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Studies on the Surface Area of Fe(III) and Cu(II) Ion Exchanged Zeolites of Type A and X Using Sorption and X-ray Powder Diffraction

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The determination of surface areas and pore size distribution is discussed. Good agreement is obtained between surface areas determined using the B point method and areas determined from the Langmuir isotherm. Furthermore the loss of microporosity as obtained from adsorption measurements was related to the background intensities of X-ray powder patterns. In addition an independent method for estimation of loss of crystallinity by using a plane intensity least affected by ion exchange is discussed.

Introduction

There is a considerable volume of work dealing with adsorption on zeolites, but very little on the relationship between surface area and pore size distribution of ion exchanged zeolites.

The surface area and pore size distribution are known to be important factors in sorption and diffusion of adsorbates in solids and hence are of importance in catalytic studies [1].

In general, the equation derived by Brunauer, Emmett and Teller (B.E.T.) is widely used for determining surface areas of solids. The B.E.T. equation is based on the assumption of multilayer adsorption. The monolayer capacity of a solid characterized by an isotherm following the B.E.T. equation is given by point B.

Zeolites are characterized by their microporous structure the dimensions of which are of the same order as the adsorbate molecules. Consequently the Langmuir isotherm (Type I) provides a reasonable representation of adsorption in zeolites although other isotherms have been proposed [2].

For zeolite surface area measurements various investigators have chosen different methods some using B.E.T. [3–6] and others the Langmuir equation [7].

Barrer introduced the concept of monolayer equivalent area for zeolites [8]. Later Yates [9] provided an independent method of measuring surface areas in crystalline zeolites by using the X-ray technique. The loss of crystallinity determined from the loss of peak heights of a few low angle line intensities was successfully related to the loss of surface area, provided that the loss of surface area was not due to ion exchange.

In this work surface area measurements obtained mainly on Fe(III) and Cu(II) exchanged zeolites of type A and X are used to investigate the relation between the loss of surface area and the background peak height. In addition the surface areas measured are compared with the peak height of a particular line intensity which was observed to be least affected by ion exchange.

Experimental

Apparatus and Materials

All isotherms were determined volumetrically using N_2 at 77°K. Conventional (Pyrex) glass cells and vacuum systems were used and the pressures were measured with mercury manometers using a kathetometer. The apparatus used was similar in design to that described by Lippens *et al.* [10]. The N_2 used was of spectroscopic purity.

The X-ray equipment consisted of a Phillips diffractometer, using Cobalt K_α radiation for Fe(III) ion exchanged zeolites and Copper K_α radiation for Cu(II) exchanged zeolites. The zeolite samples were in the hydrated form and during the X-ray process they were exposed to air.

The ion-exchanged zeolites were obtained by exchanging NaX and CaA (Union Carbide) by $Fe(SCN)_3$ or $Cu(CH_3COO)_2$. The samples did not include binder material.

Procedure

For surface area measurements a sample of zeolite (0.2 to 0.5 g) was loaded into glass cells and evacuation begun. The temperature was raised stepwise from 20 °C to 400 °C within a period of three hours. The sample was left under vacuum overnight at 400 °C. The cell was then closed, cooled to 77°K with liquid N_2 and He was added to measure the dead

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TABLE I. Surface Areas

Sample	B-point Method			Langmuir Equation		
	Monolayer capacity (10^4 molg^{-1})	S.S.A. (m^2 g^{-1})	% Microporosity retained[a]	Monolayer capacity (10^{-4} mol g^{-1})	S.S.A. (m^2 g^{-1})	% Microporosity retained[a]
Ca5A	68.52	668	100	79.5	688	100
Fe5A (3)	67.45	660	98.8	69.3	676	98.2
Fe5A (4)	67.25	656	98.4	69.5	680	98.6
Cu5A (3)	63.80	598	89.5	69.2	676	98.3
Cu5A (4)	58.73	564	84.5	63.6	620	90.2
Na13X	86.59	845	100.0	89.0	869	100.0
Fe13X (3)	84.81	826	97.9	86.7	845	97.3
Fe13X (4)	80.0	780	92.3	82.3	804	92.6
Cu13X (4)	72.3	705	83.4	75.2	734	84.4
Cu13X (5)	66.0	645	76.3	67.8	662	76.2

[a] Determined by taking ratios of sample to 'parent' sample.

