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Mechanism of Adsorption of Water, Benzene, and Nitrogen on Al-MCM-41 and Effect of Coking on the Adsorption

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Water, benzene, and nitrogen were adsorbed on Al-MCM-41 molecular sieves, both unmodified and modified via controlled deposition of coke, and adsorption isotherms were determined. The mechanism of adsorption most probably includes multilayer adsorption at lower relative pressures, followed by capillary condensation. It is similar for all the adsorbates studied. The sorption capacity of the parent samples for benzene and nitrogen is relatively high and independent of the Al content. Thus, the Al centers do not substantially influence the lyophilic character of MCM-41 in relation to these adsorbates. In the case of water, however, a decrease in sorption capacity with an increase in the Al amount implies that clusters of the adsorbate molecules formed around the Al centers cause a partial clogging of the pores. The Al content is a factor controlling adsorption of water both directly, as a number of adsorption centers, and indirectly via influencing the content of coke. Coke strongly decreases both the surface area and the sorption capacity of the materials. It also causes a random formation of additional macropores. From the adsorption energy distributions, it is inferred that the carbonaceous deposits create centers capable of bonding the benzene molecules.

Introduction

Porous materials with high surface area, e.g., molecular sieves, are widely utilized as adsorbents and catalysts for industrial processes. Crystalline structures of exactly defined geometry and of pore sizes within a relatively narrow range of dimensions are characteristic of microporous molecular sieves, whereas the mesoporous ones exhibit no order within the solid walls and their pore sizes can be adjusted within a wide range of dimensions. During the last years, the family of the M41S materials[1,2] and especially MCM-41 and its derivatives containing various metals[3–5] have reached high scientific and application interest.

Measurements of the adsorption of gases and vapors constitute an important method for characterizing porous solids. These investigations allow for the determination of specific surface area, pore volume, pore size, and pore size distribution and for the examination of surface properties of the adsorbents.[6–8] Although the techniques of gas adsorption and the methods of adsorption data analysis are apparently well established, an accurate and reliable evaluation of those properties is still a difficult task.[6,7]

The number of papers dealing with adsorption of gases and vapors other than nitrogen on MCM-41 is very limited.[2,9–13] Beck et al.[2] determined the sorption capacities for benzene. Rathousky et al.[9] investigated adsorption of cyclopentane. Other groups, e.g., Chen et al.,[10] compared adsorption of cyclohexane on all-silica MCM-41 with that on Al-MCM-41. Adsorption of different alcohols and water was investigated by Branton et al.[11] who found a narrow hysteresis loop for alcohols. The isotherms of water showed a hydrophobic behavior of the investigated materials[10–12] and a pronounced hysteresis between the adsorption and desorption branches.[12] Boger et al.[13] concluded from the experimentally determined adsorption isotherms of nitrogen, water, aromatics, and alcohols that the sorption capacity of MCM-41 was only slightly affected by varying aluminum content. Consequently, it was accepted that the course of adsorption on such solids should mainly depend on the size of the pores.

In accordance with the IUPAC classification,[14] the dimensions below 2 nm, between 2 and 50 nm, and above 50 nm correspond to micropores, mesopores, and macropores, respectively. In the case of micropores, adsorption proceeds via volume filling of the pores even at low relative pressures. In mesopores, adsorption proceeds via formation of multilayers of adsorbate molecules followed by

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capillary condensation. Adsorption in macropores takes place only through formation of multilayers. Thus, the adsorption process on a porous solid may proceed via different mechanisms depending on the pore size.

Though numerous studies have been devoted to the examination of the properties of the MCM-41 type materials after various modifications (e.g., incorporation of metals), no attention has been paid to the determination of the exact effects of coking on adsorption properties. Obviously, the main trend is a lowering of sorption capacity. However, correlation between the material composition, the parameters of the coking process, and their effects on adsorption characteristics has not been studied in detail so far.

More detailed characteristics of the studied Al-MCM-41 materials are given in separate papers.[15,16] The investigations with X-ray diffraction (XRD)[15] as well as thermogravimetric analysis (TGA), diffuse reflectance IR Fourier transform (DRIFT), UV−vis, and ^{13}C NMR methods[16] yielded broader characteristics of structural and surface properties of the molecular sieves as well as the composition, properties, and behavior of the coke deposits.

The aim of the current study was to elucidate the influence of both the Si/Al ratio and the coke deposited during a catalytic process on adsorption properties of MCM-41 type materials. Adsorption of nonpolar (benzene, nitrogen) and polar (water) compounds chosen as probe molecules was studied to learn more about both the lyophilic properties of the examined mesoporous solids and the adsorption mechanisms.

