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Optimization and Modification of Offretite Sorbents

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Abstract

The effective free diameter of the parallel, nonintersecting channel system of offretite has been modified in various ways using synthetic crystals initially containing K and tetramethylammonium (TMA) ions. Objectives were to optimize the openness of the channels and to produce sorbents having regulated molecule sieving properties. Removing all TMA from the wide, parallel channels by exchange and enriching the crystals in Li, Na, K, or Cs yielded open sorbents which sorbed *n*-hexane very rapidly and which differed only marginally in rapid rates of uptake of 2,2-dimethylbutane. Removal of all TMA from gmelinite cages and wide channels by heating in air or oxygen also yielded open M,K,H-offretites (where M = Li, Na, K, or Cs). However, the sieve behavior and capacity were further modified according to the temperature and number of oxidative treatments. Crystals enriched in methyl-, dimethyl-, and trimethylammonium sorbed *n*-hexane at rates which differed inter se. Small amounts of TMA in the wide channels also strongly influenced the kinetics of sorption of *n*-hexane and large amounts prevented any uptake at all.

INTRODUCTION

The zeolite offretite has been synthesized free of stacking faults (*1*, *2*) and its structure has been determined (*3*, *4*). It has wide parallel channels like those in mordenite or zeolite L and is of much interest as a sorbent

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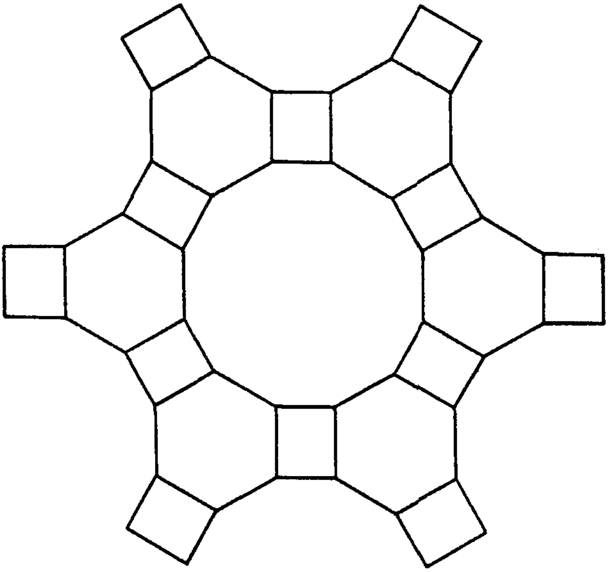

FIG. 1. Cross section of the channel in offretite. Al or Si are centered at each corner, oxygens near but not on the midpoint of each edge.

and catalyst. In the structure, columns of alternating 11-hedral cancrinite cages and hexagonal prisms, and also columns of 14-hedral gmelinite cages, run parallel to the *c*-direction. A cross section of the wide channel and its surroundings is shown in Fig. 1.

A previous study of diffusion in a "narrow port" mordenite (*5*), another zeolite with wide parallel channels (*6*), showed that its molecule-sieving properties were altered by ion exchange with ions of different size or valence. The same possibility appeared to arise in Li-, Na-, and K-enriched offretites (*7*) and led to the further investigation reported in this paper. The overall width of channel (free diameter ~ 6.9 Å) is such that with channel occupancy by cations of differing sizes one might hope to develop a range of sieves which could, for example, separate *n*- from iso- or iso- from neo-paraffins. For such molecules (with methyl side-groups for iso- and neo-paraffins) the respective critical van der Waals dimensions are approximately 4.9, 5.6, and 6.2 Å.

EXPERIMENTAL METHODS

The offretite, synthesized according to the procedure of Aiello and Barrer (*2*) and provided by Air Products and Chemicals, had the oxide

TABLE 1

Ions per Unit Cell in Offretites

Cation	Parent	Li-enriched	Na-enriched	K-enriched
		Exchange forms		
Li	—	0.75	—	—
Na	—	—	1.23	—
K	2.9	1.66	1.15	2.6
TMA	1.4	1.29	1.31	1.11
Total	4.3	3.70	3.69	3.71

composition (where TMA is tetramethylammonium) 0.79 K_2O, 0.38 $(TMA)_2O$, Al_2O_3, 7.78 SiO_2, 4.8 H_2O, corresponding with a unit cell content of $K_{2.9}(TMA)_{1.4}[Al_{3.7}Si_{14.2}O_{36}]8.7H_2O$. X-ray diffraction patterns and electron micrographs indicated that the sample was highly crystalline. The zeolite was enriched with various cations by three treatments at 80°C, each of 12 hr duration, with the appropriate 1 *M* metal or organic chloride solutions. The product was then washed free of chloride and the extent of ion exchange determined by standard analytical techniques including, where relevant, organic microanalyses of C and N. The cation contents of the Li-, Na-, K-, and TMA-enriched forms are given in Table 1. Those of the forms containing methyl-, dimethyl-, and trimethylammonium ions are given later in Table 5.

