Adsorption of Hydrocarbons and Water on ZSM 5 and on ZSM 5 Converted by Dealumination into Silicalite

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Abstract. Adsorption measurements of hydrocarbons and water have been performed on ZSM 5 (Si/Al = 30) and on two samples prepared from this by dealumination. The properties of the highly dealuminated sample agree essentially with those of silicalite obtained by direct synthesis.

The pecularities in the adsorption of benzene at more than one molecule per $\frac{1}{4}$ unit cell are discussed.

Key words: Adsorption, hydrocarbons, water, ZSM 5, silicalite, dealumination.

1. Introduction

The catalytic activity and selectivity of ZSM 5 zeolites are directly associated with the framework aluminium content [1,2]. In addition to the synthesis, subsequent dealumination allows us to decrease the framework aluminium content. Highly dealuminated ZSM 5 samples have been obtained in this way, and it was demonstrated by high-resolution solid-state MASNMR spectroscopy [3] that they are isostructural with silicalite prepared by direct synthesis.

In this paper, adsorption data of ZSM 5 and dealuminated ZSM 5 zeolites are presented with the aim of answering the question whether the highly dealuminated products have adsorption properties similar or identical to those of silicalite.

2. Experimental

2.1. SAMPLES

The samples are summarized in Table I. Sample A was synthesized in the following way: Silica sol (30 wt % SiO_2), sodium aluminate solution (1.5 Na_2O/Al_2O_3), water and 1 M tetrapropylammoniumhydroxide solution (TPAOH) were mixed together resulting in a final composition of 60 $SiO_2 \cdot Al_2O_3 \cdot 2.5\ Na_2O \cdot 2.9$ TPAOH $\cdot$ 550 H_2O. The mixture was stirred for 10 min at room temperature and then treated at 160°C for ten hours.

The two dealuminated samples B and C were prepared from the NH_4^+ form of sample A by steaming at 550 and 850°C, respectively.

As shown by electron microscopy, the crystals are uniform hexagonal prisms with the dimensions $1 \times 2 \times 5$ μm. No change in crystal size and surface could be detected after dealumination.

Table I.   Characterization of the samples

	Sample prepared		Si/Al ratio
	From	By	
A (ZSM 5)		synthesis	30
B	sample A	steaming at 550°C, 100 h	100
C	sample A	steaming at 850°C, 100 h	> 300

2.2. ADSORPTION MEASUREMENTS

Adsorption isotherms were measured gravimetrically in the temperature range 25–65°C using a quartz spring type McBain balance. The equilibrium pressure was determined by a capacitance pressure meter (MKS Baratron) calibrated from 0.01 to 10^5 Pa.

The differential molar heat of adsorption was measured by means of a Tian-Calvet type calorimeter at 28°C.

The uptake rate of different molecules was determined by weighing tubes containing the samples ($\sim$ 1 g) at different operating times.

3. Results and Discussion

Adsorption isotherms for n-hexane, benzene, and water on the three samples are represented in Figure 1. For comparison, the corresponding isotherms on silicalite are given (dotted curves). Figure 1 demonstrates the changes in the adsorption capacity and in the shape of the isotherms by dealumination.

The n-hexane adsorption is influenced only insignificantly by the loss of framework aluminium. The adsorption capacity decreases by about 5% due to the loss of AlO_4 tetrahedral units in this order. Furthermore, a small hysteresis loop appears in the isotherms
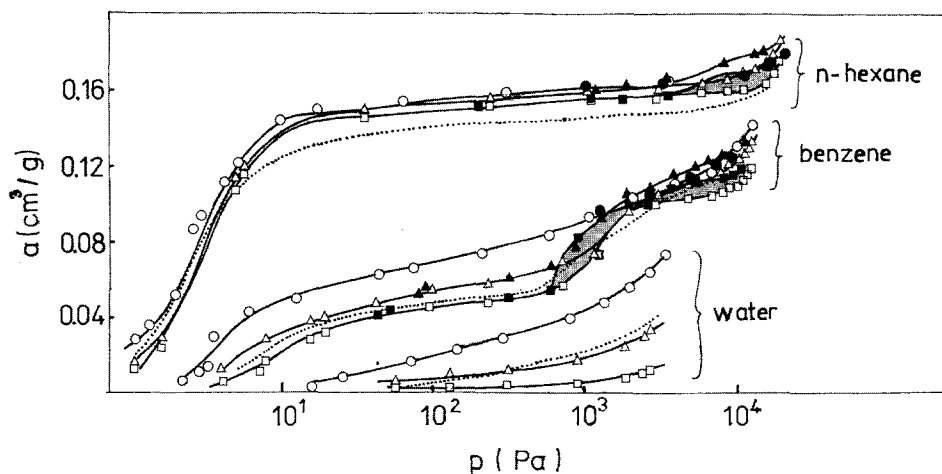

Fig. 1.   Adsorption isotherms of n-hexane, benzene and water at 25°C: ○ sample A, △ sample B, □ sample C; ·······silicalite, ● ▲ ■ desorption.

