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# Sorption Properties of Zeolite Rho

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Zeolite rho possesses an unusual combination of selectivity and activity for the synthesis of dimethylamine from ammonia and methanol. Sorption measurements were used to examine the synthesis of zeolite rho and how it evolves to become a superior catalyst, to distinguish various preparations, and to determine the effects of calcination under different conditions. A term "packing ratio" was defined as the ratio of adsorbed weights at equilibrium of different molecules for the same sorption volume and was shown to provide a measure of the steric constraints imposed on guest molecules by the host framework. Statistical analysis of the sorption data for many samples reveals that methanol fills the available framework volume and packs according to its liquid density. Because of this feature, methanol sorption provides a measure of the crystallinity of the rho framework. Larger molecules are constrained by the framework in the order: *n*-hexane > *n*-propanol > ethanol > methanol. Reproducible packing ratios, ethanol/methanol and *n*-propanol/ethanol, were determined for the rho framework. Rates of filling used in conjunction with the packing ratios show the presence of extra-lattice material and its proximity to the double 8-rings of rho.

## INTRODUCTION

Recent publications have described the acid-catalyzed reaction of methanol and ammonia by zeolites to selectively produce dimethylamine, DMA (*1–6*). It was shown that zeolites with medium or large pores produce nearly an equilibrium product distribution where trimethylamine, TMA, is the dominant species (*2*). A wide range of selectivities toward DMA were found for small-pore zeolites. Surprisingly, mineral chabazites provide a range of selectivities but they should have performed similarly, if not identically, as catalysts on the basis of various characterization techniques, other than adsorption. A study of the sorption of alcohols into mineral chabazites provided a rational basis for the observed differences in their catalytic selectivities (*3*).

Zeolite rho was found to provide very high selectivity to DMA as well as very high catalytic activity (*4*). This combination of selectivity and activity is unusual and permits the reaction to be run at 325°C instead of 400°C using conventional amorphous silica–alumina catalysts or the chabazites noted above. For this reason, we explored various aspects of the chemistry of zeolite rho to understand the basis of its selectivity and activity. For example, as previously described (*5*), calcination conditions affect the selectivity of a rho catalyst for several reasons:

- Deactivation of impurity phases (*6*): rho is a relatively stable zeolite in the acid form. Calcination of an ammoniated rho to produce the H-form under "severe" conditions, i.e., 600°C in the presence of steam, causes other less-stable impurity phases (zeolite or crystalline) to be converted to the relatively inactive amorphous forms. Thus, steaming generally lowers the catalytic activity somewhat by the destruction of the impurity phases but enhances the selectivity of the catalyst by destroying the nonselec-

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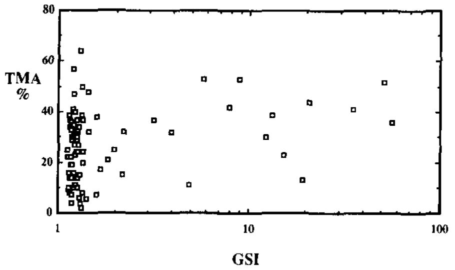

FIG. 1. Relationship of GSI to the yield of trimethylamine in the methylamines synthesis reaction from methanol and ammonia as catalyzed by zeolite rho; the TMA value is the percentage of the product stream at 90% methanol conversion.

tive impurity phases (i.e., rho is the only active component).

- High-temperature calcination causes some decomposition and dealumination of the rho framework. The resulting calcined materials are similar in selectivity but produce more dimethyl ether.
- Modification of acid site chemistry: calcination seems to reduce the number of very strong acid sites while increasing the population of somewhat weaker sites.

Previously (*3*), we described how sorption measurements of aliphatic alcohols were used to characterize zeolites used as catalysts in a novel process to preferentially synthesize dimethylamine, DMA, from ammonia and methanol. A Geometric Selectivity Index, GSI, was defined as the ratio of the sorbed amounts (at 20 h) of methanol to *n*-propanol. For chabazite minerals, GSI was shown to correspond to the selectivity of synthesizing DMA or inhibiting the synthesis of TMA. GSI measurements, however, do not correlate with product selectivity for the catalyst of choice, H-rho (*4*). Shown in Fig. 1 is the selectivity toward TMA as a function of the GSI measured for samples of zeolite rho.

Despite the detailed characterization efforts presented in our previous publications, we were left with a less-than-completely fulfilled mission. We did not achieve a satisfactory answer to the question: Why is rho such a selective catalyst? In the search for this answer, (*7*), we made extensive use of sorption measurements to examine the synthesis of zeolite rho and how it evolves to become a superior catalyst, and to distinguish various rho preparations and the effect of their treatment conditions. This paper summarizes those findings and demonstrates the utility of carefully performed sorption measurements in characterizing subtle differences in batch samples prepared and calcined under identical conditions.

## METHODS

The description and operating protocol for the apparatus used to gravimetrically measure sorption were described previously (*3*). Essentially, a zeolite sample is loaded into a preweighed cell employing a leak-tight vacuum stopcock. The sample is slowly heated to 425°C and kept there until the residual pressure is $<2 \times 10^{-5}$ Torr (1 Torr = 133.3 pa). The outgassed sample is then cooled and weighed. Subtraction of the cell weight provides the weight of dried sample. The cell is then attached to a chamber where the sample is exposed, at room temperature (20–25°C), to a solvent at a relative vapor pressure in the range 0.2–0.3. After some time, the cell is removed and weighed and the weight gain per 100 g of dry sample is recorded. Typically, sorption weights are recorded after 3 and 20 h of exposure to a solvent's vapor. When the sorption process was slow or if it was questionable that equilibrium was reached, the duration of exposure was increased until reproducible values were obtained. Equilibrium sorption measurements performed in this manner were reproducible to better than 1%. Unless specifically stated, all values reported in this manuscript are equilibrium sorption values.

