Catalysis Letters 5 (1990) 333–348

HIGH RESOLUTION, QUASI-EQUILIBRIUM SORPTION STUDIES OF MOLECULAR SIEVES

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Received 14 March 1990; accepted 21 May 1990

Quasi-equilibrium sorption studies of molecular sieves, high resolution sorption isotherms of molecular sieves

Argon, nitrogen, and neopentane adsorption isotherms from molecular sieves are recorded at 87 K, 77 K, and 273 K, respectively, by a quasi-equilibrium, high resolution gas sorption technique. The molecular sieves used in this study are alkali exchanged zeolite X, $AlPO_4$-11, $AlPO_4$-5, VPI-5, KL, CaA, ZSM-5, and ZSM-11. Little relation is observed between the transition pressure for microporous nitrogen adsorption and pore size. Small changes in the effective pore size resulting from variations in cation size are detected in the transition pressure for argon adsorption. Large shifts in the transition pressure for argon adsorption are found for the 10-, 12-, and 18-membered ring pores of $AlPO_4$-11, $AlPO_4$-5, and VPI-5, respectively. Argon adsorption combined with neopentane adsorption on microporous materials provides additional information regarding transitions in the isotherm that result from dual pore systems and effects that may be due to adsorbate packing. The step in the nitrogen isotherm at $P/P_0 > 0.1$ from ZSM-5 is not observed in the nitrogen isotherm from ZSM-11.

1. Introduction

The use of gas sorption for characterizing the properties of solid materials spans many decades. The determination of properties such as surface area, pore volume, and pore size have been the center of considerable attention and numerous techniques have been proposed for their elucidation, e.g., [1–6]. More recent is the development of high resolution adsorption (HRADS) which can generate high resolution isotherms over a wide range of pressures ($10^{-6} < P/P_0 < 1$). HRADS appears very promising in its application towards the study of molecular sieves [7–9] which possess pore sizes of less than approximately 20 Å. It is in the micropore region (< 20 Å as defined by IUPAC) that surface curvature effects from the pore wall become increasingly important. As the pore

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size reaches atomic dimensions, the number of surface atoms interacting directly with the adsorbate atom is increased and thus generates an enhanced energy of adsorption. This enhanced adsorption energy has been suggested to result from an overlapping of adsorption fields due to the close proximity of the adsorbent atoms with one another [10]. Derouane et al. [11] have described this enhanced interaction for zeolites by a simple van der Waals model. This model predicts that when a curved surface or pore reaches the dimensions of the adsorbate, the energy of attraction is increased by a factor of 8. Moreover, the pressure required for microporous adsorption (otherwise known as the transition pressure for microporous adsorption) decreases as the pore size reaches atomic dimensions (*vide infra*). This relationship between pressure and pore size does not lend itself to all adsorbates [7], but it does appear to work well for molecules which do not possess dipole or quadrupole moments. Therefore, HRADS should provide a viable technique to investigate how systematic changes in surface curvature, i.e., pore size, influences the transition pressure for microporous gas adsorption.

The use of quasi-equilibrium HRADS involves the construction of the HRADS isotherm via a "continuous" procedure that obtains sorption data at quasi-equilibrium conditions [8]. One advantage of quasi-equilibrium HRADS is that the adsorbate is introduced into the sample chamber at a fixed flow rate thus reducing the long experimental time required by static HRADS. One disadvantage in quasi-equilibrium HRADS is that unlike static HRADS true equilibrium is only approximated. However, Rouquerol et al. [8] have proposed a method for establishing confidence levels in the isotherms generated by quasi-equilibrium sorption. This method has been applied here (*vide infra*).

The goal of this study is to explore the feasibility of using quasi-equilibrium HRADS to quickly characterize microporous solids. Here, we present sorption data from molecular sieves with known structure in order to test the limits of this technique.

2. Experimental

ADSORBENTS

The synthesis of NaX and exchange procedure with the group 1A metal hydroxides have been described earlier along with resulting chemical compositions, pore volumes, and BET surface areas [12].

$AlPO_4$-11 and $AlPO_4$-5 were synthesized by the procedures outlined in Example 32 and 3 respectively, in the Union Carbide patent [13]. $AlPO_4$-11 and $AlPO_4$-5 were then calcined in air at 600 °C to remove the organic template prior to sorption. The synthesis of VPI-5 and activation prior to sorption have been described earlier [14,15]. The topological properties (e.g., pore size, framework densities, etc.) and adsorption capacities (both experimental and calculated) of

$AlPO_4$-11, $AlPO_4$-5, and VPI-5 have been given earlier [15]. However, a figure concerning their topology will be provided below.

Silicon ZSM-5 was synthesized using procedures outlined by Fegan and Lowe [16]. Silicon ZSM-11 was synthesized using the gel composition: 5.75 TBA · 2.8 Na_2O · SiO_2 · 880 H_2O where TBA denotes tetrabutylammonium hydroxide (from 55 wt% aqueous solution) and Na_2O is from NaOH. The gel was heated at autogenous pressure for 24 hours at 150 °C after aging at ambient conditions for 24 hours. Both silicates were prepared with no added alumina in the synthesis gel and calcined at 600 °C to remove the organic template prior to sorption.