Table II.   Effective diffusion coefficients ($D \times 10^{-12}$)

Adsorbate	Degree of pore filling (%)	Sample A	Sample B	Sample C	Silicalite (ref. [18])
n-hexane	20	3.9	3.9	3.0	7.5
benzene	20	3.4	3.4	2.7	8.6
cyclohexane	20	1.1	0.91	0.55	
water	20	1.2	0.082	0.038	
n-hexane	80	16.0	16.0	15.0	
benzene	80	9.7	13.0	8.7	
cyclohexane	80	0.52	0.12	0.072	
water	80	0.66	0.048	0.033	
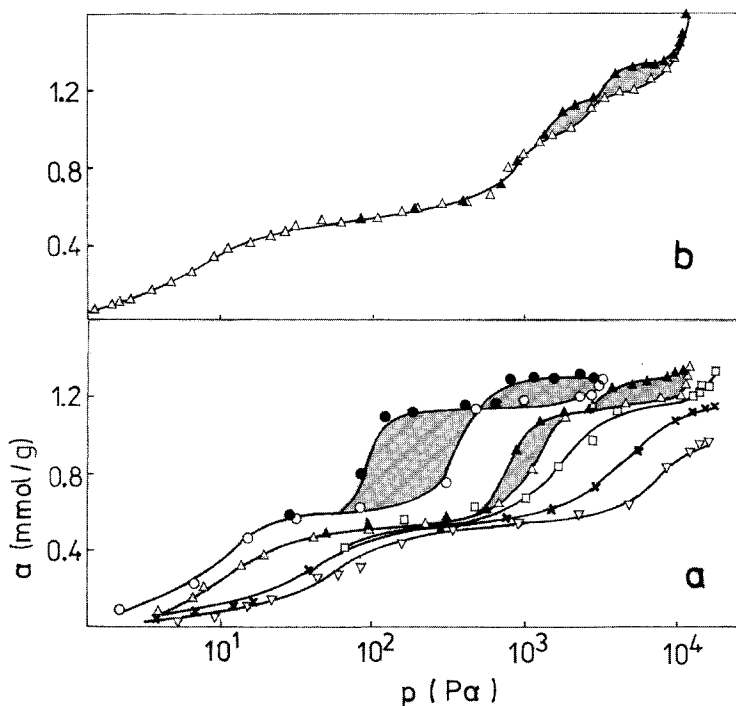
Fig. 2.   (a) Adsorption isotherms of benzene on sample C (○ 0°C, △ 25°C, □ 35°C, × 45°C, ▽ 55°C; ● ▲ desorption). (b) Adsorption (△) and desorption (▲) isotherms of benzene on silicalite at 25°C.

of the dealuminated samples whereas no hysteresis is observed for the parent sample A. It has been reported for Y type zeolites that dealumination is associated with the creation of mesopores [4, 5]. Therefore, the small hysteresis loop observed above $p/p_0 = 0.2$ is probably due to capillary condensation in mesopores.

Dealumination has more effect on the adsorption of benzene. Here the shape of the isotherms is changed drastically and pronounced hysteresis loops are observed after dealumination. The hysteresis loops may be discerned better in Figure 2a where for sample C benzene isotherms at different temperatures are given. The isotherms of sample C are characterized by:

- plateaus at about 0.6 and 1.2 mmol/g.
  (As 0.69 mmol/g is equal to 1 molecule per cross-section of the two pore types ($\frac{1}{4}$ unit cell) the plateau correspond to about 1 and 2 molecules per cross-section.)
- two hysteresis loops separated from each other by a point of inflection at 2×10^3 Pa ($25\,^\circ$C).
  (The upper small hysteresis probably arises from the same reason as in the case of *n*-hexane adsorption, whereas capillary condensation can be ruled out in the range of adsorption of the second molecule per $\frac{1}{4}$ unit cell. This phenomenon will be discussed later.)

