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Mössbauer Spectroscopy and Catalytic Studies of Iron-Exchanged, Silicon-Substituted Y-Zeolite

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Iron-exchanged zeolites with Si/Al ratios ranging from 2.49 to 8.88 were characterized by Mössbauer spectroscopy and studied for the decomposition of N_2O. Mössbauer spectra were collected at room temperature after pretreatments in H_2 and O_2 at 700 K, and after exposure of the samples to CO or H_2O. Nitrous oxide decomposition activities were determined at 800 K under a N_2O partial pressure of 3.5 kPa. Mössbauer spectra collected after pretreatment in H_2 showed that silicon-substituted Fe–Y had a larger fraction of iron cations in sites I′, II′, and/or II than conventional Fe–Y, in which most iron cations were in site I. The silicon-substituted Fe–Y catalysts had higher turnover frequencies for the decomposition of N_2O than conventional Fe–Y. Mössbauer spectra collected after pretreatment in O_2 showed that a fraction of the iron cations in silicon-substituted Fe–Y was more difficult to oxidize to Fe^{3+} than the iron in conventional Fe–Y. This result suggests that pairs of iron cations in close proximity are needed for the oxidation process to occur readily. Finally, exposure of the zeolites to CO or H_2O produced Mössbauer spectroscopy doublets due to iron cations associated with adsorbate molecules. These doublets indicate that ferrous cations at sites I′, II′, and/or II serve as adsorption centers for H_2O, the adsorption process increasing the coordination of the ferrous cations, and that ferrous cations at site II can serve as adsorption centers for CO as well.

INTRODUCTION

Zeolites are unique among oxide catalysts because of the wide range over which their physical and chemical properties can be varied. There are many natural and synthetic zeolites having unique crystal structures and pore systems; furthermore, each zeolite may have its catalytic and chemisorptive properties modified by changing the base-exchange cation, the degree of hydration, and the silicon-to-aluminum ratio. In addition, these cationic species, because of the nature of their interaction with the anionic sites within the zeolite lattice, exist as isolated cations. Therefore, zeolites provide the opportunity to study the relationship between catalytic properties and both the state of these isolated cations and the structure of zeolite lattice. Mössbauer spectroscopy has proved to be a useful technique for the study of cation coordination in zeolites covering a range of physical and chemical properties. In the past, the technique has been used to characterize zeolites Y, A, L, mordenite, and ZSM-5, exchanged with Fe, Co, and Eu cations in different oxidation states and under various degrees of hydration (*1–9*). Nonetheless, no Mössbauer spectroscopy study has been reported of zeolites having the same crystal structure, exchanged with the same cation species, but with varying silicon-to-aluminum (Si/Al) ratios. Hence, experiments were undertaken in which a series of Fe-

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exchanged Y-zeolites having varying Si/Al ratios were characterized using Mössbauer spectroscopy.

In addition, the catalytic properties of these same zeolites were studied for the decomposition of N_2O into its elements. This reaction provides the simplest example of the redox chemistry associated with the clean-up of combustion exhaust gases, and it has been shown to be catalyzed by zeolites containing iron cations (*10, 11*). The mechanism by which the reaction occurs involves a regenerative, oxidation–reduction cycle. Starting with the oxidized catalyst, N_2O first removes an oxygen atom from a ferric cation, reducing it to Fe^{2+} and forming N_2 and O_2. Next, a second molecule of N_2O decomposes on the reduced iron site, forming N_2 and reoxidizing the iron. An interesting feature reported earlier was that the reaction rate per gram of catalyst was approximately the same for Fe–Y and Fe–M, although the amount of Fe in the mordenite structure was significantly less than that in the Fe–Y (*11*). This was thought to result from differences in the environment of the Fe within the structures. By comparing the kinetic results with the Mössbauer spectroscopic results, a correlation between catalytic activity and the chemical environment of the exchange cations was sought in the present study.

EXPERIMENTAL

Sample Preparation

The starting material for the zeolites reported here was crystalline Linde Y-zeolite (SK-40, Lot 1280-133). One sample was exchanged with Fe without modification of the Si/Al ratio. The others were subjected to a treatment with ammonium hexafluorosilicate (*12*) after two exchanges with ammonium nitrate (1 *M*, 363 K, 3 h). The silicon substitution was carried out with a predetermined amount of $(NH_4)_2SiF_6$ (based on the total amount of aluminum in the zeolite being treated) in a buffered solution of pH 6.5 at 358 K for 3 h. After this reaction the zeolite was washed with hot distilled–deionized water until the pH of the effluent was 6.95–7.05 (about 1 liter per gram of zeolite). Following this procedure, the samples were dried overnight and calcined at 770 K. They were then converted back to their ammonium form by treatment with anhydrous NH_3 and exchanged with NaOAc twice to obtain the same sodium form used in the Fe exchange of the first sample. The sample with Si/Al ratio of 4.64 was exchanged with NaOAc immediately after silicon substitution and washing, but without an intervening calcination. All samples were dried and calcined at 770 K following the exchange with Na. The procedure used for the final exchange with $FeSO_4$ has been reported elsewhere (*1*).

The unit cell compositions of the four samples, according to the analytical data provided by Galbraith Laboratories, are given in Table 1. The Si/Al ratios determined by MAS–NMR analysis were found to agree qualitatively with those obtained from chemical analysis. The crystallinities of the final preparations were determined by X-ray diffraction and nitrogen adsorption capacities. These data are also presented in Table 1. The given X-ray diffraction crystallinities were determined from the five strongest peaks having 2θ values between 10 and 20°. To obtain the percentage crystallinities, the sums of the height-to-area ratios of these peaks were computed and normalized against the corresponding ratios of the parent Na–Y. A word of caution is of note. All samples were subject to line broadening from the X-ray fluorescence of iron, explaining why this method yielded percentage crystallinities that are lower than those expected from the nitrogen adsorption capacities.