Experimental Section

Materials. The Al-MCM-41 samples were prepared using the following gel compositions: $SiO_2/0.17$ CTMACl/0.4 TEAOH/25 H_2O/x Al_2O_3, where CTMACl and TEAOH are cetyltrimethylammonium chloride and tetraethylammonium hydroxide templates, respectively, and x was equal to 0.0083, 0.0167, or 0.0333. The reaction mixture was heated at 378 K under autogenous pressure for 8 days. The obtained materials were calcined initially in nitrogen and then in air. More details on the synthesis can be found elsewhere.[15]

The samples are referred to as Al-MCM-41(n) where n denotes the Si/Al molar ratio in the reaction gel equal to 15, 30, and 60. The products were analyzed using the methods of atomic absorption spectroscopy (AAS) and nuclear magnetic resonance (NMR). The ^{27}Al NMR spectra were obtained with a Bruker AMX300 WB spectrometer, employing an aqueous solution of $Al(NO_3)_3$ as a reference and the techniques of high-power proton decoupling and magic angle spinning with a 4-mm o.d. zirconia rotor spun at 7 kHz.

Deposition of Coke. A parent Al-MCM-41 sample was placed in a shallow-bed flow reactor under a set helium flow. When a preselected temperature of the reactor was reached, a mixed stream of helium and cyclohexene was applied. The gas mixture was accomplished by injecting liquid cyclohexene into the helium stream. After 12 h, the cyclohexene injection was terminated and the sample was purged with pure helium for another 12 h. More details are given elsewhere.[15] The reactions for the deposition of coke were carried out at 483, 513, 543, 573, 603, and 663 K. The coked samples are designated as Al-MCM-41(n)+CT_c, C standing for coke, and T_c for temperature (K) of coking.

Coke Content Determination. The contents of deposits in the coked samples were determined according to the modified procedure by Bibby et al.[17,18] The samples were taken from the

reactor at certain time intervals, and each was quickly transferred into a weighed glass container equipped with a Teflon stopper. For taking a sample, the injection of cyclohexene was stopped and the Al-MCM-41 bed purged with pure helium for about 20 min. The samples were weighed and then calcined at 823 K for 5 h under flow of oxygen. The deposit content was derived from the difference in the mass before and after calcination. More details can be found elsewhere.[15]

Adsorption Measurements. The adsorption isotherms of nitrogen were determined with the ASAP 2010 instrument from Micromeritics.[15] The measurements were performed at 77 K in a static mode. Before the measurements, the parent and coked samples were degassed at 700 and 363 K, respectively, all for at least 8 h and under vacuum of less than 0.7 Pa.

The adsorption isotherms of water and benzene were determined at 298.2 K using a vacuum device equipped with a McBain quartz spring balance and an MKS Baratron gauge. The samples (ca. 0.1 g) were activated in situ under stationary vacuum of 10^{-3} Pa at 700 and 363 K for the parent and coked materials, respectively, to attain a constant mass ($\Delta m \leq 10^{-5}$ g within 12 h). Water and benzene were carefully degassed using the freeze-and-thaw technique. The adsorption equilibrium was assumed to be reached when the change of mass was lower than 10^{-5} g for at least 12 h under constant pressure of adsorbate.

Calculation Methods and Equations. The specific surface area of the samples was assessed with the BET method[19] using the data of nitrogen adsorption. It was found, however, that condensation of nitrogen inside the pores occurred for all the samples within the relative pressure range of 0.05−0.3. Therefore, the relative pressure limits used in the BET calculations had to be adjusted for individual samples; they varied from 0.078−0.297 to 0.058−0.176.[15]

The surface area was also evaluated from the nitrogen adsorption isotherms transformed into α_s plots.[15] The total surface area, S_t, was calculated from the slope of the initial part of the α_s plot. The total pore volume, V_t, was derived from a single-point adsorption of nitrogen at the relative pressure of 0.99 by converting the volume of the adsorbed gaseous nitrogen to that of the liquid one. The primary mesopore volume, V_p, and the external surface area, S_{ext}, were calculated from the slope of a linear part of the α_s plot in the pressure range between the value corresponding to the termination of nitrogen condensation in the primary mesopores and that associated with the onset of capillary condensation in the secondary mesopores and in the macropores. (For definition of the primary and secondary mesopores, see Results and Discussion). The $S_t - S_{ext}$ difference yielded the surface area of the primary mesopores, S_p.

We attempted to use the equations of Dubinin and Astakhov (DA),[20] Dubinin and Radushkevich (DR),[21] Dubinin, Radushkevich and Stoeckli (DRS),[22] modified DRS (DRSI),[23] Jaroniec and Choma (JC),[24] as well as Langmuir and Freundlich (LF)[25] to describe the isotherms of the benzene adsorption on the Al-MCM-41 samples. These equations, being applicable generally to microporous adsorbents, were tested since no equations are known that would take into account the energetic or structural heterogeneities of the sample surface and have been derived specifically for mesoporous adsorbents.

