

## FACTORS INFLUENCING SORPTION AND DIFFUSION IN PENTASIL ZEOLITES

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### ABSTRACT

Pentasil zeolites (Si:Al= 20-50) have been prepared with different templates (TPA,  $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ ,  $\text{NH}_2(\text{CH}_2)_3\text{NH}_2$ , and  $\text{NH}_3$  (organic free)) in the hydrogen form; they were characterized by XRD and by chemisorption of pyridine. Equilibrium sorption of hexane, benzene, toluene and p-xylene was studied at 298 K; the uptake of hydrocarbons varies regularly with the nature of the template which had been used in the synthesis of the zeolite. Diffusivities (obtained from sorption rates at 298 K) of aromatic hydrocarbons are independent of the method of preparation of the zeolite. Chemisorbed pyridine does not affect the diffusivity of aromatic hydrocarbons in pentasil zeolite synthesized with TPA as template, whereas it reduces the diffusivities substantially in zeolites prepared with other templates. This observation indicates that the template influences the location of acid sites in the structure of the solid.

### INTRODUCTION AND SCOPE

The generic name "pentasil-zeolites", which has been introduced by Meier and Kokotailo (1), covers a family of similar structures with nearly identical lattices containing five-membered rings of tetrahedral silicon or aluminium. The end members of this series are represented by the ideal structures of ZSM-5 (sinusoidal channels) and ZSM-11 (straight channels). Real crystals seem to be an intergrowth of these structures and they also contain stacking faults and disordered domains (2-4). These zeolites are synthesized through crystallisation from silica-rich gels containing nitrogen bases as templates. The classical synthesis relies on tetrapropylammonium for ZSM 5 (5) and tetrabutylammonium for ZSM-11 (6) as templates. It has been found that pentasil zeolites can also be

obtained if the gel contains N-bases other than these, such as 1,6 diaminopropane (8) or no organic template (9). The XRD-patterns of zeolites prepared by different methods are very similar with nearly identical lattice-spacing, whereas sorption of hydrocarbons and catalytic properties have been found to vary with the method of preparation (10, 11). In order to exemplify the influence of the template used for synthesis on the properties of the resulting pentasil zeolites we have prepared pentasil zeolites using 3 different organic templates as well as no organic template. The properties of these zeolites with respect to sorption and diffusion of various hydrocarbons and chemisorption of pyridine are reported here; the catalytic properties of these materials will be the subject of a later publication.

Synthesis and characterization of zeolites. Zeolites were prepared by crystallization from gels at 170°C in a teflon-lined autoclave. The gels were formed by first heating slurries of precipitated silica (Merck) in aqueous solution of NaOH and the template to boiling for 30 minutes and then adding under stirring either a hot solution of AlCl<sub>3</sub> (preparation A and B) or a hot slurry of freshly precipitated aluminium hydroxide (preparation D). The molar compositions of the gels were Al<sub>2</sub>O<sub>3</sub> - 75 SiO<sub>2</sub> - x template - 6.2 Na<sub>2</sub>O - 870 H<sub>2</sub>O, where x = 9.2, 21.0 and 71.6 for TPA-Br, HMD and NH<sub>3</sub>, respectively. The crystallization periods were 6 days for TPA- and HMD-zeolites and 12 days for NH<sub>3</sub>-zeolite. Sample C (template: 1,3 diaminopropane) was kindly supplied by Dr. Hölderich (BASF Aktiengesellschaft).

The crystalline solids resulting from the gels were filtered, washed several times with distilled water, dried at 120°C and calcined in air at 500°C for 4 h. After cooling to room temperature the zeolites were ionexchanged at 80°C 6 times with 20 ml of 1 m NH<sub>4</sub>NO<sub>3</sub> solution per g of zeolites. The ionexchanged solids were dried and deammoniated in air at 500°C for 6 h to obtain the hydrogen forms.

The composition of the resulting zeolites as obtained by wet analysis and AAS and the size of the crystals (which were nearly monodisperse in all preparations as shown by SEM) are given in Table 1.