KL (#Lot 13443-32) was obtained from Union Carbide. CaA was purchased from Aldrich (#Lot 01122DV).

All materials were characterized by X-ray powder diffraction and were found to contain no other crystalline phases. From the low background intensity, significant amounts of amorphous material are not present. Also, argon adsorption capacities are within experimental error of those expected from each molecular sieve in its pure form.

ADSORBATES

Nitrogen and argon were purchased from AIRCO at > 99% purity. Neopentane (2,2-dimethylpropane) was purchased from Wiley Chemicals at > 99% purity.

ANALYSIS

Elemental analysis of the group 1A metal hydroxide-exchanged NaX zeolites was performed by Galbraith Laboratories, Inc. (Knoxville, TN). A Siemens I2 X-ray diffractometer was used to collect X-ray powder diffraction data with Cu Kα radiation. All sorption data were obtained using an Omnisorp 100 analyzer [7] purchased from Omicron Technology.

3. Procedure

Sorption was carried out by a quasi-equilibrium, volumetric technique which has been described in greater detail elsewhere [7,8]. However, a brief description is given to familiarize the reader.

The sample is first outgassed *in vacuo* to 350 °C in a calcination furnace to remove water of hydration. The sample is then transferred under vacuum to a constant temperature bath for sorption studies. With a mass flow controller, helium or adsorbate is fed into the sample chamber at known flow rates (here helium is used to establish the volume of the sample chamber and assumed to have a relatively low affinity for adsorption at the temperatures used for sorption, i.e., at or greater than 77 K). Once the volume of the sample chamber has been determined via He capacity, the sample chamber is evacuated and the adsorbate

is introduced into the sample chamber at a known flow rate. Under quasi-equilibrium conditions the adsorbate is introduced into the sample chamber at a predetermined flow rate (*vide infra*) so that disruption in adsorption/desorption equilibrium is minimized. Thus, by monitoring the chamber pressure as a function of time the isotherm can be generated. Data acquisition is started at $P/P_0 \simeq 10^{-6}$ and is ended as high as 0.9. Here, nearly all isotherms presented have been recorded to a maximum of 300 Torr. Isothermal sorptions of nitrogen, argon and neopentane have been obtained at 77 K, 87 K, and 273 K, respectively. Argon isotherms have been recorded at 77 K also. All of the isotherms obtained in this study are of Type I. However, since it is our interest to analyze the adsorption behavior in the microporous region, i.e., P/P_0 below approximately 10^{-2}, the isotherms are given as the semi-Log of P/P_0 versus the normalized uptake W/W_0 so that the microporous sorption is more readily displayed. W_0 represents the total uptake.

QUASI-EQUILIBRIUM

It has been suggested by Rouquerol et al. [8] that the onset of quasi-equilibrium conditions (no appreciable difference between the isotherm generated by quasi-equilibrium and static conditions) can be tested for by varying the ratio of the weight of the adsorbent to the flow rate of the adsorbate (W/F). Ideally, the higher this ratio the less equilibrium is disturbed. However, the time required to generate the complete isotherm increases with lowering the adsorbate flow rate. Figure 1 illustrates the influence of W/F on the argon isotherm of $AlPO_4$-11. Assuming that diffusional resistance plays the dominant role in establishing adsorption/desorption equilibrium, it is necessary to choose an adsorbent which offers a limiting case for this study. $AlPO_4$-11 is chosen because it possesses two excellent properties for diffusional resistance: (i) a unidimensional pore structure and (ii) a slightly elliptical 10-membered ring pore (*vide infra*) which is slightly larger than the kinetic diameter of 3.5 Å and 3.8 Å reported for argon and nitrogen, respectively [17]. Note that in this experiment the amount of adsorbent ($AlPO_4$-11) was held constant at 110 mg while the flow rate of the adsorbate (argon) introduced into the sample chamber was systematically increased from 0.11 CC STP/min to 0.34 CC STP/min.

As shown in fig. 1, W/F ratios above 0.48 g · min · CC STP^{-1} show no appreciable variation in the transition pressure for microporous adsorption (defined here as the initial inflection point (second derivative equals zero) of the isotherm occurring at $P/P_0 \simeq 2 \times 10^{-5}$). At a W/F of 0.32 g · min · CC STP^{-1} the isotherm is shifted towards higher P/P_0 indicating that quasi-equilibrium has not been established. Listed in table 1 are the run times required to reach 20 Torr of argon in the experiments used to generate fig. 1. Note that it is our desire to develop a quick characterization technique but yet allow for near equilibrium to be established. Therefore, based upon the data given in table 1, the W/F ratios

