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Expressiveness of Adsorption Measurements for Characterization of Zeolitic Materials—A Review*

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Abstract. This critical review concerns the author's results and experience in adsorption studies on molecular sieves comprising crystalline microporous aluminosilicates and aluminophosphates as well as amorphous mesoporous aluminosilicates. The discussion is mainly based on three distinctly different standard adsorbates: nitrogen, benzene, and water. The highlights or advantages and the shortcomings or limitations are considered from the points of view of the experimental procedures and expressiveness or concluding. The results are compared to several other zeolitic materials and adsorbates. Adsorption technique is a valuable tool for characterization of the molecular sieves. Since the measurements are very sensitive to modification of the materials, the investigations require sufficiently thorough procedures and the results a careful interpretation. A comparison between the results for larger series of materials yields valuable conclusions that are much more expressive than those from a single measurement or material.

Keywords: adsorption, isotherms, adsorbent heterogeneity, adsorption centres, sorption capacity, adsorption mechanism, adsorption theory, adsorption equation

1. Introduction

High porosity of zeolitic materials causes their good adsorption properties. Large surface area of the pores is a preliminary condition for significant adsorption processes. Structure and/or composition of an adsorbent and especially of its surface are other important factors. These features relate to the presence of definite centres that determine mutual interactions between the surface centres and adsorbed species. Generally, such interactions enable the adsorption processes to occur. Thus, the pore dimensions delimit which molecules can penetrate the pores, while the surface state determines affinity of an adsorbate to adsorbent. Both parameters together set the "static" feature of adsorbents, sorption capacity, defining the full filling of the pores with an adsorbate under studied experimental conditions.

Mobility of the adsorbate molecules inside the pores concerns penetration depth, diffusion rate, internal distribution, interpenetration between potentially existing various pore systems, desorption, etc. Both the diffusivity and the sorption capacity are temperature dependent phenomena that result in their own thermal effects coinciding with the whole process. The adsorption processes run this way only when no reactions occur simultaneously. Otherwise, the processes are more complicated. Therefore, numerous parameters and conditions have to be considered for evaluation of the adsorption measurements.

Zeolitic materials comprise molecular sieves from several groups. The most important are: crystalline microporous zeolites (aluminosilicates) and aluminophosphates (Baerlocher et al., 2001; Breck, 1974; Wilson et al., 1982), layered aluminosilicates of semicrystalline structure with micro- and mesopores (Roth et al., 1995; He et al., 1998), amorphous mesoporous

*Dedicated to the memory of Professor Wolfgang Schirmer.

(alumino-)silicates (Beck et al., 1992; Kresge et al., 1992), and derivatives thereof substituted with various metals in their framework or skeleton. All the crystalline microporous materials exhibit regular pore systems with exactly defined geometry, directions, and dimensions below 15 Å corresponding to smaller chemical molecules. The pores of mesoporous materials have the dimensions from those of micropores to 50 Å although are not as exactly regular as in the crystalline solids. Thus, the zeolitic materials are well suitable and promising samples for modelling adsorption processes and analytical description of adsorption results. This is opposed to classic adsorbents such as carbons, oxides, glasses, etc., which exhibit undefined pore structures and a broad distribution of dimensions. Consequently, any modelling or calculation requires a number of arbitrary, hypothetic assumptions that are hardly revisable.

Nitrogen, benzene, and water have been chosen as standard adsorbates. These molecules exhibit different dimensions and shapes, various electron structures, dipole moments, and interaction abilities. Nitrogen has inert, large, cylindrical molecules with a quadrupole moment due to a multiple bond, benzene has large and flat rings with π electrons able of interactions, and water has small molecules strongly interacting due to a high dipole moment. This choice covers the three principal domains of interactions affecting adsorption. Other adsorbents have been used for special purposes or comparison.

The presented adsorption measurements focus on two main aspects considered below:

– characterization of the pore system of the studied zeolitic materials and
– description of adsorption isotherms with use of various adsorption equations.

Adsorption results give important information on the adsorbent structure, supplementary to X-ray examinations, especially concerning the pores and their accessibility to adsorbates. The X-ray diffraction is insensitive to possible amorphous deposits in the pores or other hindrances to diffusion, e.g., interfaces in overgrown crystals. The second aspect includes both the verification of the existing adsorption models and the search for correlation between the adsorption theory and experimental results. The present review is predestined to evoke more general considerations and search for more common tendencies, dependences, influences, mechanisms, etc., which might offer a broader insight into adsorption processes in regular pores of zeolitic materials.

2. Experimental Basis and Results

The samples of all considered materials were synthesized hydrothermally from the reaction mixtures containing mostly organic templates (structure directing agents) as described for particular materials in respective references. All the materials were thoroughly calcined under shallow-bed conditions to remove fully the templates from the pores. Typical calcination was performed in two steps, at 673–773 K under a slow stream of dry air and at 773–823 K under a slow stream of oxygen for at least 48 h each. Prior to the adsorption measurements, each sample of ca. 0.1 g was freshly activated *in situ* at 673–800 K under stationary vacuum of less than 10^{-3} bar until constant mass was achieved ($\Delta m \leq 10^{-5}$ g/12 h), for at least 8 h.

The adsorption isotherms for nitrogen were recorded with use of an automated volumetric analyzer ASAP 2010 (Micromeritics Instr. Corp., USA) or Omnisorp 100 (Omicron Corp., USA) at 77 K, mainly in the dynamic mode. Static measurements revealed no significant differences. The adsorption isotherms for benzene and water were determined gravimetrically at 298.2 K in a temperature-controlled vacuum device equipped with a McBain quartz spring balance and MKS Baratron gauge. Each point was recorded after the sorption equilibrium was attained (Δm $\leq 10^{-5}$ g/12 h) under a constant pressure of the adsorbate vapour. The adsorbates were degassed in several cycles of a freeze-and-thaw procedure. The adsorption isotherms for other adsorbates, like alcohols, *n*-hexane, etc., were measured analogously. The obtained results have been presented in the respective refs. and are not reproduced here except exemplary illustrations of adsorption isotherms for particular adsorbates and adsorbent groups.

3. Summarizing Considerations

3.1. General Notices

Adsorption ability of porous solids results from their surface and structural heterogeneity, being the reason for mutual interactions and bonding of adsorbate molecules with adsorbent surface. In zeolitic materials with a regular structure, heterogeneity may be due to defects in the framework and/or on the inner (pore)

or external (crystal) surfaces. For aluminophosphate molecular sieves, an additional effect arises from the charge discontinuity of the structure composed of alternating $(AlO_{4/2})^-$ and $(PO_{4/2})^+$ tetrahedra that generate strong hydrophilic properties. Modification by isomorphous substitution of metal ions in the framework or skeleton results in a compositional heterogeneity. All the above structural irregularities are adsorption centres of various affinities to different adsorbates and create together the final adsorption effect. However, adsorption properties also depend on crystal size (Shiralkar et al., 1991), crystal morphology (Foger et al., 1984; Kornatowski et al., 2003a, 2004), Si/Al ratio (Müller and Unger 1988; Choudhary et al., 1990), Al distribution (Zikanova and Derewinski, 1995; Müller et al., 1988), acidity and degree of ion exchange (Müller et al., 1988; Shiralkar et al., 1991; Choudhary et al., 1990), and the sorption history (Karsli et al., 1992). Adsorption on zeolitic materials with a highly ordered pore structure is more sensitive to modifications than that on amorphous micro-/mesoporous adsorbents. This is a chance for verification of the meaning of the parameters of adsorption isotherm equations (Kornatowski et al., 1995).

3.2. *Adsorption of Nitrogen*

Inert nitrogen molecules should not interact with and penetrate the adsorbents following the simple mechanism of volume filling of the pores and adsorption isotherms of type I (IUPAC classification). The aluminophosphate molecular sieves [Cr substitution evidenced by UV-Vis, NMR, EPR, and X-ray absorption spectroscopy] (Fig. 1; Kornatowski et al., 1998, 1999a,b,c, 2001a, 2003a, 2004) confirm apparently a lack of interactions. The isotherms usually exhibit an almost vertical increase to nearly the full sorption capacity under low relative pressures and no or minor further increase, i.e., a course parallel to the pressure axis (Fig. 1). Such a picture is characteristic of exclusively microporous adsorbents as well as of the lack of diffusion hindrances and phase transitions. An isotherm, sloped over a wide pressure range, may indicate diffusion hindered by adsorbate-adsorbent interaction, a partial clogging/narrowing of the pores, a non-uniform pore system as, e.g., micro- and mesopores in the layered molecular sieves (Fig. 2; Barth et al., 2002, 2004), etc. The sorption capacities of the MeAPO-5 materials (Fig. 1) are generally higher than that of $AlPO_4$-5 and follow rising metal contents. An opposed tendency

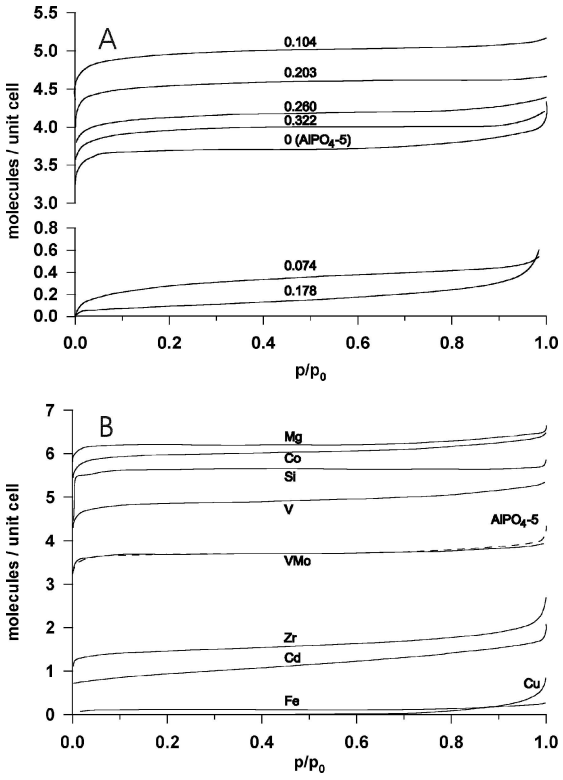

Figure 1. Isotherms of nitrogen adsorption on large AFI type crystals of (A) CrAPO-5 (upper part: framework Cr, bottom part: mainly extra-framework Cr, numbers denote Cr contents in atom%) and (B) other MeAPO-5 derivatives; Me contents as in Figs. 7 and 13 [after Kornatowski et al., 1999b].

for CrAPO-5 results likely from partial clogging of the pores by extra-framework Cr^{6+} species, very low amounts of which slightly increase with rising total Cr content.