Mössbauer Spectroscopy

Mössbauer spectra were recorded with an Austin Associates Model S-600 Mössbauer Spectrometer Controller and a Tracor-Northern Model N6-900 multichannel analyzer. A 50-mCi single-line ^{57}Co source

TABLE 1

Fe-Y-Zeolite Properties

Unit cell compositions[a]	Si/Al ratio[b]	N_2 adsorption capacity at 77 K[c]	X-ray crystallinity (%)
$H_{5.3}Na_{22.6}Fe_{13.6}(AlO_2)_{55.0}(SiO_2)_{137.0}$ $[H_{10.1}Na_{22.6}Fe_{13.6}(AlO_2)_{59.9}(SiO_2)_{134.1}]$	2.49	180	63
$H_{3.5}Na_{12.0}Fe_{9.3}(AlO_2)_{34.1}(SiO_2)_{157.9}$ $[H_{11.7}Na_{12.0}Fe_{9.3}(AlO_2)_{42.3}(SiO_2)_{150.7}]$	4.64	183	64
$H_{8.6}Na_{5.6}Fe_{6.3}(AlO_2)_{26.8}(SiO_2)_{165.2}$ $[H_{13.9}Na_{5.6}Fe_{6.3}(AlO_2)_{32.1}(SiO_2)_{161.9}]$	6.17	161	44
$H_{2.0}Na_{4.4}Fe_{6.5}(AlO_2)_{19.4}(SiO_2)_{172.6}$ $[H_{9.5}Na_{4.4}Fe_{5.5}(AlO_2)_{24.9}(SiO_2)_{169.1}]$	8.88	171	42

[a] The unit cell compositions given in square brackets are those which account for the Si/Al ratio determined by MAS–NMR.

[b] Determined from unit cell compositions based on chemical analysis. MAS–NMR analysis for the zeolites prior to Fe exchange had Si/Al ratios of 2.24, 3.59, 5.04, and 6.78, respectively. The ^{27}Al spectra for all the samples here did not show the presence of amorphous, octahedral aluminum.

[c] Units are cc/g.

in a Pd matrix was used. The velocity scale of the spectrometer was calibrated with a sodium nitroprusside standard absorber. Isomer shifts are reported relative to metallic iron at room temperature. Each sample was pressed into a self-supporting wafer (ca. 0.2 g, 1.8 cm diameter) and loaded into a glass cell with thinned Pyrex windows. The cell was equipped with heating coils and was attached to a diffusion-pumped gas handling system. This allowed operation of the cell at temperatures up to 700 K and pressures as low as 10^{-3} Pa. The spectra were fit to several quadrupole doublets with the program MFIT (*13*).

Oxidized samples were prepared by treatment in flowing oxygen for 5 h at 700 K, and reduced samples were prepared by treatment of the oxidized samples with flowing H_2 (150 cm^3/min) for 5 h at 700 K. The O_2 was dried by passage through a 13X molecular sieve trap cooled in dry ice–acetone (200 K), while the H_2 was purified by passage through a Deoxo unit (Fisher Scientific), followed by a 13X molecular sieve trap thermostated at 77 K. The CO used for adsorption experiments was purified by passage through a glass bead trap at 550 K, followed by a 13X molecular sieve trap at 200 K. Samples were exposed to water using a flowing stream of He (150 cm^3/min) which had been bubbled through a water saturator at 298 K (2 kPa partial pressure of H_2O). Oxygen was removed from the He by passage through a tube of hot Cu turnings (550 K). All treatments were carried out *in situ*, and all reported spectra were collected at ambient temperatures.

Catalytic Studies

Catalytic activity studies were carried out in a continuous-flow, single-pass microreactor operating at near-atmospheric total pressure. Fractional conversions were determined by mass spectral analysis of the effluent gas. The mass spectrometer used was a UTI Model 100C-02. It was equipped with a UTI Spectrolink process control computer linked to an IBM-PC. The flow system was interfaced to the mass spectrometer by a two-stage pressure letdown. The first stage dropped the pressure to be-

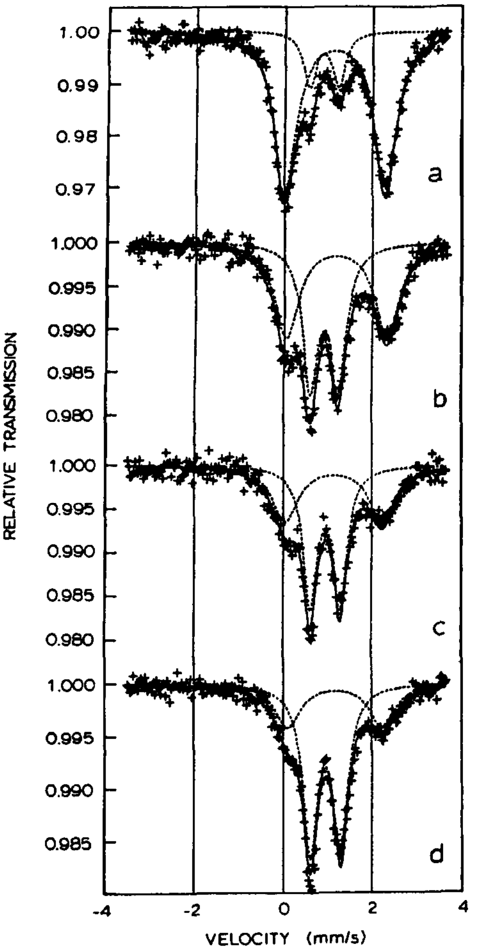

FIG. 1. Mössbauer spectra and computer fits after reduction in H_2. The Si/Al ratio of the samples in the spectra are (a) 2.49, (b) 4.64, (c) 6.17, and (d) 8.88.

tween 3 and 0.3 Pa, while the second stage reduced the pressure to that of the mass spectrometer (10^{-4} Pa range during operation). The catalyst samples (0.037 to 0.3 g) were initially pretreated by heating in He to 570 K and then in O_2 at incrementally higher temperatures until reaching 870 K. Between experiments the catalyst was treated with O_2 at 770 K, either overnight or for 2 h. After the O_2 treatment, the samples were brought to reaction temperature in He. After reaching reaction temperature the samples were exposed to 3.5% N_2O in He carrier gas for 1 to 2 h before measurements were commenced.

Differential reaction rates were determined from the initial slope in the plots of fractional conversion versus the space time $[W/F(N_2O)]$, where W was the weight of catalyst and F was the flow rate of N_2O. Values of F/W ranged from 400 to 9000 cm^3 (STP)/g-min^{-1}. The reaction temperature was 800 K for all samples and the concentration of N_2O was held constant at 3.5 mol%.

Microbalance Studies

Redox chemistry and rates of reduction and oxidation were studied in a Cahn Electrobalance, Model RG-2000, operated in the flow mode. The electronic portion of the balance was continually flushed with dry N_2. The reactant gases (mixed with 75% He) entered the weighing arm, passed across the sample, and exited at the top of the arm. Constant flow rates of the different gases were maintained during the experiments by individual Moore flow controllers with corresponding needle valves. Aliquots of zeolites were dehydrated in flowing dry He from room temperature up to 573 K at a temperature rise of 5 K per minute. At 573 K, 25% dry O_2 was added to the He flow and the temperature program continued to 825 K. The temperature was then held constant overnight. Steady-state weights were taken after a brief flush in pure dry He.