Table 1

Composition and size of crystals, Sorption capacity for nitrogen, Chemisorption of pyridine

sample designation (template)	Crystal-diameter ( $\mu\text{m}$ )	Composition Si/Al	$\text{N}_2$ -Sorption	Chemisorption of pyridine	
			at 77 K and $P_{\text{N}_2} = 1$ torr (m mol/g)	at 400°C $\frac{\text{m mol}}{\text{g}}$	$\frac{n_{\text{pyridine}}}{n_{\text{Al}}}$
A (TPA Br)	0.5	36	4.2	0.21	0.48
B $(\text{NH}_2(\text{CH}_2)_6\text{NH}_2)$	0.5	36	3.9	0.26	0.58
C $(\text{NH}_2(\text{CH}_3)_2\text{NH}_2)$	0.8	22	3.6	0.28	0.39
D $(\text{NH}_3)$	0.5	36	2.3	0.28	0.64
ZSM-5 *	1.0	50	-	0.17	0.53

\* sample of zeolite ZSM-5 in the hydrogen form, kindly supplied by Mobil Research and Development corporation

Na content in zeolites A, B, C and D  $< 0.05$  wt %.

Chemisorption of pyridine was determined with an electro-balance by evacuating the zeolite at 400°C for 2 h, cooling to room temperature, contacting with pyridine vapour at 13 mbar at this temperature and then evacuating to  $10^{-3}$  mbar at 400°C for 2 h. The amount of pyridine retained thereafter and its ratio to the amount of Al in the zeolite is also listed in Table 1. The main X-ray diffraction reflexes with Cu  $K_{\alpha}$  -radiation and their relative intensities (peak heights) are given in Table 2 as well as the degree of crystallinity which is defined by the ratio of sum of heights of major XRD peaks of test sample to the sum of heights of major XRD peaks of standard (Sample A) multiplied by 100.

Table 2

XRD-data of zeolites in the hydrogen form

Sample:	A	B	C	D	ZSM-5(Mobil)
2 $\theta$	100 I/I <sub>0</sub>				
7.8	(100)	(100)	(100)	(100)	(100)
8.7	58	56	62	60	56
23.0	49	49	46	78	48
23.8	25	25	26	39	24
24.2	13	14	17	26	13
crystallinity (%)	(100)	98	100	91	99

## SORPTION OF HYDROCARBONS INTO THE ZEOLITES IN THE HYDROGEN-FORMS

Sorption equilibria and sorption kinetics were observed gravimetrically with a Cahn RG electrobalance hooked up to a grease-free vacuum system which can be evacuated through a turbomolecular pump to  $10^{-3}$  mbar. Pressure was measured with a capacitance pressure transducer (MKS baratron Type 170 M-6B). The experimental procedure has been described in detail by Doelle and Riekert (12); sorption equilibria were observed on samples weighing about  $70 \pm 10$  mg, equilibrium being defined by coincidence of isotherms obtained at increasing and decreasing pressures; sorption rates were observed on much smaller samples (about 10 mg each) spread in a monolayer of crystals in order to avoid intercrystalline mass transfer resistance and to minimize the excursion of temperature due to the heat of sorption. Pretreatment of the zeolites consisted in degassing at  $400^\circ\text{C}$  for 1 h at  $p 10^{-3}$  mbar.

Figure 1 shows the isotherms at 298 K of n-hexane, benzene, toluene and p-xylene on zeolite A and figure 2 shows sorption isotherms of toluene on zeolites A, B, C and D at 198 K. Values of equilibrium-sorption of different hydrocarbons at 298 K and a pressure of 1.33 mbar of the respective hydrocarbon are given in Table 3.