The type I isotherms might be expected for all crystalline zeolites. However, the nitrogen isotherms for aluminosilicate zeolites and mesoporous materials are usually of type IV, indicating either a non-uniform adsorption mechanism or a significant presence of mesopores. Isotherm steps for the MFI type zeolites are accompanied by a clear desorption hysteresis. The step is commonly accepted as an indication to a liquid-solid phase transition of nitrogen in micropores and is distinctly observed for Silicalite-1 (Sil-1, pure silica framework) (Müller et al., 1988). The step and hysteresis loop for Sil-1 exhibit a regular vertical increase/decrease. This implies a non-perturbed mechanism of the nitrogen adsorption in two separate stages. Deviations appear for the materials lacking the ideal "monotonic" (pure SiO_2) structure of Sil-1, i.e., those

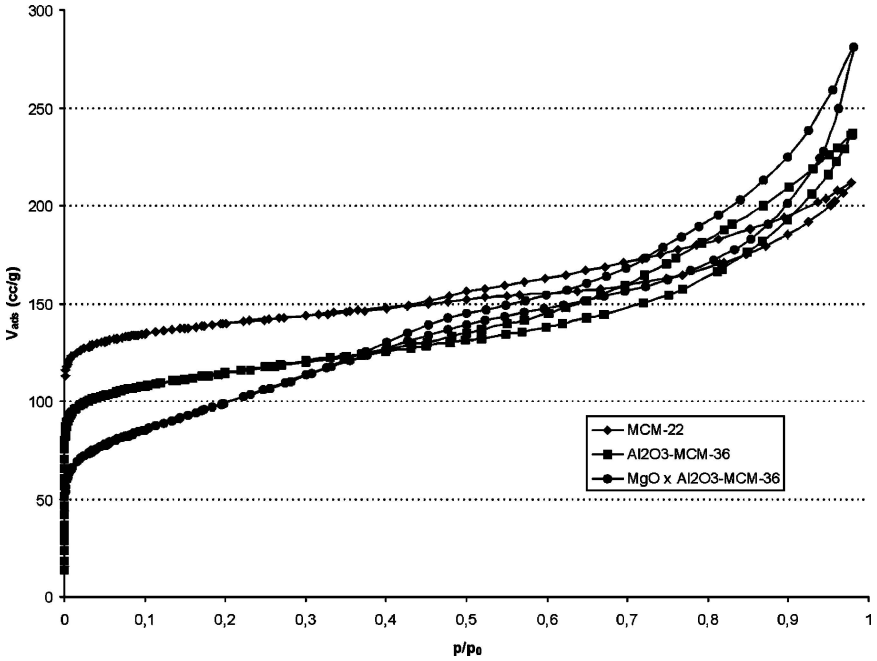

Figure 2. Examples for isotherms of nitrogen adsorption on layered MCM-36 materials [*cf.* Barth et al., 2002].

with substituted metals or a perturbed structure. Dealuminated ZSM-5 samples are informative examples for these two kinds of materials (Fig. 3; Kornatowski et al., 1995). The relevant adsorption isotherms show (i) the influence of Al centres on adsorption (parent sample), (ii) influence of the degree and the method of dealumination on the structure and adsorption, (iii) formation of mesopores after leaching Al ions from the framework, (iv) formation of macropores as larger structure defects, and (v) sensitive response of the adsorption results to fine changes in the material structure or composition. Increasing content of Al is reflected in a considerable and systematic weakening and inclination of the step and hysteresis loop without significant changes in the sorption capacity. Thus, with a growing dealumination level, the isotherms become more and more similar to that of Sil-1, which is to be expected. Metal substitution may cause transformation of the isotherm from type I to IV, as found for V and Ti derivatives of Sil-1, i.e., VS-1 (KVS-5) and TS-1 (Fig. 4; Kornatowski et al., 1997). These regular dependences suggest that the nitrogen molecules behave not completely inert and some interactions presumably occur between the multiple bond electrons and adsorption centres of the framework metal ions. This agrees with the simple isotherm shape and adsorption mechanism for aluminophosphates in which the strong effect of periodic framework structure may predominate local interactions with particular heterocentres.

Mesoporous molecular sieves of the M41S family (Beck et al., 1992; Kresge et al., 1992) exhibit the type IV isotherms (Kruk et al., 1997; Rozwadowski et al., 2000, 2001, 2002) of a sloped course and a flat, elongated hysteresis loop under higher pressures (Fig. 5), similar to the layered MCM-36 materials. This results from the properties of the two material groups, an amorphous structure and not exactly defined mesopores. Thus, the isotherms are a resultant of overlapping adsorption processes and phase transitions in various pores. Substitution of metals (e.g. Corma et al., 1994) and other modifications, e.g., tailoring the pores by coke deposition (Rozwadowski et al., 2000, 2001, 2002), do not change the structure from the point of view of the course and mechanism of adsorption. This reminds the aluminophosphates: the main influence of the structure and properties of the skeleton cannot be overbalanced by even significant effects of non-numerous heterocentres. Note that large mesopores enable the adsorbate molecules to overcome possible diffusion hindrances at the heterocentres. Stronger effects might be expected for larger molecules of dimensions comparable with the pores.

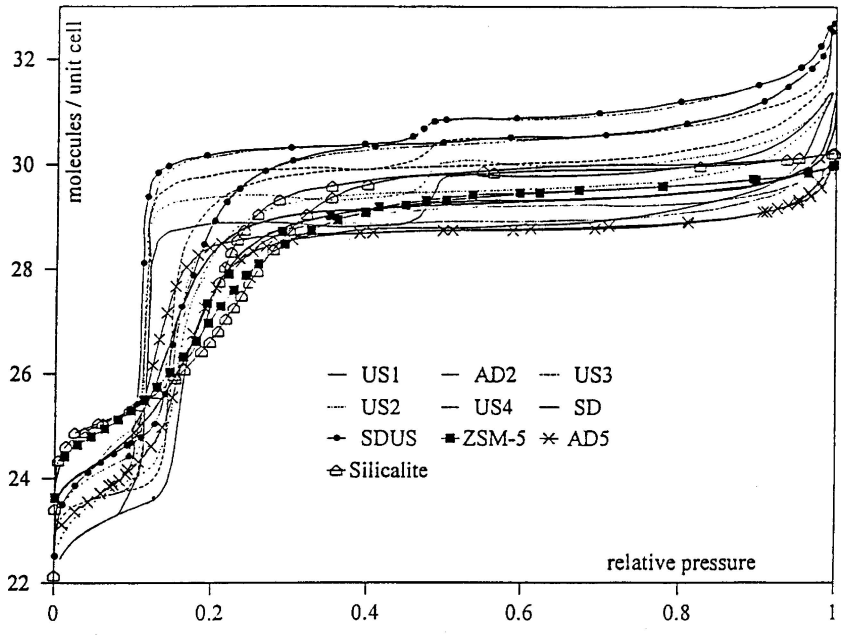

Figure 3. Isotherms of nitrogen adsorption on large crystals of ZSM-5 zeolites (MFI type, initial Si/Al = 39.5) dealuminated with different treatments to various extents (*cf.* Fig. 6(A) and 11); AD2 and 5 mean leaching with 1.25 N HCl at the boiling point for 2 and 5 h, [Si/Al 93.4 and 120.3]; SD—leaching with 0.3 M $AlCl_3$ at RT for 24 h, [67.0]; US1—steaming at 1200 K for 12 h after AD for 1 h [129.4]; US2—1100 K, 6 h after AD for 1 h [140.7]; US3—900 K, 65 h after NH_4^+ ion exchange [79.9]; US4 as US3 but 12 h [67.0]; SDUS—SD steamed as US4 [93.4]; [after Kornatowski et al., 1995].