The *n*-hexane and 2,2-dimethylbutane (2,2-DMB) used as probe molecules had purities better than 99%. Sorption measurements were made using a McBain-Bakr balance in conjunction with conventional vacuum apparatus, attaining an ultimate vacuum of $\sim 10^{-6}$ Torr. Sorbents containing TMA were outgassed at 300°C for 16 hr whereas sorbents without TMA were outgassed at 360°C for a similar period of time.

RESULTS AND DISCUSSION

Interpretation of Analyses

The analysis confirmed previous observations (*1*, *8*) that the total cations are in excess of the lattice aluminum. This is attributed to occlusion of excess alkali, which was removed during the exchange with neutral salt solutions as seen in Table 1. After treatment with the exchange solutions the total cations per unit cell equal the number of Al atoms per unit cell (3.70).

Previously, it was found that one TMA ion could not be exchanged, and it was suggested that this ion was trapped in the one gmelinite cage per unit cell (*2*, *7*). The remaining potentially exchangeable TMA was necessarily in the wide channels since TMA is too large to occupy the cancrinite cages. The results in Table 1 thus mean that before outgassing there are, respectively, ~0.4, 0.27, 0.31, and 0.11 TMA ions per unit cell in the wide channels in the parent offretite and in the forms enriched in Li, Na, and K ions. Exchange of the organic ions in these channels is not complete in any form but is most extensive in the K-enriched offretite.

From Table 1 the maximum K^+ content of this form is 2.6 ions per unit cell, compared with 2.9 in the parent crystals. Therefore not less than 0.3 K^+ ions must be present in the parent crystals as excess KOH, and so there is not more than 0.3 free TMAOH and not less than 1.1 TMA cations per unit cell, the latter neutralizing framework charge.

Sorption of *n*-Hexane and Role of TMA Ions

When the offretites of Table 1 were outgassed at 300 °C, *n*-hexane was unexpectedly more rapidly sorbed in the parent material than in the ion-exchanged forms (Fig. 2a). Moreover, contrary to an earlier report (*7*), the rates did not decrease with increasing size of the exchange ions Li^+, Na^+, and K^+. Therefore the TMA content was determined for several exchanged forms after outgassing at 300 °C (Table 2). The parent material lost considerable TMA during outgassing, but after exchange the exchange forms lost very little. The rates of uptake recorded in Fig. 2a are therefore governed primarily by the TMA content of the wide channels which, with about 1 TMA per unit cell locked in the gmelinite cages, is in the sequence:

parent < K-enriched < Na-enriched < Li-enriched < TMA-enriched

The TMA-enriched offretite did not imbibe any *n*-hexane. It was concluded from the above results that the rate sequence reported earlier (*7*) (K-enriched < Na-enriched < Li-enriched) was governed not by the size of the inorganic ions, but by the amount of TMA still remaining in the wide channels. This TMA is a sensitive means of modifying the sieve properties.

The greater loss of TMA from the parent crystals during the outgassing is attributed to the entrained base referred to in the previous section, which has been largely washed out during the exchange reactions. In the wide channels of the parent offretite there is a mixture of K^+, TMA^+, and OH^-, and therefore TMAOH, which has a melting point of only 63 °C, is eliminated at 300 °C. On the other hand the TMA^+ ions neutralizing the framework charge remain (Table 2).

