

Ferric Ion Exchange and Breakdown of Crystalline Structure in Zeolites

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Fe(III) ion exchanged samples of type X and A zeolites were prepared in a modified ion exchange process using an ethereal solution of $\text{Fe}(\text{SCN})_3$. These samples were thoroughly characterised by measurement of % ion exchange, SSA, unit lattice parameter and % crystallinity. The effect of pH, temperature and the extent of exchange during the ion exchange process on the loss of crystallinity of the samples was investigated. Furthermore the drying procedures and vacuum treatments at high temperature were investigated as potential factors in structure breakdown.

Introduction

Fe(III) ion exchanged zeolites were examined for selective oxidation reactions and it was reported by Skalkina and coworkers [1] that these zeolites showed selectivity in oxidative ammonolysis of propylene. Furthermore Fe(III) exchanged 13X type zeolites were shown to be selective in ammoxidation reaction of toluene and of alkyl pyridines [2].

Difficulties in preparing Fe(III) exchanged zeolites without breakdown were also reported by Malashevich and coworkers [3-6] who studied the structure, absorption characteristics and catalytic reactions (e.g. oxidation of propane). The authors used X-ray diffraction data and reported that zeolites with low silica content (type A and X) retain their crystalline structure up to 15-17% substitution of sodium by ferric ions. Morice and Rees [7] reported that short times of exposure of zeolite to $\text{Fe}(\text{NO}_3)_3$ solution enabled exchange without decomposition.

Delgass [8] reported that Fe(III) ion exchanged zeolites can be prepared without breakdown by exchanging them with FeSO_4 under a N_2 stream and further oxidizing them.

In general it was reported that temperature and ion-concentration influences the % of exchange [9, 10], and the amount of breakdown in the samples is influenced by both the pH and the ion concentration of the solutions used for the ion-exchange [11].

Experimental

Preparation of Ferric Ion Exchanged Zeolites

Method

FeCl_3 was treated with an excess of KSCN and the resulting complex was extracted by ether. The ethereal solution was found to contain only the $\text{Fe}(\text{SCN})_3$, in particular manganese salts (impurities) were not present. This purified solution of ferric thiocyanate in ether was used for ion exchange.

The ethereal ferric salt was added dropwise to the aqueous slurry (in some cases this was buffered) on top of which a thin layer of ether was present. The exchanging system was stirred vigorously in order to ensure complete distribution of the two phases, so that the resulting sample was homogeneous. The ferric thiocyanate partitioned between the two phases and when the ferric ions entered the aqueous phase they exchanged into the zeolite. Eventually transfer of ferric ions into the zeolite was complete. At this stage the ethereal and aqueous solutions were decolorized and the zeolite sample was pale brown.

When the ion exchange process was completed, the slurry was filtered using a porosity 3 sinter. The zeolite was washed several times with distilled water until no metal ions or anions (thiocyanate) were detected in the filtrate.

Materials

Ferric Chloride: Analar; Potassium Thiocyanate: Analar; Ether: Analar; NaX: ex Union Carbide; CaA: ex Union Carbide; pH buffer tablets ex BDH. In Table I are listed the samples prepared without use of a buffer.

These samples were analysed and the % exchange was calculated from the equation

$$\% \text{ exchange} = \frac{a \times 100}{b} \quad (1)$$

where a = actual weight of ion per g of zeolite, and $b = (96/e \times M_1)/M_2$ for A sieves or $(86/e \times M_1)/M_2$ for 13X (M_1 = atomic weight of metal ion, M_2 = "molecular weight" of fully exchanged dry zeolite, e = oxidation state of metal ion).

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TABLE I. Preparation of Samples.

Zeolite Type	Volume Fe(SCN) ₃ Ether Solution per g (zeolite)	Designation	pH (final)
CaA	20/50	Fe5A(1)	6.5
CaA	40/50	Fe5A(2)	6.2
CaA	60/50	Fe5A(3)	5.5
CaA	80/50	Fe5A(6)	5.2
CaA	100/50	Fe5A(9)	5.0
NaX	50/75	Fe13X(1)	8.1
NaX	100/75	Fe13X(2)	7.1
NaX	150/75	Fe13X(3)	6.2
NaX	200/70	Fe13X(4)	5.5
NaX ^a		Fe13X(5)	5.0

^a Buffered to pH 5.0.

Investigation of the Physical Properties

The surface area of the highest exchanged zeolites was found using conventional volumetric or gravimetric techniques, and the unit cell parameters (a_0) were determined using the X-ray powder technique.

The loss of crystallinity in Fe13X exchanged zeolites was followed using a single plane intensity. The single plane chosen was that found to be least affected by ion exchange (533) [12]. Results are quoted in Table II.

TABLE II. Exchange and Structure Retention.