TABLE II. Mesopore Areas (from 15 Å to 100 Å radius).

Sample	Mesopore Surface Area (m^2 g^{-1})
CaA	38.0
Fe5A (3)	44.1
(4)	60.3
Cu5A (3)	68.2
(4)	78.6
NaX	14.0
Fe13X (3)	38.0
(4)	57.0
Cu13X (4)	36.3
(5)	67.0

space. Then the liquid nitrogen trap was removed and the sample was evacuated at room temperature for one hour. The cell was then recooled to 77°K and the N_2 was added for the adsorption isotherm. When P/P_0 was close to unity the desorption isotherm was followed. After adsorption and desorption isotherms were determined the sample was taken out of the cell and weighed. The surface area values are given per gram of anhydrous zeolite.

For the X-ray powder diffraction measurements the samples being in powder form of 2 to 5μ after ion exchange were pressed into a holder using McCreery's procedure as discussed in detail by Klug and Alexander [11].

Samples

A complete list of the ion exchanged zeolites studied is given in Table IV. Samples studied for loss of microporosity by adsorption measurements were Ca5A, Fe5A(4), Fe5A(3), Cu5A(4), Cu5A(3), Na13X, Fe13X(4), Fe13X(3), Cu13X(4) and Cu13X-(5) (Table I).

Results

Adsorption Isotherms

All isotherms showed a reasonably good fit to Langmuir's equation. The fit was poorer as the percentage of exchange increased. It was very clearly shown from the isotherms that a mesopore region became apparent at the highest levels of exchange. A hysterisis loop was also observed in all samples but this was very small for the parent zeolite NaX.

Surface Areas

Table I shows the surface areas calculated using the B point method and from the Langmuir equation. The agreement between the two methods is quite good.

Pore Size Distribution

Table II records the mesopore area of each sample.

Determination of Changes in Crystallinity

Changes in crystallinity usually lead to the production of amorphous material. The amorphous material produces a diffraction halo in a certain region of 2θ values. The increase of background intensity in the region of 2θ values where the halo due to amorphous material is observed could be used as a measure of the amount of amorphous material.

Table III shows the background peak height of samples at a 2θ region around 10°.

On the basis of the measurements shown in Table III a plot was made of the % S.S.A. retained *vs* background peak height (cm) which showed in all cases linear correlation for the three points measured (Fig. 1).

TABLE III. Background Intensity Measurements at 2θ ≅ 10°.

Radiation Source	2θ in degrees	Sample		Background Intensity (cm)	% S.S.A. Retained[a]
Cobalt	10	Ca5A		1.10	100
	10	Fe5A	(1)	1.15	–
	10		(2)	1.10	–
	10		(3)	1.15	98.8
	10		(6)	1.15	–
	10		(4)	1.15	98.4
Copper	11	Ca5A		1.10	100
	11	Cu5A	(1)	1.10	–
	11		(2)	1.10	–
	11		(3)	1.25	89.5
	11		(4)	1.33	84.5
Cobalt	9	Na13X		1.18	100
	9	Fe13X	(1)	1.15	–
	9		(2)	1.15	–
	9		(3)	1.22	97.9
	9		(4)	1.30	92.3
Copper	8	Na13X		1.20	100
	8	Cu13X	(1)	1.30	–
	8		(2)	1.40	–
	8		(3)	1.50	–
	8		(4)	1.50	83.4
	8		(5)	1.65	76.3

[a]Calculated from surface area measurements.

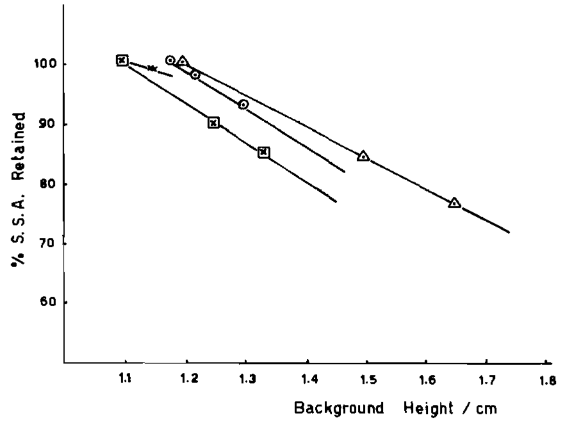

Figure 1. Correlation between % S.S.A. retained and the peak height of the background X-ray diffraction halo due to amorphous material. ⊠ Cu5A zeolites, × Fe5A zeolites, ⊙ Fe13X zeolites, △ Cu13X zeolites.