Using surface areas obtained from mercury porosimetry, a correction is made for the amount adsorbed on the exterior surface of the particles to determine the amount sorbed into the framework (*3*). It is important to note that the same sample was used to sorb a variety of solvents to provide information on their packing density within the same framework volume (see "packing ratio" below). Generally, the same samples were used for a series of adsorption and desorption experiments. Sample weights were checked after heating under vacuum at 425°C and, if warranted, the samples were returned to the desorption rack for an oxygen treatment. The alcohols, methanol, ethanol, and *n*-propanol, were used for this study because they readily sorbed into the framework, desorbed cleanly upon calcination at 425°C in vacuum, and therefore permitted the same sample to be used for several measurements. Typically, the order of sorption experiments was: methanol (MeOH), ethanol (EtOH), *n*-propanol (*n*POH), *i*-propanol (*i*POH), hexane (*n*Hex), methanol, ethanol, *n*-propanol, etc. Virtually all of the data reported in this manuscript were from replicate runs agreeing within 1% of the reported values.

Na,Cs-Rho was prepared using AlOOH (Catapal SB), NaOH, CsOH, and Ludox LS-30 according to the method described by Robson *et al.* (*8*). Wet chemical analysis of the resultant batch preparations indicated a typical composition of $(NH_4)_{9.6}Cs_{1.0}Al_{10.5}Si_{37.5}O_{96}$ after ammonium exchange. Within analysis error, the $SiO_2/Al_2O_3$ ratios of all batches were identical (*5*). The particle size of all preparations was in the range from 0.4 to 0.6 μm. The $NH_4$-forms were calcined at conditions noted in the text to provide the different H–rho catalysts. Over 200 samples of zeolite rho (differing in preparation conditions, ion exchange, and calcination conditions) were examined in the course of this study.

## GEOMETRIC CONSIDERATIONS OF THE RHO FRAMEWORK

The structure of zeolite rho is illustrated in Fig. 2 and consists of a body-centered arrangement of α-cages (truncated cubooctahedrons) connected to each other via double 8-ring channels formed by the $TO_2$ ($T$ = Si, Al) groups. There are two independent networks such that there are two α-cages per unit cell, length $a \sim 15$ Å. Assuming that the structural $TO_2$ groups have the same volume as in quartz, some parameters concerning adsorption may be calculated:

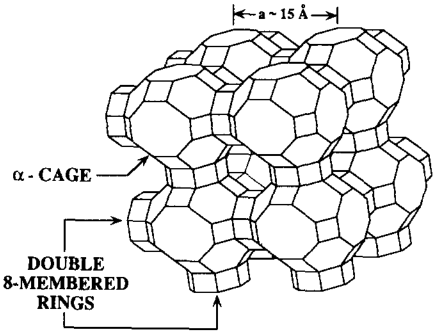

FIG. 2. The structure of zeolite rho showing the two independent networks formed by the body-centered arrangements of α-cages. The 6-ring windows of each α-cage are connected to the 6-rings of other cages thereby forming the double 8-rings shown in this schematic.

For a sample with only protons as the charge compensating cation, i.e., H–rho, the volume of a unit cell, uc, is $a^3$ or 3375 $Å^3$. Using the volume of the $TO_2$ group of quartz, ~38 $Å^3$, the solid's contribution is 1805 $Å^3$ per unit cell. The remaining volume, 3375–1805 = 1570 $Å^3$, is the unit cell pore volume such that the calculated void fraction, $V_f$, is 1570 ÷ 3375 = 0.465. The number of unit cells per gram is $6.023 \times 10^{23} \div$ MW, or $\sim 2 \times 10^{20}$. The calculated volume for 1 g is $\sim 2 \times 10^{20} \times 3375$ $Å^3 \times 10^{-24}$ $cm^3/Å^3$, or 0.701 cc, yielding a density of 1.427 g/cc. Thus, 1 g of H–rho occupies 0.701 cc and has a pore volume of 0.701 × 0.465 = 0.326 cc. Most of the H–rho samples contain varying amounts of residual cesium, typically ~1 Cs/uc; the calculated effect of cesium content on the sorption parameters is summarized in Table 1.

From equilibrium adsorption data, we can get some idea of how molecules pack into a zeolite framework. For example, if two substances pack into a zeolite according to their packing in the liquid state, then the ratio of their adsorbed weights must be