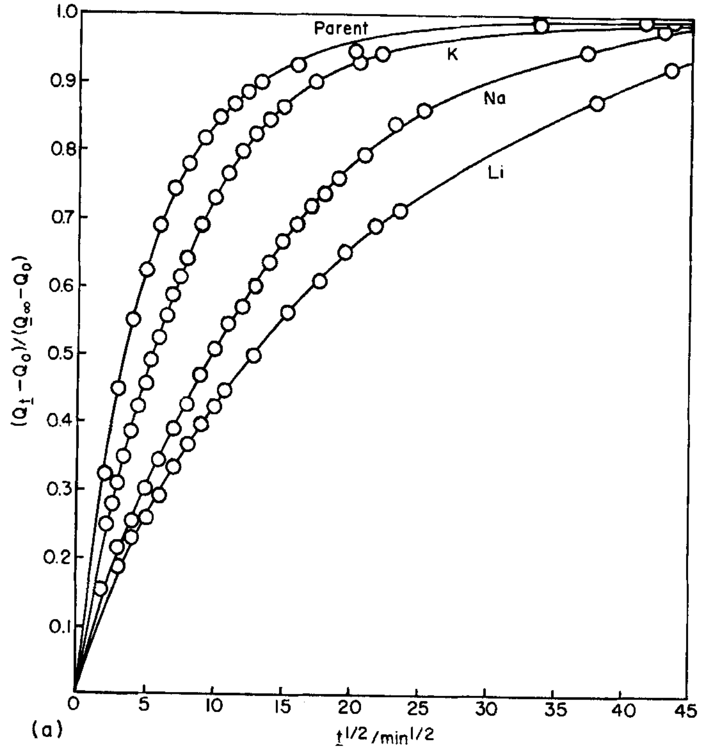

FIG. 2a. Plots of $(Q_t - Q_0)/(Q_\infty - Q_0)$ against $t^{\frac{1}{2}}/\mathrm{min}^{\frac{1}{2}}$ for the uptake of *n*-hexane by ion-exchanged offretites at 30°C. Q_0, Q_t, and Q_∞ are the uptakes at time $t = 0$, time t, and equilibrium ($t = \infty$), respectively.

TABLE 2

TMA Ions per Unit Cell before and after Outgassing at 300°C

Exchange form	Before	After
Parent	1.4	0.9
TMA-enriched	1.74	1.71
Li-enriched	1.31	1.21
K-enriched	1.12	1.09

Optimization and Modification of Sorbent Properties

Residual TMA in the wide channels in the Na-enriched offretite could not be removed by extraction either with cold water or with water at 80°C as judged from rates of uptake of *n*-hexane before and after these treatments (Fig. 2b). This confirms that the TMA ions are neutralizing framework charge. On the other hand, washing with *M* NaCl solution substantially improved these rates while still further exchange with *M* KCl and with *M* NaCl yielded offretites which sorbed *n*-hexane extremely

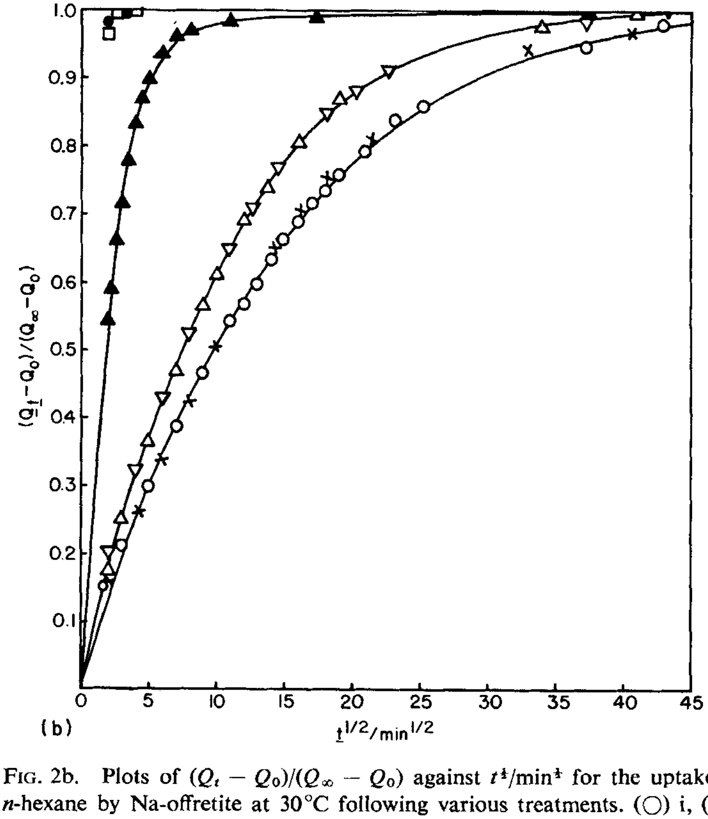

FIG. 2b. Plots of $(Q_t - Q_0)/(Q_\infty - Q_0)$ against $t^{1/2}/\text{min}^{1/2}$ for the uptake of *n*-hexane by Na-offretite at 30°C following various treatments. (○) i, (Na, TMA)-offretite as prepared; (×) repeat with i; (△) Sample i washed a further 10 times with cold water; (▽) Sample i extracted with water at 80°C for 8 hr; (▲) Sample i treated three more times with *M* NaCl at 80°C for 12 hr; (●) Sample i treated three more times with *M* KCl, then three times with *M* NaCl, all at 80°C for 12 hr; and (□) Sample i heated to 650°C in air to give (Na, H)-offretite.

rapidly. Further experiments showed that the heavier alkali metal salts (e.g., KCl and CsCl) exchanged and so removed residual wide channel TMA more readily than salts of Li and Na. Table 3 shows that the uptakes of *n*-hexane and of 2,2-DMB at fixed relative pressures were also improved by such treatments. Moreover, offretites with small amounts of TMA in the wide channels differentiate well between these two sorbates (e.g., Line 3, Table 3).