Loss of Crystallinity from Single Plane Intensities

Loss of crystallinity (on samples showing constant a_0 value) was determined from the intensities of a single plane least affected by ion exchange.

The ion exchanged 13X zeolites had constant a_0 but ion exchange of 5A zeolites lead to slight changes in a_0.

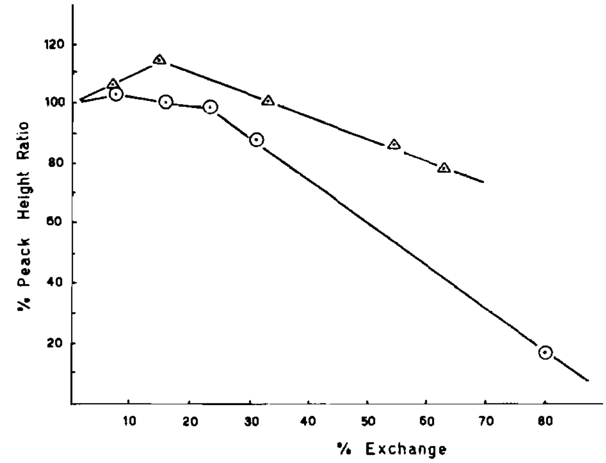

Figure 2. The dependence on ion exchange of the relative intensities for the 533 plane in X type zeolites (I_{533}M13X/I_{533}Na13X). ⊙ Fe13X zeolites, △ Cu13X zeolites.

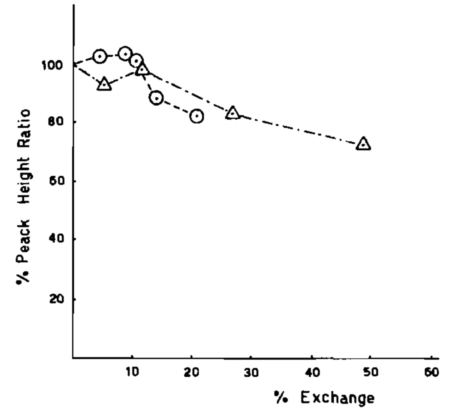

Figure 3. The dependence on ion exchange of the relative intensities for the 111 plane in A type zeolites (I_{111}M5A/I_{111}Ca5A). ⊙ Fe5A zeolites. △ FeCuA zeolites.

In the X type zeolites where a_0 was constant the 533 plane was found to be only very slightly affected by ion exchange of Cu(II) for Na(I) and hardly affected at all by exchange of Fe(III). The cell parameters decreased slightly with % exchange of Cu(II) and of Fe(III) into 5A zeolites [11] and in these materials the intensity of the 111 plane was least affected both by changes in a_0 and in %exchange.

Plots showing the % peak height ratio between exchanged and unexchanged zeolites vs percentage of exchange are shown for the 13X ion exchanged zeolites in Fig. 2 and for the 5A ion exchanged zeolites in Fig. 3.

The loss of % peak height is presumed to be due to loss of crystallinity especially in 13X ion exchanged sieves where no a_0 changes are observed. Table IV shows the % retained crystallinity (as obtained from peak height ratio of the particular plane between exchanged and unexchanged sample) and the retained

TABLE IV. % Retained Crystallinity.