TABLE 1

Effect of Cs Content on Calculated Sorption Parameters; Typical Formula: $Cs^a\ Al_{10.5}Si_{37.5}O_{96}$

| Cs /uc | MW rho | cc/G[b] | Density (g/cc) | Voids/uc (Å/uc) | $V_f$ (voids/3375) | $V_p$ (cc/G) | MeOH (g/100 G)[c] |
|---|---|---|---|---|---|---|---|
| 0 | 2890 | 0.7007 | 1.427 | 1570.0 | 0.4652 | 0.3260 | 25.82 |
| 1 | 3022 | 0.6701 | 1.492 | 1550.5 | 0.4594 | 0.3078 | 24.38 |
| 2 | 3154 | 0.6420 | 1.558 | 1531.0 | 0.4536 | 0.2912 | 23.07 |
| 3 | 3286 | 0.6163 | 1.623 | 1511.5 | 0.4479 | 0.2760 | 21.86 |
| 4 | 3418 | 0.5925 | 1.688 | 1492.0 | 0.4421 | 0.2619 | 20.74 |
| 5 | 3550 | 0.5704 | 1.753 | 1472.5 | 0.4363 | 0.2489 | 19.71 |
| 6 | 3682 | 0.5500 | 1.818 | 1453.0 | 0.4305 | 0.2368 | 18.75 |
| 7 | 3814 | 0.5309 | 1.883 | 1433.5 | 0.4247 | 0.2255 | 17.86 |
| 8 | 3946 | 0.5132 | 1.949 | 1414.0 | 0.4190 | 0.2150 | 17.03 |
| 9 | 4078 | 0.4966 | 2.014 | 1394.5 | 0.4132 | 0.2052 | 16.25 |
| 10 | 4210 | 0.4810 | 2.079 | 1375.0 | 0.4074 | 0.1960 | 15.52 |

[a] Protons are assumed to make up the remainder of the charge-compensating ions, Cs/uc.

[b] Volume per gram of rho, cc/G = 3375 $Å^3$/uc × $10^{-24}$ cc/$Å^3$ × 6.023 × $10^{23}$ uc/mole ÷ MW (g/mole).

[c] Multiplication of $V_p$ by 0.792 g/cc, the density of liquid methanol at 25°C. Sorption values are expressed in g (grams of solvent)/100 G (grams of dried, evacuated sample).

equal to the ratio of their liquid densities. If $W_i$ equals the weight of a species adsorbed into a zeolite framework of pore volume $V_p$, then the density, $\rho_i$, of the adsorbed phase is

$$\rho_i = W_i/V_p.$$

For two different liquids sorbing into the same framework volume, the ratio of the sorbed weights at equilibrium is

$$W_1/W_2 = \rho_1 \times V_p/\rho_2 \times V_p = \rho_1/\rho_2.$$

Departure from the liquid density ratio for differently sized adsorbed molecules indicates that steric constraints are imposed. Because of the utility of this ratio, the term packing ratio is defined as the ratio of adsorbed weights at equilibrium of different molecules into the same framework volume.

## CHARACTERISTIC SORPTION VALUES FOR ZEOLITE RHO

In preparing a sample for sorption studies, the initial weight loss upon evacuation at 425°C is recorded as shown in Table 2; water desorption generally accounts for this loss. The samples had different degrees of crystallinity; hence, the different weight loss percentages. Water adsorption was very slow for every sample examined and the amount sorbed, even after prolonged exposure (1 month), did not equal the initial weight loss. Calcination of rho seems to make it somewhat hydrophobic. Methanol sorption was relatively rapid, however, and almost equilibrated within 3 h of exposure. Furthermore, the framework volume occupied by water (prior to activation) is virtually identical (within experimental error) to the volume filled by methanol assuming that both species pack according to their liquid densities.

Shown in Table 3 are the mean sorption values for 20 (of 200) samples of highly crystalline (via X-ray diffraction) H–rho with an average residual cesium content of ~1/uc. The sorption value for methanol, 24.0, corresponds to an accessible void volume of 0.303 cc/G assuming that methanol packs as a liquid with a density of 0.792 g/cc. Within experimental error, this is in excellent agreement with the sorption value of 24.38 g/100 G calculated in Table 1 for a sample with 1 Cs/uc. Thus, under the experimental conditions, methanol fills the available rho framework and packs according to its liquid

TABLE 2

Water and Methanol Sorption Data for Some Rho Samples[a]

| Form | Calc. cond.[b] | Fraction weight loss[a] | g sorbed/100 G dry sample | | | | $V_p$[c] (cc/g) |
|---|---|---|---|---|---|---|---|
| | | | Water | | | MeOH 20 h | |
| | | | 3 h | 66 h | 100 h | | |
| Ca,H | 425/Vac | 0.150 | 0.10 | 5.90 | | 9.71 | 0.123 |
| La,H | 425/Vac | 0.126 | 0.00 | 2.56 | | 11.07 | 0.140 |
| H | 725/Air | 0.174 | 2.59 | 12.14 | 12.49 | 14.12 | 0.178 |
| H | 600/Ar | 0.243 | 7.25 | 18.62 | 18.99 | 19.53 | 0.247 |
| H | 600/Air | 0.250 | 15.10 | 19.48 | 19.71 | 20.17 | 0.255 |
| H | 550/Air | 0.269 | 15.83 | 18.62 | 19.47 | 21.11 | 0.267 |
| Li,H | 425/Vac | 0.291 | 0.98 | 7.48 | | 22.42 | 0.283 |
| H | 550/Air | 0.314 | 4.47 | 21.99 | 22.02 | 24.58 | 0.310 |
| H | 500/Air | 0.300 | 11.61 | 23.81 | 23.86 | 24.72 | 0.312 |

[a] Dry sample weight basis, sample activated at 425°C and evacuated to $<2 \times 10^{-5}$ Torr.

[b] Calcination conditions, temperature °C, and atmosphere; time generally 10 h.

[c] Pore volume, $V_p$, calculated using a density of 0.792 g/cc for methanol.

