

# Zeolite Phi: A Physical Mixture of Chabazite and Offretite

Raul F. Lobo, Michael J. Annen and Mark E. Davis\*

Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

Zeolite Phi is synthesized by two methods reported previously. Results from X-ray powder diffraction and scanning electron microscopy suggest that the materials are physical mixtures of chabazite and offretite; one sample has a small amount of phillipsite. The X-ray powder diffraction data from these samples, and those reported previously, are indexed and their unit-cell parameters compare well to those obtained from a physical mixture of chabazite and offretite. These samples show multiple particle morphologies that are indicative of physical mixtures. Zeolite Phi is concluded to be a physical mixture of chabazite and offretite and we suggest that the use of the name zeolite Phi be discontinued.

The synthesis of novel materials is a continuing challenge in molecular sieve science. New materials with channels comprised of 12-membered rings (12MR) or larger are of particular current interest.<sup>1</sup>

Zeolite Phi, first reported by Union Carbide in 1978,<sup>2</sup> was synthesized from a reaction mixture consisting of soda, silica, alumina, tetramethylammonium hydroxide and water. The source of silica was an ammonium-exchanged mineral that contained chabazite. The solid was washed in 30 wt.% sulfuric acid, calcined and leached with hot water prior to use in the synthesis of zeolite Phi. The zeolite Phi sample synthesized in this manner sorbed 3.5 wt.% neopentane and 8.0 wt.% perfluorotributylamine [(C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>N, kinetic diameter of 10.2 Å]. For comparison, zeolite X sorbs 15.6 wt.% neopentane and 3.1 wt.% (C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>N at 25 °C.<sup>3</sup> From the results of cracking *n*-decane, Martens *et al.*<sup>4,5</sup> speculate that zeolite Phi contains intersecting channels formed by 12MR. In addition, Franco *et al.* postulate that zeolite Phi is structurally related to offretite and may be another member of the ABC-6 family of molecular sieves.<sup>6</sup> As Franco *et al.* point out, the sparsity of literature data on zeolite Phi is surprising in view of the fact that it has been reported to contain intersecting 12MR channels and to have adsorption capacities of more than two times that of zeolite X for (C<sub>4</sub>F<sub>9</sub>)<sub>3</sub>N.

We have observed that the diffraction data reported in the literature for zeolite Phi show a strong correlation to that obtained from a physical mixture of chabazite and offretite, with chabazite being the abundant phase. The objective of this work is to show that zeolite Phi is a physical mixture of the zeolites chabazite and offretite.

## Experimental

### Samples

Zeolite Phi was synthesized in a manner similar to that employed by Franco *et al.*<sup>6</sup> (Synthesis I) and to that of Jacobs and Martens<sup>7</sup> (Synthesis II).

### Synthesis I

A gel composition 1.12 Na<sub>2</sub>O : 0.36 K<sub>2</sub>O : 3.16 (TEA)<sub>2</sub>O : 10 SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> : 150 H<sub>2</sub>O was prepared as follows: 12 g of tetraethylorthosilicate (TEOS, Aldrich, 98%) were added to a mixture of 13.4 g of tetraethylammonium hydroxide (40 wt.%, TEAOH, Aldrich), 0.27 g of potassium hydroxide (KOH 85%+, Aldrich), 0.11 g of sodium hydroxide (50 wt.% aqueous solution, Fisher Scientific), 1.26 g of sodium aluminate (NaAlO<sub>2</sub> · 1.5 H<sub>2</sub>O, VWR) and 9 g of distilled water. The mixture was stirred in a closed Teflon jar at room temperature for ca. 16 h to hydrolyse the TEOS and then stirred while exposed to ambient conditions for several hours until

the ethanol formed had evaporated. The reaction mixture was statically heated at 110 °C for 8 days at autogenous pressure in Teflon-lined autoclaves. The product was collected by centrifugation and then dried at room temperature. To remove the occluded organic molecule, sample I was heated at a rate of 3 °C min<sup>-1</sup> to 600 °C in air and kept at this temperature for 4 h. To prepare the acid form of the zeolite, the calcined sample was refluxed overnight in a 1 mol dm<sup>-3</sup> solution of ammonium nitrate and calcined at 400 °C for 4 h. The ammonium exchange and the calcination were repeated a second time to complete the transformation into the acid form. The as-made product of Synthesis I will be referred to as sample I while its acid form will be denoted H-sample I.