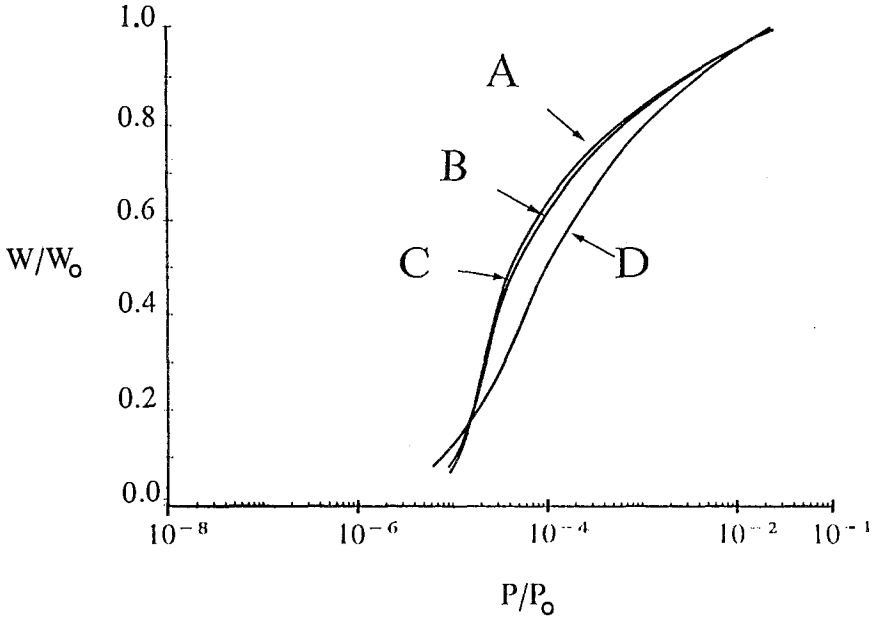

Fig. 1. Influence of argon flow rate on quasi-equilibrium for $AlPO_4$-11. (A) $W/F = 1.0$ g·min·CC STP^{-1}, (B) $W/F = 0.65$ g·min·CC STP^{-1}, (C) $W/F = 0.48$ g·min·CC STP^{-1}, (D) $W/F = 0.32$ g·min·CC STP^{-1}. Recorded at 87 K.

used for argon and nitrogen in this study were typically fixed between 0.50 and 0.70 g · min · CC STP^{-1}.

On the same sample of NaX, quasi-equilibrium (flow) and equilibrium (static) argon adsorption isotherms at 87 K were obtained. The isotherms were the same while the data collection time for the static isotherm was approximately ten times longer than that at quasi-equilibrium conditions. Finally, the N_2 adsorption isotherms at 77 K for VPI-5 collected at flowing (Omnisorp) and static (on a separate instrument) [19] conditions were within experimental error of one another. These data are consistent with those in fig. 1 which show that quasi-equilibrium can be established.

Table 1
Experimental times required to reach 20 Torr of argon

Experiment	*W/F	Time (min)
A	1.0	66.7
B	0.65	43.4
C	0.48	32.6
D	0.32	21.6

* g·min·CC STP^{-1}.

Table 2
Pore volume of NaX

Adsorbate	Source	Temp (K)	Pressure (Torr)	Pore volume (cc liq./g)
Nitrogen	ref. [18]	77	700	0.32
	This work	77	300	0.33
Argon	ref. [18]	90	700	0.29
	This work	87	300	0.29
Neopentane	ref. [18]	298	50	0.23
	This work	298	50	0.21

Ref. [18]: Si/Al ~ 1.25.
This work: Si/Al ~ 1.34.

PORE VOLUME

After determining the W/F limits for quasi-equilibrium conditions, the pore volume of NaX was ascertained from the quasi-equilibrium isotherm to ensure that it was within the known range for the adsorbates used here. Given in table 2 are the pore volumes of NaX (cc liq./g) as determined by quasi-equilibrium sorption for nitrogen, argon, and neopentane at 77 K, 87 K, and 298 K, respectively. Listed also are the pore volumes of NaX reported from other laboratories [18]. For all three adsorbates, the pore volumes determined by quasi-equilibrium sorption are within experimental error of the reported values. Thus, the system was sufficiently calibrated to begin our studies.

4. Results and discussion

INFLUENCE OF THE ADSORBATE

Nitrogen and argon were used as adsorbates to determine the sensitivity of their transition pressure to small changes in pore size. The adsorbent chosen was NaX exchanged with the group 1A metal cations. By increasing the ionic radius of the balancing cation the effective pore size should, in principle, be slightly lowered in the direction of Li^+ to Cs^+. In light of the arguments presented in the Introduction above, this decrease in the effective pore size should shift the transition pressure for microporous adsorption, i.e., the initial inflection point of the isotherm should shift to lower P/P_0 when going from Li^+ to Cs^+. As illustrated in fig. 2A, no distinguishable difference occurs in the transition pressures for nitrogen adsorption. This result is consistent with those reported by Venero and Chiou [7] who found no relationship between pore size and transition pressure for microporous nitrogen adsorption. The inability of nitrogen to distinguish subtle changes in pore size may result from a preferential adsorption on the zeolite surface generated by surface-quadrupole interactions. For argon