TABLE 3

Characteristic Sorption Values for Zeolite H–Rho[a]

| | Methanol[b] MeOH | Ethanol[b] EtOH | | *n*-Propanol[b] *n*POH | | *n*-Hexane[b] *n*Hex | | *iso*-Propanol[b] *i*POH |
|---|---|---|---|---|---|---|---|---|
| Time, h | 20 | 3 | 20 | 3 | 20 | 3 | 20 | 20 |
| Mean | 24.00 | 21.31 | 22.15 | 19.93 | 20.80 | 9.34 | 10.85 | 0.89 |
| SD | 0.89 | 0.96 | 0.97 | 0.91 | 0.88 | 2.12 | 1.66 | 0.39 |

Packing and rate of filling ratios[c]

| | Packing ratios | | | Rate-of-filling Ratios | | | |
|---|---|---|---|---|---|---|---|
| | $\frac{\text{EtOH}}{\text{MeOH}}$ | $\frac{n\text{POH}}{\text{EtOH}}$ | $\frac{n\text{POH}}{\text{MeOH}}$ | MeOH 3/20 | EtOH 3/20 | *n*POH 3/20 | *n*Hex 3/20 |
| Mean | 0.923 | 0.939 | 0.867 | 0.986 | 0.962 | 0.958 | 0.861 |
| SD | 0.016 | 0.013 | 0.015 | 0.010 | 0.025 | 0.028 | 0.136 |
| Liquid Density Ratio | 0.996 | 1.019 | 1.015 | | | | |

*Note.* g sorbed/100 G dry sample (20 samples).[d]

[a] Average cesium content ~1/uc; typical formula: $Cs_1Al_{10.5}Si_{37.5}O_{96}$; the remainder of the charge compensating cations are protons.

[b] The specific solvent and its abbreviation used throughout this article.

[c] The packing ratio is defined as the ratio of equilibrium amounts of sorbed species and the rate-of-filling ratio is the ratio of amounts sorbed at 3 and 20 h.

[d] Unless stated otherwise, all sorption values have been corrected for solvent adsorbed on the external and nonzeolitic surfaces. Sorptions were performed at 20–25°C at a relative pressure of 0.2–0.3.

density. A 100% crystalline rho sample should adsorb an amount of methanol equivalent to its pore volume whose value depends on its Cs content as shown in Table 1. Lower values of methanol sorption indicate that the sample is <100% crystalline, a fraction of the framework is inaccessible, another phase may be present, or a combination of these possibilities. Thus, methanol adsorption provides a reasonable measure of the crystallinity of a rho sample.

The values in Table 3 represent the sorption properties that might be considered "typical" of a highly crystalline sample of zeolite rho and serve as a basis of comparison. As noted above, methanol sorption is virtually complete within 3 h of exposure; the rate-of-filling ratio, i.e., the ratio of the 3-h sorption value to the 20-h value, is ~99%. Solvents, such as ethanol and *n*-propanol, which are larger than methanol equilibrate somewhat slower as shown by their lower rate-of-filling ratios which suggests that the framework hinders their adsorption.

The packing ratios, EtOH/MeOH, *n*POH/EtOH, calculated from the sorption data are 92–94% of their respective liquid density ratios as shown in Table 3. As the guest molecules become larger, the packing ratio becomes smaller. The difference in measured vs calculated values (from liquid densities) of the packing ratios provides a measure of the constraint imposed on the ethanol and *n*-propanol molecules by the rho framework. A calculation of constraint imposed upon the guest molecules in the rho framework is shown as Table 4. The inability to assume all configurations of the liquid state is manifested by a packing ratio lower than that of the pure liquids or a higher constraint. As the molecular chain length increases, the packing ratio (compared to methanol) drops and the constraint on the sorbed species increases.

As noted above, methanol apparently fills the rho framework as a liquid; ethanol and larger-sized molecules are constrained depending on their size. The values of the packing ratios in Table 3 are reproducible and serve to characterize the rho framework. The packing ratios are not only sensitive to the framework geometry but herald the presence of materials within the framework, for example, extra-lattice alumina. This is an extremely important point and is demonstrated later in this article.

Over 200 samples of zeolite rho (differing in preparation conditions, ion exchange, and calcination conditions) were examined in this study. Interestingly, all of the samples with crystallinity >94% (based on methanol adsorption) were calcined at or below 550°C. In general, the higher the calcination temperature above 550°C, the lower the crystallinity of the product (*5*). A reduction in crystallinity accompanied the appearance of an amorphous background in the X-ray diffraction patterns of some samples (*6*). Table 5 illustrates the effect of calcination temperature on the same rho preparation. The sample calcined at 600°C has the maximum crystallinity (~90.4% according to the methanol sorption value) for this series as well as higher sorption values for the other solvents. Furthermore, the packing and rate-of-filling ratios for this sample are close to those of the typical rho preparation. Both the 500 and 700°C samples have different sorption profiles but for entirely different reasons. The sample calcined at 500°C has some residual ammonium within the framework (as shown by IR (*5*)) because the calcination period was not sufficiently long. The residual ammonium ion slightly reduces the packing ratio, EtOH/MeOH, while the *n*POH/EtOH ratio of 0.675 is significantly smaller than that of the typical rho. The large reduction in crystallinity imposed by calcination at 700°C is accompanied by significant framework dealumination resulting in the production of extra-lattice alumina (*5*). Again, the reduction in packing ratios provides vivid evidence for the presence of material inside the framework. The use of the packing ratio amplifies the effect of small changes in the volume available for adsorption because of significant changes on the