### Synthesis II

Franco *et al.*<sup>6</sup> found that the presence of potassium is necessary for the synthesis of zeolite Phi. They note that while Jacobs and Martens did not explicitly add potassium, TEAOH from Fluka typically contains 'appreciable amounts of potassium'. It has been reported that a sample of 20 wt.% TEAOH from Fluka contains 400 ppm of Na<sup>+</sup> and 5400 ppm of K<sup>+</sup>.<sup>8</sup> We attempted to account for the potassium impurity in the Fluka 40 wt.% TEAOH by assuming a potassium content of 1.08 × 10<sup>4</sup> ppm and then simulating this impurity by explicitly adding equimolar amounts KOH and KNO<sub>3</sub>. Both potassium salts are used so that the pH of the reaction mixture is not significantly altered from that in the absence of potassium.

A reaction mixture of composition 1.1 Na<sub>2</sub>O : 0.42 K<sub>2</sub>O : 9.3 TEA<sub>2</sub>O : 20 SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> : 558 H<sub>2</sub>O was prepared by mixing 25.8 g TEOS (Aldrich, 98%), 42.4 g TEAOH (40 wt.%, Aldrich), 0.36 g KOH (Aldrich, 85%+) and 0.59 g KNO<sub>3</sub> (Fisher, 99+%). The resulting solution was stirred at room temperature for 24 h. A second solution was prepared by mixing 1.6 g NaAlO<sub>2</sub> · 1.5 H<sub>2</sub>O (VWR), 0.13 g NaOH (Aldrich) and 36.2 g deionized H<sub>2</sub>O. The two solutions were combined and stirred for 5 min at room temperature. The reaction mixture was statically aged at 5 °C for 2 days. After the ageing period, the gel was transferred to Teflon-lined stainless-steel autoclaves and statically heated at 100 °C under autogenous pressure for 14 days. The final product was washed with deionized H<sub>2</sub>O and recovered by filtration. This product will be referred to as sample II.

### Analytical Methods

X-Ray powder diffraction (XRD) patterns were collected on a Scintag XDS 2000 diffractometer using Cu-Kα radiation and a solid-state Ge detector cooled with liquid nitrogen. The diffractometer was aligned with silicon as an external standard. Synchrotron diffraction data (λ = 1.2995 Å) were collected at

the Brookhaven National Laboratory. All reflections were individually deconvoluted to obtain accurate peak positions and widths.

Thermogravimetric analyses (TG) were performed on a DuPont 951 thermogravimetric analyser. A heating rate of  $10^{\circ}\text{C min}^{-1}$  was used for all data collections. Nitrogen adsorption isotherms were collected at 77 K on an Omicron 100 analyser. The scanning electron micrographs (SEM) were recorded on a JEOL 840-A scanning electron microscope.

### Results and Discussion

The SEM of H-sample I (Fig. 1) shows two distinctive crystal morphologies suggesting the simultaneous crystallization of two different phases. The synchrotron X-ray powder diffraction pattern of H-sample I, shown in Fig. 2(a), reveals the presence of chabazite and offretite. The data illustrated in Fig. 2(a) can be indexed to a physical mixture of chabazite and offretite (see Table 1). Only one  $d$  spacing at 8.24 Å cannot be indexed. It is not possible to identify which phase produces this single reflection. Franco *et al.*<sup>6</sup> show that other phases (GIS, OFF, SOD, GME, LTL and zeolite Beta) often