This shape of the benzene isotherm is similar to that of the silicalite sample used for comparison (Figure 2b, refs. [6–8]). As detected from the ^{29}Si MASNMR spectrum the structure of sample C is more regular than that of the silicalite sample. This may be the reason for the more distinctly marked plateaus, steps and hysteresis loops in the isotherms.

For the adsorption of benzene on silicalite, an unusual dependence of the differential heat of adsorption on the adsorbed amount, showing minima and maxima, has been described by Thamm *et al.* [10,11]. Therefore, it is interesting to compare the heat curve of silicalite with that of the highly dealuminated ZSM 5 zeolite (Figure 3). Indeed, the heat curve of benzene on sample C shows a similarly complicated dependence to that of silicalite (dotted curve from [11]), but does not agree completely with it. For sample C the minimum is more shallow and only one maximum at about 1 mmol/g is observed. In the evaluation of these differences, it must be taken into account that sample C contains a small amount of nonframework aluminium species which may modify the interaction of the benzene molecule with the adsorbent and with one another.
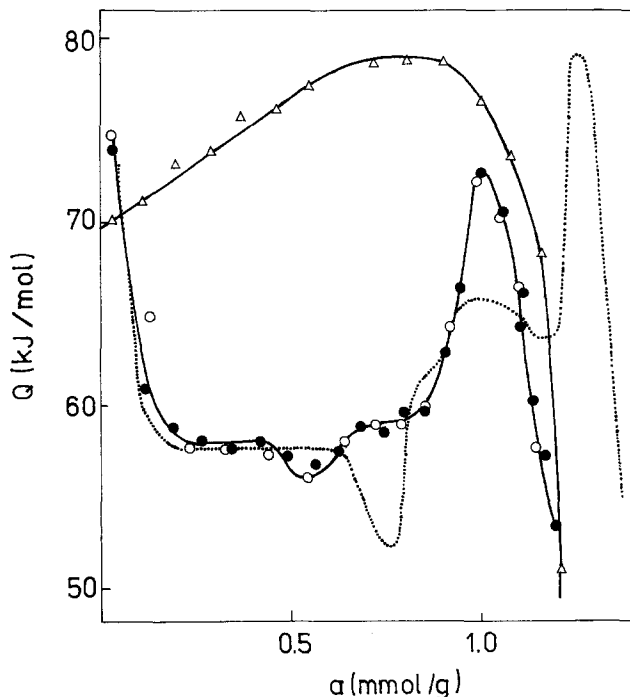

Fig. 3.   The dependence of the differential molar heat of adsorption Q at $28\,^\circ$C on the adsorbed amount a: $\triangle$ *n*-hexane, $\bigcirc$ benzene ($\bullet$ second run) on sample C; ⋯⋯ benzene on silicalite.
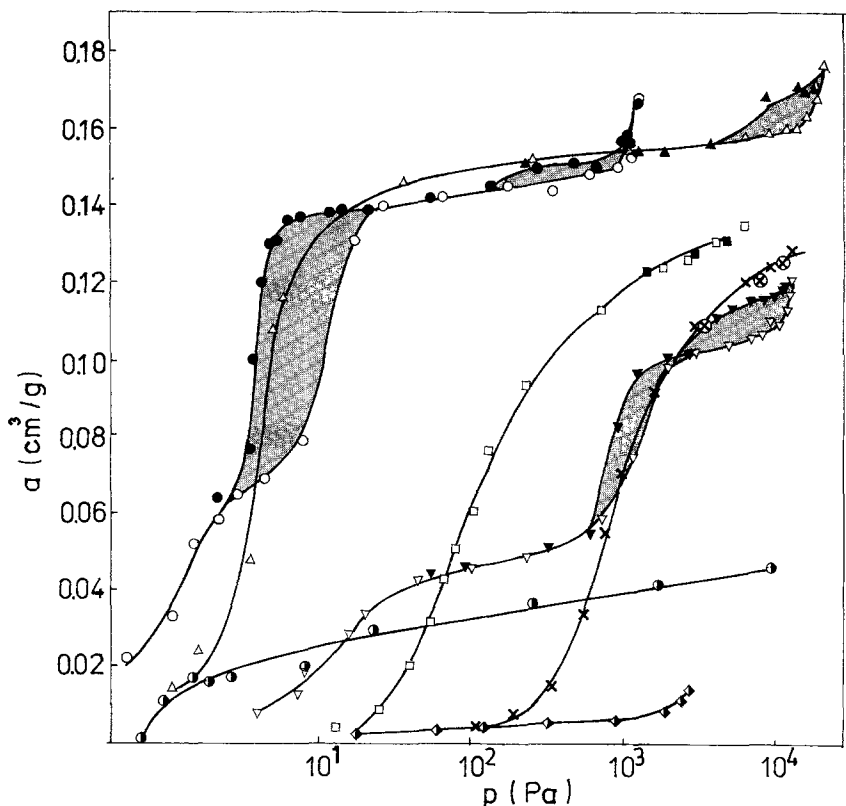
Fig. 4.   Adsorption isotherms at 25°C: ○ p-xylene, △ n-hexane, ▽ benzene, □ ethanol, × methanol, ◑ cyclo-hexane, ◈ water; ● ▲ ■ ⊗ desorption.