2,2-DMB (critical dimension ~6.2 Å) should reflect in a more sensitive way than *n*-hexane (critical dimension ~4.9 Å) the resistance to penetration offered by ions or adventitious impurities in the wide channels. TMA ions may be removed by oxidation from both wide channels and gmelinite cages. The kinetics of sorption of 2,2-DMB in several ion-exchanged

TABLE 3

Influence of Washing with Aqueous Electrolyte on Sorption Capacities at 30°C. Capacities Are in Molecules/Unit Cell of Outgassed Zeolite

Cations[a]	*n*-Hexane, $p/p_0 = 0.36$	2,2-Dimethylbutane, $p/p_0 = 0.16$	Treatment
Parent	0.93		
K,TMA	0.99		No further treatment following ion-exchange with KCl
K,TMA	1.08	0.18	Washed three times with *M* KCl
Na,TMA	0.95		No further treatment following ion-exchange with NaCl
Na,TMA	0.97		Extracted with boiling water
Na,TMA	1.08		Washed three times with *M* NaCl
Na,TMA (vi)	1.17	0.47	Reexchanged with *M* KCl and then with *M* NaCl
Na,H (ix)	1.29	0.49	Ignited at 650°C for 1 hr after three washings with *M* NaCl
Na,H		0.40	Sample ix ignited at 460°C for 6 hr in air
Li,TMA	0.91		No further treatment following ion exchange
Li,TMA	1.12	0.25	Reexchanged with *M* KCl then *M* LiCl
Li,H	1.31	0.64	Ignited at 650°C for 1 hr

[a] *K* is also present in the forms enriched in Na and Li.

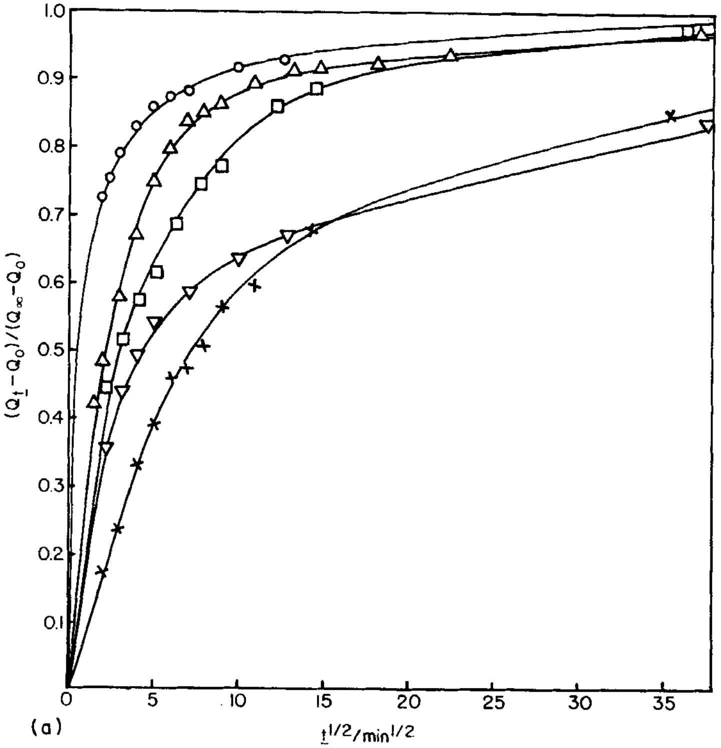

FIG. 3a. Plots of $(Q_t - Q_0)/(Q_\infty - Q_0)$ against $t^{\frac{1}{2}}$/min$^{\frac{1}{2}}$ for the uptake of 2,2-dimethylbutane by ion-exchanged offretite at 30°C. (○) (Li,H)-offretite after 4 hr in air at 450°C; (△) (Li,H)-offretite after the above treatment, then 16 hr in oxygen at 450°C; (×) (Na,TMA)-offretite as prepared; (□) (Na,H)-offretite after 1 hr in air at 650°C; and (▽) (Na,H)-offretite after 1 hr in air at 650°C, then 6 hr in air at 460°C.

offretites subjected to heat treatments in air are shown in Fig. 3a. Calcination of the Na-enriched form at 650°C increased the rate of uptake of 2,2-DMB but not the capacity [Table 3, Samples Na,TMA(vi) and Na,H (ix)]. On the other hand the capacity for *n*-hexane was improved by such treatment as shown for the above two Na-enriched forms and by the corresponding Li-enriched forms. The increased capacity arises from removal of TMA from gmelinite cages which can then be entered by *n*-hexane.