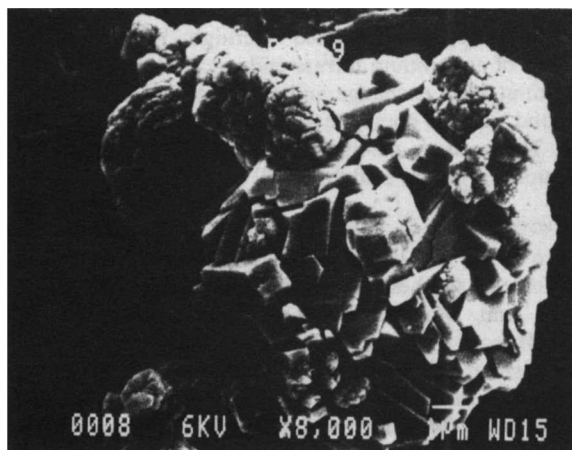


Fig. 1 Scanning electron micrograph of H-sample I

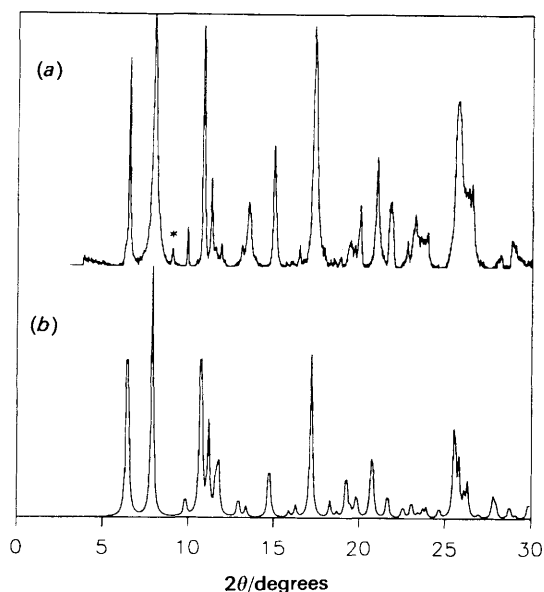


Fig. 2 (a) Background-corrected synchrotron X-ray powder diffraction pattern of H-sample I. The peak marked with an asterisk was not assigned to chabazite or offretite. (b) Simulated X-ray powder diffraction pattern for a physical mixture of chabazite and offretite

Table 1  $d$  spacings for H-sample I

$d/\text{Å}$	$I/I_0$	chabazite <sup>a</sup> $hkl$	offretite <sup>b</sup> $hkl$
11.43	79		100
9.33	100	101	
8.24 <sup>c</sup>	5		
7.52	15		001
6.87	94	110	
6.59	35		110
6.27	10		101
5.70	5		200
5.53	23	201	
4.98	48	003	
4.55	5		201
4.31	97	211	
3.86	7	212	
3.80	5		300
3.76	10		002
3.74	17		211
3.59	5	104	
3.57	43		102
3.43	23	220	
3.29	7		220
3.23	12	311	
3.17	10	204	310
3.14	7		202
2.92	66	401	311
2.86	25		400
2.83	17	223	212
2.67	5		302
2.61	7		320
2.59	5	410	
2.57	2	322	
2.50	2		003

<sup>a</sup> Chabazite cell constants (Å): hexagonal,  $a = 13.745(7)$ ,  $c = 15.02(1)$ . <sup>b</sup> Offretite cell constants (Å): hexagonal,  $a = 13.191(5)$ ,  $c = 7.510(4)$ . <sup>c</sup> This reflection was not indexed to chabazite or to offretite. The reflection was not used for calculation of the cell constants.

crystallize simultaneously with zeolite Phi. However, they do not report the presence of chabazite in any of their samples.