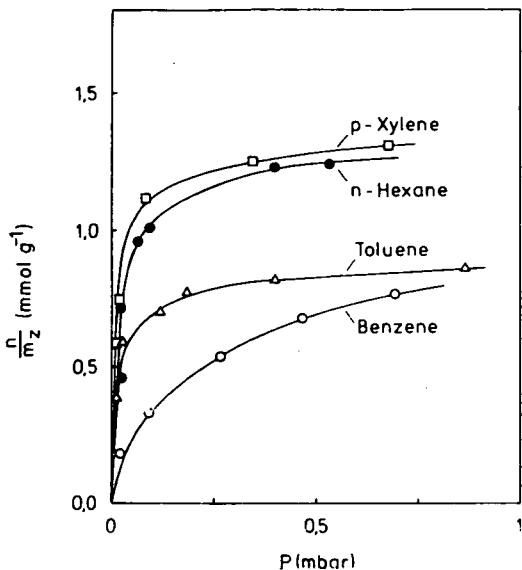


Fig. 1. Equilibrium isotherms of sorption of hydrocarbons in sample A at 298 K

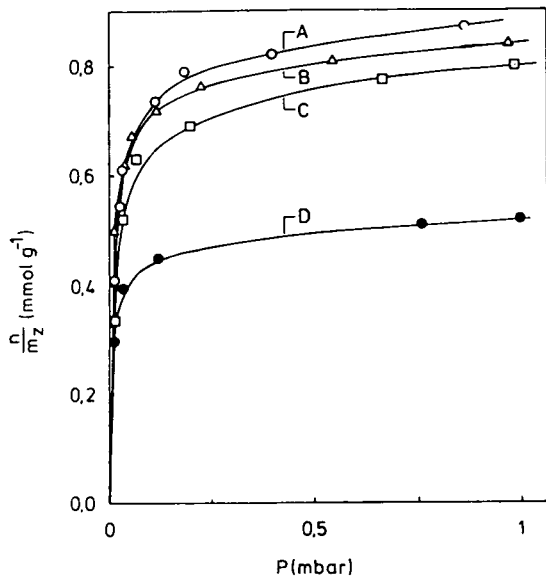


Fig. 2. Equilibrium isotherms for sorption of toluene in samples A, B, C, D at 298 K

Table 3

Equilibrium sorption  $n_s/m_z$  in  $\text{mmol g}^{-1}$  of different hydrocarbons i at 298 K and  $p_i = 1.33$  mbar in different pentasil zeolites

Zeolite	A	B	C	D
hydrocarbon				
m-hexane	$\frac{n_s}{m_z} = 1.28$	1.21	1.12	0.62
benzene	0.91	0.79	0.83	0.42
toluene	0.94	0.87	0.85	0.52
p-xylene	1.33	1.01	0.98	0.67

Sorption of p-xylene at 298 K did show hysteresis on all samples investigated, values in desorption (decreasing p) exceeding the values found in sorption (increasing p). Sorption of o-xylene at 298 K was also investigated on sample A and D where the same loadings are approached as for p-xylene, albeit much more slowly.

The kinetics of sorption of benzene, toluene and p-xylene at 298 K into all zeolites investigated can be described by  $n/n_\infty$  ( $n_\infty$  = final uptake at equilibrium) being linear in  $\sqrt{t}$ , up to about  $n/n_\infty = 0.5$  (see fig. 3). In this range the kinetics of sorption is controlled by intracrystalline diffusion under the

conditions of these experiments with monolayers of crystals (12). Assuming diffusion in a homogeneous isotropic medium we have independent of the shape of the crystals for the initial slope of  $n/n_\infty$  vs.  $\sqrt{t}$

$$\lim_{t \rightarrow 0} \frac{d(n/n_\infty)}{d\sqrt{t}} = \frac{2}{\sqrt{\pi}} \cdot \left( \frac{D}{L^2} \right)^{1/2} \quad (1)$$

where  $L = V/a$  is the ratio of volume to external surface of the solid; e. g.  $L = \frac{d}{6}$  for spherical crystals of diameter  $d$ . Intra-crystalline diffusion coefficients  $D$  of hydrocarbons in the zeolites which were obtained on the basis of eq. (1) are listed in Table 4.