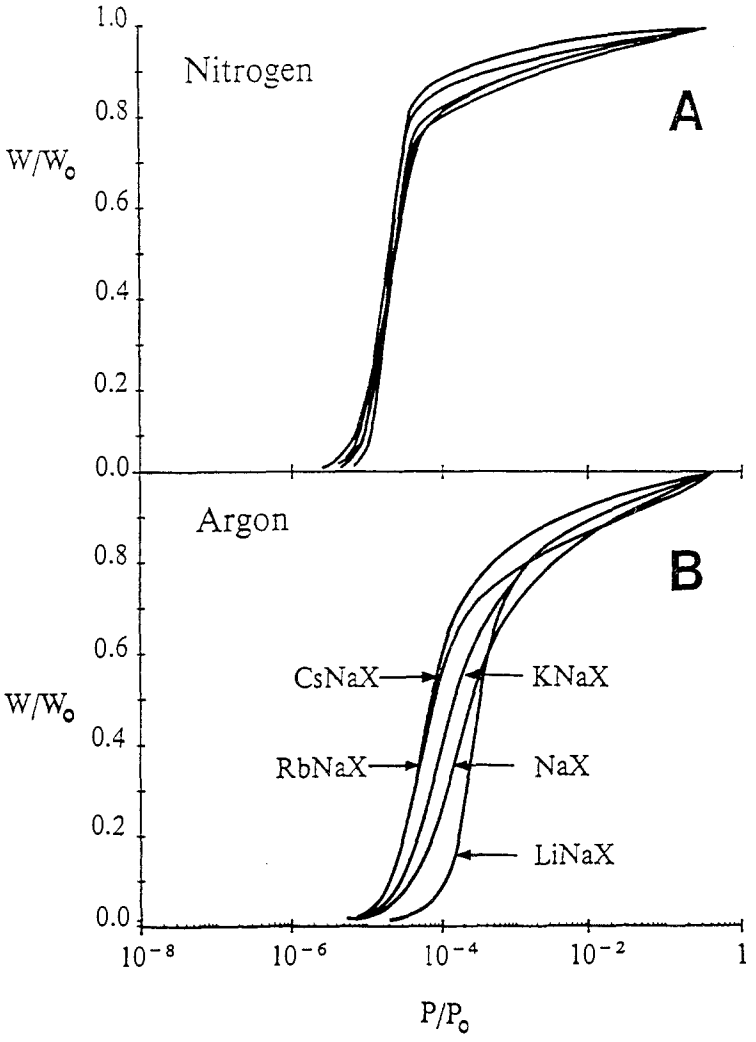

Fig. 2. Influence of effective pore size of alkali exchanged, zeolite X on transition pressure for microporous adsorption. (A) Nitrogen isotherms recorded at 77 K and (B) Argon isotherms recorded at 87 K.

adsorption (fig. 2B), the expected shift in transition pressure when going from Li^+ to Cs^+ is observed. Interestingly, little difference is observed in the transition pressure between RbNaX and CsNaX and may indicate equivalence in pore size. The similarity in isotherms between RbNaX and CsNaX may be due to the fact that the level of Cs exchange is less than that for Rb [12].

It may be argued that the observed shift in the transition pressure for argon adsorption is not influenced by pore size but by surface composition. However, one might expect the cation-adsorbate interaction energy of lithium-argon to be higher than that of cesium-argon [18]. If this were the case, then LiNaX should

give the lowest transition pressure for adsorption. Thus, we conclude that the argon transition pressure is sensitive to small changes in pore size while the nitrogen transition is not. This may be due to that fact that nitrogen possesses a quadrupole moment [7].

The data in fig. 2 also show that the slope of the argon adsorption isotherm is larger for LiNaX than for the other alkali-zeolites. This may indicate a stronger cation-argon interaction for Li. If such is the case, the strength of the cation-argon interactions is only a "second-order" effect since it is not sufficient to destroy the relationship between the pore size and the transition pressure for microporous Ar adsorption (as is the case with N_2).

INFLUENCE OF THE ADSORBENT

From the results shown in fig. 2, argon was chosen to determine the influence of pore size on the transition pressure for microporous adsorption. Figure 3 illustrates the framework [100] projection of $AlPO_4$-11 and the framework [001] projections of $AlPO_4$-5 and VPI-5. These aluminophosphates are similar in that they possess a unidimensional pore structure and because the frameworks are neutral they contain no balancing cations. Moreover, the samples used here were well characterized [15]. Thus, the sorption isotherms from these materials were used to establish the relationship between the pore size and the transition pressure for microporous, argon adsorption. Shown in fig. 4B are the argon isotherm from $AlPO_4$-11, $AlPO_4$-5, and VPI-5 measured at 87 K. The change in pore size is reflected by the shift in transition pressure for argon adsorption. Interestingly, for VPI-5 a second transition is observed at $P/P_0 \simeq 2 \times 10^{-2}$. Because the pores of VPI-5 (~ 12.5 Å) can accommodate argon adsorption above