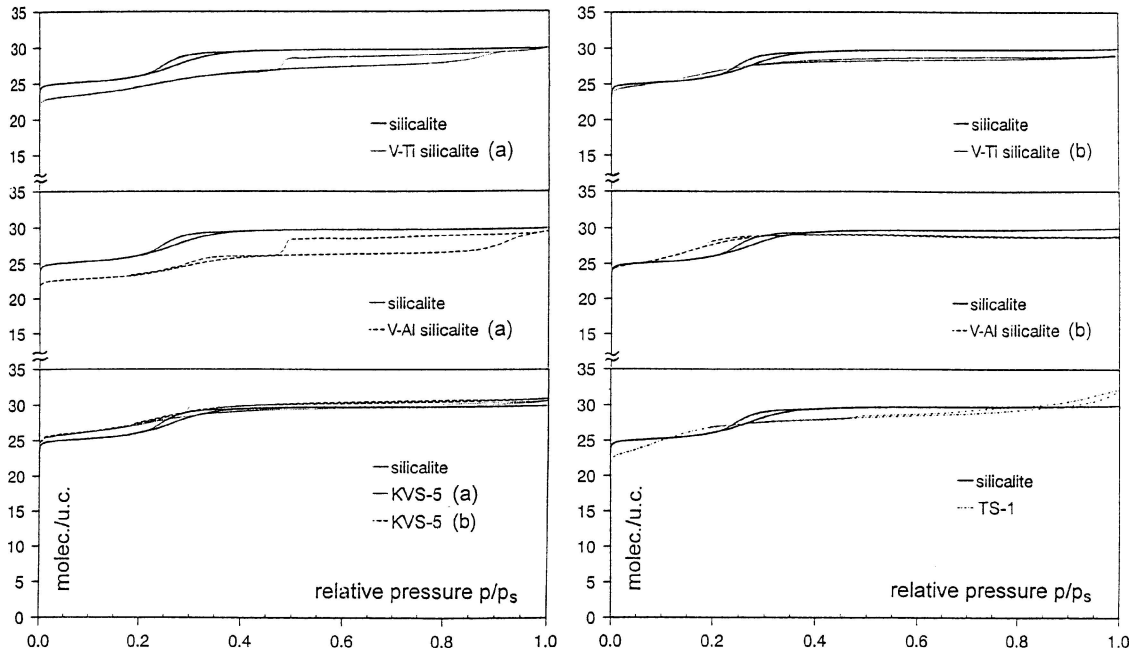

Figure 4. Isotherms of nitrogen adsorption on large crystals of MFI type zeolites substituted with V (KVS-5 or V-Al-Sil-1) and Ti (TS-1 or V-Ti-Sil-1); V, Ti, Al contents in atoms/u.c. are: V-Ti-Sil-1 (a) 0.61, 1.88, 0.17; (b) 0.44, 0.37, 0.12; V-Al-Sil-1 (a) 0.10, -, 1.86; (b) 0.05, -, 0.81; KVS-5 (a) 0.07, -, 0.14; (b) 0.05, -, 0.10; TS-1 0.03, 2.76, 0.14; Sil-1 -, -, 0.14; [after Kornatowski et al., 1997].

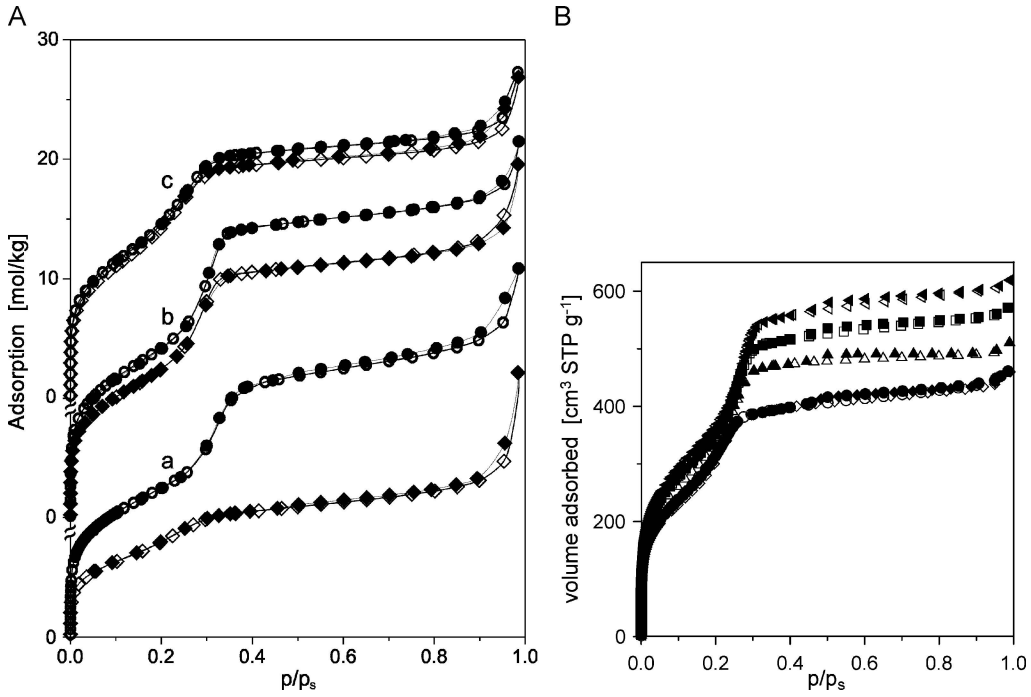

Figure 5. Isotherms of nitrogen adsorption (open symbols) and desorption (filled symbols) on mesoporous materials of: (A) the parent (circles) and coked (diamonds) MCM-41 samples with Si/Al ratios 15 (a), 30 (b), and 60 (c) [after Rozwadowski et al., 2001], and (B) the parent (◁) and Al-grafted MCM-48 samples with Si/Al ratios 34.5 (□), 12.7 (△), 3.8 (◯), and 3.5 (◇) [after Rozwadowski et al., 2002].

Sorption capacity is indicative of the pores accessibility. For open pores and a correct structure, the capacity (STP conditions) should be close to the geometric pore volume. Reduced capacities prove obstacles for nitrogen penetration. In microporous molecular sieves, the obstacles mean either clogging of the pores or inaccessible crystal domains. The latter can origin from overgrowth or aggregation of crystals and formation of borders for diffusion at the interfaces. The geometric pore volume of a mesoporous material cannot be calculated and an evaluation of the sorption capacity can be made by comparison to analogous materials. Higher perturbations in the capacities of mesoporous materials are rather seldom and indicate considerable problems with the structure (Rozwadowski et al., 2000, 2001, 2002).

3.3. Adsorption of Benzene

Benzene is an inert species with respect to its low reactivity, but it can interact with its vicinity via the π electrons of the aromatic ring. The benzene molecule has dimensions close to those of nitrogen. The latter has the form of a slightly elongated, thick rod while benzene resembles a round, thick plate or coin. These shapes differ from that of water molecule, which is much smaller, almost spherical, and strongly polar particle. Thus, benzene is the adsorbate of intermediate properties between the two poles represented by nitrogen and water.

Large crystals of MFI type zeolites exhibit the type I isotherms which reveal a not so steep increase under low relative pressures as those of nitrogen and adsorption rises over the whole pressure range (Fig. 6; Kornatowski et al., 1989, 1995, 1997). Noticeable differences occur between materials containing Al (Kornatowski et al., 1989, 1995), V, and Ti (Kornatowski et al., 1997). The ZSM-5 materials exhibit a steeper increase in adsorption under low relative pressures and a slower increase under higher pressures than the V and Ti derivatives. Severely dealuminated ZSM-5 samples exhibit type IV isotherms with a slight step at $p/p_s \approx 0.07$ (Fig. 6(A)). The step has been assigned to a surface barrier due to interactions of the π electrons with the non- or slightly acidic surface OH groups. In the non- or mildly dealuminated samples, this effect is likely overbalanced by interac-