RESULTS

Reduced and Oxidized Samples

Mössbauer spectra of the reduced samples are shown in Fig. 1. The spectrum of the standard Fe–Y (1a) sample exhibits the two characteristic Fe^{2+} doublets observed previously by Delgass *et al.* (*1*). The area of the doublet with the smaller quadrupole splitting accounts for 16% of the total spectral area. This doublet has been denoted as the inner doublet while the doublet with the larger quadrupole splitting and isomer shift is called the outer doublet. The spectra of the silicon-substituted samples (1b–1d) exhibit the same peaks, but in different proportions. They show that the fraction of the total spectral area contributed by the inner doublet increases with the degree of silicon substitution, reaching 67% in the sample with a Si/Al ratio of 8.88. This result indicates that the distribution of ferrous cations in the different ion-exchange sites in the lattice is dependent on the Si/Al ratio.

The spectra of the oxidized samples are shown in Fig. 2. The spectrum of the standard Fe–Y sample (2a) is essentially identical to that reported previously by Garten *et al.* (*2*). The silicon-substituted samples (2b–2d) show similar spectra, but with extra peaks appearing at higher velocity. In the spectrum of the sample with a Si/Al ratio of 8.88, it is clear that the extra peaks are due to a doublet with an isomer shift (IS) characteristic of Fe^{2+}, having a small quadrupole splitting (QS). Indeed, the parameters of this doublet are identical to those of the inner doublet of the reduced samples. This result indicates that a fraction of the ferrous cations in the silicon-substituted Fe–Y remains unoxidized after treatment with O_2 at 700 K for 5 h. These data show that the higher Si/Al ratio Fe zeolites are more difficult to oxidize than conventional Fe–Y, which is readily oxidized under these conditions, and the former samples may require more time or higher temperature as will be discussed below.

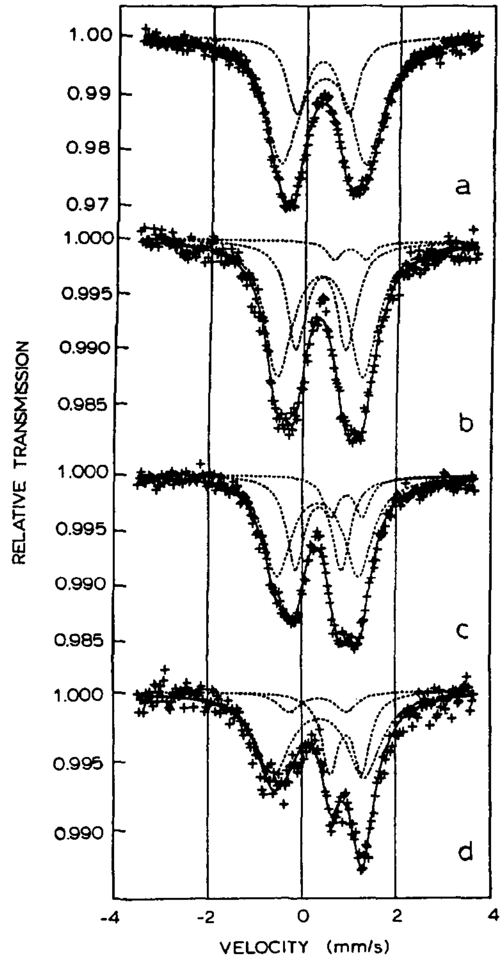

FIG. 2. Mössbauer spectra and computer fits after O_2 oxidation. The Si/Al ratio of the samples in the spectra are (a) 2.49, (b) 4.64, (c) 6.17, and (d) 8.88.

To test whether a fraction of the iron cations in the silicon-substituted Fe–Y is difficult to oxidize, oxygen uptakes were measured during oxidation of the samples with Si/Al ratios of 2.49 and 8.88. This was done using a standard volumetric adsorption apparatus. When standard Fe–Y was first reduced in H_2 and then equilibrated with 28 kPa of O_2 at 700 K, the oxygen uptake corresponded to an O/Fe ratio of 0.51, in agreement with previous work. In contrast, when the sample with a Si/Al ratio of 8.88 was treated in a similar manner, the oxygen uptake corresponded to an O/Fe ratio of 0.39. Additionally, flow microbalance experiments were carried out at 700 K with 10% O_2 in He to determine if the oxidation stopped at this point. The oxidation was defined to be complete when the weight remained constant for 1 h. With the standard Fe–Y sample, the oxidation was complete after about 0.75 h and the O/Fe ratio was 0.52. In contrast, under the same conditions a sample having a Si/Al ratio of 8.88 displayed an O/Fe ratio of 0.35 after 1.5 h. However, after about 20 h the weight became constant and the O/Fe ratio was 0.45. Thus, the difficulty in using O_2 to oxidize all ferrous cations in the silicon-substituted samples is demonstrated by Mössbauer

TABLE 2

Mössbauer Spectroscopy Fitting Parameters

Si/Al ratio	After Reduction Fe^{2+} outer doublet			Fe^{2+} inner doublet		
	IS (mm/s)	QS (mm/s)	Area (mm/s %)	IS (mm/s)	QS (mm/s)	Area (mm/s %)
2.49	1.15	2.28	5.76	0.89	0.66	1.12
4.64	1.19	2.28	2.24	0.92	0.63	2.16
6.17	1.14	2.19	1.42	0.95	0.68	1.86
8.88	1.17	2.14	0.90	0.95	0.68	1.96

Si/Al ratio	Fe^{3+} outer doublet			After Oxidation Fe^{3+} inner doublet			Fe^{2+} inner doublet		
	IS (mm/s)	QS (mm/s)	Area (mm/s %)	IS (mm/s)	QS (mm/s)	Area (mm/s %)	IS (mm/s)	QS (mm/s)	Area (mm/s %)
2.49	0.38	1.81	5.48	0.33	1.11	2.02	—	—	—
4.64	0.36	1.82	2.70	0.36	1.08	1.48	0.95	0.68	0.18
6.17	0.34	1.74	1.94	0.35	0.98	1.14	0.95	0.68	0.44
8.88	0.36	1.96	1.62	0.34	1.22	0.26	0.95	0.68	0.74

spectroscopy, volumetric measurements, and gravimetric measurements, and this oxidation process appears to be kinetically limited.