X-ray Source	Sample	Ion Exchange (%)	X-ray single plane ((111) Plane)^a	Adsorption Measurements^b
Cobalt	Ca5A	0.00	100.0	100
	Fe5A (1)	4.26	102.9	–
	(2)	8.49	102.9	–
	(3)	10.23	100.0	98.8
	(6)	14.36	88.2	–
	(4)	20.80	82.3	98.4
Copper	Ca5A	0.00	100.0	100.0
	Cu5A (1)	5.35	93.3	–
	(2)	12.50	98.3	–
	(3)	26.5	83.3	89.5
	(4)	48.5	73.3	84.5
			((533) Plane)	
Cobalt	Na13X	0.00	100.0	100.0
	Fe13X (1)	7.30	103.0	–
	(2)	15.60	100.0	–
	(3)	23.00	99.0	97.9
	(4)	31.00	87.5	92.3
	(5)	80.00	15.0	29.0
Copper	Na13X	0.00	100.0	100.0
	Cu13X (1)	7.15	104.9	–
	(2)	14.57	115.3	–
	(3)	33.10	100.0	–
	(4)	53.85	85.4	83.4
	(5)	62.35	77.7	76.3

[a] Data refer to 100 (Peak height of exchanged sample/Peak height of parent zeolite).
[b] Data refer to 100 (Surface area of exchanged sample/Surface area of parent zeolite).

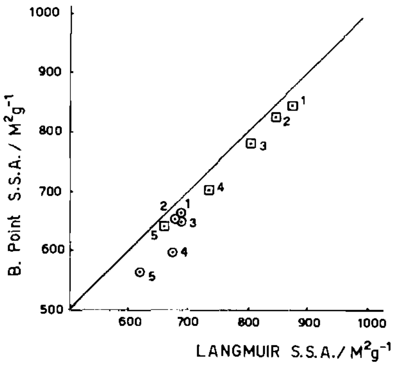

Figure 4. Correlation between surface areas determined by the B point method and calculated using the Langmuir equation.

1 ⊡ Na13X	1 ⊙ Ca5A
2 ⊡ Fe13X(3)	2 ⊙ Fe5A(3)
3 ⊡ Fe13X(4)	3 ⊙ Fe5A(4)
4 ⊡ Cu13X(4)	4 ⊙ Cu5A(3)
5 ⊡ Cu13X(5)	5 ⊙ Cu5A(4)

microporous structure obtained from surface area measurements.

Discussion

Adsorption Measurements

It has been known from the early stages of research that most zeolites show type I(13) adsorption isotherms according to the Brunauer classification, which indicates monolayer adsorption while capillary condensation is negligible. Furthermore Yates [9] found that the B-point method is more appropriate than a BET or Langmuir plot for correct estimation of the S.S.A. of zeolites.

The isotherms obtained in this work fairly clearly belonged to type I, especially in the case of the CaA and NaX samples. The isotherms also show a hysterisis loop in the mesorpore region, which increases with loss of specific surface area as determined either by B-point or from the Langmuir equation. The increase in the hysterisis loop also changed the type of isotherm from type I towards type II.

The surface areas specifically obtained by B-point and Langmuir equation show good agreement (Fig. 4). From Tables I and IV it is evident that the S.A.A. decreases with increase in % ion exchange.

TABLE V. Retention of Crystallinity from Background Intensity Measurements.

Samples	% Crystallinity	Samples	% Crystallinity
Ca5A	100.0		
Fe5A (1)	98.4	Cu5A (1)	100.0
(2)	100.0	(2)	100.0
(3)	98.4	(3)	89.5
(5)	98.4	(4)	84.5
(4)	98.4		
Na13X	100.0		
Fe13X (1)	100.0	Cu13X (1)	95.0
(2)	100.0	(2)	90.0
(3)	97.9	(3)	83.4
(4)	92.3	(4)	83.4
		(5)	76.3

The pore size distribution of the samples tested showed the increase of pores in the mesopore region. In most cases the maximum was obtained in the region of pores with radius about 18Å.

In general Fe(III) ion exchanged zeolites showed significant increase in pores of radius 18Å, even when considerable S.S.A. was lost, while in the Cu(II) exchanged zeolites the increase in mesopores was not restricted to mesopores of 18Å radius but was spread to mesopores of greater radius.

Fig. 5 shows the correlation between micropore surface area as obtained from B-point method and mesopore surface area as obtained from calculations using the procedure of Pierce [14] (modified by Orr and Dalla Vale [15]) over the range $P/P_0 = 0.3$ to $P/P_0 = 1.0$. In Fig. 5 it is shown that in Fe(III) ion exchanged zeolites the mesopore surface area obtained is high with small loss of microporous surface area indicating that mesopores of small radius are obtained. For Cu(II) ion exchanged zeolites it is observed that more micropores need to be lost in order to obtain a mesopore surface area equivalent to that of the Fe(III) exchanged zeolites.