Sample	% Exchange	B-point % Retained SSA	a_0	% Retained Crystallinity (533) Plane
CaA		100	12.30	
Fe5A(1)	4.26	—	12.30	
Fe5A(2)	8.49	—	12.30	
Fe5A(3)	10.2	98.8	12.26	
Fe5A(6)	14.4	—	12.24	
Fe5A(4)	20.8	98.4	12.23	
NaX		100.0	24.87	100
Fe13X(1)	7.30	—	24.90	100
Fe13X(2)	15.6	—	24.92	100
Fe13X(3)	23.0	97.9	24.89	99
Fe13X(4)	31.0	92.3	24.86	88
Fe13X(5)	80.0	29.0	—	15

TABLE III. The Effect of Temperature and pH during the Exchange Process.

Designation	% Exchange	Aqueous Sol.	Temp. of Exchange	Drying Process	% Retained Crystallinity
A25	25	7.0	Room	Acetone	109
B25	25	7.0	80 °C	Acetone	104
A50	50	7.0	Room	Acetone	61.8
B50	50	7.0	80 °C	Acetone	72.2
C50	50	4.0	Room	Acetone	73.2
D50	50	4.0	80 °C	Acetone	65.0

Results

From Table II it is observed that for the CaA zeolites, Fe(III) ion exchange is limited to a value of 20% at room temperature. Moreover the Fe5A sieves do not lose microporosity and a_0 values decrease with increase in ion exchange especially when the percent exchange reaches the equivalent of one univalent ion per unit cell, which corresponds to $\approx 10\%$ exchange.

For NaX the percent of exchange may proceed to completion at room temperature but the microporous structure and the crystallinity is destroyed at high levels of exchange. Finally the a_0 value of NaFeX does not change much when crystallinity is retained.

These observations provided motivation for further investigation of Fe13X zeolites in connection with the conditions used for ion exchange and for the drying process.

The results demonstrating the effect of temperature and the use of a buffer during the ion exchange process on the crystallinity are presented in Table III.

Using the X-ray powder technique and the ratio:

$$a = \frac{\text{(533) plane intensity for exchanged NaX}}{\text{(533) plane intensity for NaX}}$$

as a measure of % retained crystallinity for Fe13X samples the following results were obtained (Table III).

Values greater than 100% are obtained because of: (a) experimental errors, (b) small effects of ion exchange on (533) plane intensity.

From Table III it is observed that at low levels of exchange when pH is 7.0 there is no significant difference in crystallinity with temperature of ion exchange. However the difference is significant at the higher level of exchange where an increase in crystallinity with increase in temperature is observed.

The most crystalline sample was obtained by ion exchange at room temperature and at pH 4.0. Using these conditions (room temperature, pH 4.0), two new samples were prepared and analysed and then examined by the powder X-ray technique, to examine the dependence of % crystallinity on the drying process. The samples studied are shown in Table IV.

TABLE IV. Dependence of % Crystallinity on the Drying Process.

Sample Designation	% Exchange	pH of Aqueous Phase	Temp. of Exchange	Drying Process	% Crystallinity
CA30	30	4.0	Room Temp.	Acetone	102.0
CB30	30	4.0	Room Temp.	80 °C in air	92.8
CC30	30	4.0	Room Temp.	Room Temp. in vacuum	95.9
CD30	30	4.0	Room Temp.	Room Temp. in vacuum at 180 °C	95.9
CE30	30	4.0	Room Temp.	Acetone + in vac. at 20 °C for 15 hr	115.5
CF30	30	4.0	Room Temp.	Acetone + in vac. at 20 °C for 15 hr + in vac. at 110 °C for 15 hr	104.1
CA50	50	4.0	Room Temp.	Acetone	74.4
CB50	50	4.0	Room Temp.	80 °C in air	58.8
CC50	50	4.0	Room Temp.	Vac. at 20 °C	78.3
CD50	50	4.0	Room Temp.	Vac. at 20 °C + vac. of 110 °C	75.3
CE50	50	4.0	Room Temp.	Acetone + vac. (20 °C) (15 hr)	83.5
CF50	50	4.0	Room Temp.	Acetone + vac. (20 °C) (15 hr) + Vac. at 110 °C (15 hr)	73.2

The ratio of the (533) plane intensity between exchanged NaX and unexchanged NaX was chosen as a criterion for the % retained crystallinity (Table VI).

From the figures obtained in Table IV it is obvious that drying in air at 80 °C leads to the greatest loss in crystallinity for both the low and higher exchanged samples. On the other hand drying first with acetone and then further *in vacuo* at 20 °C shows best structure retention for both low and higher exchanged samples. Further drying at higher temp. (110 °C) *in vacuo* shows no significant effect on % crystallinity whether the sample was previously dried with acetone or not.

The effect of vacuum treatments at higher temp. (up to 400 °C) on the loss of crystallinity was also studied (Table V).

The crystallinity of zeolites in Table V was determined after treatment at 200 °C and 400 °C. The vacuum treatment used is outlined below.

TABLE V. % Retained Crystallinity.