The Mössbauer spectroscopy parameters and spectral areas obtained by computer fitting the spectra of the reduced and oxidized samples are summarized in Table 2. The spectra of the reduced samples were fit with two Fe^{2+} doublets. The fits indicate that the parameters of the inner doublet are independent of the degree of silicon substitution, while the quadrupole splitting of the outer doublet decreases slightly with silicon substitution. The spectrum of the oxidized, standard Fe–Y was fit with two overlapping Fe^{3+} doublets. This is in contrast to Garten *et al.* (*2*), who fit the same spectrum with one doublet; however, the widths of the peaks, their asymmetry, and the fact that the spectra of the reduced samples show two doublets are evidence that a two-doublet fit is appropriate. The spectra of the oxidized, silicon-substituted samples were fit with three doublets. Two of these were the same Fe^{3+} doublets used to fit the spectrum of the oxidized standard Fe–Y sample, while the third was the inner doublet present in the spectra of the reduced samples. In these fits, the positions of the Fe^{2+} inner doublet peaks were constrained to be constant. The fits of the oxidized samples show that the fraction of the total spectral area contributed by the Fe^{3+} doublet with the smaller quadrupole splitting increases with the degree of silicon substitution in the samples with Si/Al ratios of 2.49, 4.64, and 6.17, but then decreases for the sample with a Si/Al ratio of 8.88. Some variation was observed in the Mössbauer spectroscopy parameters of the Fe^{3+} doublets, but since no trend was observed, these variations are believed to be artifacts of computer simulation.

Adsorption Studies

Figure 3 shows spectra of the reduced, silicon-substituted samples after exposure to 100 kPa of CO. While Delgass *et al.* (*1*) reported little change in the spectrum of the

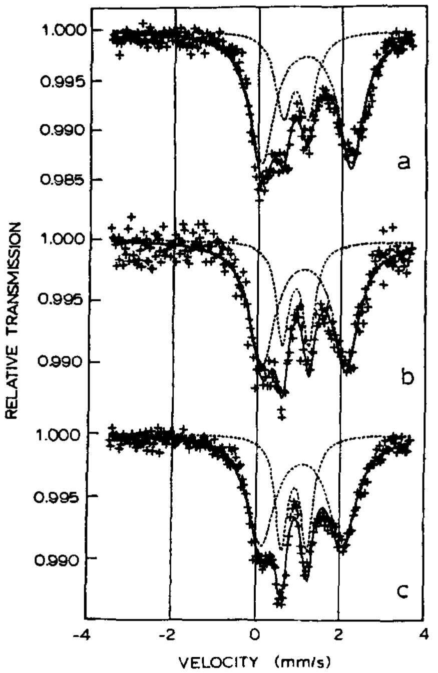

FIG. 3. Mössbauer spectra and computer fits after CO exposure. The Si/Al ratio of the samples in the spectra are (a) 4.64, (b) 6.17,and (c) 8.88.

reduced, standard Fe–Y after exposure to CO, substantial changes occur in the spectra of the silicon-substituted Fe–Y. The spectral area of the inner doublet decreases, and a new doublet appears with parameters that are nearly identical to those of the Fe^{2+} outer doublet. This doublet will be denoted as the Fe–CO product doublet.

The effect of exposure to H_2O after reduction of the sample having a Si/Al ratio of 8.88 is shown in Fig. 4. When the sample was completely hydrated, no spectrum resulted, indicating that the cations were solvated and did not have a sufficiently high recoil-free fraction to exhibit a Mössbauer spectrum at room temperature. The spectrum shown in Fig. 4a was collected after evacuating the completely hydrated sample at 400 K for 1 h, while the spectrum in Fig. 4b was collected after evacuation at 500 K for 1 h. These spectra show that water converts the Fe^{2+} inner doublet of the silicon-substituted Fe–Y to a Fe–H_2O doublet that has parameters similar to the Fe^{2+} outer doublet.

The spectra collected after exposure of the silicon-substituted samples to CO and H_2O were fit with two overlapping doublets. One was the Fe^{2+} inner doublet, while the other was the appropriate product doublet. Because of the similarity of their parameters, no attempt was made to resolve the Fe^{2+} outer doublet from the product doublets. The parameters obtained from these fits are summarized in Table 3.

Catalytic Activity Studies

Figure 5 shows the fractional conversion at 800 K versus space time for the N_2O decomposition reaction over Fe–Y samples with Si/Al ratios ranging from 2.49 to 8.88. The data show that as the Si/Al ratio increases the conversion increases at each flow rate. The reaction rates were determined from the initial slopes of these curves. These data together with the turnover frequencies (based on total iron content) and the activation energies are shown in Table 4. From the data it can be seen that

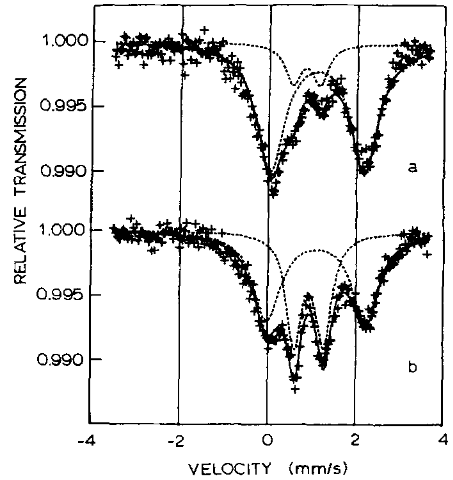

FIG. 4. Mössbauer spectra and computer fits after exposure to water. The Si/Al ratio of the samples was 8.88. Spectrum a was collected after a 1-h evacuation at 400 K, while spectrum b was obtained after a 1-h evacuation at 500 K.

TABLE 3

Mössbauer Spectroscopy Fitting Parameters

Si/Al ratio	After Exposure to CO Fe–CO product doublet			Fe^{2+} inner doublet		
	IS (mm/s)	QS (mm/s)	Area (mm/s %)	IS (mm/s)	QS (mm/s)	Area (mm/s %)
4.64	1.14	2.13	2.86	0.88	0.59	1.14
6.17	1.12	2.00	2.26	0.91	0.63	0.90
8.88	1.10	1.93	2.10	0.92	0.61	0.94

Evacuation temperature (K)	After Exposure of 8.88 Si/Al Ratio Sample to H_2O Fe–H_2O product doublet			Fe^{2+} inner doublet		
	IS (mm/s)	QS (mm/s)	Area (mm/s %)	IS (mm/s)	QS (mm/s)	Area (mm/s %)
400	1.10	2.13	2.32	0.83	0.61	0.40
500	1.10	2.22	1.62	0.94	0.66	1.12

the rate of N_2O decomposition per gram of sample increases by a factor of 40 in going from Si/Al of 2.49 to 8.88, despite a twofold decrease in the number of iron atoms per unit cell (Table 1). Accordingly, the activity per iron atom increases by nearly two orders of magnitude. The activation energy for the reaction decreased by about 50 kJ/mol over this range of Si/Al ratios, implying that the Fe cations were moving into sites that have more favorable energetics for N_2O decomposition.