Sample II also exhibits two crystal morphologies (Fig. 3); one of which is the same as that reported by Jacobs and Martens.<sup>7</sup> The material synthesized by Jacobs and Martens is claimed to be zeolite Phi but no characterization data other than crystal morphology are provided. The large spheres shown in Fig. 3 are most likely phillipsite while the smaller spheres formed of agglomerate plates are probably chabazite. The XRD powder pattern for this sample reveals the presence of chabazite, phillipsite and a very small amount of offretite (Table 2).

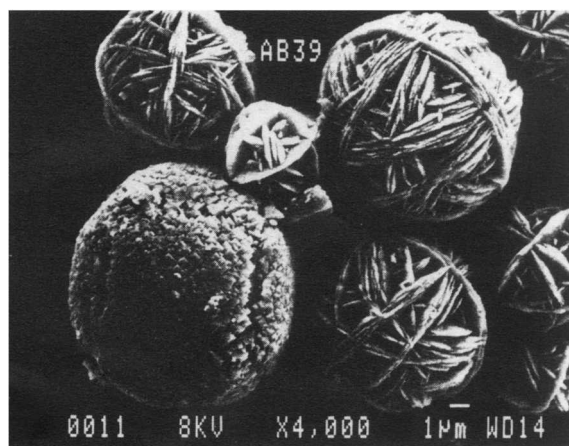


Fig. 3 Scanning electron micrograph of sample II

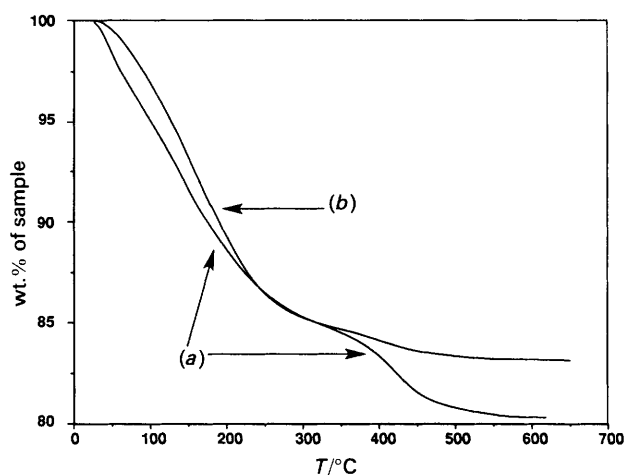
**Table 2** *d* spacings for sample II

<i>d</i> /Å	<i>I</i> / <i>I</i> <sub>0</sub>	chabazite <sup>a</sup> <i>hkl</i>	offretite <sup>b</sup> <i>hkl</i>	phillipsite <sup>c</sup> <i>hkl</i>
11.77	2		100	
9.40	12	101		
8.16	13			101
7.13	59			020
7.08	15			111
6.89	13	110		
5.54	6	201		
5.36	24			121
5.02	44	003		
4.97	47			200
4.32	29	211		
4.28	7			130
4.08	25			220
3.98	5	300		
3.88	7	212		
3.52	4			222
3.44	10	220		
3.26	31			141
3.23	26	311		
3.18	100			024
2.94	12			321
2.93	45	401		
2.90	3			240
2.88	10	214		
2.74	14			143
2.68	31	205		
2.60	19	410		

<sup>a</sup> Chabazite cell constants (Å): hexagonal, *a* = 13.78(1), *c* = 15.01(2).  
<sup>b</sup> Offretite cell constants (Å): hexagonal, *a* = 13.59, insufficient data to calculate *c* cell edge. <sup>c</sup> Phillipsite cell constants (Å): orthorhombic, *a* = 9.95(1), *b* = 14.23(1), *c* = 14.23(1).

The thermogravimetric analyses for both samples (Fig. 4) exhibit weight-loss events around 380 °C which are assigned to the combustion of TEA<sup>+</sup> cations in a 12MR pore.<sup>6</sup> The amount of TEA<sup>+</sup> within sample II is less than in sample I and is consistent with the argument that it resides in the offretite portion of the sample.