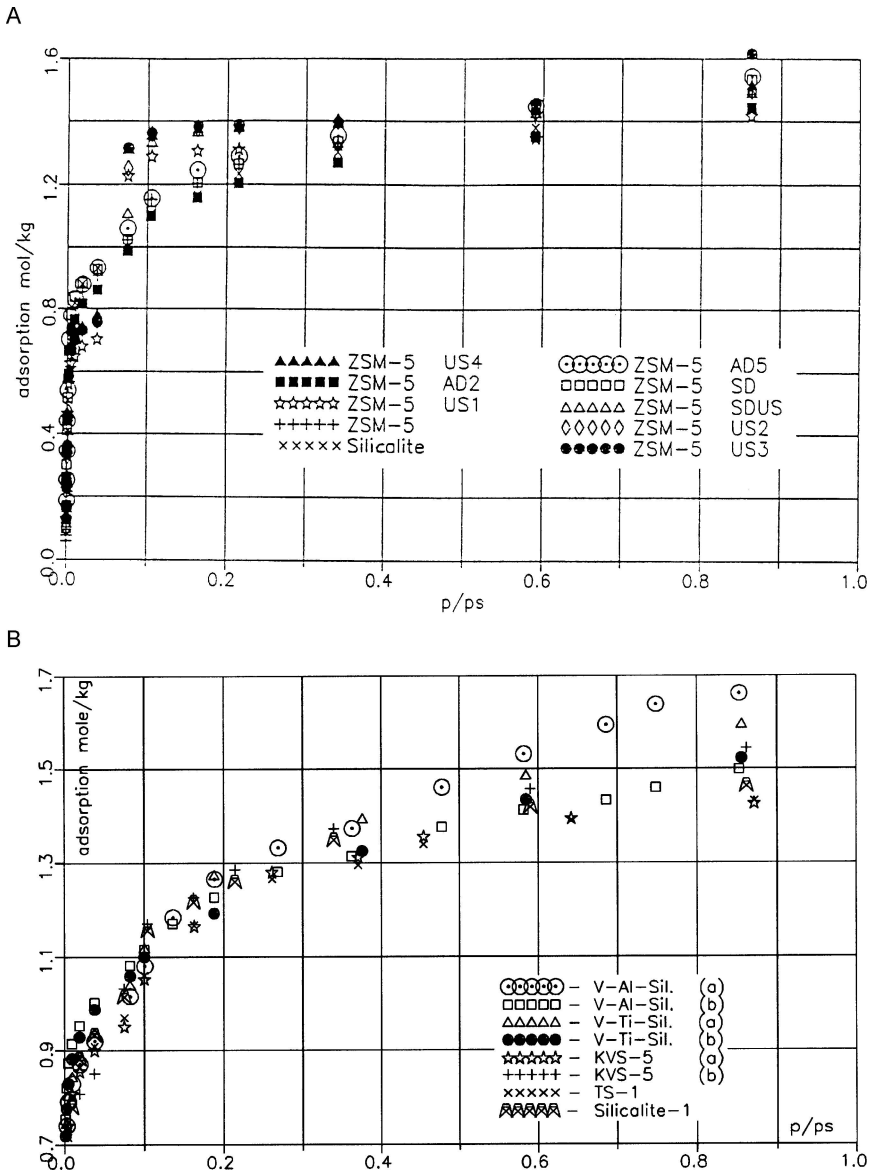

Figure 6. Isotherms of benzene adsorption on large crystals of MFI type zeolites: (A) ZSM-5 samples dealuminated with different treatments to various extents (details see in Fig. 3, *cf.* Fig. 11) [after Kornatowski et al., 1995]; (B) V and Ti substituted samples (metal contents as in Fig. 4) [after Kornatowski et al., 1997].

tions of the π electrons with strongly acidic OH groups at the Al centres, resulting in "sucking" the benzene molecules into the channels. Interestingly, the powder ZSM-5 materials often exhibit the type IV isotherms (Zikanova et al., 1995). This may result from larger external surface of the powders, which can comprise a sufficiently high number of surface OH groups to overcome other interactions and display the surface barrier effect in spite of the strongly acidic OH groups at the Al centres. Such relations coincide with adsorption of benzene on the other derivatives. The V and Ti centres are not as acidic as the Al ones and exert no distinct influence on adsorption (Kornatowski et al., 1997). The isotherms are more inclined (Fig. 6(B)) and reflect a filling of the pores driven by pressure and capillary forces. A smooth isotherm course without steps indicates a

non-perturbed diffusion and the lack of hindrances or phase transitions. Note that Sil-1, composed of pure SiO_2, exhibits the same "quiet" course as the V and Ti derivatives (Fig. 6(B)).

The experimental sorption capacities support the above considerations. Their values are higher than the geometrical pore volume (Kornatowski et al., 1995). This implies a significant participation of the external crystal surface in the total adsorption. Such an effect would be impossible without actual interactions of benzene with the surface OH groups.

The AFI type structure, homogeneously composed of alternating $(AlO_{4/2})^-$ and $(PO_{4/2})^+$ tetrahedra, is comparable to uniform Silicalite-1 built of neutral SiO_2, but has much wider pores. A possible heterogeneity comprises structure defects and substituted metals. The type I adsorption isotherms are similar to those of nitrogen with a steep increase under low pressures and an almost flat further course, although with large differences in the sorption capacities between various metal derivatives (Fig. 7; Kornatowski et al., 1994a, 1999a,b,c, 2001a,b, 2003a,b, 2004; Rozwadowski et al., 1999). The isotherms show almost no increase over $p/p_s \approx 0.15$ and are parallel to each other, independently of the kind of metal, its amount, etc. Thus, all the materials attain the full sorption capacity under a low pressure. The similar shape and the parallel isotherm course indicate the same adsorption mechanism as for nitrogen.

The strong variations of sorption capacities from ca 0.5 to ca 1.5 mmol/g do not indicate clogged pores since the materials exhibit high nitrogen adsorption. Moreover, the capacities increase with the metal content. Deviations from this effect are not numerous, e.g., SAPO-n materials (substitution for P, not Al). The parent $AlPO_4$-5 exhibits the capacity of a middle value. The systematic increase and distribution of the capacities below and over that of the parent $AlPO_4$-5 indicate that the adsorption of benzene is controlled by more factors and does not correspond to simple volume filling of micropores alone. The main additional factor is interaction of benzene with adsorption centres.

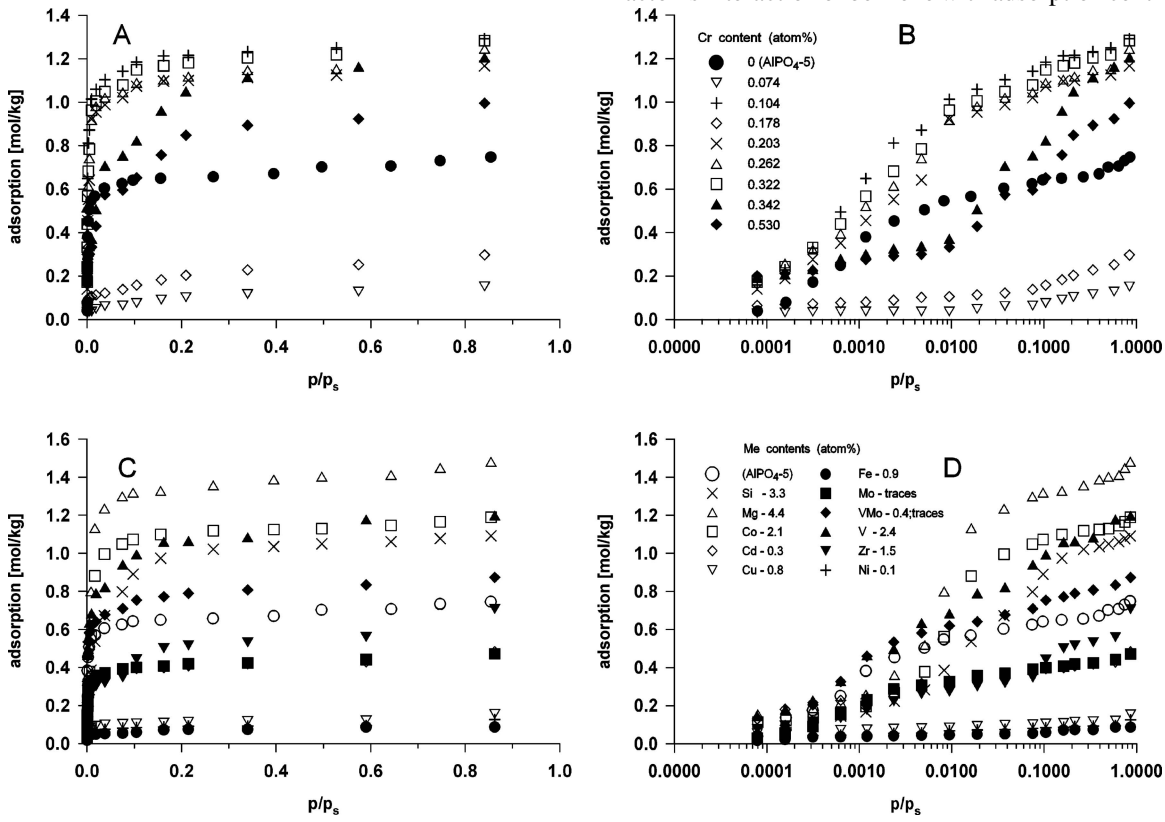

Figure 7. Isotherms of benzene adsorption on large AFI type crystals of CrAPO-5 (A, B) and other MeAPO-5 derivatives (C, D) together with parent $AlPO_4$-5. Plots B and D are logarithmic transformations of plots A and C, respectively, for a better illustration of the low-pressure ranges [after Kornatowski et al., 1999b].

Non-substituted $AlPO_4$-5 reveals numerous structure defects that hinder diffusion/adsorption (Lehmann et al., 2002, 2003a,b; Müller et al., 1999, 2004; Bódis et al., 2001, 2002; Kornatowski et al., 1998, 1999b,c, 2001a,b, 2003a,b, 2004; Rozwadowski et al., 1999). Substitution of metals usually results in a more perfect structure (Kornatowski et al., 2001a,b, 2003a,b, 2004, 2005) and a higher sorption capacity. A reduction in the capacity after incorporation of smaller amounts of metals indicates that interactions of benzene with the metal centres may be strong enough to form adsorbate islands around the centres (localized adsorption effect). These islands are large and stable enough to clog the pores, stop diffusion, and cause a not full filling of the pores. With increasing amount of substituted metals, the adsorption centres become closer to one another. The shorter distances enable a deeper penetration of the adsorbate molecules by jumping from one centre to another. The kind of metal has a secondary meaning for such increased diffusion, provided that interactions of benzene with the metal centres are sufficiently strong.

Adsorption measurements on various ground MeAPO-5 samples support the above findings (Fig. 8; Kornatowski et al., 2003a; Rozwadowski et al., 1999). Grinding large crystals should increase adsorption if it is limited by structure hindrances, e.g., interfaces between overgrown, inaccessible crystal regions. However, these effects are insignificant. The maximum increase in adsorption, found as expected for $AlPO_4$-5, was ca 13% only. Thus, the material heterogeneity and the interactions of adsorbate with adsorption centres are most important for adsorption.