Further heat treatments in air or oxygen were given to some of the

TABLE 4

Sorption Capacity of Ion-Exchanged Forms of Offretite for 2,2-Dimethylbutane Following Various Heat Treatments. Capacities[a] Are in Molecules/Unit Cell of Outgassed Zeolite

Cation	Sorption capacity	
		Single Treatments
Li,H	0.94	Four hours at 450 °C in air. Carbon content = 0.8 %
Li,H	0.89	Four hours at 450 °C in air then 16 hr at 450 °C in oxygen. Carbon content = 0.27 %.
Li,H (i)	0.98	Six hours at 480 °C in air
Li,H	0.92	Sample i after two sorption runs[b] at 17 °C then repeat of experiment at 30 °C
K,H (ii)	0.70	Four hours at 450 °C in air then 16 hr at 450 °C in oxygen
K,H	0.61	Sample ii after two sorption runs[b] at 17 °C then repeat of experiment at 30 °C
		Progressive Treatments
Li,H	0.96	Six hours at 480 °C in air
Li,H	0.81	Plus 5 hr at 480 °C in air
Li,H	0.50	Plus 5 hr at 480 °C in air
Li,H	0.42	Plus 5 hr at 650 °C in air
K,H	0.75	Six hours at 480 °C in air
K,H	0.61	Plus 5 hr at 480 °C in air
K,H	0.43	Plus 5 hr at 480 °C in air
K,H	0.37	Plus 5 hr at 650 °C in air

[a] Capacities for single treatments were measured at 30 °C and $p/p_0 = 0.16$; those for progressive treatments were measured at 24 °C and $p/p_0 = 0.19$. Li,H-forms also contain K see (Table 1).

[b] Each followed by outgassing at 360 °C for 16 hr.

ion-exchanged offretites (Table 4). The table shows that at 450 °C it is not easy to remove all carbon from offretites containing some TMA, but that nevertheless at $p/p_0 = 0.16$ fairly consistent uptakes of 2,2-DMB can be achieved, which are better than those in Table 3. However, the capacities declined when the zeolites were subjected to the progressive treatments indicated in the table. Parallel with loss in capacity for 2,2-DMB, the rate of sorption of this molecule also decreased (Fig. 3b), but