Nearly all the *d* spacings reported for zeolite Phi<sup>2,6</sup> are found in the X-ray diffraction data for chabazite. The remaining few reflections can be assigned to offretite. Accordingly, the diffraction data reported for zeolite Phi, both in the orig-



**Fig. 4** Thermogravimetric analyses: (a) H-sample I, (b) sample II

inal patent<sup>2</sup> and by Franco *et al.*,<sup>6</sup> have been indexed to offretite or chabazite (Table 3). The calculated cell constants for these materials are in good agreement with the cell constants reported for chabazite and offretite (Table 4).

The relative intensities of the diffraction peaks reported for zeolite Phi in the original patent<sup>2</sup> and those published by Franco *et al.*<sup>6</sup> are different. The differences are most likely due to varying amounts of offretite and chabazite in each

**Table 4** Cell constants for chabazite and offretite calculated from published zeolite Phi reflections<sup>a</sup>

material	chabazite cell (hexagonal)		offretite cell (hexagonal)	
	<i>a</i> /Å	<i>c</i> /Å	<i>a</i> /Å	<i>c</i> /Å
zeolite Phi <sup>b</sup>	13.76(1)	15.11(4)	13.43 <sup>c</sup>	7.69
zeolite Phi <sup>d</sup>	13.76(1)	15.03(2)	13.28	7.57
chabazite, <sup>e</sup> offretite	13.78	15.06	13.29	7.58

<sup>a</sup> Standard deviation in parentheses. <sup>b</sup> Calculated from *d* spacings given in ref. 2 (see Table 3). <sup>c</sup> Standard deviation not assigned owing to lack of data. <sup>d</sup> Calculated from *d* spacings given in ref. 6 (see Table 3). <sup>e</sup> From ref. 3.

**Table 3** *d* spacings reported for zeolite Phi and indexing to chabazite or offretite

zeolite Phi <sup>a</sup>				zeolite Phi <sup>b</sup>			
<i>d</i> /Å	<i>I</i> / <i>I</i> <sub>0</sub> <sup>c</sup>	<i>hkl</i>	phase <sup>d</sup>	<i>d</i> /Å	<i>I</i> / <i>I</i> <sub>0</sub> <sup>c</sup>	<i>hkl</i>	phase <sup>d</sup>
11.63	m	100	O	11.5	5	100	O
9.51	s	101	C	9.3	24	101	C
7.69	vw	001	O	6.9	15	110	C
6.97	s	110	C	5.53	16	201	C
5.61	s	201	C	5.01	27	003	C
5.04	s	003	C	4.31	66	211	C
4.31	s	211	C	3.97	9	300	C
3.97	vw	300	C	3.86	13	212	C
3.43	vs	220	C	3.77	4	211	O
2.92	vs	401	C	3.58	22	104	C
2.69	vw	205	C	3.44	24	220	C
2.61	w	410	C	3.23	8	311	C
2.51	vw	215	C	2.92	100	401	C
2.09	w	333	C	2.69	5	205	C
1.90	w	520	C	2.60	25	410	C
1.81	w	611	C	2.50	10	215	C
1.74	vw	434	C	2.30	7	330	C
1.72	w	440	C	2.08	15	333	C

<sup>a</sup> From Table A in ref. 2. <sup>b</sup> From Table 1 in ref. 6. <sup>c</sup> Relative intensity: vw = very weak; w = weak; m = medium; s = strong; vs = very strong. <sup>d</sup> C = chabazite; O = offretite.

sample. In general, the amount of offretite in zeolite Phi is less than chabazite. This explains why only very few, typically intense, offretite reflections are reported for zeolite Phi. Franco *et al.* claim that offretite co-crystallizes with zeolite Phi when the potassium concentration in the reaction mixture is increased above  $K_2O/Al_2O_3 = 0.36$ . It is most likely that the amount of offretite is greater in such products than in those synthesized by Union Carbide. Additionally, it is claimed that zeolite G<sup>9</sup> is an intergrowth of offretite and chabazite.<sup>10</sup> Comparison of the X-ray powder diffraction pattern of H-sample I with that reported by Franco *et al.*<sup>6</sup> indicates that our sample contains more offretite.