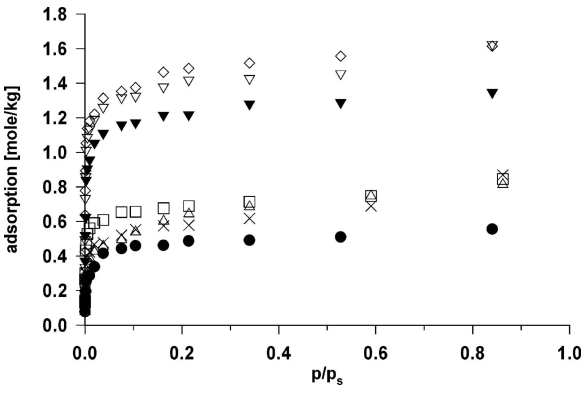

Figure 8. Isotherms of benzene adsorption on ground MeAPO-5 samples (AFI type): (◇) MgAPO-5 (4.4), (▽) MgAPO-5 (2.8), (▼) MgAPO-5 (1.6), (●) MgAPO-5 (0.6), (△) ZrAPO-5 (1.8), (×) VAPO-5 (0.1), (□) $AlPO_4$-5; the figures in brackets denote Me content in atom% [after Rozwadowski et al., 1999].

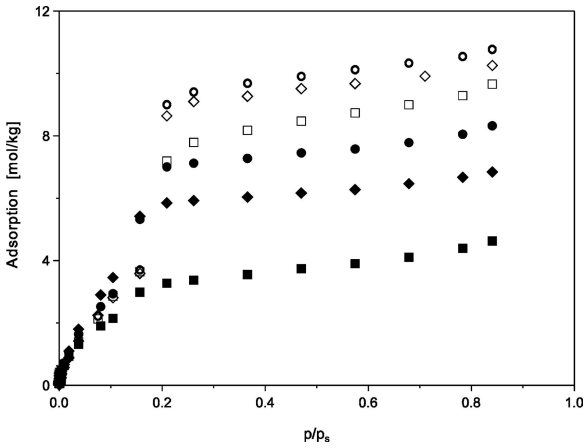

Figure 9. Isotherms of benzene adsorption on mesoporous Al-MCM-41 materials: the parent (open symbols) and coked (filled symbols) samples with Si/Al ratios 15 (squares), 30(circles), and 60 (diamonds) [after Rozwadowski et al., 2001].

Similar relations for benzene adsorption emerge from a series of $AlPO_4$-31 materials substituted with various metals in different amounts (Rozwadowski et al., 1998).

Adsorption of benzene on mesoporous MCM-41 and MCM-48 materials follows type IV isotherms (Figs. 9, 10; Rozwadowski et al., 2001, 2002, 2005). The benzene uptake proceeds via multilayer adsorption under low pressures, which is followed by capillary condensation reflected in a minor isotherm step. The shape and position of the steps are independent of the

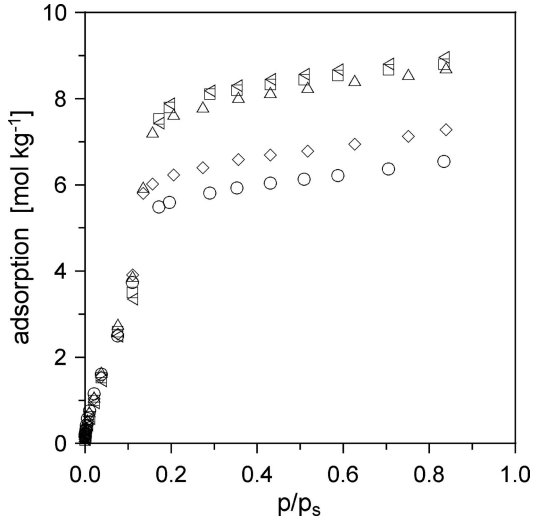

Figure 10. Isotherms of benzene adsorption on mesoporous MCM-48 materials: the parent (◁) and Al-grafted samples with Si/Al ratios 34.5 (□), 12.7 (△), 3.8 (◯), 3.5 (◇) [after Rozwadowski et al., 2002].

Al content. Only the height of a step and the relevant sorption capacity increase with the decreasing Al content, similarly as observed for other zeolitic materials (*cf.* above). Thus, these samples also reveal benzene-adsorbent interactions. They are weaker than even those in the MFI type zeolites, as the skeleton Al atoms of the mesoporous materials do not form strongly acidic OH groups. Coking the MCM-41 samples causes a stepwise transformation of the isotherms into type I and a drastic reduction in sorption capacity. This results from a decrease in both the mesoporosity (reduction of the pore dimensions) and the interaction strength after covering the adsorption centres with coke. Analogous effects appear after grafting Al onto MCM-48, which also implies a reduction in the pore dimensions due to significant deposition of Al species in the pores (Rozwadowski et al., 2002).

3.4. Adsorption of Water

Pure silica zeolites are hydrophobic and hardly adsorb water as the surface OH groups are weak adsorption centres. Al or other metals, incorporated into the framework, create (mostly) charged centres being stronger centres and adsorption becomes noticeable. This way, sorption capacities of microporous alumino- or metallosilicate zeolites depend primarily on the metal amounts and, additionally, on the kind of counterions located in the pores and balancing the framework charge. The "strength" of the counterions as adsorption sites depends on their charge and ionic radius. The highest adsorption of ca 22 mmol/g occurs on MgA zeolite of Si/Al = 1 (Rozwadowski et al., 1989). The faujasite type zeolites X and Y with Si/Al ratios ca 1.5 and over 2, respectively, exhibit lower capacities that also depend on ion-exchange and coking (Rozwadowski et al., 1992a,b, 1993a,b,c, 1994). The MFI type zeolites, containing much less metal centres, as dealuminated ZSM-5 zeolites (Fig. 11; Kornatowski et al., 1995) and the samples substituted with V, Ti, V-Al, and V-Ti (Fig. 12; Kornatowski et al., 1994b, 1997), exhibit further reduced sorption capacities. The first group demonstrates a straight relation of the capacity to the actual content of Al in the framework and insensitivity to extra-framework Al species (Kornatowski et al., 1995). The other group presents the same general dependence of the capacity on the metal content, independently of its kind and, additionally, fine differences between the metals. Namely, under the lowest relative pressures, increase in water adsorption also follows the metal contents but in a different way as compared to the

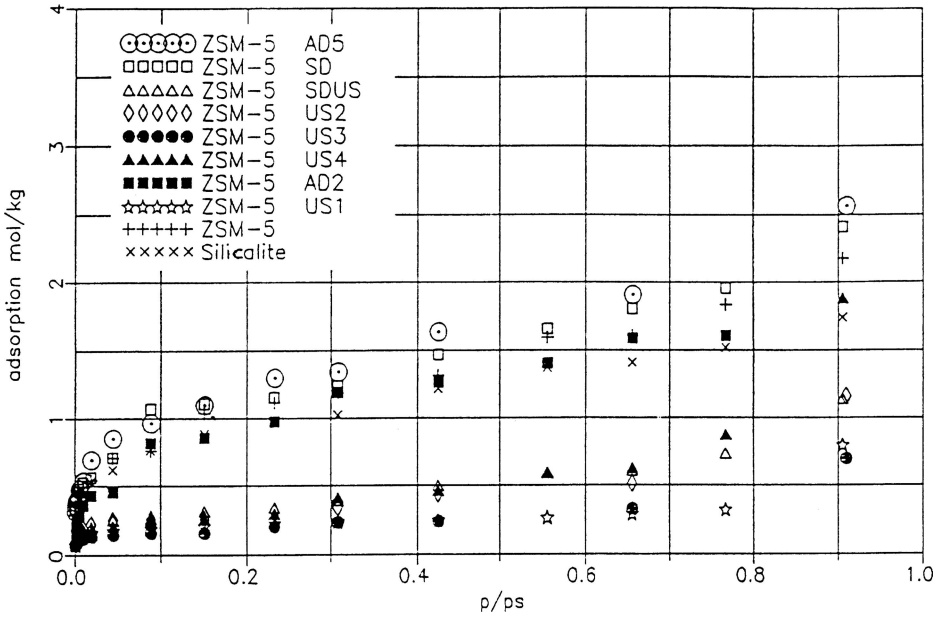

Figure 11. Isotherms of water adsorption on large crystals of ZSM-5 (MFI type) dealuminated with different treatments to various extents (details in Fig. 3, *cf.* Fig. 6(A)) [after Kornatowski et al., 1995].