Background X-ray Intensities

In all ion exchanged zeolites a 2θ value around 10° was found to give a linear relationship between % S.S.A. retained and background intensity (height in cm). In practice care was taken that the chosen 2θ value represented the background intensity and was not interferring with a peak associated with the crystalline material.

From Fig. 1 and from the background heights of the X-ray patterns of ion exchanged zeolites, the % retained crystallinity is obtained. Table V quotes values for % retained crystallinity obtained from background heights and % retained microporosity from adsorption measurements.

The values obtained are in reasonable agreement and the use of background X-ray intensities seems to be justified as far as the present samples are concerned (*i.e.* Fe(III) or Cu(II) ion exchanged zeolites with structure breakdown less than 25–30%).

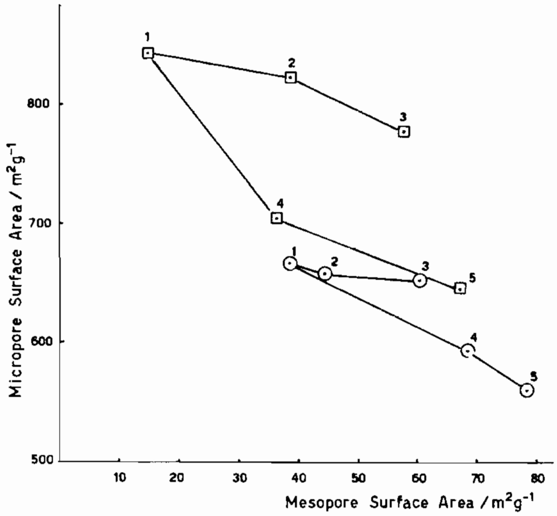

Figure 5. Correlation between micropore and mesopore surface areas.
1 ▫ Na13X 1 ⊙ Ca5A
2 ▫ Fe13X(3) 2 ⊙ Fe5A(3)
3 ▫ Fe13X(4) 3 ⊙ Fe5A(4)
4 ▫ Cu13X(4) 4 ⊙ Cu5A(3)
5 ▫ Cu13X(5) 5 ⊙ Cu5A(4)

When using this X-ray method, care should be taken that the materials under comparison have been pretreated strictly in the same way (*i.e.* water content should be the same), because background intensity receives a contribution from adsorbates or air occluded in the cavities of the solid material.

Loss of Crystallinity Measured from a Single Plane

From Table IV it is observed that: (a) Using the (111) plane as reference plane to determine the retained crystallinity (for 5A zeolites) the figures obtained are somewhat lower than those obtained from surface area measurements (*i.e.* % retained S.S.A.).

This might be because of two reasons: (i) The (111) plane is affected by ion-exchange. (ii) The (111) plane is affected by changes in a_0 value. The second reason seems the more likely because a_0 does change due to ion exchange [11], while the (111) plane should not be greatly affected by ion exchange if the incoming ions occupy the site I available in 5A zeolites. (b) Using the (533) plane for ion exchanges 13X sieves it is found that the % retained crystallinity is very close to the value obtained from surface area measurements (% retained S.S.A.). (c) In the lower exchanged samples where the crystallinity is close to 100% the method is not particularly good because the small effects which ion exchange imposes on the (533) line intensity appears to be the major factor and therefore values higher than 100% crystallinity are obtained.

Conclusions

The adsorption isotherms of Fe(III) and Cu(II) exchanged zeolites were found to be of type I when the loss of microporosity is low. As the loss of microporosity increases the isotherms show characteristics of type II. The B-point method was found adequate and in good agreement with the Langmuir equation method for measuring S.S.A. The pore size distribution of the mesopore region was found to be different for the Fe(III) exchanged and the Cu(II) exchanged zeolites.

Background intensities of X-ray patterns of samples of $2\,\theta \cong 10^\circ$ were found to be in approximately a linear relationship with % retained S.S.A. from adsorption measurements.

The loss of crystallinity measured from the line intensity of the 533 plane for 13X ion exchanged zeolites was in reasonable agreement with measurements using adsorption techniques.

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