The variations of the specific reaction rate and the turnover frequency (TOF) with the number of aluminum atoms per unit cell are shown in Fig. 6. Qualitatively, both curves are S-shaped. The implication from these data is that there is a balance between the effectiveness of the iron for carrying out N_2O decomposition and the amount of iron present within the structure. The point at which the decreasing iron content starts to

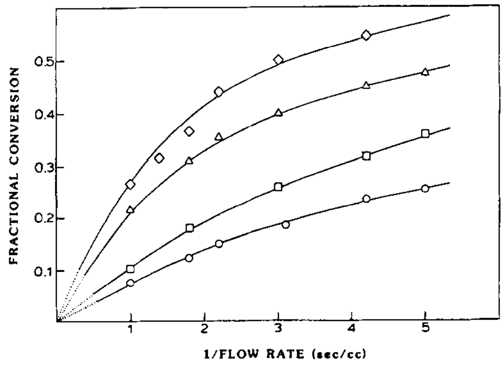

FIG. 5. Variation in fractional conversion as a function of reciprocal space velocity ($1/F$) for Fe–Y (2.49) (○), Fe–Y (4.64) (□), Fe–Y (6.17) (△), and Fe–Y (8.88) (◇). Using a 0.2-g constant weight basis.

TABLE 4

Catalytic Activities of Fe–Y-Zeolites for the Decomposition of N_2O

Si/Al ratio[a]	Al per unit cell[a]	TOF[b] (molec./Fe-sec^{-1})	E_{act}[c] (KJ/mol)	Rate[d] (initial)
2.49(2.24)	55.0(60.0)	0.0012	175	0.77
4.64(3.59)	34.1(42.3)	0.032	137	14.9
6.17(5.04)	26.8(32.1)	0.12	125	35.9
8.88(6.78)	19.4(25.0)	0.14	117	41.2

[a] Based on chemical analysis. Numbers in parentheses are based on NMR of unexchanged zeolite.

[b] Turnover frequency at 800 K as molecules/Fe per second.

[c] Activation energies were determined from these rate data and data (not shown) at 723 and 773 K.

[d] Rate units are molecules/g sec^{-1} × 10^{18}.

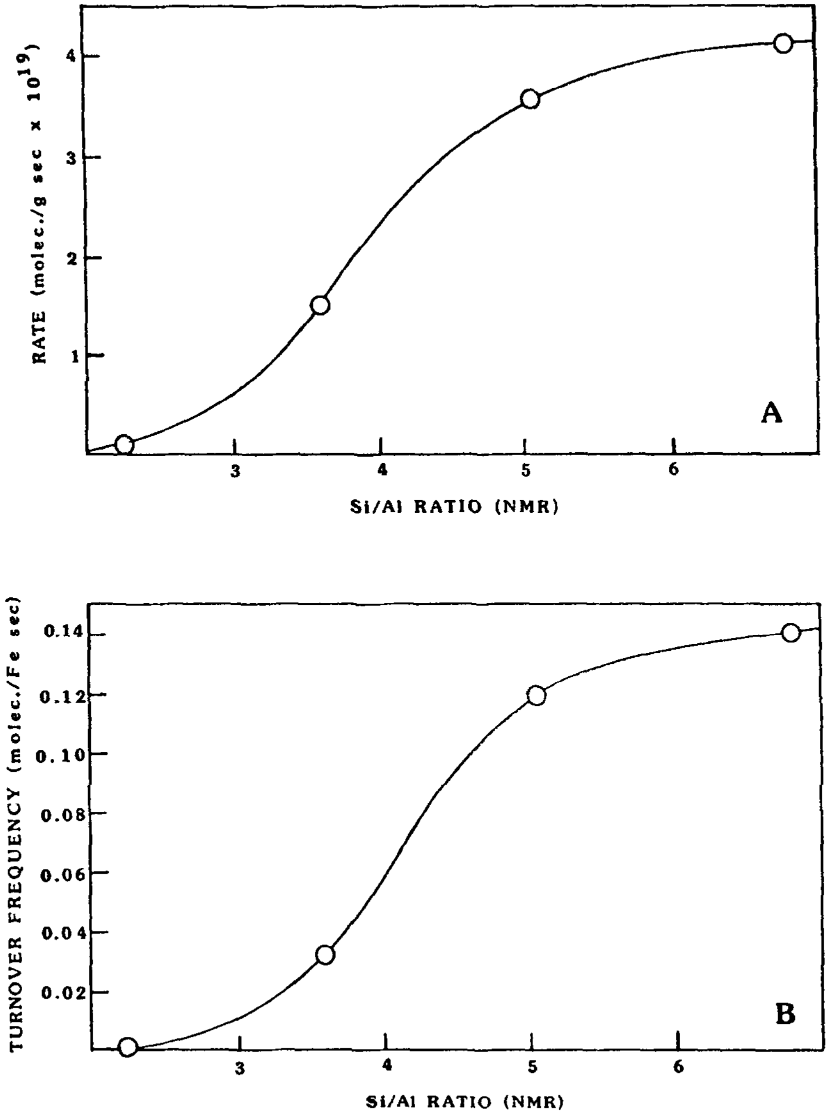

FIG. 6. (A) The variation of the initial reaction rate of the different Fe–Y catalysis with silicon-to-aluminum ratio (NMR). (B) The variation in the turnover frequency of the different Fe–Y catalysts with silicon-to-aluminum ratio (NMR).

become the limiting factor appears to be near a Si/Al ratio of 8. This could be better resolved by samples with higher Si/Al ratios, but attempts to prepare them by this method yielded samples with substantial crystal degradation.

Figure 7 shows the variation in the logarithm of both the specific reaction rate (7A) and the turnover frequency (7B) with activation energy. In both cases there is a nearly linear relationship. This suggests that the variation in the measured reaction rates may be related primarily to the activation energy, although there is also a small contribution from variations in the preexponential factor.