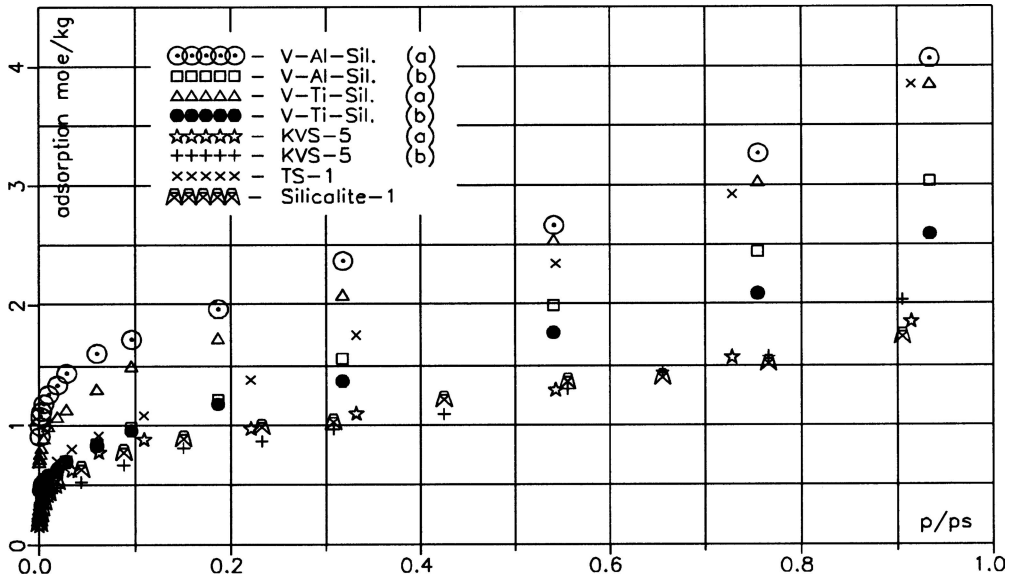

Figure 12. Isotherms of water adsorption on large crystals of MFI type zeolites substituted with V, Ti, and Al in combinations indicated in the legend; (a) means samples higher substituted than (b) [after Kornatowski et al., 1997].

high saturation region (Fig. 12). The shape of particular isotherms under low pressures illustrates differences in the interaction between the V, Ti, and Al framework centres and water. The fastest and highest adsorption is observed for the negative $(AlO_{4/2})^-$ centres, a weaker one for uncharged and/or differently coordinated V(IV) and/or V(V) centres with a double vanadyl bond or V-OH and V-ONa groups, and the weakest effect for the neutral TiO_2 centres. Note also that the differences can partially be due to the counterions in the pores.

The type I isotherms of highly adsorbing zeolite A and faujasites (not shown) indicate a quick filling of micropores with water up to the (almost) full sorption capacity. The further isotherm course shows an unperturbed diffusion of water into the whole pore system. After coking, the materials become less hydrophilic and the pores get narrower, which hinders diffusion and is reflected in the type II isotherms (Rozwadowski et al., 1992a,b, 1993a,b,c, 1994). This type is common for MFI type zeolites and reflects a slower diffusion dependent on pressure as a driving force. It is justified to assume that the isotherms mirror a weak adsorption on (mostly) isolated adsorption sites, which can be broken by increased pressure.

Adsorption of water on aluminophosphate molecular sieves is a distinct phenomenon. Their neutral frameworks are hydrophilic due to the charged $(AlO_{4/2})^-$ and $(PO_{4/2})^+$ tetrahedra and easily adsorb large water amounts. The AFI and ATO structure types exhibit isotherms of type IV or V (Fig. 13; Kornatowski et al., 1994a, 1998a,b, 1999a,b,c,d, 2001a,b, 2003a,b, 2004; Kornatowski, 2004, 2005; Rozwadowski et al., 1998). Both types are characteristic of a phase transition and change in the adsorption mechanism under a certain pressure. This is presumably connected with the pore diameters being over 7 Å, i.e., almost twice as large as those in zeolites. Large surface area and pore diameter together with a high affinity of the adsorbate cause a monolayer adsorption under low relative pressures. After the whole surface is covered by water, capillary condensation (phase transition) occurs and leads to the volume filling of the pores with a quasi-liquid adsorbate (Kornatowski and Rozwadowski, 1999d). The condensation is reflected in an almost upright step of the isotherms and steep increase in the adsorbate amount almost to the full sorption capacity. An accompanying distinct hysteresis loop confirms the occurrence of a phase transition. With growing contents of introduced metals, the step shifts to lower pressures and becomes less steep, the hysteresis loop diminishes, and the isotherm transforms in direction of type I (Fig. 13; Kornatowski et al., 1999b,c,d, 2001a,b, 2004; Kornatowski, 2004, 2005). These changes indicate that the capillary condensation occurs earlier, faster, and more fluently than that following a sharp step. This is justified by the growing number of adsorption sites able of strong interactions and by the shorter distances between the new sites. These effects are practically

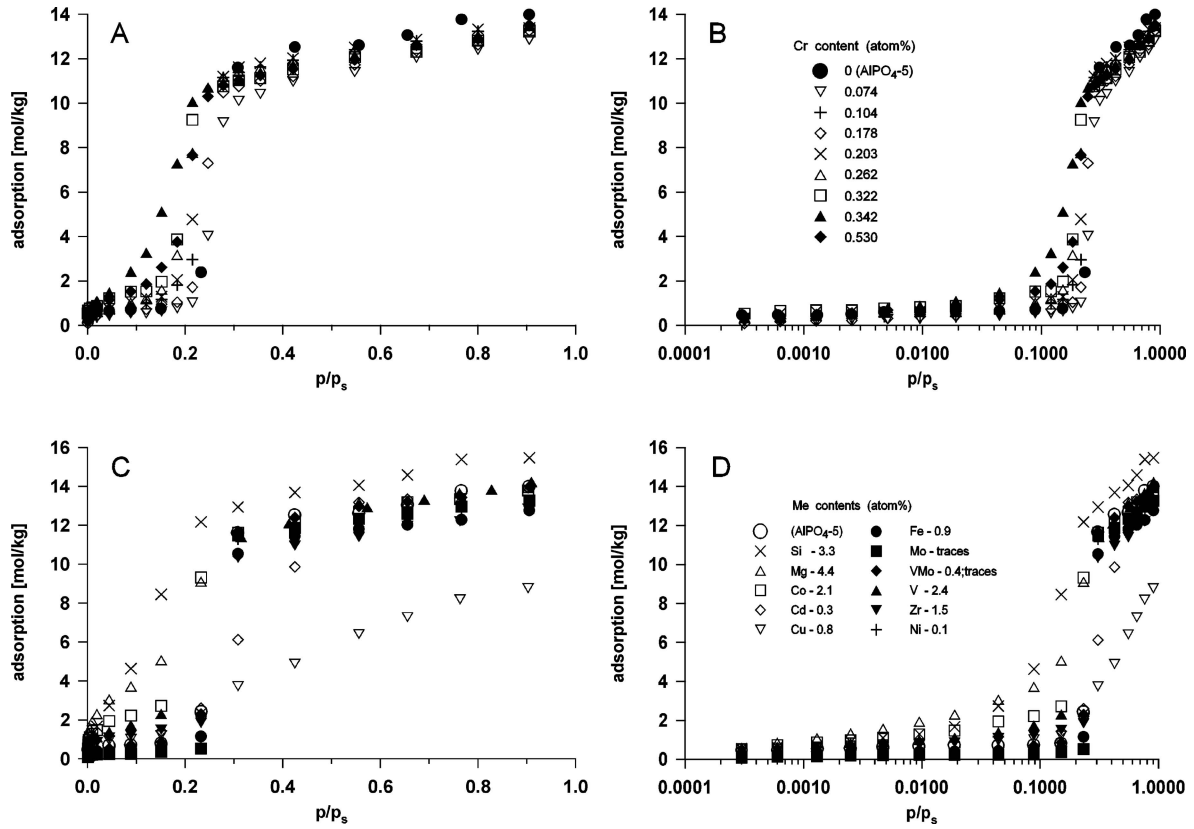

Figure 13. Isotherms of water adsorption on large AFI type crystals of CrAPO-5 (A, B) and other MeAPO-5 derivatives (C, D) together with parent $AlPO_4$-5. Plots B and D are logarithmic transformations of plots A and C, respectively, for a better illustration of the low-pressure ranges [after Kornatowski et al., 1999b].

independent of both the metal kind and the charge of the framework centres. Neutral Cr centres act similarly to, e.g., Mg ones (refs. as above). Almost no effect comes from extra-framework metal species. Consequently, the adsorption isotherms of water offer sensitive evidence for framework incorporation of metals into aluminophosphates.

The sorption capacity is practically constant for particular structure types and independent of modifications. Water molecules are small enough to pass by hindrances possibly present in the pores. They penetrate through the 6-membered rings of the structure, i.e., as through the walls, and fill the whole adsorption volume. Thus, the adsorption of water does not offer an indication for open or closed pore system of aluminophosphates.

In spite of the above relations, adsorption of water does not proceed fully homogeneously. Under low relative pressures, water (and methanol) distributes in accordance with structure irregularities and reflects the interfaces between overgrown crystal regions, creating the image of a dumbbell core (Kornatowski and Zadrozna, 2003b; Lehmann et al., 2002, 2003a,b). This indicates that the structural factors can also influence interactions with polar adsorbates. However, it is noticeable only at the initial stage of adsorption, before the phase transition.

Two other findings confirm the above picture. The crystal morphology and dimensions do not significantly influence the adsorption course. Grinding large crystals also does not change their adsorption behaviour (Kornatowski et al., 1999d, 2003a; Kornatowski, 2004). However, it may cause an apparent increase in the sorption capacity above the geometrical pore volume likely due to formation of numerous surface defects by the grinding (refs. as above).

