On the Stability of Fe-Y under Redox Conditions

The present note relates to the question of the thermal stability of the Fe-Y zeolite under redox conditions. Pearce et al. (1) used in situ X-ray diffraction to reinvestigate the location and coordination environment of the Fe cations after a variety of pretreatment procedures. Among other things, these workers concluded that the bridged extra-lattice oxygen held between two Fe cations in the oxidized form (2–4) does not exist and that the structure breaks down after a couple of redox cycles with H_2 and O_2. The latter conclusion has found support in the recent work of Iwamoto et al. (2). On the other hand, many other experimental data (3–10) suggest that the Y-zeolite lattice is quite stable under similar experimental conditions. The present experiments were made to assess this question and to isolate the cause of the lattice breakdown.

The activity of the Fe-Y in the oxidation of CO with O_2 or NO has been studied by several authors (8, 10–13) and recently Fu et al. (9) showed that the fully oxidized form of Fe-Y acted as a catalyst for N_2O decomposition. The catalytic activity was stable in these experiments. Garten et al. (5) reported that the Fe-Y could be oxidized and reduced reversibly with O_2 and H_2 at 400°C between the valence state Fe^{2+} and Fe^{3+}. The zeolite acted as an oxygen carrier with a capacity O/Fe = 0.5. By measurement of the capillary condensation of N_2 they showed that the crystallinity of the sample was maintained throughout the oxidation and reduction cycle. In the picture developed from their data, it was supposed that the oxygen formed a bridge between two Fe^{3+} ions centered on the six rings inside the cubo–octahedra. Fu et al. (8), using both gravimetric and volumetric tech-

niques, also found Fe-Y to be reversible (stable) over many oxidation–reduction cycles at 500°C. It was confirmed that the oxygen carrying capacity was about 0.5 O/Fe or 1e/Fe and that temperatures as high as 700°C could be used without seriously damaging the oxygen-carrying capacity. Moreover, NO and N_2O could be used as oxidizing agents instead of O_2 and CO worked as well as H_2 as a reducing agent. The results of Pearce et al. appeared to be in contradiction with these data. For example, if the zeolite decomposed, the valence change of the Fe might be expected to increase (above 1) and the strict reproducibility of weights in flow microbalance experiments would be lost. According to Pearce et al. X-ray data showed framework decomposition after one redox cycle at 400°C and nearly total lattice disruption after an additional cycle. We were, therefore, motivated to test our preparations carefully for lattice breakdown. We do not question their other finding, viz., that the carried oxygen atom is not held as a bridge between two iron cations inside the cubooctahedron. In fact, we have advanced an alternative explanation (7) which locates the extra-lattice oxygen in the supercages.

Pore filling factors were determined from the amount of N_2 adsorbed at $P/P_0 = 0.5$ at liquid nitrogen temperatures. X-Ray diffraction was also employed to assay the crystallinity of the zeolites. Our equipment did not, however, permit in situ studies as did that used by Pearce et al. Three different Fe-Y zeolites were investigated. The Fe-Y (45%) was that used by Fu et al. (8, 9) and two new samples were prepared with special care being taken in the control of the variables. The starting material was pure crystalline Linde Y zeolite (SK-40,

261

Sample	Anhydrous cell composition	H^+ required to balance CEC	Loading No. of TMI/g^a
Fe-Y (14%)[b]	$Na_{50}Fe_4(AlO_2)_{58}(SiO_2)_{134}$	—	2.00×10^{20}
Fe-Y (21%)	$Na_{43}Fe_6(AlO_2)_{58}(SiO_2)_{134}$	3	3.01×10^{20}
Fe-Y (45%)	$Na_{19}Fe_{13}(AlO_2)_{58}(SiO_2)_{134}$	13	6.13×10^{20}
Na-Y	$Na_{57}(AlO_2)_{57}(SiO_2)_{134}$	—	—

[a] TMI = transition metal ions.

[b] In parentheses are the percentages of the base exchange capacity satisfied by Fe^{2+}.