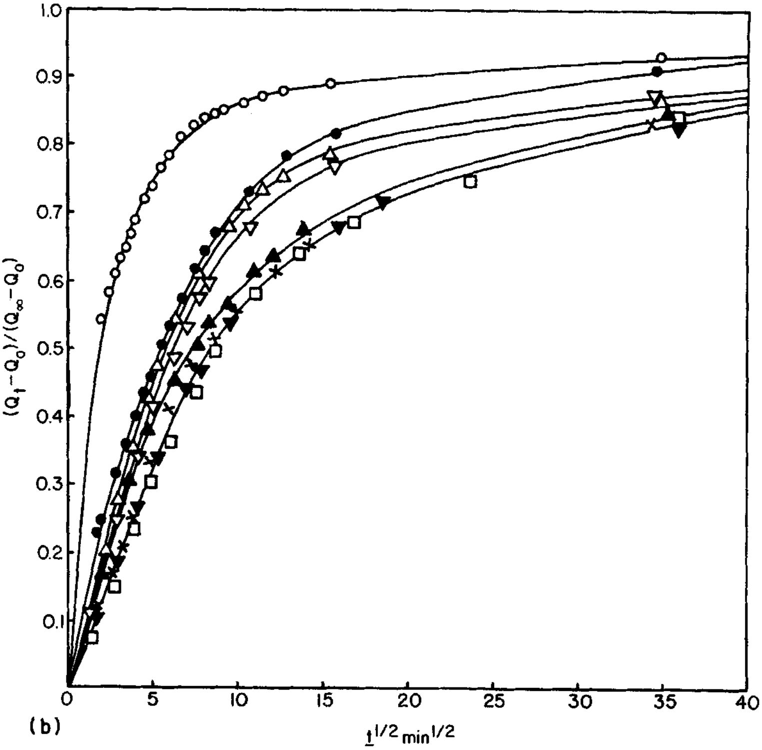

FIG. 3b. Plots of $(Q_t - Q_0)/(Q_\infty - Q_0)$ against $t^{\frac{1}{2}}/min^{\frac{1}{2}}$ for the uptake of 2,2-dimethylbutane by (Li,H)- and (K,H)-offretite at 24°C after the successive heat treatments noted in Table 4. (Li,H)-offretite: Experiment 1 (○); Experiment 2(●); Experiment 3 (□); and Experiment 4 (×). (K,H)-offretite: Experiment 1(△); Experiment 2(▽); Experiment 3(▼); and Experiment 4 (▲).

appeared to be stabilized near the lowest value obtained with treatment at 480°C when a further heating was carried out at 650°C.

Controlled heat treatment appears to be a further way of yielding sorbents which differentiate between *n*-hexane and 2,2-DMB (e.g., Table 3, Na,H-offretite ix). Since organic matter should all have been removed, these effects can only be ascribed to silanol hydroxyls of the partial H-offretites which in air at 480°C result in progressive lattice changes unfavorable for uptake of 2,2-DMB (Table 4). At 650°C, however, dehydroxylation should be nearly complete, leaving electron-deficient sites (*9*) and tending to stabilize the structure by freeing it of hydroxyls.

Relationships between Cation Size and Sorption Capacity

Offretites enriched in H, Li, Na, K, Cs, methylammonium (MA), dimethylammonium (DMA), trimethylammonium (TriMA), and TMA were compared as sorbents of water, *n*-hexane, and in some cases 2,2,-DMB (Table 5). Because of the tendency of the organic ions to decompose on heating, the forms enriched in MA, DMA, TriMA, and TMA were outgassed at 190, 150, 200, and 300°C, respectively.

From the results recorded in Table 5 one may make the following observations:

(1) Removal of the organic ions increases the uptakes of water and *n*-C_6H_{14} although not in a constant ratio. From the increased uptakes one obtains the following apparent equivalences for space filling: TMA $\sim$ $2.8H_2O$ or $0.3C_6H_{14}$; MA $\sim 1.2H_2O$; DMA $\sim 1.6H_2O$; TriMA $\sim 0.9H_2O$. The results for TriMA is anomalous, but in all cases the increase, especially for *n*-C_6H_{14}, is also smaller than expected from the respective ionic and molar volumes.

(2) For K,Cs,TMA-offretite the removal of TMA improves only slightly the uptake of *n*-hexane. This, together with the kinetic data reported in the next section, indicates that the Cs cations and hence other exchangeable cations may be recessed into the 8-ring windows of the gmelinite cages. Earlier (*3*) it was concluded that the K ion in the specimen (*7*) could only be located near the windows of a gmelinite cage on account of spatial considerations. Complete blocking of all entrances to the gmelinite cages is not possible since each gmelinite cage has three windows and there is a maximum of 1.7 exchangeable cations available. The exchangeable cations are limited to about 1.7 ions per unit cell since initially 1 TMA ion is locked in the gmelinite cage (*2*, *7*) and approximately 1 K ion is nonexchangeably located in the cancrinite cage (*3*, *10*, *11*). Confirmation has been given to these observations in the present work. Thus even if K^+ migrated out of the cancrinite cages and other ions migrated into them under the high temperature conditions to which the sorbents had been subjected, there are still insufficient ions to seal gmelinite cages completely, unless the number of cations in 8-ring windows was to vary among cages.

(3) In offretites from which all the organic ions have been removed, the capacity in molecules per unit cell is always less for 2,2-DMB than for *n*-hexane. This difference may arise in part from the different relative pressures of 0.16 and 0.36 at which the capacities were measured. However, at 30°C the isotherms are expected to be very rectangular in shape so that

TABLE 5

Sorption Capacities at 30 °C in Molecules/Unit Cell of Outgassed Offretite for Water, *n*-Hexane, and 2,2-Dimethylbutane