Adsorption on mesoporous Al-MCM-41 and Al-MCM-48 proceeds similarly to that on aluminophosphates and corresponds to the above picture (Fig. 14; Rozwadowski et al., 2001, 2002, 2005). The course as

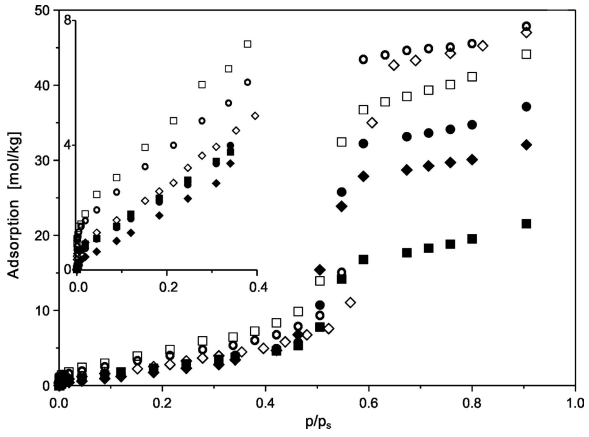

Figure 14. Isotherms of water adsorption on mesoporous Al-MCM-41 materials: the parent (open symbols) and coked (filled symbols) samples with Si/Al ratios 15 (squares), 30 (circles), and 60 (diamonds) [after Rozwadowski et al., 2001].

well as the position and height of the step of the type IV isotherms depend on the content of Al similarly as for aluminophosphates. The growing content of skeleton Al causes a shift of the step to lower pressures and decrease in its height. This indicates a higher adsorption of water under low pressures and an earlier capillary condensation. Modification by coking causes a reduction in hydrophilicity and, thus, in adsorption. The only difference in relation to aluminophosphates is that increase in the Al content results in lowering the sorption capacity. This is presumably the consequence of a low number of the Al centres, which may cause formation of clusters of liquid water around them and clogging the pores by adsorbate itself (strongly localized adsorption). The practically isolated Al centres are too rare and distributed too far from one other to yield the full filling of pores with condensed water.

3.5. Other Remarks and Brief Comparison with Other Adsorbates

The above findings reveal high sensitivity of adsorption, which can be seen in two aspects: (i) an extreme role of heterogeneity of adsorbents and (ii) an extreme response in adsorption results to changes or modifications of the adsorbents. The first relates directly to the adsorbent features, such as metal content, number of structure defects, distribution of both the metal atoms and the defects, etc. The second aspect deals more with adsorbates that, in response to the interactions with modified adsorbent, amplify the adsorption effects via an apparently over-proportional increase in the adsorbate-adsorbate interactions. However, such effects are hardly visible from a single measurement or for one system and become noticeable from comparison of the results for a larger series. For instance, one, two, or even three measurements could not demonstrate a relation between the isotherm step and metal content.

Postulated influence of crystal dimensions (Shiralkar et al., 1991) and morphology (Foger et al., 1984) on adsorption might be justified for two- or three-dimensional pore systems. For the one-dimensional pore systems (e.g., AFI type), these parameters have a secondary meaning. Their influence is indirect and expressed only via or in synergy with the substitution of metals that control the crystal shape or size and constitute simultaneously the main adsorption sites (Kornatowski et al., 2001b, 2003a, 2004; Kornatowski, 2004, 2005). The same holds for the ATO structure type (Rozwadowski et al., 1998). Thus, the actual effect of the crystal size and morphology itself on adsorption is hardly possible for explicit separation and determination.

An intriguing adsorption behaviour occurs under low relative pressures. It is not observable on the isotherms as it deals with the adsorbate distribution and requires special techniques. The investigations (cf. 3.4. above) with interference and FTIR microscopy of methanol and water adsorbed on the AFI type crystals under the pressures up to 1 mbar reveal an inhomogeneous distribution of both adsorbates, mirroring the intergrowth domains of the crystals (Lehmann et al., 2002, 2003a,b). The effect seems to be independent of the metal amount and distribution but depends on mutually connected parameters of the kind of metal and crystal morphology. The effect vanishes at higher saturation of the pores with the adsorbates. This is explicit evidence for a definite interaction and interdependence between the framework structure and the diffusion of polar adsorbates under low pressures. The adsorbate-framework interactions are likely weaker than the adsorbate-adsorbate ones. The former can therefore be manifested only under low pressures (for a thin, sparse adsorbate phase) and the latter become more significant in a denser adsorbate phase. These measurements give a new insight into the crystal structure itself as well as into the adsorption mechanisms and interactions occurring at various stages.

Relations between the crystal structure and diffusion are also visible form adsorption of iodine on large Sil-1

crystals (Kocirik et al., 1998; Masarik et al., 1998). Iodine penetrates the entire pore system uniformly only from gas phase or solution. A counter-diffusion in crystals initially saturated with solvent vapour is by up to three orders of magnitude slower than under co-diffusion conditions. At the initial adsorption stage, the colouring of the crystals by entering iodine is non-uniform and images the crystal intergrowth pattern. The counter-diffusion proceeds primarily along the interfaces of the crystal sections and then in the pores.

Mobility of adsorbate molecules during the adsorption processes can be divided into three stages: (a) external transport to the adsorbent surface, (b) passing the surface and entering the pores, and (c) diffusion inside the pores under interactions with adsorption centres of the pore walls and changing between various pore systems. The first stage does not deal with adsorbents. The last one has partially been discussed above. The middle point is controversial in the literature. Mostly, various surface barriers are assumed and accepted, e.g., the surface concentration and distribution of Al (Zikanova et al., 1995). However, thermal effects due to the adsorption heat have commonly been accepted as one of the most significant barriers for adsorbates passing the adsorbent surface. Recent experiments with adsorption of *n*-hexane on large crystals of the MFI type materials, carried out with use of an improved experimental device, have demonstrated that the thermal effects of adsorption influence neither the rate nor the diffusion coefficient, i.e., a thermal surface barrier does not exist (Wloch et al., 2004a,b). Earlier experiments with adsorption of *n*-hexane have yielded the method for measuring the diffusion coefficients in particular crystallographic directions (Caro et al., 1993).

At appropriate interactions between adsorbates and framework, molecular sieves can serve as host matrices to orient polar and polarizable molecules. *p*-Nitroaniline and other dies can form pearl-string-like oriented chains in the pores of AFI and MFI type crystals. Such macro domains reveal extraordinary optical properties that can be used for lasers, optical second harmonic generation, etc. (Werner et al., 1992; Marlow et al., 1996; Hill et al., 1994; Caro et al., 1997). The same holds for (dimethylamino)benzonitrile in the $AlPO_4$-5 channels (Marlow et al., 1993). Orientation of *p*-xylene proceeds with the molecule long axis parallel to the channel axis of SAPO-5 (Schüth et al., 1994).

The occurrence of discrete bridging OH groups and their strength in various MeAPO-5 materials have been discovered from adsorption of ammonia and pyridine (Müller et al., 1999; Bódis et al., 2002), and water and methanol (Bódis et al., 2001; Müller et al., 2004).

3.6. Analytical Approach and Description of Isotherms

Adsorption measurements give extensive information about adsorbate-adsorbent interactions that can be characterized by adsorption energy or adsorption potential. The adsorption energy distribution function gives a quantitative characterization of the global energetic heterogeneity of solids. The total heterogeneity of adsorbents is the sum of the structural and surface heterogeneities and is characterized by the adsorption potential distribution function. This function is evaluated from the isotherm equations that are based on the Polanyi-Dubinin potential theory developed as the theory of volume filling of micropores (Dubinin, 1966). The theory has been developed for classic adsorbents of non-ordered pore systems, like carbons, glasses, oxides, etc. The equations derived from this theory are best useful for nonpolar solids with a homogeneous micropore structure (Rozwadowski et al., 1993c). They should generate isotherms fitting the experimental data. A measure for the fit of a calculated isotherm is the determination coefficient (DC) that reflects an almost ideal fitting at a value of at least 0.999, while 1.0 means exact covering.

In relation to the classic adsorbents, zeolitic materials can be regarded as model systems due to their perfectly ordered structures and constant dimensions and directions of the pores, fully reproducible in each synthesis. Systematic modifications of zeolitic materials by ion exchange, dealumination, incorporation of heterometals, etc. affect adsorption properties due to increased adsorption potentials in the pores, consisting of van der Waals, electrostatic, and capillary forces. Thus, adsorption properties reflect possible variations in heterogeneity.