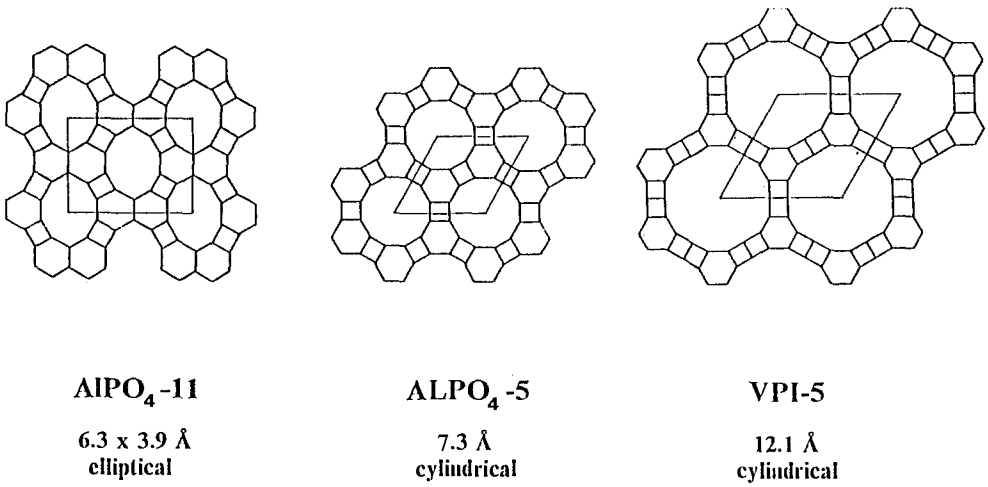

Fig. 3. Framework [100] projection of $AlPO_4$-11 and framework [001] projections of $AlPO_4$-5 and VPI-5.

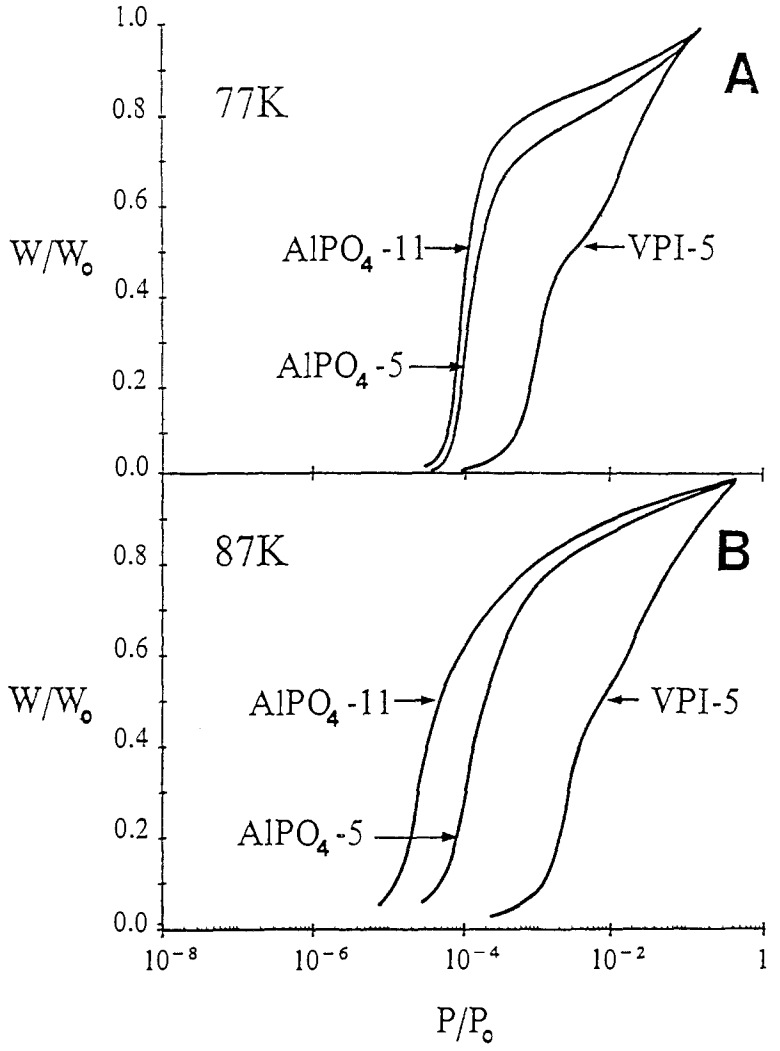

Fig. 4. Influence of pore size on transition pressure for argon adsorption. (A) 77 K and (B) 87 K.

monolayer coverage it is speculated that this second transition may result from adsorbate/adsorbate interactions, i.e., molecular packing (*vide infra*).

Argon adsorption at 77 K was performed also on $AlPO_4$-11, $AlPO_4$-5, and VPI-5. As illustrated in fig. 4A, the change in pore size is reflected by the shift in the transition pressure. However, the separation in transition pressures is not as large as that observed at 87 K. Thus, small changes in pore size will probably not be recognizable at 77 K.

If the sorption of argon onto the aluminophosphate molecular sieves followed the ideal behavior for physical adsorption then figs. 4A and 4B should be identical. Since they are not, the sorption deviates from ideal. The deviation from ideal behavior is not surprising and has been observed on ZSM-5 with N_2 [20].