Table 4

Diffusivities (in  $\text{cm}^2/\text{s}$ ) of hydrocarbons at 298 K, obtained from initial slopes of  $n/n_\infty$  vs.  $\sqrt{t}$ -curves

Sample: (L in $\mu\text{m}$ )	A (0.08)	B (0.08)	C (0.13)	D (0.08)
Hydrocarbon				
Benzene	$D = 5.7 \cdot 10^{-12}$	$6.0 \cdot 10^{-12}$	$6.3 \cdot 10^{-12}$	$6.3 \cdot 10^{-12}$
Toluene	$1.6 \cdot 10^{-12}$	$1.8 \cdot 10^{-12}$	$2.0 \cdot 10^{-12}$	$2.2 \cdot 10^{-12}$
p-Xylene	$2.8 \cdot 10^{-11}$	$2.9 \cdot 10^{-11}$	$3.6 \cdot 10^{-11}$	$2.8 \cdot 10^{-11}$

These diffusivities should be considered as rough estimates only, because the characteristic length  $L$  obtained from SEM micrographs cannot be considered to be very accurate. Furthermore the patterns of  $n/n_\infty$  vs.  $\sqrt{t}$  at  $n/n_\infty > 0.8$  seem to indicate that the solids are not always homogeneous, containing disordered domains where diffusivities are lower. The data in Table 4 nevertheless indicate that the order of magnitude of the diffusivity of a given hydrocarbon is the same in all preparations and that p-xylene always diffuses more rapidly into the solid than benzene or toluene. O-xylene on the other hand diffuses much more slowly, in sample A the rate of sorption of o-xylene at 298 K corresponds to  $D \approx 6 \cdot 10^{-13} \text{ cm}^2/\text{s}$ .

#### SORPTION OF HYDROCARBONS INTO ZEOLITES CONTAINING CHEMISORBED PYRIDINE

Equilibria and kinetics of sorption of aromatic hydrocarbons were also investigated in pentasil samples A, B, C and D after these had been modified by chemisorption of pyridine at the acid

sites in the crystal. For this purpose the zeolites were contacted with pyridine-vapour (13 mbar) at 25°C and then degassed at 400°C under vacuum ( $p=10^{-3}$  mbar) for 1 h, the amounts of pyridine retained thereafter are given in Table 1. The equilibrium isotherms of hydrocarbons in zeolites modified by chemisorbed pyridine were compared to the isotherms for the unmodified zeolites. It was found throughout that sorption in the modified zeolites at  $p > 1$  mbar is reduced by an amount which corresponds roughly to the amount of chemisorbed pyridine. The kinetics of sorption of benzene and p-xylene in the H-forms as well as in the pyridine-modified forms of the same zeolites (A, C and D) is shown in Fig. 3.

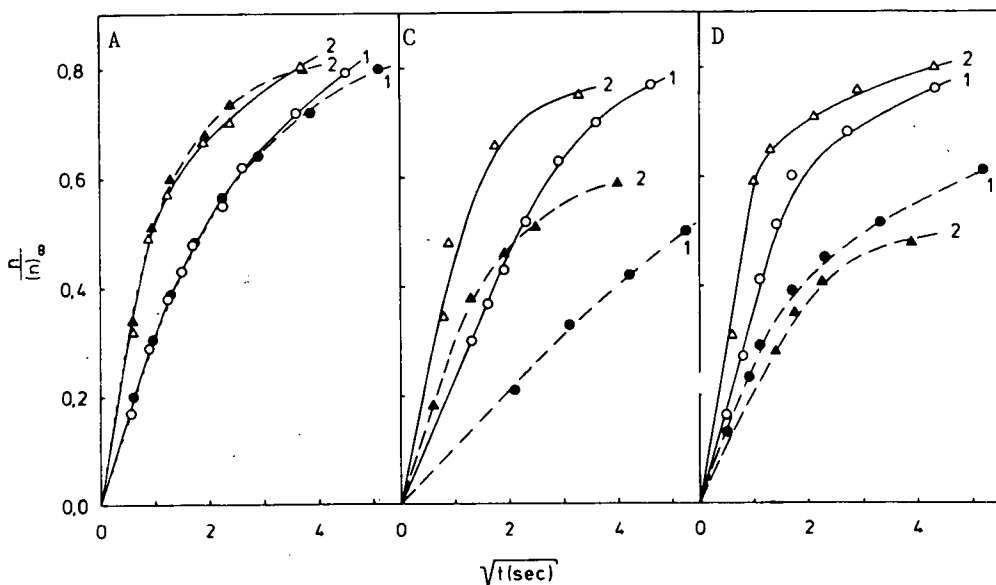


Fig. 3. Kinetics of sorption of benzene (1) and p-xylene (2) into H-forms of zeolites (-o-o-, -Δ-Δ-) and into H-forms containing chemisorbed pyridine (-●-●-, -▲-▲-).  $T = 298$  K.