Oxidation/Reduction Studies

Whereas a fraction of the iron cations in silicon-substituted Fe–Y was found to be

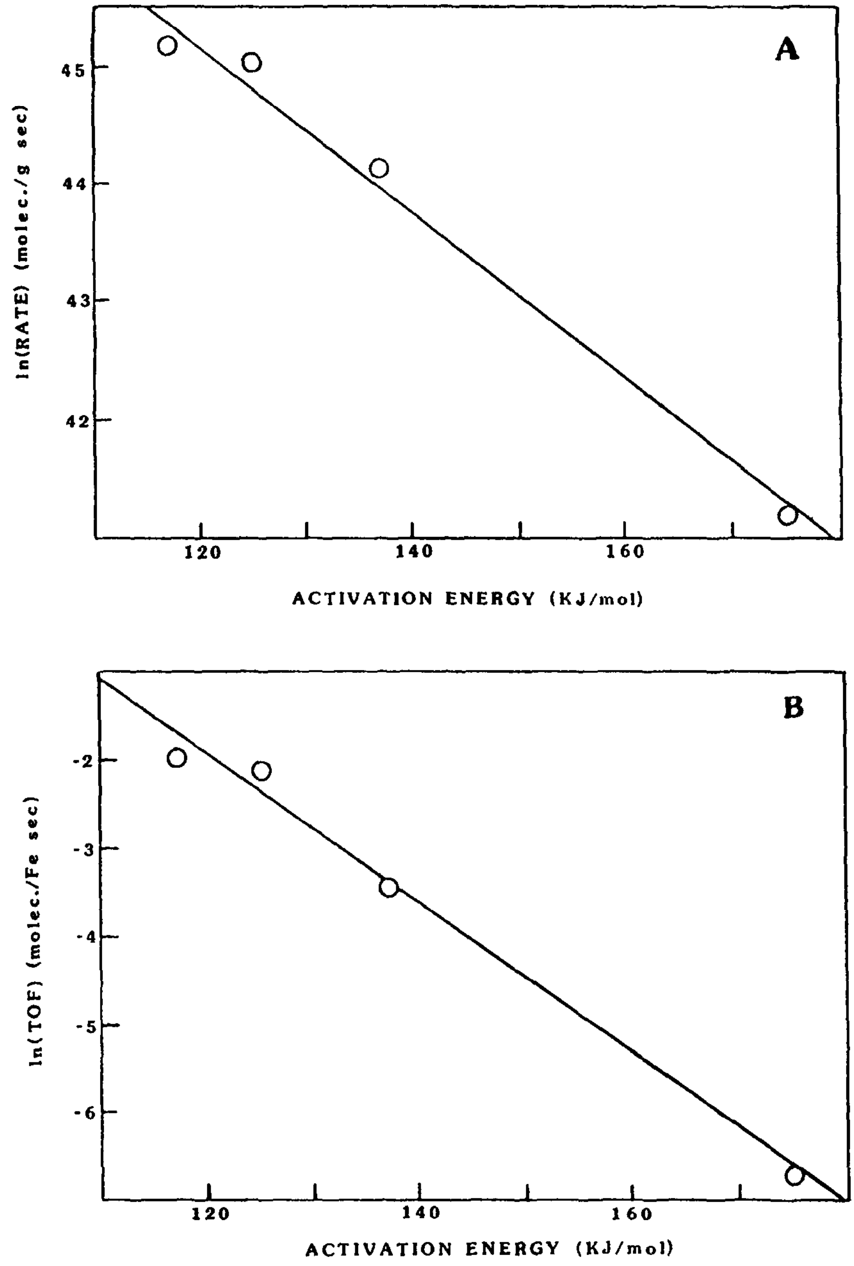

FIG. 7. (A) The variation of the ln(rate) versus the activation energy. (B) The variation of the ln(TOF) with activation energy. The data are from Table 4.

difficult to oxidize with O_2, the same effect was not observed when N_2O was used as the oxidizing agent. When the sample having a Si/Al ratio of 8.88 was treated with N_2O at 700 K for 5 h, the resulting Mössbauer spectrum showed that all the iron had been oxidized to Fe^{3+}. In agreement with this, flow microbalance experiments showed that the rate of oxidation was faster for this sample when N_2O was the oxidizing agent compared to O_2. These results, along with results obtained for standard Fe–Y,