Lot 1280-133). It was first washed with excess NaAc–HAc buffer solution (pH 5). The exchange procedures followed that described by Delgass *et al.* (*3*). The ratio zeolite/solution was 10 g/liter. $FeSO_4 \cdot 7H_2O$ (analytical reagent grade) was used; the final solution concentration was 0.04 M. The pH was maintained between 3.8 (initial) and

3.85 (final) with H_2SO_4. The exchange was conducted in a prepurified N_2-washed glove bag overnight at room temperature for Fe-Y (14%) and at 50°C for Fe-Y (21%). The exchanged zeolite was first rinsed with acidified, deoxygenated H_2O and then with redistilled H_2O. It was later dried with ultra-high purity N_2 at room temperature. Table 1 shows the unit cell compositions of the different samples based on chemical analyses made by Galbraith Laboratories.

The N_2 adsorption isotherms were determined with a conventional BET system. To this a circulation loop was added for different pretreatments. The zeolite (0.5–1 g) was weighed into a quartz reactor which was attached to the system and evacuated at room temperature for 1 to 2 h to a vacuum of 10^{-6} Torr. The temperature was then raised to 400°C over a period of 9 h with 3 h at 100°C. The sample was then
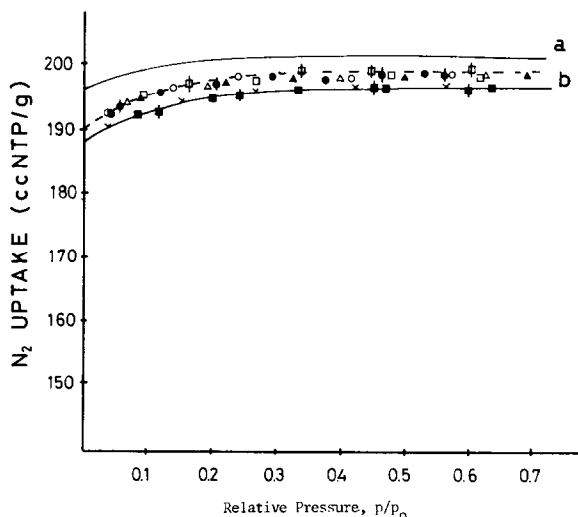

FIG. 1. Nitrogen adsorption isotherms at −196°C on Fe-Y (21%) after the following treatments: (○), fresh sample; (●), 1 h in flowing dry O_2 at 400°C; (◆), 1 h in flowing dry oxygen at 500°C; (△), 1 h in flowing dry oxygen at 400°C followed by 1 h in circulating H_2 at 400°C; (□), four H_2/O_2 redox cycles (1 h each gas) at 400°C; (⊡), four H_2/O_2 redox cycles (1 h each gas) at 500°C; (■), 1 h in circulating H_2 at 400°C, evacuation at the same temperature and then contacted 1 h with H_2O vapor followed by 1 h in a flow of dry oxygen; (▲), 1 h in circulating H_2, 1 h in H_2O vapor at room temperature, evacuation for 1 h at the same temperature; (X), 1 h in flowing O_2 at 400°C, 1 h in H_2O vapor at room temperature; (⬢), 1 h in flowing dry O_2 at 400°C, 1 h in H_2O vapor at room temperature, 1 h evacuation at the same temperature, 4 H_2/O_2 redox cycles (1 h each gas) at 400°C. Note: In all cases standard pretreatment preceded nitrogen adsorption and a new aliquot of zeolite was used in each experiment. Curve a is for Na-Y and curve b represents the lower boundary achieved in all these measurements.