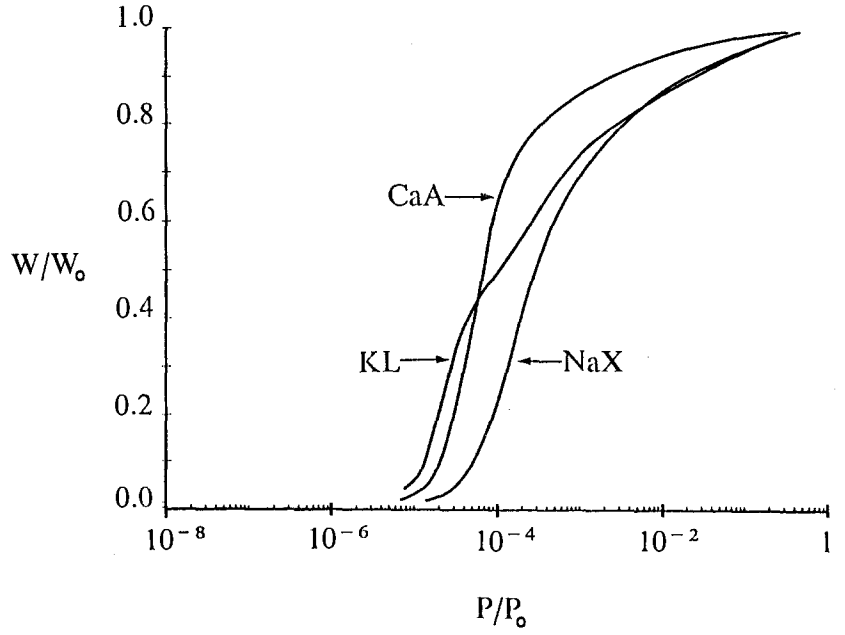

Fig. 5. Influence of a bimodal pore distribution on the argon isotherm. Recorded at 87 K.

INFLUENCE OF DUAL PORE SYSTEMS

KL, CaA, and NaX were used to investigate how sieves which possess pores of more than one size influence the argon isotherm. CaA and NaX have only 8- and 12-membered ring pores, respectively. KL, however, possesses both 8- and 12-membered ring pores. Figure 5 shows the argon isotherms from KL, CaA, and NaX. The first transition for argon adsorption on KL is consistent with the interaction of argon with an 8-membered ring (see isotherm from CaA). Interestingly, a second transition is observed on KL and is consistent with the interaction of argon with a 12-membered ring (see isotherm from NaX). This result suggests that sieves with two pore sizes can show two transition pressures in the argon isotherm. Note that the first transition pressure for KL is shifted slightly below that observed for CaA. This may be due to the fact that the 8-membered ring pores found in KL are elliptical resulting in perhaps a greater adsorbate/adsorbent interaction than that found from the circular 8-membered ring pores of CaA.

NEOPENTANE ADSORPTION

Neopentane isotherms from NaX (fig. 6B) and VPI-5 (fig. 6C) show that the transition pressure increases with increasing pore size in a manner similar to that observed with the argon isotherms. This suggests that information concerning pore size can be obtained also from neopentane isotherms. Moreover, neopentane is considerably larger than argon with a kinetic diameter of approximately 6.2 Å

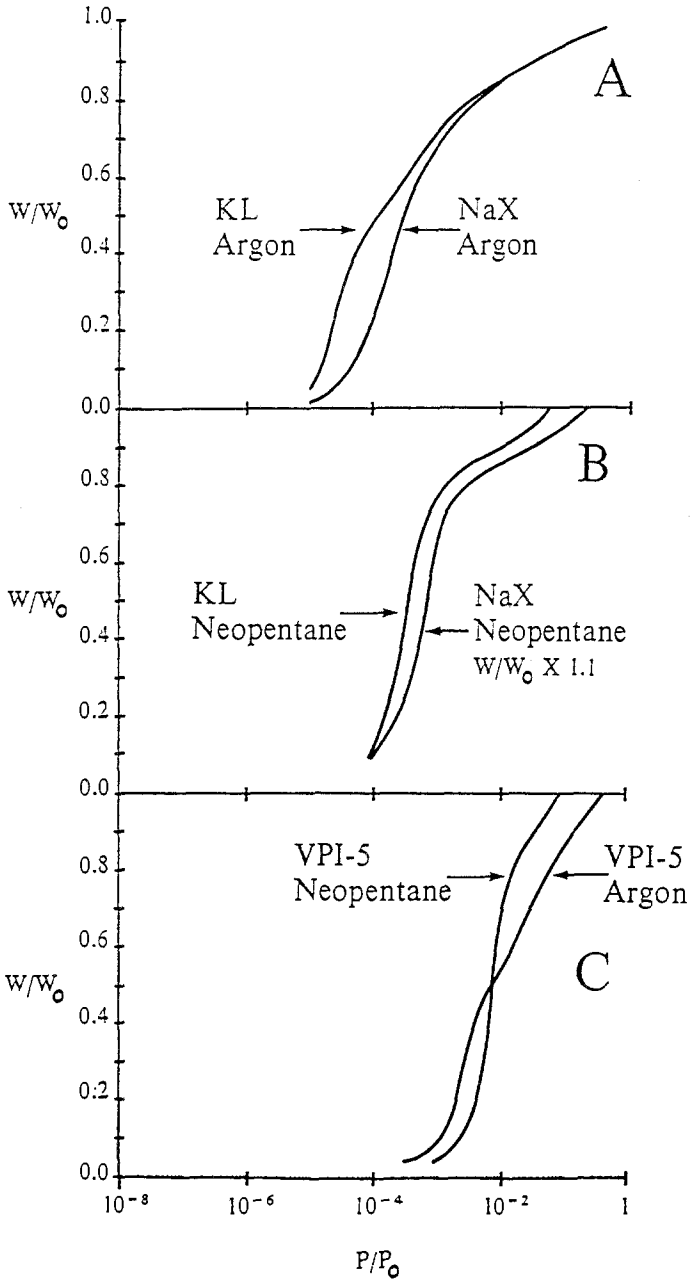

Fig. 6. Neopentane adsorption. Recorded at 273 K and 87 K for neopentane and argon, respectively.