Sample	% Crystallinity
NaX	100.0
Fe13X(2)	100.0
Ca3O	95.9
CaA	100.0
Fe5A(4)	—

TABLE VI. % Crystallinity Relative to the Hydrated Sample.

Sample	Temp. of Vac. Dehydration (°C)		
	200	400	600
NaX	103.5	103.5	97.6
Fe13X(2)	101.0	96.9	
Fe13X(5)	90.3	78.7	
CaA	95.4	93.8	
Fe5A(4)	91.0	86.4	

Method of Treatment at High Temperatures

The samples were treated in vacuum overnight at 5×10^{-4} torr, at room temp. The temperature was then raised to 200 °C, 400 °C or 600 °C gradually over about three hours, until the vacuum reached about 10^{-5} torr. The temperature was then held constant for one hour. The sample was then allowed to cool under vacuum.

X-ray patterns were obtained when the samples were sufficiently rehydrated, and compared with patterns prior to vacuum treatment. Table VI shows the % crystallinity obtained.

Apart from Fe13X(5) treated at 400 °C, the loss of crystallinity relative to the hydrated sample was, in all cases, small.

Discussion

Structure breakdown is evident in Fe(III) ion exchanged X type zeolites starting from moderate levels of exchange (31%) and building up as the percentage of exchange increases. The breakdown phenomenon was strongly evident in Fe13X(5) (80% exchanged) from both SSA measurements and corresponding loss of crystallinity (Table II). Slight structure breakdown is observed at 23% exchange but not at 16% exchange which is in agreement with Levina and coworkers [3–6] who found that for A and X type zeolites the crystal structure is retained up to 15–17% exchange. The fact that in this work no breakdown was observed for Fe5A zeolites is possible due to the low % exchange obtained in this work. The low levels of exchange achieved are probably related to the fact that Ca(II) ions are not so readily replaced by exchange at room temperature. No attempt was made to ion exchange at higher temperatures. From the analytical results it appeared that Fe(III) was exchanged for Na(I) ions (which were present in the parent CaA zeolite) only and not for Ca(II) [12]. It is also evident that the a_0 value of the zeolites in Table II changed with percentage of exchange which is indicative of internal strains in the zeolitic structure. It is possible that at higher levels of exchange the internal strain would increase and lead to structure breakdown.

Ion Exchange Conditions and Loss of Crystallinity

From Table III it is evident that the samples obtained with a buffered dispersing medium show higher crystallinity than the samples of Table II of similar exchange prepared without a buffer. Samples A25, and B25 although exchanged to more than 20% do not show loss of crystallinity. Samples of moderate (50%) exchange show loss of crystallinity. The loss of crystallinity appears to be dependent on both temperature and pH, for example we obtain nearly the same results if we operate at 80 °C and pH 7 or at room temperature and pH 4. According to Malashevich and coworkers [3] at pH 7.6 the Fe(III) ion enters the zeolites largely as $\text{Fe}(\text{OH})_2^+$ whilst at pH 4.0 it enters as $\text{Fe}(\text{OH})^{2+}$. The exchanging species may also be affected by temperature and it seems likely that such species effect the distribution of Fe(III) between the zeolitic sites, and influence the extent of structure breakdown.

Drying Process and Loss of Crystallinity

From Table IV it is observed that a greater loss of crystallinity takes place when the zeolites are dried in air (CB30, CB50). Vacuum drying either at room temperature or at 110 °C gives less loss in % crystallinity than drying in air (CC30, CD30, CC50, CD50). Results in Table VI imply that structure breakdown due to heating under vacuum is very limited for low exchanged samples but is greater for higher exchanged samples.

The greater loss of crystallinity on drying in air may be connected with the oxidation state of the iron atoms (which in the presence of air is always Fe(III)), with their positions of stabilization in the zeolitic structure and possibly with rate of drying, which for the same temperature is faster in the presence of a good vacuum.

It is worth mentioning here that samples pre-treated for a long time in air at high temperatures (400 °C) or for short times at very high temperatures (800 °C) were found completely broken down while samples heated at the same levels under vacuum kept their crystalline structure (e.s.r. and X-ray) [12, 13]. From studies of the vacuum treatment of Fe(III) zeolites by Delgass and coworkers [8] it was shown that some Fe(III) ions are reduced to Fe(II) and these may be stabilized at different positions in the zeolitic structure.

Conclusions

Loss of crystallinity starts at a level of exchange between 15% and 23%, but if the exchange process is carried out at room temperature and pH 4 the zeolitic structure can be retained up to 30% exchange for 13X type zeolites. It is also found that the Fe(III) exchanged zeolites of type A with low percentage exchange have a smaller unit cell parameter (a_0) than the original CaA zeolites. The method of drying affects the crystallinity of the solid. Drying the NaFeX zeolites in air leads to a decrease in crystallinity while treatments at high temperature under vacuum show only a small effect on crystallinity of the zeolites. The major part of structure breakdown occurs during the ion-exchange process and is related to % exchange.

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