TABLE 2

N_2 Adsorption after Various Treatments

Sample	Treatment	Pore filling factor[a] $(cm^3(NTP)/g)$	Symbol
Na-Y	Standard	202	
Fe-Y (21%)	Standard	198	○[b]
Fe-Y (21%)	1 h O_2 at 400°C, standard	199	●[b]
	1 h O_2 at 500°C, standard	196	◆[b]
Fe-Y (21%)	1 h O_2, 1 h H_2 at 400°C, standard	198	△[b]
Fe-Y (21%)	4 H_2/O_2 redox cycles at 400°C, standard	197	□[b]
	4 H_2/O_2 redox cycles at 500°C, standard	198	⊡[b]
Fe-Y (21%)	1 h H_2 at 400°C, 1 h in H_2O vapor and 1 h in O_2 at room temperature, standard	192	■[b]
	1 h in H_2 at 400°C, 1 h in H_2O vapor 1 h in O_2 at room temperature, standard up to 500°C	190	
Fe-Y (21%)	1 h in H_2 at 400°C, 1 h in H_2O vapor at room temperature, standard	198	▲[b]
Fe-Y (21%)	1 h in O_2 at 400°C, 1 h in H_2O vapor at room temperature, standard	191	X[b]
Fe-Y (21%)	1 h in O_2 at 400°C, 1 h in H_2O vapor at room temperature, 1 h evacuation at the same temperature, 4 H_2/O_2 redox cycles at 400°C, standard	192	▮[b]
Fe-Y (21%)	1 h in H_2O vapor, heating in one step up to 500°C with closed reactor	140	⊡[c]
Fe-Y (45%)	Standard	148	□[c]
Fe-Y (45%)	1 H_2/O_2 redox cycle at 400°C, standard	150	○[c]
	3 H_2/O_2 redox cycles at 500°C, standard	146	⊘[c]

[a] N_2 uptake at $P/P_0 = 0.5$.
[b] See Fig. 1.
[c] See Fig. 3.

evacuated at 400°C for 4 to 10 h to a final pressure of 10^{-6} Torr. This was the standard pretreatment.

Diffraction patterns were taken with a General Electric reflection diffractometer (Model XRD-5) using Cu$K\alpha$ radiation. The samples were recorded from $2\theta = 5°$ up to $2\theta = 40°$ at 2°/min at room temperature. The samples examined were first treated in the circulation system described above. In all cases the preparations were examined in their oxidized states. They were exposed briefly to the atmosphere as they were transferred to the diffractometer for measurement.

The cell constant a_0 was determined by applying the Bragg equation to the various lines characteristic of the zeolite structure. The values reported were obtained by the method of Klug and Alexander (*14*) by extrapolating a plot of a_0 versus $(\cos^2 \theta/\sin \theta) + (\cos^2 \theta/\theta)$ to 90°.

The flow microbalance technique determines weight changes of the zeolites when the chemical environment is changed (oxidation to reduction and vice versa); it does not necessarily provide direct evidence that structural change has not occurred. Measurement of adsorption isotherms of N_2 at −195°C should detect such changes, however, via the amounts adsorbed and their shape. These measurements should provide a measure of the crystallinity of the exchanged samples with respect to the Na-Y starting material, since the large internal pore volume of a zeolite is the result of its crystalline structure.

Figure 1 summarizes the results of experiments designed to test the stability of Fe-Y (21%). Isotherms, after various treatments,
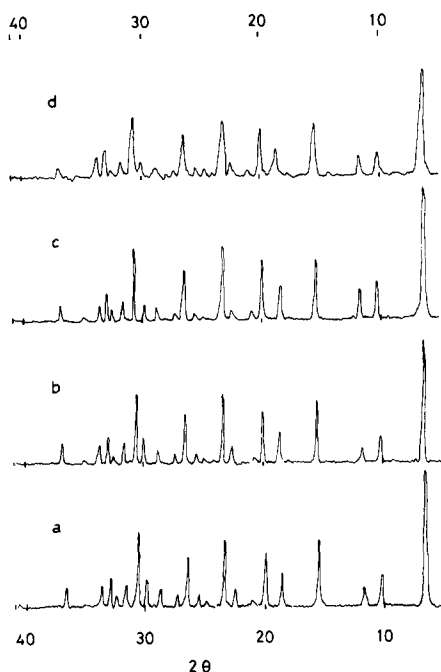
FIG. 2. XRD diffractogram (I vs 2θ); (a) Na-Y parent material; (b) fresh Fe-Y (21%); (c) Fe-Y (21%) after four H_2/O_2 redox cycles (1 h each gas) at 411°C; (d) Fe-Y (45%) after 2 years storage and reactivation.

are compared with that from the parent Na-Y (Curve a). Up to at least 500°C, the zeolite could be put through several redox cycles without undergoing serious damage. As shown in Table 2 (first 12 lines), the pore filling factors decreased by no more than about 5% as a result of any of these treatments.