TABLE 4

Molecular Constraint of Packing in the Rho Framework

| Solvent | Amount sorbed (g/G) | Packing ratio vs MeOH | Liquid density (g/cc) | Liquid volume (cc/g) | Constraint[a] (%) |
|---|---|---|---|---|---|
| Methanol | 0.2400 | 1.000 | 0.792 | 0.3030 | 0 |
| Ethanol | 0.2215 | 0.923 | 0.789 | 0.2807 | 7.36 |
| *n*-Propanol | 0.2080 | 0.867 | 0.804 | 0.2587 | 14.62 |
| *n*-Hexane | 0.1085 | 0.452 | 0.659 | 0.1646 | 45.7 |

[a] Constraint is defined as the percentage difference in the volume accessible for methanol adsorption, $V_p$, vs the volume filled according to packing via liquid density, constraint = ($V_p$ − volume sorbed of solvent) ÷ $V_p$.

constraint imposed on the larger guest molecules. Furthermore, the lower rate-of-filling ratios indicate that migration into the framework is also inhibited and suggests that extra-lattice material is near the double 8-rings such that it impedes the sorption process.

## RHO PREPARATION SERIES

Sorption measurements were used to track the crystallization of a zeolite rho preparation. Using the same starting mixture at 100°C, samples were extracted at various times during the synthesis of zeolite rho. All of the samples have the same Si/Al ratio, were exchanged with $NH_4^+$, and calcined under the same conditions at 550°C. The development of crystallinity as a function of residence time at temperature is shown in Fig. 3. Samples with short residence times show no crystallinity and, at very long residence times, other phases appear. The precise moment to stop the reaction is not well defined; hence, there is considerable art involved in the synthesis of a zeolite. Analysis of these samples by sorption and catalysis (*9*) has provided some insights into the chemistry and reactivity of an alumino–silicate mix as it forms zeolite rho; the data are summarized in Tables 6a and 6b.

Samples with less than 32 h prep. time at 100°C are X-ray amorphous; however, as shown in Table 6a, they sorb a fair amount of alcohols (uncorrected sorption data). These samples were not catalytically inert but required a reactor temperature of 375°C to produce a 90% methanol conversion in the methylamines (*2*) synthesis reaction from methanol and ammonia. The products included both high dimethyl ether and the equilibrium methylamines product distribu-

TABLE 5

Effect of Calcination on Sorption Values

| Calc. temp. | g sorbed/100 G dry sample | | | | Packing ratios | | Rate-of-filling ratios | |
|---|---|---|---|---|---|---|---|---|
| | MeOH | EtOH | *n*POH | *n*Hex | EtOH/MeOH | *n*POH/EtOH | EtOH 3/20 | *n*POH 3/20 |
| 500°C | 20.20 | 18.18 | 12.27 | 4.77 | 0.900 | 0.675 | 0.97 | 0.58 |
| 600 | 21.13 | 19.51 | 17.95 | 9.58 | 0.923 | 0.920 | 0.88 | 0.71 |
| 700 | 12.66 | 9.16 | 1.99 | 0.37 | 0.723 | 0.218 | 0.81 | 0.44 |
| Typical | 24.00 | 22.15 | 20.80 | 10.85 | 0.923 | 0.939 | 0.96 | 0.96 |

*Note*. Preparation 3 calcined in a shallow bed for 4 h under flowing nitrogen.

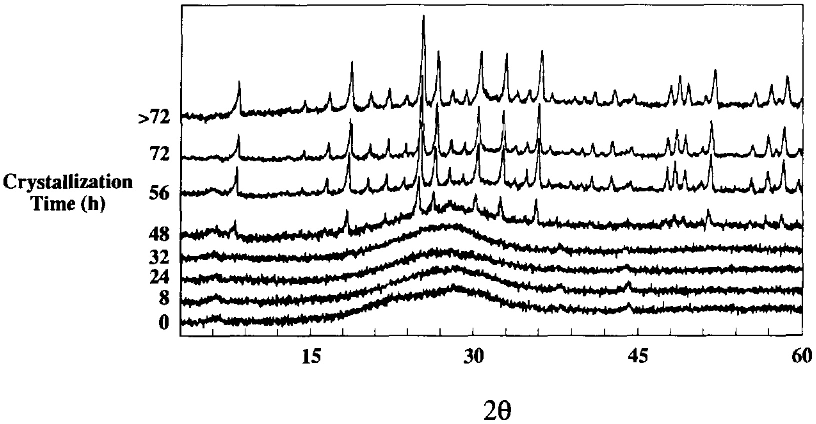

FIG. 3. X-ray diffraction patterns of samples after extraction at different times from the synthesis reactor (at 100°C), washing, $NH_4NO_3$ exchange, and calcination.

tion; that is, there was no selectivity toward mono- or dimethylamine vs trimethylamine. The sorption of methanol, *iso*-, and *n*-propanol are almost equal at 3–5% which suggests that these are high surface-area solids with no framework sorption; i.e., no zeolite is present. The ratio of methanol to *i*-propanol sorption is almost 1 while a value >20 is typical for highly crystalline rho preparations. The surface areas of these preparations were very high, >100 $m^2/g$, as calculated from mercury porosimetry measurements. For these samples, the amount adsorbed on the surface corresponds to the total amount sorbed such that sorption measurements also indicate the absence of a framework or zeolitic structure as shown in Table 6b.

Some zeolite rho is evident in the 48-h sample from the X-ray diffraction data. Sorption measurements, after correction for the amount adsorbed on the surface, indicate that the sample is ~20% crystalline. This amount of zeolite rho is sufficiently active to reduce the amines synthesis reactor temperature to 300°C to achieve 90% methanol conversion. The packing and rate-of-filling ratios for this sample are close to those of a typical rho sample even though the crystallinity is not well developed. This observation clearly demonstrates that these ratios are characteristic of the rho framework and independent of the crystallinity of the sample.