Ion-enriched form	Cations per unit cell	Unit cell weight	H_2O (p/p_0 = 0.76)	Change in H_2O capacity when original cation is removed	*n*-Hexane (p/p_0 = 0.36)	Change in *n*-hexane capacity when original cation is removed	2,2-DMB (p/p_0 = 0.16)
Parent	3 K, 1.4 TMA	1290	7.6		0.93		
Parent (ign[a])	3 K, 1.4 H	1188	10.6	3.0	1.14	0.21	0.89
H	0.8 K, 1.8 H, 1.2 TMA	1195	8.3		1.02		
H (ign)	0.8 K, 3 H	1107	12.2	3.9	1.43	0.41	0.99
Li	1.6 K, 0.8 Li, 1.3 TMA	1240	9.7		0.91		
Li (ign)	1.6 K, 0.8 Li, 1.3 H	1146	12.8	3.1	1.31	0.40	0.98
Na	1.1 K, 1.2 Na, 1.3 TMA	1238	8.3		0.95		
Na (ign)	1.1 K, 1.2 Na, 1.3 H	1145	11.7	3.4	1.29	0.34	0.86
K	2.7 K, 1.1 TMA	1262	8.1		0.99		
K (ign)	2.7 K, 1.1 H	1179	10.8	2.7	1.27	0.28	0.70
Cs	1 K, 1.7 Cs, 1 TMA	1413	7.8		1.07		
Cs (ign)	1 K, 1.7 Cs, 1 H	1340	10.3	2.5	1.16	0.09	0.71
MA[b]	0.8 K, 2 MA, 1 TMA	1243	6.5		0.76		
MA (ign)	0.8 K, 3 H	1108	11.6	5.1			
DMA	0.8 K, 2 DMA, 1 TMA	1270	6.0		0.49		
DMA (ign)	0.8 K, 3 H	1108	12.0	6.0			
TriMA	0.8 K, 2 TriMA, 1 TMA	1299	6.7		0.47		
TriMA (ign)	0.8 K, 3 H	1108	11.6	4.9			
TMA	1.8 K, 2 TMA	1292	7.0		0.23		
TMA (ing)	1.8 K, 2 H	1146	12.4	5.4			

[a] ign = heated in air to remove organic material. Heating was normally in air at 490 °C for about 4 hr.

[b] The K contents of the samples containing MA, DMA, and TriMA were determined by difference, assuming 3.8 ions per unit cell.

this factor should not be important. It seems likely that the difference mainly reflects the inability of the 2,2-DMB to enter the gmelinite cages.

Relationships between Cation Size and Sorption Kinetics

The kinetics of uptake of *n*-hexane are shown in Fig. 4a in a number of ion exchanged forms of offretite. Only the curve for K,H-offretite is given for the sake of clarity as being a representative example for the following cationic forms: parent (after ignition), K,Li,TMA-, K,Li,H-, K,Na,TMA-, K,Na,H-, K,TMA-, and K,Cs,H-. The rate curves for all these forms show only minor differences from that for K,H-offretite which shows that *n*-hexane was sorbed very rapidly in all these forms. The rates of uptake were

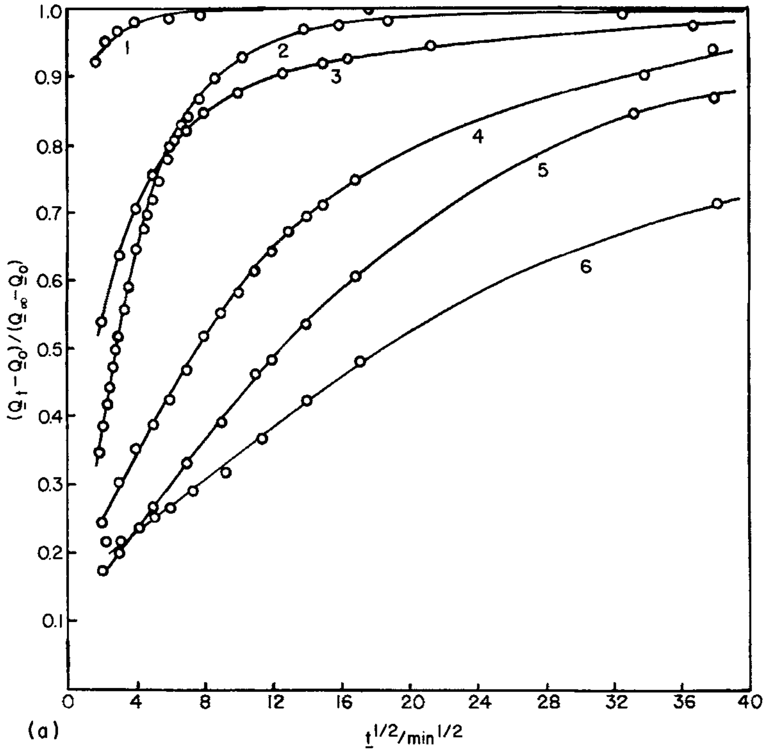

FIG. 4a. Plots of $(Q_t - Q_0)/(Q_\infty - Q_0)$ against $t^{\frac{1}{2}}/\mathrm{min}^{\frac{1}{2}}$ for the uptake of *n*-hexane by ion-exchanged offretite at 30 °C. Curves 1 to 6 are, respectively, for K,H-; K,NH_4,TMA-; K,Cs,TMA-; K,DMA,TMA-; K,MA,TMA-; and K,TriMA,TMA-offretites.