The stability of the zeolitic structure was confirmed with XRD measurements. The diffractograms obtained for Na-Y and Fe-Y (21%) under carefully controlled conditions are shown in Figs. 2a and b. These were almost the same; no significant change could be observed in the position, intensity or linewidth of the lines. The values of a_0 for the Na-Y and Fe-Y were the same and equaled 24.7 Å. The diffractogram of the Fe-Y after several redox cycles also did not show any significant changes (Fig. 2c). Thus, the redox cycles used in our work (8–10) evidently did not lead to significant disruption of structure.

The effects of the hydration and dehydra-tion (under controlled conditions) on the structure of the Fe-Y were next investigated. After the standard pretreatment, the reduced sample was rehydrated by contacting it with water vapor at room temperature for one hour, after which it was dehydrated through the standard pretreatment. As shown in Fig. 1 and Table 2, the nitrogen isotherm showed a small decrease (<4%). A repetition of the experiments starting with the oxidized form of the Fe-Y (21%) also produced a similar change in the N_2 adsorption isotherm which was again observed when, after hydration, the reduced sample was treated for 1 h in flowing dry O_2 at room temperature. The XRD diffracto-grams, however, did not detect significant changes in the zeolitic lattice in these experiments. Moreover, further redox cycles did not further alter the N_2 adsorption isotherm. These small changes which occurred when H_2O was condensed into the pore system (Curve b of Fig. 1) could be interpreted as follows: the solvation of some of the Fe ions occurred on filling the pore system with H_2O at room temperature, and the mobility of iron in the intra-crystalline fluid made possible the oxidation of the Fe^{2+} to Fe^{3+} in solution; this has been suggested before (3–6, 13). These processes could be represented by:

$$2Fe^{2+} + 3H_2O + \tfrac{1}{2}O_2 \rightarrow 2FeOOH + 4H^+ \tag{1}$$
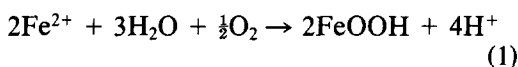
The precipitated oxide would occupy space, thus lowering the filling factor. If this were the case, then the amount of Fe participating in this process would be less than 10% of that present, assuming that the density of FeOOH was 5.24 g/cm^3.[1]

When the structure of FeY (21%) was deliberately destroyed by heating the sample to 900°C for 5 h, the typical reddish color of the Fe_2O_3 was observed. The nitrogen iso-