Interestingly, the most crystalline sample of this series at 72 h has some unusual sorption behavior as indicated by the *n*POH/EtOH packing ratio and the rate-of-filling ratio. The framework is fully developed as shown by the X-ray diffraction pattern and >23% methanol sorption. The slow diffusion of methanol, ethanol, and *n*-propanol suggest that the channels might be constricted or partially blocked. This point is examined later.

## DIFFERENTIATION OF RHO PREPARATIONS

Shown in Table 7 are the sorption data for H–rho samples from calcination of four different batches prepared under similar conditions. Sorption measurements of these preparations calcined at higher temperatures underscore the fact that thermal stability is batch dependent. The packing ratios for the 600°C calcined samples are similar and close to those for a typical rho sample showing that the frameworks available for adsorption of these preparations are well developed. For preparation 1, the amount of methanol adsorbed, packing ratio *n*POH/EtOH, and rate-of-filling

TABLE 6

Preparation of Zeolite Rho

6a. Uncorrected sorption data[a]

| Prep. time | g sorbed/100 G dry sample | | | | SA[b] (m$^2$/g) | Rx*n*[c] (*T*, °C) |
|---|---|---|---|---|---|---|
| | MeOH | EtOH | *n*POH | *i*POH | | |
| 0 h | 3.75 | 4.52 | 5.16 | 4.86 | 218 | 375 |
| 8 | 4.56 | 4.31 | 4.80 | 4.60 | 208 | 375 |
| 24 | 2.83 | 2.69 | 3.06 | 2.96 | 131 | 375 |
| 32 | 2.55 | 2.25 | 2.60 | 2.52 | 112 | 375 |
| 48 | 6.76 | 5.58 | 5.50 | 1.97 | 87 | 300 |
| 56 | 18.55 | 15.27 | 15.11 | 1.21 | 48 | 300 |
| 72 | 24.18 | 24.55 | 7.00 | 1.14 | 44 | 300 |

6b. Corrected sorption data[d]

| Prep. time | g sorbed/100 G dry sample | | | Xtal (%)[e] | Packing ratios | | Rate-of-filling ratios | | |
|---|---|---|---|---|---|---|---|---|---|
| | MeOH | EtOH | *n*POH | | EtOH/MeOH | *n*POH/EtOH | MeOH 3/20 | EtOH 3/20 | *n*POH 3/20 |
| 0 h | 0.00 | | | | | | | | |
| 8 | 0.00 | | | | | | | | |
| 24 | 0.00 | | | | | | | | |
| 32 | 0.11 | | | 0.5 | | | | | |
| 48 | 4.86 | 4.69 | 3.38 | 20.2 | 0.964 | 0.721 | 0.92 | 0.89 | 0.53 |
| 56 | 17.50 | 16.30 | 13.94 | 72.9 | 0.931 | 0.855 | 0.96 | 0.96 | 0.51 |
| 72 | 23.22 | 21.60 | 5.93 | 96.7 | 0.930 | 0.275 | 0.34 | 0.14 | 0.04 |
| Typical | 24.00 | 22.15 | 20.80 | | 0.923 | 0.939 | 0.99 | 0.96 | 0.96 |

[a] Total sorbed amounts: no correction for sorption on external surfaces.

[b] Surface areas, ±2 m$^2$/g, determined by adsorption and mercury porosimetry.

[c] Methylamines synthesis reaction from methanol and ammonia; temperature required to produce a 90% methanol conversion at the same feed rates.

[d] Total amount sorbed (Table 6a) minus the amount sorbed on external surfaces.

[e] Percentage crystallinity calculated on the basis of 0.2438 g/100 G of methanol being equivalent to 100% crystallinity.

ratios are lower than the expected norms and suggest that there is extra-lattice material within the structure lowering the equilibrium sorption values and the rates of sorption for the various solvents. Although preparation 1 has the lowest crystallinity (at 600°C) in comparison to preparations 2 and 3, it resists decomposition better than these preparations after calcination at 700°C. Preparation 1 shows a slight amount of decomposition upon heating from 600 to 700°C while the packing ratios remain unchanged. The rate-of-filling ratio for *n*POH has dropped further suggesting that something in the framework may have resited closer to the double 8-rings opening into the α-cages.

Although suffering >10% lattice decomposition at 700°C and ~20% at 800°C, preparation 2 shows no decrease in either the packing or rate-of-filling ratios. Apparently, there was no migration of the destroyed framework into the remaining zeolitic framework. Preparation 4 shows less than 10% decomposition after heating to 800°C and the decomposed phase, once more, did not migrate within the remaining framework as suggested by the similar values of the 600 and 800°C packing and rate-of-filling ratios. Preparation 3, however, not only shows a significant loss of crystallinity, ~40%, but also has large reductions in the packing and rate-of-filling ratios. This result suggests that some of the framework decomposition products migrate within the remaining framework reducing the volume of the $\alpha$-cages as well as siting near the double 8-rings. Apparently, the presence of small amounts of moisture during calcination facilitates migration of the decomposition products within the remaining framework. Thus, sorption measurements, combined with a controlled calcination process, are able to distinguish rho batch preparations on the basis of their crystallinity and their framework stability as well.