comparable but less rapid for K,NH_4,TMA- and K,Cs,TMA-offretites and still less rapid for offretites containing MA, DMA, and TriMA in the wide channels. The sorption of *n*-hexane in all the latter three forms is notable because, as already indicated, this molecule was excluded from offretite enriched in TMA. It is thought that with MA, DMA, and TriMA the ionic groups $-\overset{+}{N}H_3$, $-\overset{+}{N}H_2$, and $-\overset{+}{N}H$ may be recessed into the anionic 8-ring windows of the gmelinite cages (or possibly the 6 rings of cancrinite cages), thus drawing the methyl groups well to the side of the wide channel. In TMA, however, the nitrogen is surrounded by the four methyl groups so that no large part of this ion is recessed, and it effectively blocks the wide channels if present in sufficient numbers.

The rate sequence for *n*-hexane uptake was DMA > MA > TriMA

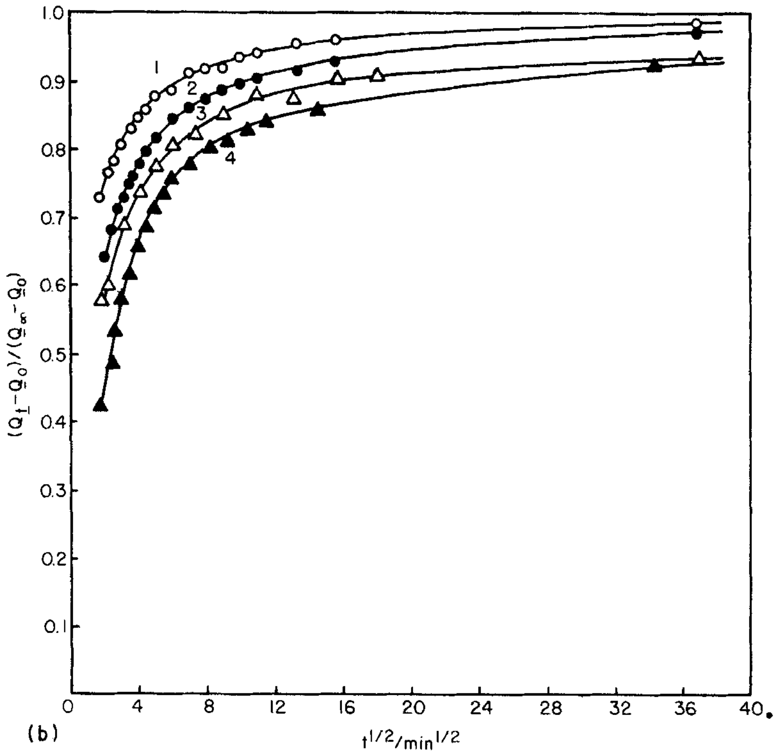

FIG. 4b. Plots of $(Q_t - Q_0)/(Q_\infty - Q_0)$ against $t^{1/2}/min^{1/2}$ for the uptake of 2,2-dimethylbutane at 30°C by ion-exchanged offretites. Curves 1 to 4 are, respectively, for K,Li,H-; K,Na,H-; K,H-; and K,Cs,H-forms.

(Fig. 4a) and requires explanation. It seems possible that the $\overset{+}{N}H_3CH_3$ ion with the ionic group recessed into 8- or 6-ring windows may be oriented vertically to the ring and may then protrude farther into the wide channel than $\overset{+}{N}H_2(CH_3)_2$. In the latter ion this orientation results in the two CH_3 groups leaning away from the vertical and from each other and so obtruding less far into the wide channel.

The kinetics of sorption of 2,2-DMB seemed more likely to differ among these offretites because of the closer fit between molecule and channel, and correspondingly the greater sensitivity to resistances due to ions protruding, for example, from positions in or near 8-ring windows into the channels. This is clearly demonstrated in the rate sequence of Fig. 4b. However, because K^+ ions from the cancrinite cages can mix, during heat treatment to remove TMA and also during outgassing, with the ions in the wide channels (*12*), the effects are probably less pronounced than they would be in the complete absence of the common ion, K^+.

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