Fig. 2(b) shows a simulated X-ray powder diffraction pattern for a mixture of chabazite and offretite. The powder diffraction patterns of chabazite and offretite<sup>11,12</sup> were simulated using the program CERIUS version 2.3 from Cambridge Molecular Design with silicon positioned in all tetrahedral sites. Since the relative amounts of each phase are unknown, the two patterns were averaged such that the relative intensities of the first reflections of offretite and chabazite match the relative intensities of the peaks in the X-ray synchrotron powder diffraction pattern. Although this procedure is partly arbitrary, the similarity of the two patterns is noticeable. Differences in the relative intensities of the two patterns are likely to be due to the presence of water, cations and aluminium in H-sample I, that were not accounted for in the simulation.

Zeolite Phi shows moderate oxygen, *n*-butane, isobutane and neopentane adsorption capacities (Table 5); these adsorption capacities are lower than those for offretite. However, the  $(C_4F_9)_3N$  adsorption capacity reported by Union Carbide<sup>2</sup> is over two times larger than that of zeolite NaX. This result suggests that zeolite Phi has at least 12MRs and a void fraction capable of adsorbing  $(C_4F_9)_3N$  that is larger than in NaX. This is in disagreement with the other adsorption capacities given in the patent.<sup>2</sup>

The  $(C_4F_9)_3N$  adsorption capacity of zeolite Phi may be due to adsorption in the mesopores of the material. The existence of mesopores in sample II is confirmed by nitrogen adsorption data recorded at 77 K. The adsorption isotherm shown in Fig. 5(a) exhibits almost no uptake at pressures of  $P/P_0 \leq 0.1$ . The sharp uptake after this pressure is indicative of adsorption within the mesopores of the material. For comparison, a standard zeolite Y sample was also analysed; the resulting isotherm is shown in Fig. 5(b). The zeolite Y adsorption isotherm exhibits virtually no adsorption after micropore filling ( $P/P_0 = 10^{-3}$ ). Aside from the  $(C_4F_9)_3N$  adsorption datum point, all other adsorption data reported for zeolite Phi can be rationalized in terms of the adsorption obtained from a physical mixture of offretite and chabazite. It is most likely that the  $(C_4F_9)_3N$  adsorption capacity is the result of extracrystalline adsorption.

The results from a catalytic probe reaction indicate that zeolite Phi contains multidimensional channels consisting of

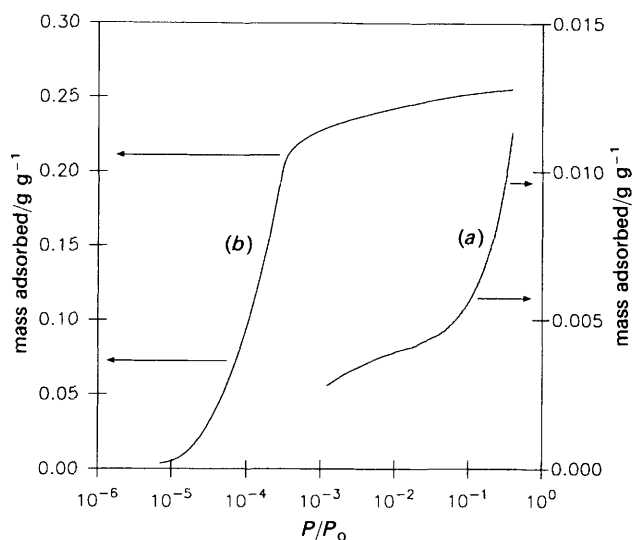


Fig. 5 Nitrogen adsorption isotherm at 77 K: (a) sample II, (b) NaY;  $P_0 = 760$  Torr

12MRs.<sup>4,5</sup> These catalytic results may be influenced by the 12MR microporous channels of the offretite portion of the sample as well as the extracrystalline mesopores. Although the exact relation between the catalytic results and the pore structure of the material is not understood, it is clear that zeolite Phi does not contain multidimensional 12MR channels.