[18]. Therefore, by combining the results obtained from argon sorption with those observed from neopentane sorption, more information concerning sieve topology or pore size/pore size distribution can be obtained. Consider KL as an example.

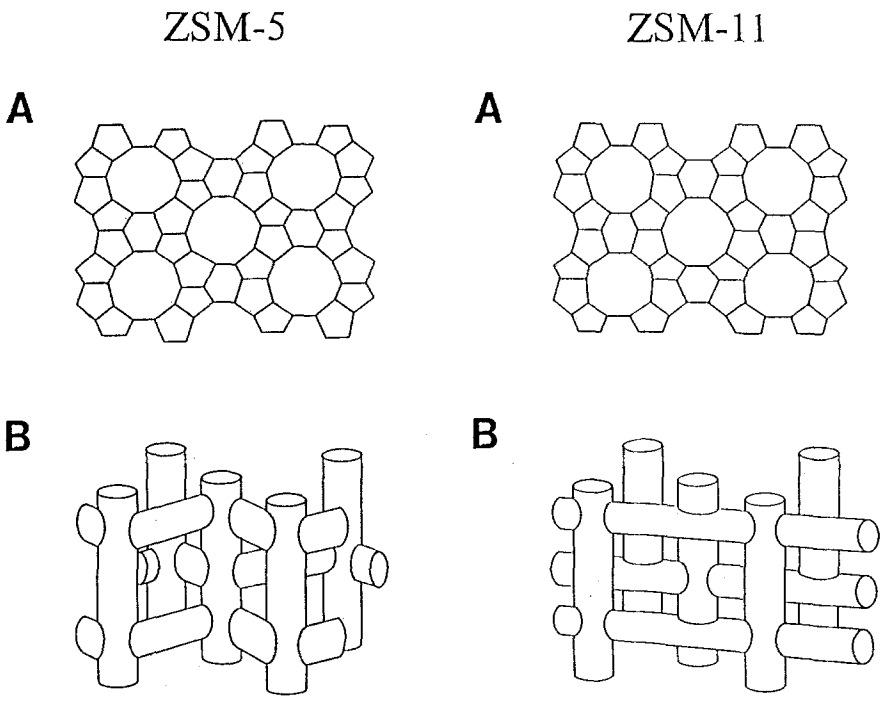

Fig. 7. Topology of ZSM-5 and ZSM-11. (A) Framework [010] and [100] projections of ZSM-5 and ZSM-11, respectively, and (B) Idealized framework channel structure.

Since the first transition in the argon isotherm of KL results from the interaction of argon with the 8-membered ring, then the neopentane isotherm should show only one transition pressure from the 12-membered ring due to neopentane's inability to penetrate an 8-membered ring. Figure 6A and B show the argon and neopentane isotherms, respectively, from KL and NaX. Note that the first transition pressure observe for argon adsorption on KL (fig. 6A) does not appear on the neopentane isotherm of KL (fig. 7B). Thus, the combination of argon and neopentane adsorption isotherms can distinguish the presence of dual pore system. Although we illustrate a 8–12 dual pore system, the technique is also applicable to a 10–12 dual pore system since neopentane adsorbs into 12-membered ring pores only.

Consider the argon isotherm recorded from VPI-5 (fig. 4B). The isotherm reveals a second transition pressure at $P/P_0 \simeq 2 \times 10^{-2}$. We attribute this second transition to molecular packing within the extra-large pores of VPI-5. Adsorption of the larger neopentane molecule will not allow for this type of molecular packing and thus should not reveal a second transition in the adsorption isotherm. Figure 6C illustrates the argon and neopentane isotherms recorded from VPI-5. Note that the second transition observed in the argon adsorption isotherm does not occur for neopentane adsorption.

NITROGEN SORPTION

Unlike most microporous materials, nitrogen and argon sorption on ZSM-5 does not result in a Langmuir-type isotherm but rather in a step like isotherm [9,20,21]. Work by Muller et al. [9] using HRADS coupled with microcalorimetry revealed several steps in both the argon and nitrogen isotherms of ZSM-5 and were found to occur at 20, 22, and 24 molecules/unit cell (standard deviation of 0.8 molecules/unit cell). From atom-atom approximation (AAP) and independent model building, 24 minima in the potential energy were calculated to exist in the unit cell of ZSM-5 and are associated with complete filling of pores and intersections [9]. This number agrees well with their experimental value of 24 molecules/unit cell determined from the argon and nitrogen isotherms. Unlike argon, however, a large step occurs in the nitrogen isotherm at P/P_0 between 0.15 and 0.18 and calculates to an increase from 24 to 30.5 molecules/unit cell [9]. This large step in the nitrogen isotherm has been suggested by Muller et al. [9] to result from the transition of a fluid-like phase (24 molecules/unit cell) to a more dense solid-like phase (30.5 molec/unit cell). Furthermore, the sharpness of this step has been shown to depend on the Si/Al ratio, balancing cation, and sorption temperature [20].