## EFFECT OF IONS ON SORPTION PROPERTIES

Shown in Table 8 is a comparison of the sorption properties of the same rho preparation with differing amounts of cesium as the charge compensating cation (protons composed the remainder). The decrease in methanol sorption with increasing cesium content follows the expected trend shown in Table 1. The presence of 2.67 Cs/uc strongly influences the packing and rate-of-filling ratios by virtually eliminating molecules larger than ethanol from entering the framework. For the 1.62 Cs/uc sample, the sorption of molecules the size of *n*-propanol and larger seems to be hindered and suggests that some cesium is in or near the double 8-rings. The packing and rate-of-filling ratios become independent of Cs content below ~1 Cs/uc.

Nonuniform distribution of ions can wreck havoc upon the interpretation of results as the data set at the bottom of the page clearly shows. The "control" was inadvertently washed with a small amount of solution containing cesium ions to produce the "after-contact" sample. The additional amount of cesium uptake was too small to be detected by conventional methods for bulk analysis but the effect on the rate of methanol sorption was significant and ethanol was virtually excluded from entering the framework. In effect, the cesium ion content of the surface layers of the rho crystallites was sufficiently high, ~4–6 Cs/uc, to prevent migration of molecules the size of ethanol and larger into the interior of the crystallites. A similar effect was observed for the 72-h sample of the preparation series noted in Table 6. Although the sample had an overall cesium content of 1.4 Cs/uc, the sorption results indicate an enrichment in the surface layers of the crystallites as evidenced by the low rates of filling ratios for all of the solvents. Subsequently, all ion-exchanged samples were calcined under modest thermal conditions to permit ions to resite homogeneously throughout the framework.

Shown in Table 9 are the sorption data for samples containing the ions noted. Arranging the data by increasing MeOH sorption also sorts the samples in terms of decreasing ion size. The same trend was observed by Barrer *et al.* for water contents of various cationic forms of rho *(10)*. They attributed this behavior to these factors: the cationic size and number (volume occupied) and the affinity (bonding) of water to the cations. The sorption data for Cs, Na, and Li show some effects of ion size. For example, the cesium ion virtually excludes molecules

| Sample ID | g sorbed/100 G dry sample | | | | Packing ratio | Rate-of-filling ratios | |
|---|---|---|---|---|---|---|---|
| | MeOH 3 h | MeOH 20 h | EtOH 3 h | EtOH 20 h | EtOH/MeOH | MeOH 3/20 | EtOH 3/20 |
| Control | 21.11 | 21.51 | 18.63 | 19.52 | 0.907 | 0.98 | 0.95 |
| After-contact | 8.40 | 18.68 | 1.10 | 1.19 | 0.064 | 0.45 | 0.92 |

TABLE 7

Comparison of Different Preparations

| Prep. | Calc. temp (°C)[a] | g sorbed/100 G sample | | | Packing ratios | | Rate-of-filling ratios | | Crystallinity[b] retention, % | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | MeOH | EtOH | nPOH | EtOH/MeOH | nPOH/EtOH | EtOH 3/20 | nPOH 3/20 | 700/600 | 800/600 |
| 1 | 600 | 19.37 | 18.35 | 15.67 | 0.947 | 0.854 | 0.89 | 0.54 | | |
| 1 | 700 | 18.62 | 17.71 | 15.36 | 0.951 | 0.867 | 0.88 | 0.31 | 96.1 | |
| 2 | 600 | 22.23 | 20.93 | 18.71 | 0.942 | 0.894 | 0.99 | 0.98 | | |
| 2 | 700 | 19.77 | 18.01 | 16.93 | 0.911 | 0.940 | 0.96 | 0.95 | 88.9 | |
| 2 | 800 | 17.64 | 15.76 | 15.25 | 0.894 | 0.968 | 0.95 | 0.94 | | 79.4 |
| 3 | 600 | 21.13 | 19.51 | 17.95 | 0.923 | 0.920 | 0.88 | 0.71 | | |
| 3 | 700[c] | 12.66 | 9.16 | 1.99 | 0.723 | 0.218 | 0.81 | 0.44 | 59.9 | |
| 4 | 600 | 20.85 | 19.95 | 17.10 | 0.957 | 0.857 | 0.96 | 0.97 | | |
| 4 | 800 | 19.11 | 17.35 | 15.32 | 0.908 | 0.883 | 0.94 | 0.94 | | 91.7 |
| Typical | | 24.00 | 22.15 | 20.80 | 0.923 | 0.939 | 0.96 | 0.96 | | |

[a] Except for the sample denoted by [c], all samples were calcined under dry flowing nitrogen for 4 h at the temperatures noted.

[b] Calculated from the ratio of methanol sorption values for the temperatures noted.

[c] Sample was calcined under flowing nitrogen (not dried) for 4 h.

larger than methanol, 3.7 Å, from entering the lattice while the sodium ion inhibits the sorption of molecules larger than ethanol, 4.0 Å. In order for the ions to exert such control on the sorption mechanism, they must be situated in or near the double 8-ring of rho as first suggested by Barrer *et al.* (*10*). Subsequent neutron diffraction studies have shown that these ions do indeed site in or near the double 8-rings. The 3/20-h sorption ratio of methanol and the packing ratio *n*POH/EtOH are lower than expected for the Li sample. Neutron diffraction studies show that the lithium ions are not situated near the double 8-ring but site at the 6-rings within the α-cage (*11*). The resulting framework is significantly distorted and has a small unit cell which would account for the lower packing ratio and the low rate-of-filling ratios.

