

The production of α-Fe on heating to 1066 K is a strong indication that the product on heating to lower temperature is a reduced form of iron, possibly very small particles showing superparamagnetism at room temperatures or an even more highly dispersed form.

2. *Reaction with $NaBH_4$*

The Mössbauer spectrum of the sodium borohydride reaction product (Fig. 4) can be separated into two six-line spectra. The parameters measured from the spectrum are given in Table 2. The stronger of the two spectra can be identified as α-Fe, and the weaker as γ-Fe_2O_3. There is some additional absorption in the region -1.0 to 3.0 mm s^{-1} including a strong doublet with isomer shift of 0.83 mm s^{-1} and a quadrupole splitting of 0.82 mm s^{-1} which is identified as Fe^3.

Electron diffraction of the material confirms the presence of α-Fe and γ-Fe_2O_3, although only one diffraction ring from γ-Fe_2O_3 is apparent. The electron micrograph (Fig. 5) reveals that the α-Fe is present in a skin of amorphous material surrounding the zeolite particles, indicating that the reduction by sodium borohydride in solution led to leaching of the iron from the zeolite.

CONCLUSIONS

We have used Mössbauer spectroscopy to study the reduction of ferrous-exchanged Y-zeolite by sodium vapor. Iron particles of ~3.5 nm were produced by this reaction at 1066 K, and it is likely that at lower temperatures smaller particles were produced. It is possible to produce metallic iron by this reaction without first producing an oxide. The reaction with sodium borohydride, on the other hand, appears to have been a

FIG. 5. Electron micrograph (dark field) of the product of the reaction of Fe^{2+}–Y with sodium borohydride.

reaction with solvated ferrous ions, and therefore independent of the zeolite support.

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