The X-ray powder diffraction data reported for zeolite Phi reveal that these samples are mixtures of chabazite and offretite. Previously reported TG, adsorption capacities and data from a catalytic probe reaction can be rationalized as resulting from the physicochemical properties of a physical mixture of chabazite and offretite. We suggest that use of the designation zeolite Phi be discontinued.

Support of this work is provided by the NSF Alan T. Waterman Award to M.E.D. We want to thank Dr. John B. Higgins at Mobil Research and Development Corporation, Central Research Laboratory (MRDC-CRL), for reviewing the manuscript and Noel Goeke, also at MRDC-CRL, for collecting the SEMs. We acknowledge Dr. D. E. Cox for assistance in collecting the synchrotron data. The data were collected at X7A beam line, National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the US Department of Energy, Division of Material Sciences and Division of Chemical Sciences.

## References

- 1 M. E. Davis, *Chem. Ind. (London)*, 1992, 137.
- 2 R. W. Grose and E. M. Flanigen, *US Pat.*, 4124686, 1978, assigned to Union Carbide.

Table 5 Adsorption data for zeolite Phi, chabazite, offretite and zeolite NaX

adsorbate	pressure/Torr	temperature/°C	g (adsorbate) g <sup>-1</sup> (dry zeolite)			
			Phi <sup>a</sup>	chabazite <sup>b</sup>	offretite <sup>b</sup>	NaX <sup>b</sup>
O <sub>2</sub>	100	-183	0.121	0.116	0.180	0.30
O <sub>2</sub>	750	-183	0.184	0.220 <sup>c</sup>	0.230 <sup>c</sup>	
<i>n</i> -butane	750	25	0.081		0.122 <sup>c</sup>	0.18 <sup>c</sup>
isobutane	750	25	0.027		0.08 <sup>c</sup>	0.18 <sup>c</sup>
neopentane	750	25	0.035		0.069 <sup>c</sup>	0.156 <sup>c</sup>
$(C_4F_9)_3N$	0.5	50	0.08			0.031 <sup>c</sup>

<sup>a</sup> From ref. 2. <sup>b</sup> From ref. 3. <sup>c</sup> Adsorption measured at 700 Torr [1 Torr = (101 325/760) Pa].

- 3 D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974, p. 606.
- 4 J. A. Martens, M. Tielen, P. A. Jacobs and J. Weitkamp, *Zeolites*, 1984, **4**, 98.
- 5 J. A. Martens and P. A. Jacobs, *Zeolites*, 1986, **6**, 98.
- 6 M. J. Franco, J. Pérez-Pariente and V. Fornés, *Zeolites*, 1991, **11**, 349.
- 7 P. A. Jacobs and J. A. Martens, *Stud. Surf. Sci. Catal.*, 1987, **33**, 15.
- 8 D. R. C. Huybrechts, Ph.D. Dissertation, Fakulteit der Landbouwwetenschappen van de K. U. Leuven, 1991.
- 9 R. M. Barrer and J. W. Baynham, *J. Chem. Soc.*, 1956, 2882.
- 10 J. M. Thomas and D. E. W. Vaughan, *J. Phys. Chem. Solids*, 1989, **50**, 449.
- 11 M. Calligaris, G. Nardin and L. Randacio, *Zeolites*, 1983, **3**, 205.
- 12 J. A. Gard and J. M. Tait, *Acta Crystallogr. Sect. B*, 1972, **28**, 825

*Paper 2/01700H; Received 31st March, 1992*