TABLE 8

Effect of Cesium on Sorption Properties

| Cs/uc[a] | g sorbed/100 G sample | | | | Packing ratios | | Rate-of-filling ratios | | |
|---|---|---|---|---|---|---|---|---|---|
| | MeOH | EtOH | nPOH | nHex | EtOH/MeOH | nPOH/EtOH | MeOH 3/20 | EtOH 3/20 | nPOH 3/20 |
| 2.67 | 20.76 | 13.01 | 1.00 | 0.00 | 0.627 | 0.077 | 0.73 | 0.54 | 0.42 |
| 1.62 | 21.86 | 19.61 | 16.33 | 0.64 | 0.897 | 0.833 | 0.95 | 0.91 | 0.69 |
| 0.87 | 22.96 | 20.65 | 17.86 | 11.14 | 0.899 | 0.865 | 0.95 | 0.92 | 0.96 |
| 0.50 | 22.81 | 20.57 | 17.84 | 11.71 | 0.902 | 0.867 | 0.96 | 0.95 | 0.97 |
| Typical | 24.00 | 22.15 | 20.80 | 10.85 | 0.923 | 0.939 | 0.99 | 0.96 | 0.96 |

[a] Cesium ions per unit cell; the remainder of the charge compensating cations are protons.

TABLE 9

Effect of Charge Compensating Ions on Sorption

| Ion[a] | Radius (Å) | g sorbed/100 G sample | | | | Packing ratios | |
|---|---|---|---|---|---|---|---|
| | | MeOH 3 h | MeOH 20 h | EtOH 20 h | *n*POH 20 h | EtOH/MeOH | *n*POH/EtOH |
| Cs | 1.67 | 1.0 | 1.39 | 0 | | | |
| Na | 1.02 | 16.3 | 18.13 | 1.82 | | 0.1 | |
| Li | 0.76 | 10.0 | 21.33 | 19.52 | 2.75 | 0.915 | 0.14 |
| H (typical) | | 23.7 | 24.00 | 22.15 | 20.80 | 0.923 | 0.939 |

[a] At least six cations/uc, the remaining charge compensating cations are protons.

## CONCLUSIONS

Adsorption measurements for a variety of zeolite rho samples show that methanol equilibrates rapidly and fills the available framework volume according to its liquid density. Statistical analysis of the adsorption data for different rho preparations with a variety of calcination histories yields a mean value of 24.0 ± 0.9 g methanol adsorbed/100 G dry sample (cesium content ~1/uc). Within experimental error, this value corresponds to a 100% crystalline zeolite rho sample with complete framework accessibility. Sufficient data were collected to provide "expectation values" for the adsorption of simple alcohols characteristic of a highly crystalline sample of H–rho.

Packing ratio was defined as the ratio of adsorbed weights, at equilibrium, of different solvent molecules for the same sorption volume and was shown to provide a measure of the steric constraints imposed on guest molecules by the host framework. Packing ratios for the rho framework indicate the order of constraint: *n*POH > EtOH > MeOH as compared to packing in the liquid state. Packing ratio values were determined that are characteristic of the zeolite rho framework and independent of sample crystallinity. Packing ratios are very sensitive to the framework geometry and to materials within the framework, such as extra-lattice alumina and charge compensating cations. Sorption measurements show that different rho preparations behave differently under identical calcination conditions and provide a means for assessing those differences.

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## REFERENCES

1. Weigert, F. J., *J. Catal.* **103,** 20 (1987).
2. Keane, M., Sonnichsen, G. C., Abrams, L., Corbin, D. R., Gier, T. E., and Shannon, R. D., *Appl. Catal.* **32,** 361 (1987).
3. Abrams, L., Shannon, R. D., and Sonnichsen, G. C., U.S. Patent 4,737,592 (1988); Abrams, L., Keane, M., and Sonnichsen, G. C., *J. Catal.* **115,** 410 (1989).
4. Gier, T. E., Shannon, R. D., Sonnichsen, G. C., Corbin, D. R., and Keane, M., U.S. Patent 4,806,689 (1989); Gier, T. E., Shannon, R. D., and Sonnichsen, G. C., U.S. Patent 4,602,112 (1986).
5. Shannon, R. D., Keane, M., Abrams, L., Staley, R. H., Gier, T. E., Corbin, D. R., and Sonnichsen, G. C., *J. Catal.* **113,** 367 (1988).
6. Shannon, R. D., Keane, M., Abrams, L., Staley, R. H., Gier, T. E., Corbin, D. R., and Sonnichsen, G. C., *J. Catal.* **114,** 8 (1988).
7. Abrams, L., Corbin, D. R., and Keane, M., *J. Catal.,* **126,** 610 (1990).

*8.* Robson, H. E., Shoemaker, D. P., Ogilvie, R. A., and Manor, P. C., *in* "Molecular Sieves" (W. M. Meier and J. B. Uytterhoeven, Eds.). American Chemical Society, Washington, DC, 1973; *Adv. Chem. Ser.*, No. 121, 106.

*9.* Corbin, D. R., Abrams, L., and Keane, M., manuscript in preparation.

*10.* Barrer, R. M., Barri, S., and Klinowski, J., *in* "Proc. 5th Intl. Conf. Zeolites, Naples" (L. V. Rees, Ed.), p. 20. Heyden Publ., 1980.

*11.* Corbin, D. R., Abrams, L., Jones, G. A., Eddy, M. M., Harrison, W. T. A., Stucky, G. D., and Cox, D. E., *J. Amer. Chem. Soc.* **112,** 4821 (1990).