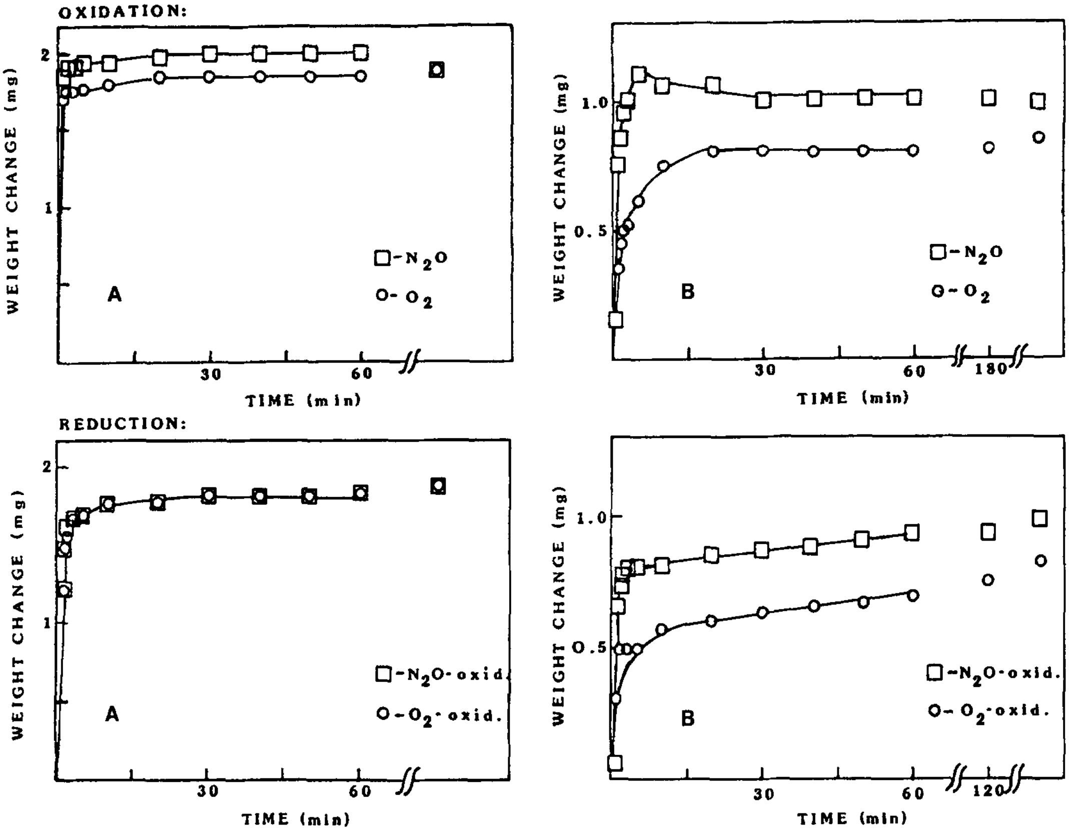

FIG. 8. The variation in weight with time for Fe-Y with oxidation in O_2 and N_2O ((A) Fe-Y (2.49), (B) Fe-Y (8.88)), and the variation of weight with time of the samples oxidized with both oxidants upon H_2 reduction. The last points, at the end of the plots, represent the weights on a constant basis in He to correct for buoyancy differences.

are shown in Fig. 8. Standard Fe-Y was completely oxidized by either O_2 or N_2O in 30 to 40 min, with some indication that oxidation might be slightly faster in N_2O. Reduction by H_2 was complete in about 45–50 min. With the silicon-substituted sample, the times required for both reduction and oxidation were significantly longer, with reduction being somewhat slower than oxidation. The rate of oxidation by N_2O was faster than oxidation by O_2. The rate of reduction of the catalyst by H_2 was faster when it had been oxidized by N_2O than when oxidized by O_2.

The oxygen-carrying capacities during oxidation/reduction cycles of Fe-Y samples having Si/Al ratios of 2.49 and 8.88 were studied gravimetrically using H_2 as the reducing agent and either O_2 or N_2O as the oxidizing agent. The data, shown in Fig. 9, demonstrate the reversibility of the redox cycles for both the H_2/O_2 and H_2/N_2O couples. As previously reported, standard Fe-Y (Si/Al = 2.49) undergoes a reversible redox cycle with both couples, corresponding to an O/Fe ratio of 0.5. With the silicon-substituted sample (Si/Al = 8.88), the redox cycles are reversible for both couples, but the extent of the redox reactions are different. With N_2O, an O/Fe ratio of 0.5 is measured, while with O_2 and O/Fe ratio is 0.45. This result also agrees with the Mössbauer spectroscopy results.

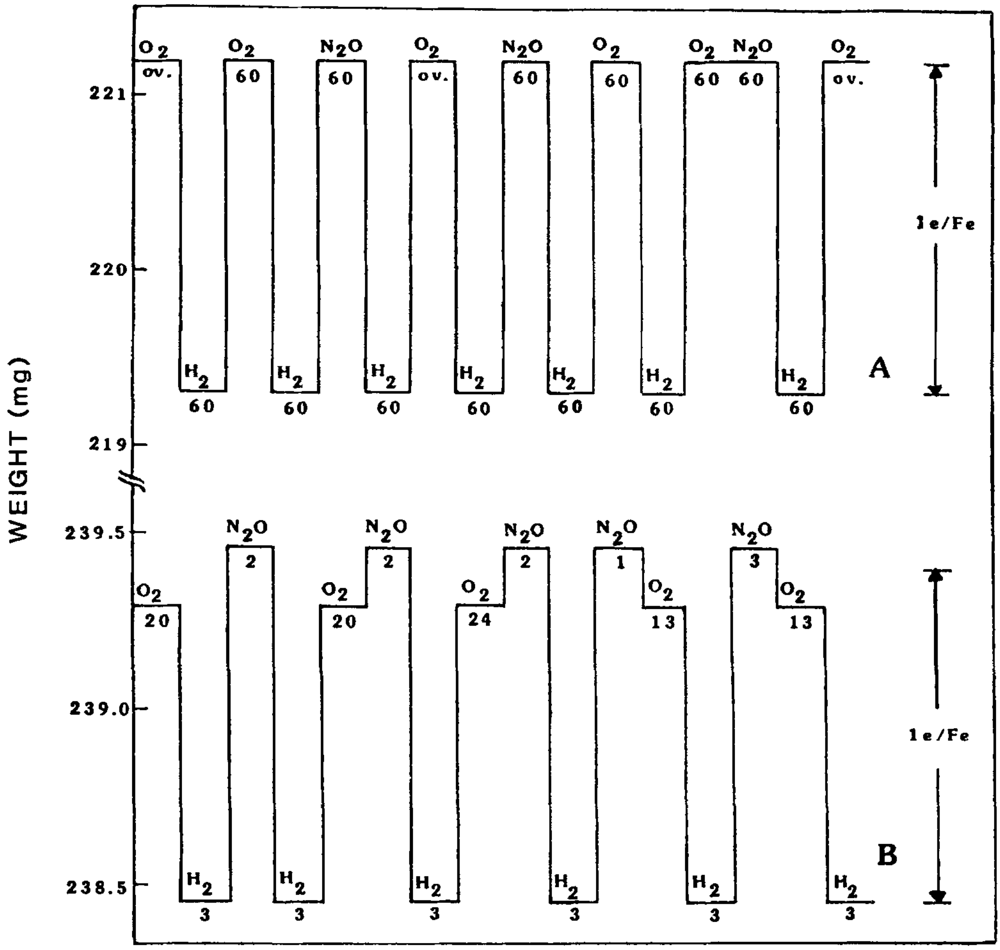

FIG. 9. The lined out weight of Fe–Y under H_2 reduction and under both O_2 and N_2O oxidation for several cycles. (A) The conventional Fe–Y (Si/Al = 2.49). Length of pretreatments is given in minutes. OV = overnight. (B) The silicon-substituted Fe–Y (Si/Al = 8.88). Length of pretreatments is given in hours.

DISCUSSION

The outer doublet in reduced Fe–Y has been assigned to ferrous cations at site I and the inner doublet to cations at sites I′, II′, and/or II (*1*). Therefore, the above results indicate that a large fraction of the ferrous cations is located at sites I′, II′, and/or II in silicon-substituted Fe–Y. Since cations at these sites are more accessible to reactant molecules and have lower coordination in the zeolite lattice than cations at site I, silicon-substituted Fe–Y can be expected to have a higher turnover frequency for reactions catalyzed by iron cations than conventional Fe–Y, in which most iron cations are in site I. In agreement with this, the catalytic activity studies for the decomposition of N_2O indicate that the activity of the samples investigated in this study increased with increased degree of silicon substitution. The decrease in the activation energy can be explained by the lower coordination number of cations at these sites, while the increase in the preexponential factors can be explained by their greater accessibility.