Initial loading of zeolite  $(n_S)_0 = 0$ ;  $\frac{P_{\infty}}{P_0} \geq 0.9$ .

In pentasil A the time-dependence of the dimensionless uptake  $n/n_{\infty}$  is not affected by the presence of chemisorbed pyridine, the diffusivities of the hydrocarbons in this zeolite are the same, whether pyridine is present or not. In zeolites B, C and D, on the other hand, the diffusivities of hydrocarbons are substantially reduced by chemisorption of pyridine. These observations are summarized in Table 5, where the ratio between the diffusivities in the pyridine-modified zeolites and the diffusivities in the

unmodified zeolites at 298 K are listed. These ratios of diffusivities obtained on the basis of eq. (1) do not suffer from uncertainties concerning shape and size of the crystals, the morphology being the same when rates of sorption on modified and unmodified crystals are compared for the same zeolite sample.

Table 5

Ratio of diffusivities  $D$  in unmodified zeolite and  $D_{py}$  in zeolite modified by chemisorbed pyridine at 298 K

Zeolite	A	B	C	D
Diffusing hydrocarbon				
Benzene	$\frac{D}{D_{py}} = 1.00$	0.3	0.25	0.4
Toluene	1.00	0.55	0.5	0.6
p-Xylene	1.00	0.2	0.4	0.05

#### DISCUSSION

Zeolites A, B, C and D agree with respect to their crystal-lattice, since x-ray reflexes occur at identical  $\theta$ -values, characteristic for Pentasil-zeolites. Their chemical composition corresponds essentially to that of silica where between 2 and 5 % of Si-atoms have been replaced by Al. The structures of these zeolites appear not to be identical, however, if the equilibria and kinetics of sorption of hydrocarbons and of pyridine in these solids are considered. Between 40 and 65 % of the Al-atoms are associated with an acidity which gives rise to chemisorption of pyridine at 400°C; the fraction being highest for the zeolite which was prepared without organic template.

The pattern of the equilibrium isotherms for sorption of different hydrocarbons is the same for all 4 zeolites. The amounts of a given hydrocarbon which are incorporated into different zeolites under otherwise identical conditions decrease in the order  $A > B > C > D$ , which corresponds to an ordering of the template molecules with their size, decreasing from A (TPA) to D ( $NH_3$ ). The effect can be due to an increasing degree of disordering in the crystals, as we go from A to D.

The amount of p-xylene which is sorbed at saturation always exceeds the amount of benzene sorbed at saturation; it seems impossible



to explain this result on the basis of space-filling in the structure. The hysteresis observed for p-xylene sorption indicates that a change of the structure of the solid takes place when p-xylene is introduced. A subtle change of the structure of ZSM-5 upon sorption of p-xylene has recently been observed by Fyfe et al. (13) through XRD and NMR spectra. The diffusivity of p-xylene in these zeolites always exceeds the diffusivity of benzene by a factor of about 5 (Table 4).

The observation that the diffusivities of benzene, toluene and p-xylene in zeolite A (prepared with TPA as template) are not affected by chemisorbed pyridine shows that in this case the chemisorbed pyridine molecules are located such that they do not obstruct the diffusion pathways of the hydrocarbons. In zeolites B, C, D on the other hand the presence of chemisorbed pyridine entails a substantial reduction of the diffusivities of hydrocarbons in the solid (Table 5). In zeolites B, C and D (prepared with primary amines or ammonia as templates) the chemisorbed pyridine molecules must therefore be located such that they obstruct the diffusion pathways of hydrocarbons in the structure. Theodorou and Wei (14) have shown how observed diffusivities will be reduced, if in a lattice of diffusion pathways a fraction of the pathways in the volume or at the boundary of the system is blocked. This effect is evidently responsible for the decrease of diffusivities in zeolites B, C and D due to chemisorbed pyridine. Since the effect is absent in zeolite A it can be concluded that chemisorbed pyridine occupies different positions in the channel-system of zeolite A than in the case of B, C or D. It follows that the location of framework Al in the lattice is influenced by the template which is used for synthesis.

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