Stoeckli started to generalize the adsorption theory to gain its better applicability by introduction of a distribution function (Stoeckli, 1977). Later, many authors tried to improve the concept and analytical description of adsorption isotherms by a further tuning of parameters (details in Rozwadowski et al. (1993c) and refs. therein). In general, an isotherm description

is based on the fundamental Dubinin-Astakhov (DA) Eq. (1)

$$W = W_0 \exp[-(A/\beta E_0)^n] = W_0 \exp[-k(A/\beta)^n] \quad (1)$$

where W is the volume of the "liquid-like" adsorbate filling the micropores under the pressure p and at temperature T, W_0 is the total volume of micropores, β is the constant characterizing the adsorbate, A is equal to RT $\ln(p_s/p)$ and determines the adsorption potential, p_s is the saturation pressure of adsorbate vapour at temperature T, E_0 is the characteristic energy of adsorption, k is the structural parameter correlated with micropore dimensions, and n is the parameter connected with the microporous structure of the adsorbent. The DA Eq. (1) illustrates the apparently natural consequence that the adsorption volume W is a part of the total pore volume W_0, determined by all parameters connected with the adsorbent and adsorbate. The relation between W and W_0, implied by the Equation (1), could not be verified for the classic adsorbents since calculation of their pore volume was impossible (non-defined pore systems). Thus, in routine calculations, initially for the classic adsorbents and later also for the zeolitic materials, the W_0 value has been accepted as one of the adjustable parameters for finding the best fit between calculated and experimental isotherms. Zeolitic materials of definite pore geometry give no justification for application of such "open" W_0 values. Therefore, we performed (i) classic calculations with "open" W_0 and (ii) modified calculations taking the actual values of micropore volume from the experimental isotherms (a) at the relative pressure of 0.1 (i.e., close to the applicability limit of the equations), (b) at the relative pressure of 0.85 (i.e., almost full saturation with adsorbate), and (c) using geometrical pore volume for various MFI type materials and with use of several different isotherm equations (Kornatowski et al., 1995, 1997). The results manifested that the actual W_0 values at $p/p_s \approx 0.1$ match best the classic "open" ones and the total volume of micropores gives no reasonable results. This holds for all the isotherm equations applied and for two different adsorbates, benzene and water. Similar tendency has also been found for water adsorption on zeolite Y (Rozwadowski et al., 1993c), for benzene adsorption on aluminophosphates of AFI type (Kornatowski et al., 1999b,c; Rozwadowski et al., 1999) and ATO type (Rozwadowski et al., 1998), and for mesoporous MCM-41 (Rozwadowski et al., 2001). This broad spectrum of materials, exhibiting similar relations, suggests that this is a rule and implies that an analytical description of the isotherms should comprise only the pores actually involved in the process of adsorption since the measured adsorption does not depend on the total pore volume existing in the adsorbent. The latter delimits only the maximum sorption capacity. Thus, the meaning of W_0 requires a re-definition, at least for the zeolitic materials.

The description of isotherms for zeolitic materials yields usually worse results (DC mostly below 0.999) than for the classic adsorbents. Adsorption of water and methanol on zeolite A that can be fully saturated with these polar adsorbates is an exception (Rozwadowski et al., 1989). This observation is difficult to explain at present. A possible reason might be that an additional type of heterogeneity occurs in the regular pores of zeolitic materials, which should be taken into account. This seems to be confirmed by a better description of the isotherms found for zeolites modified by coke deposits (Rozwadowski et al., 1992b, 1993a, 1994) and for amorphous mesoporous materials (Rozwadowski et al., 2001). In these cases, the pore systems are less regular than in original crystalline zeolitic materials.

Adsorption potential, reflecting adsorbent heterogeneity, should depend on compositional changes such as ion exchange, coking, or metal substitution. However, no dependences or at least tendencies have been found for zeolites in relation to adsorption of water and benzene (Rozwadowski et al., 1989, 1992a,b, 1993a,b,c, 1994). Nevertheless, two exceptions have been found for adsorption of benzene on MgAPO-5 (Rozwadowski et al., 1999) and CrAPO-5 (Kornatowski et al., 1999b). The values of adsorption potentials decrease surprisingly after substitution of small amounts of the metals in relation to the parent $AlPO_4$-5. With rising metal contents, the potentials grow systematically and reach the value equal to that of $AlPO_4$-5 at the substitution level of 0.5–0.65 Me per unit cell, i.e., from one Me per two unit cells to two Me per three unit cells. At higher metal contents, adsorption potentials exceed the value of $AlPO_4$-5 (Fig. 15; Rozwadowski et al., 1999; Kornatowski et al., 1999b). The decrease in the adsorption potential value at low substitution levels may reflect strongly localized adsorption on single isolated metal centres. Shortening of distances between the centres with growth of the Me content may cause weakening of the effect of the localized adsorption and increase in adsorption potential values. Only above a definite "density" of the metal centres, the adsorption potentials can overpass

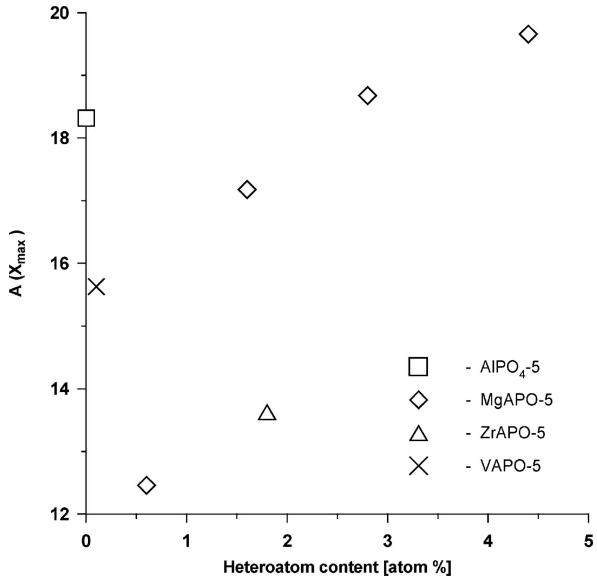

Figure 15. Dependence of adsorption potential $A(X_{max})$ on content of heteroatoms calculated with use of Dubinin-Radushkevich-Stoeckli equation from isotherms of benzene adsorption on MeAPO-5 materials [after Rozwadowski et al., 1999].

the value for the parent material. This might evidence a "distributional" heterogeneity concerning the adsorption centres.

The above exceptions seem to indicate that the adsorption potentials may relate to the composition of the adsorbents. Anyway, observation of regular changes is very difficult as the metal distribution is the only undefined feature of zeolitic materials. The regular effect has been found exceptionally for Mg that exhibits the highest affinity for framework substitution and for Cr that is very difficult for incorporation and requires special synthesis conditions causing likely its more homogeneous distribution in the crystals.

The mesoporous MCM-41 materials exhibit an increase in the adsorption potential values in relation to benzene with the growth of coking. This suggests that carbonaceous deposits increase heterogeneity of MCM-41. A distributional effect is also obvious (Rozwadowski et al., 2001).

4. Conclusions

The whole experimental work and interpretation present a consistent picture for adsorption behaviour of zeolitic materials. This holds for the type and shape of isotherms, mechanism of adsorption, sorption capacity, diffusivity of adsorbates in the pores, sensitivity of adsorption processes to modification of adsorbents, and analytical description of the isotherms. The consistency results from measurements for a relatively large series of samples. It is evident that even a large collection of single measurements could not lead to such conclusions. This can also be seen as a shortcoming. Adsorption measurements are time-consuming and require much thoroughness, often repetitions. The large series of measurements need a well-equipped laboratory and experienced operator. Such a high expenditure of work and time is finally profitable in fruitful primary results and interpretation possibilities. This equals to strong expressiveness of the serial experiments.

Particular achievements worth of conclusive presentation:

a) Homogeneous zeolitic structures like Sil-1, AlPO-n, and mesoporous materials, reveal a relatively weak influence of their regular framework/skeleton on adsorption of inert or weakly interacting adsorbates. Significant changes appear after modifications connected with creation of adsorption centres, e.g., introduction of metals that increase heterogeneity of the materials.
b) For polar adsorbates, the framework defects can be strong enough to affect adsorption process. The strong adsorption centres (*cf.* point a) can cause effects of strongly localized adsorption and an apparent decrease in adsorption.
c) Sorption capacity is the most deceptive and doubtful result of a single measurement. Even a very low capacity must not indicate a limited adsorption volume or inaccessible pore system. These effects can result from localized adsorption or other hindrances to diffusion.
d) The type and shape of isotherms may quite precisely reflect adsorption mechanism in a given system, provided that a comparison for a large series is possible. Conclusions from a single isotherm can easily be wrong.
e) Mechanism of adsorption can correctly be evaluated after elimination of possible effects of other parameters on adsorption isotherm, e.g., by applying a large series of measurements.
f) Diffusivity of adsorbates inside the pores depends practically on all parameters affecting adsorption. Evaluation is possible exclusively from serial experiments.
g) Sensitivity of adsorption to modification of adsorbents is enormously high, which can be favourable

or undesired. Serial measurements enable the correct interpretation.

h) Analytical description of the isotherms (adsorption potential distribution function) may but must not supply with additional information about the adsorption process. The potential represents an average result of all parameters. It is mostly impossible to differentiate particular influences. The number of the adsorption centres and their distribution play primary role for adsorption. The kind of the centres plays likely a secondary role.

i) Analytical description of adsorption corresponds to the volume of the pores actually engaged in the adsorption process and not to the total volume of the micropores. This is new statement in relation to the mathematical modelling of the adsorption process.

j) The BEST characterization of zeolitic adsorbents comes from comparison of the results within a series of samples AND for several different adsorbates.

Nomenclature

A	equal to RT $\ln(p_s/p)$ and determining the adsorption potential (kJ mol^{-1})
β	constant characterizing the adsorbate
DC	determination coefficient
E_0	characteristic energy of adsorption
k	structural parameter correlated with micropore dimensions
M	commonly all parameters connected with adsorbent and adsorbate
n	parameter connected with the microporous structure of the adsorbent
p	adsorbate pressure (mbar)
p_s	saturation pressure of adsorbate vapour (mbar)
p/p_s	relative pressure of adsorbate
R	universal gas constant (J mol^{-1} K^{-1})
STP	standard temperature and pressure
T	absolute temperature (K)
W	volume of the "liquid-like" adsorbate filling the micropores (cm^3 g^{-1})
W_0	total volume of micropores (cm^3 g^{-1})
X_{max}	parameter characterizing the distribution function of adsorption potential

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