A similar argument could explain why iron-exchanged mordenite, despite its smaller pore apertures, has been found to be more active per iron cation than Fe–Y for the oxidation of CO with NO, O_2, and N_2O (*14*), and more active for the decomposition of N_2O (*11*). The iron cations in iron-exchanged mordenite are believed to be located in highly accessible sites in the main channels of the structure (*3*).

The finding that a large fraction of iron cations is present in sites I′, II′, and/or II in silicon-substituted Fe–Y can be explained by assuming that site preference is influenced by the number of aluminum atoms that are adjacent to the exchangeable cation sites. To test this, we performed a Monte Carlo simulation in which aluminum atoms were randomly incorporated into isolated hexagonal prisms obeying Lowenstein's rule. The results of the simulation showed that at a Si/Al ratio of 2.49, 99% of the hexagonal prisms contain two or more aluminum atoms. At a Si/Al ratio of 8.88, this number is only 29%. If site I, in the middle of the hexagonal prism, is a favorable site for polyvalent cations (like Fe) only when the hexagonal prism contains more than one aluminum atom, then sites of lower coordination such as sites I′, II′, and/or II may become more favorable at higher Si/Al ratios.

The results obtained for the oxidized samples show that a fraction of the iron cations in silicon-substituted Fe–Y was not readily oxidized to Fe^{3+} by treatment with O_2 at 700 K for 5 h, yet these ferrous cations were oxidized by N_2O under these same conditions. Since the samples with Si/Al ratios of 6.17 and 8.88 gave similar spectra in the reduced state, but different spectra when oxidized by O_2, this phenomenon is not believed to be related in a simple way to the cation location. Rather, the appearance of Fe^{2+} peaks in the spectra of the O_2-oxidized samples may result from the larger separation between aluminum atoms in silicon-substituted Fe–Y. Two models have been proposed to describe the oxygen-carrying capacity of Fe–Y. In one model it was suggested that Fe–O–Fe bridges formed upon oxidation (*2*), whereas in a later model it was proposed that a single Fe^{3+} cation in site III′ could hold an oxygen atom, with one electron being supplied by a second Fe cation (*15*). Regardless of which model is adopted, the observation that one oxygen atom is adsorbed for every two iron cations in conventional Fe–Y suggests that the oxidation process may require pairs of iron cations within close proximity. A possible location for a pair of iron cations would be in sites I′ and II′, inside the truncated octahedra. When O_2 is used as the oxidizing agent, two pairs of iron cations must be involved in the oxidation process. If two pairs of Fe atoms are present at sites I′ and II′ in a truncated octahedron (a maximum of three pairs can be present within a truncated octahedron of X-zeolite having a Si/Al ratio of 1.0 (*16*)), then they are in close enough proximity for both oxygen atoms to be held there. However, as the silicon-to-aluminum ratio increases, the number of aluminum atoms per sodalite unit decreases, thereby decreasing the capability to adsorb dioxygen. For the sample with a Si/Al ratio of 8.88, the average sodalite cage contains approximately three aluminum atoms.

Thus, a fraction of the aluminum atoms may be sufficiently isolated that pairs of iron cations cannot readily interact with oxygen. When N_2O is used as the oxidizing agent, only one pair of iron cations is required for the oxidation process, explaining the faster rate of oxidation observed. A remaining question is how do isolated iron pairs undergo oxidation with molecular oxygen; i.e., what happens with the second oxygen atom? This may be related to the work of Leglise *et al.* (*11*) where it was found that the second oxygen atom in the formation of O_2 from the decomposition of N_2O came from the lattice, defining a "sphere of influence," the size of which increased with increasing temperature. Thus, one can envision the second oxygen atom diffusing through the lattice, as described for bismuth–molybdate catalysts (*17*), but over a smaller, temperature-dependent distance.

The relationship between the location of the iron cations and the catalytic activity of the samples poses some interesting questions. It is apparent from the results that the samples with a larger fraction of the iron in sites I′, II′, and/or II are more active for N_2O decomposition. The rate data, for example, can be correlated with the amount of iron in sites I′, II′, and/or II that is not oxidized by treatment with O_2 at 700 K for 5 h. If these are, in fact, the most active sites for N_2O decomposition, then the location of these iron cations needs to be determined in terms of sites I′, II′, II, or a special configuration of one or more of these exchange sites.

The fact that no significant changes in the Mössbauer spectra of standard Fe–Y were observed after exposure to various adsorbates led Dickson and Rees (*4*) to focus on catalytically less active zeolite A for Mössbauer spectroscopy studies of the interactions between adsorbate molecules and iron cations. The results of the present study show that such interactions can also be studied in Fe–Y zeolite, if the distribution of iron cations among the various ion-exchange sites is altered to favor iron in accessible sites. When CO or H_2O were adsorbed in the silicon-substituted Fe–Y zeolite, Mössbauer spectroscopy doublets were observed with parameters that were similar to the outer doublet in the reduced Fe–Y samples. This is clear evidence that the adsorption of CO and H_2O changes the symmetry of the ferrous cations similar to the behavior of ferrous cations supported on silica (*18, 19*). After CO was adsorbed, a significant spectral contribution from the inner doublet remained, indicating that some of the iron, presumably in sites I′ and/or II′, is not accessible to CO at room temperature. Exposure of the samples to H_2O led to a more substantial decrease in the spectral area of the inner doublet, suggesting that water is able to reach iron cations at more sites than CO, e.g., iron at sites I′ and/or II′ may be accessible to H_2O but not CO (*20, 21*). Water may reach these cations either by migrating into the sodalite unit or by bonding to the cations after they have migrated to the supercage through their own dynamic motion.

The observation that the doublets produced by the adsorption of these gases in Y-zeolite overlap the doublet due to ferrous cations at site I explains why the former doublets had been difficult to resolve in the past. It also explains why, as pointed out by Yulin *et al.* (*22*), partially hydrated, reduced Fe–Y does not exhibit the inner doublet at room temperature or at 77 K. If the absence of the inner doublet in the room temperature spectrum were due to the solvation of cations by water, then this doublet should be observable at lower temperatures as the water freezes in the lattice. The inner doublet does not appear at liquid-nitrogen temperature because the extra coordination provided by H_2O molecules causes the Fe^{2+} cations to exhibit peaks that overlap with the outer doublet.

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