Figure 3 also contains the heat curve of n-hexane on sample C. It agrees completely with the corresponding curve on silicalite [10] and is also in good agreement with values for ZSM 5 zeolites in [6]. This means that the adsorption equilibrium of n-hexane is not substantially influenced by dealumination, whereas for benzene the heat of adsorption strongly rises and its coverage dependence completely alters with increasing aluminium content of the ZSM 5 structure [12].

The water sorption in ZSM 5 is reduced significantly by dealumination (Figure 1). A strong correlation between water uptake and the content of framework aluminium atoms was published by Weisz [13] for ZSM 5 and mordenite.

Adsorption isotherms for different molecules on sample C are represented in Figure 4. As may be seen the pore volume is filled completely by n-hexane and p-xylene; it is about 66% filled by benzene, ethanol and methanol; about 20% filled by cyclohexane and is not filled by water. These differences in pore filling are due to the hydrophobic character, to the limited pore diameter excluding cyclohexane from one kind of pore and probably to the formation of adsorbate structures (benzene).

The affinity to adsorption decreases in the sequence:

p-xylene
n-hexane   > benzene (the first molecule per cross section)
cyclohexane
> ethanol > benzene (the second molecule) > methanol.

With the exception of the second benzene molecule this sequence corresponds approximately to the decreasing molecular weight of the molecules and is due to a pure dispersion interaction. This confirms the former results on silicalite [6, 10].

Up to the present, the available experimental data on the benzene/silicalite adsorption system give no clear picture on the microscopic state of the adsorbed benzene molecule. While from energetic reasons the channel sections seem to be preferred adsorption sites [11, 18], the cross-sections are more favourable from entropic reasons. The latter assumption is supported by the nonlimited isotropic mobility of the adsorbed benzene molecule concluded from Raman spectroscopy and by NMR results showing the strong hindrance of the mobility of methane by preadsorption of benzene [14].

The adsorption of one benzene molecule per $\frac{1}{4}$ unit cell represents a stable state over a wide pressure range. The uptake of the second molecule takes place above a critical pressure within a narrow pressure range and is associated with a strong increase in the heat of adsorption (Figure 3). This behaviour may be accounted for by assuming the formation of molecular associates above 1 molecule per $\frac{1}{4}$ unit cell, while the low pressure hysteresis loop indicates difficulties in the dissociation of these clusters.

The situation is further complicated by the fact that a pore widening by interaction with the adsorbate seems to be possible. The idea of a 'flexible' framework structure is supported by MASNMR spectroscopy. ^{29}Si NMR spectra obtained for adsorbate loaded ZSM 5 and silicalite samples show clearly a significant influence on the relative intensity of the different lines specific to each adsorbate molecule [15–17].

Moreover, recent calorimetric measurements with further adsorbate molecules give evidence that the 'anomalous' behaviour is not limited to aromatic molecules but is observed generally for molecules with diameters comparable with those of the pores as for example with iso-butane and iso-butan-1-ol [11].

From measurements of the uptake rate for n-hexane, benzene, cyclohexane and water effective diffusion coefficients were estimated and listed in Table II. In the case of the parent sample A at 20% pore filling no significant differences between the four molecules exist. The values of cyclohexane and water become smaller with increasing Si/Al ratio (samples B and C) and increasing pore filling. On sample C the effective diffusion coefficients for n-hexane and benzene are in satisfactory agreement with those given by Wu $et\ al.$ [18] for silicalite (Table II, column 6).

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