Because of the high degree of similarity between ZSM-5 and ZSM-11 it was of interest to determine whether a step in the nitrogen isotherm occurs from ZSM-11. As illustrated in fig. 7A, the framework [010] and [100] projections of ZSM-5 and ZSM-11, respectively, are very similar. Furthermore, the ZSM-11 and ZSM-5 framework channel structures both possess two intersecting channel systems with 10-membered ring pores (fig. 7B). However, in place of the zigzag channels of ZSM-5, straight channels are found for ZSM-11. Figure 8 shows the nitrogen isotherms recorded from ZSM-5 and ZSM-11. For ZSM-5, an uptake of 25 molecules/unit cell was calculated (from the Langmuir equation) and is in good agreement with the 24 molecules/unit cell ± 0.8 molecules/unit cell calculated by Muller et al. [9]. Observed also is the large step in the isotherm occurring at $P/P_0 \simeq 0.15$. A final uptake of 31 molecules/unit cell was calculated from the data given in fig. 8 and is in excellent agreement with the 30.5 molecules/unit cell calculated by Muller et al. [9].

Shown also in fig. 8 is the nitrogen isotherm of ZSM-11. As expected, an uptake of 25 molecules/unit cell is obtained for ZSM-11 and corresponds well with the pore and intersection filling proposed for ZSM-5. However, unlike ZSM-5 no further increase in adsorption is observed. The step in the nitrogen isotherm from ZSM-5 is suggested to be related also to the adsorption pressure [20]. Therefore, it was necessary to determine whether a step in the nitrogen would occur for ZSM-11 at perhaps higher pressures. If the sorption is carried out to 650 Torr (fig. 8 inlay), no further uptake is observed for ZSM-11. Since it has recently been shown that ZSM-5 and ZSM-11 both reveal framework flexibility [22], this transition cannot be the cause of the sorption behavior. Thus, the

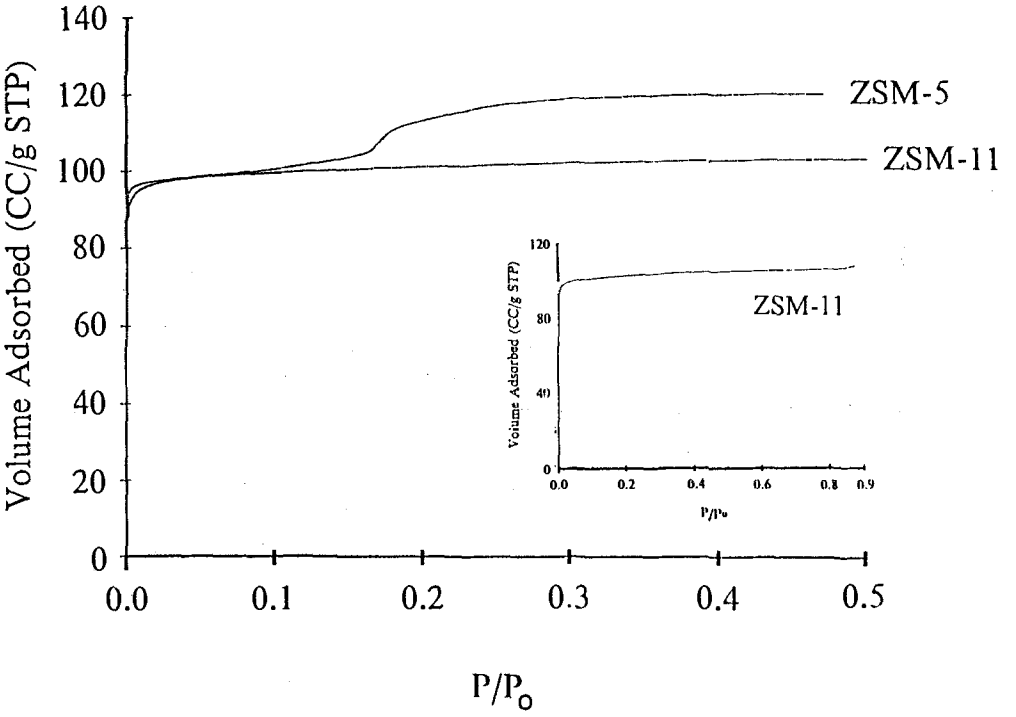

Fig. 8. Nitrogen isotherms from ZSM-5 and ZSM-11. Recorded at 77 K.

explanation for the second transition in the isotherm from ZSM-5 remains unknown.

MIXTURES OF PHASES

Finally, quasi-equilibrium HRADS has been shown by us to be capable of distinguishing mixtures of phases present in a sample [23].

Acknowledgements

We are grateful to Drs. David Young and Consuelo Montes for the preparation of sieves and for their constructive discussions and to Jennifer Groppe and Moses Chan for collecting the equilibrium N_2 adsorption isotherm on VPI-5. We wish to thank the Mobil Oil Company for the financial support of this project.

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