[1] Irreversible changes in the zeolite lattice would also be expected to result from this process as the base exchange capacity of the cations removed is compensated by protons; dehydroxylation at elevated temperatures would then be expected to follow.
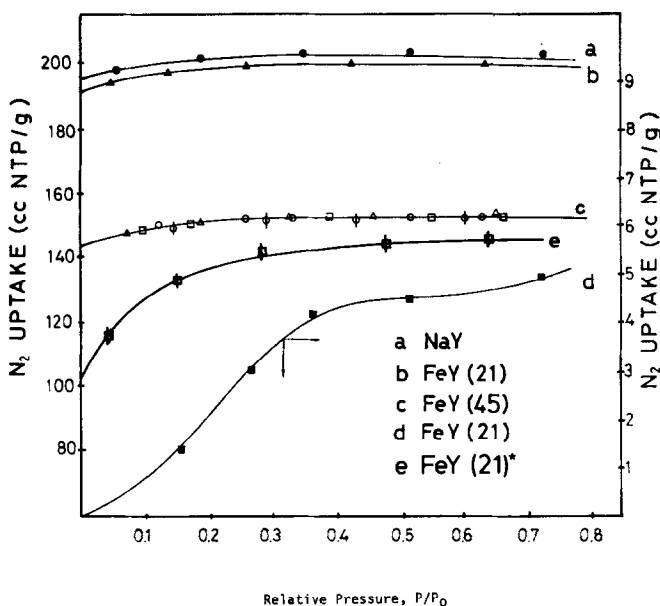
FIG. 3. Nitrogen adsorption on different Fe-Y zeolites. Curves a and b are taken from Fig. 1. They correspond to Na-Y and Fe-Y(21%) after repeated treatments, respectively. (□) Fresh Fe-Y(45%) after 2 years storage in air; (△), Fe-Y(45%) after 1 h in H_2 at 400°C; (○), Fe-Y(45%) after one H_2/O_2 cycle at 400°C; (φ), Fe-Y(45%) after several H_2/O cycles at 500°C; (■), Fe-Y(21%) after 5 h in air at 900°C; (⬚), Fe-Y(21%) after 1 h in H_2O vapor heating in one step up to 400°C in closed reactor. Note: In all cases standard pretreatment up to 400°C preceded nitrogen adsorption.

therm produced is shown in Fig. 3d. Not only was the filling factor decreased significantly from those of Fig. 1 (Curves a and b of Fig. 3), but the shape of the isotherm at low relative pressure was changed indicating a disruption and collapse of the crystalline pore system.

The effect of steam at 400°C on Fe-Y (21%) in the closed reactor was tested after filling the pore system with H_2O at room temperature. After steaming for 1 h, the preparation was evacuated overnight and cooled in vacuum. Its N_2 isotherm is shown as Curve e of Fig. 3. The altered shape and decreased filling factor [from 190 to 140 cm³(NTP)/g] are indicative of a significant change in structure which could also be observed in the XRD diffractogram as line broadening.

To test the importance of excluding air during preparations, a sample of Fe-Y (21%) was exposed to H_2O vapor at room temperature for 1 h; thus, the pore volume was filled with H_2O. Oxygen was then

added and circulated for another hour before the sample was given the standard pretreatment. The filling factor [186 cm³(NTP)/g] was close to those obtained in other experiments where the zeolite had been exposed to H_2.

In another set of experiments a 2-year-old preparation Fe-Y (45%), which had been in contact with air during this time, was tested. Unlike a newly prepared sample (white), its color was a light yellow, suggesting the presence of some iron oxide. The adsorption isotherm obtained after the standard pretreatment is shown in Fig. 3c and the filling factors after several redox cycles are given in Table 2. A decrease of 30% in the uptake of N_2 from the parent Na-Y is evident. Nevertheless, neither the shape of the isotherm differed much from that of the Na-Y nor did the H_2/O_2 redox cycles further change the structure. Moreover, as reported previously (8, 10), the ratio O/Fe determined in redox cycles remained close to 0.5 and the diffractogram

for this sample (Fig. 2d) showed all the characteristics of the zeolitic structure, although the peak intensities were somewhat lower and the peaks broader than in the Na-Y diffractogram. This could be indicative of partial lattice breakdown. It was impossible to attribute the decrease in N_2 adsorption only to the formation of the FeOOH; if that were the case it would be necessary for the sample to have considerably more Fe than was actually present. The evidence suggests that the same hydrothermal breakdown in structure has occurred at room temperature in a couple of years, as at 400°C in 1 h.

In conclusion, contrary to the report of Pearce et al. (1), Fe-Y was found to be structurally stable in successive redox cycles when these were studied under controlled conditions. Fe-exchanged zeolites, however, are sensitive to treatment with O_2 when the pore system contains H_2O. It is remarkable that these materials maintain their redox characteristics without sensible changes in their oxygen-carrying capacity even after a partial disruption of their structure.

ACKNOWLEDGMENTS

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