The distribution functions of the adsorption potential, resulting from different models of adsorption, were calculated using the benzene adsorption isotherms. The individual functions, being of the form $X(A) = -d\theta_t(A)/dA$,[6,26,27] were obtained from numerical

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Table 1. Surface Features of the Parent and Coked Al-MCM-41 Materials[a]

sample	C.c. (wt %)	S_{BET} (m²/g)	S_t (m²/g)	S_{ext} (m²/g)	S_p (m²/g)	V_t (cm³/g)	ΔV_t (%)	V_p (cm³/g)
Al-MCM-41(15)	N/A	1031	1042	249	793	1.071	N/A	0.610
Al-MCM-41(15)+C483	48.81	386	295	151	144	0.547	48.9	0.104
Al-MCM-41(15)+C513	33.80	598	524	176	348	0.674	37.1	0.254
Al-MCM-41(15)+C543	23.24	705	633	184	449	0.775	27.6	0.297
Al-MCM-41(15)+C573	28.38	720	599	176	423	0.768	28.3	0.273
Al-MCM-41(15)+C603	18.85	740	713	193	520	0.795	25.8	0.352
Al-MCM-41(15)+C663	13.46	783	752	205	547	0.967	9.7	0.384
Al-MCM-41(30)	N/A	1177	1163	158	1005	1.092	N/A	0.766
Al-MCM-41(30)+C573	13.54	1073	1004	161	843	1.023	6.3	0.631
Al-MCM-41(60)	N/A	1219	1139	128	1011	0.946	N/A	0.645
Al-MCM-41(60)+C573	6.92	1235	1081	131	950	0.931	1.6	0.609

[a] C.c. is the coke content; S_{BET}, BET surface area; S_t, total surface area; S_{ext}, external surface area; S_p, surface area of primary mesopores; V_t, total pore volume; $\Delta V_t = 100\%(V_{tp} - V_{tc})/V_{tp}$, where V_{tp} and V_{tc} are the total pore volumes of the parent and coked samples, respectively; V_p, volume of primary mesopores; and N/A, not applicable.

differentiation of the adsorption isotherms, $\theta_t(A)$, using the adsorption potential defined as a change in the Gibbs free energy of adsorption, with the negative sign: $A = -\Delta G = RT\ln(p_s/p)$.

Results and Discussion

Structural Features of the Materials. The Si/Al ratios in the Al-MCM-41(15), Al-MCM-41(30), and Al-MCM-41(60) samples are 12.2, 19.9, and 36.8, respectively, as determined with the AAS method. This means that there is an apparent enrichment in aluminum found for the products in relation to the composition of the reaction mixture.[15] The materials show a typical system of uniform cylindrical pores in a hexagonal array that is reflected in a set of peaks in the low-angle XRD powder patterns.[15] The values of interplanar spacings, d, were equal to 4.01, 3.56, and 3.35 for the samples with the Si/Al ratio of 15, 30, and 60, respectively; i.e., they increase with rising amount of Al.[15] The uniform pores characteristic of mesoporous molecular sieves are considered as primary mesopores. In addition to their surface area, one has to take into account the external surface area, i.e., mostly the exterior area of the material particles with large mesopores that do not form any ordered structures.[28-30] These mesopores are referred to as the secondary ones.[15]

All the parent samples exhibit a high specific surface area (S_{BET} above 1000 m²/g), which increases with the lowering content of Al (Table 1) and suggests a superior ordering of the pores within the individual particles of the materials with the lower amount of Al. The same is observed for the surface area of the primary mesopores (S_p). The external surface area (S_{ext}) reveals an opposite tendency, i.e., it increases with the content of Al, suggesting a decrease in particle size and/or a more developed external surface of the particles with the growing content of Al. However, the values of the total surface area (S_t) and S_{BET} correspond well.

As a result of coking the samples, both the surface area and the pore volume of the examined materials drastically decreased (Table 1). The amount of the deposited coke increases with the rising Al content and decreasing reaction temperature. Thus, the most drastic decrease in the surface area and the pore volume is observed for Al-MCM-41(15) coked at the lowest temperatures. Interest-
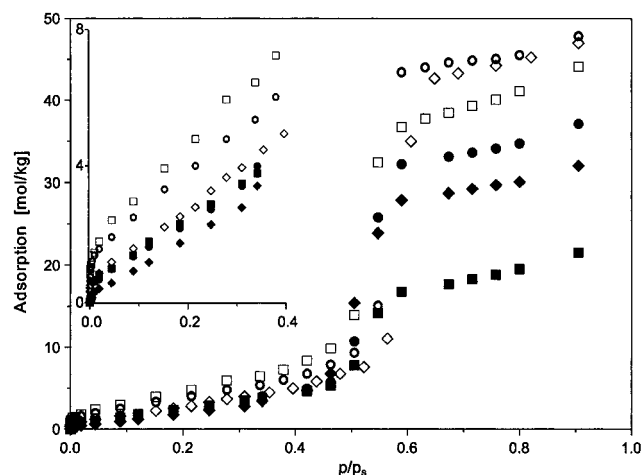
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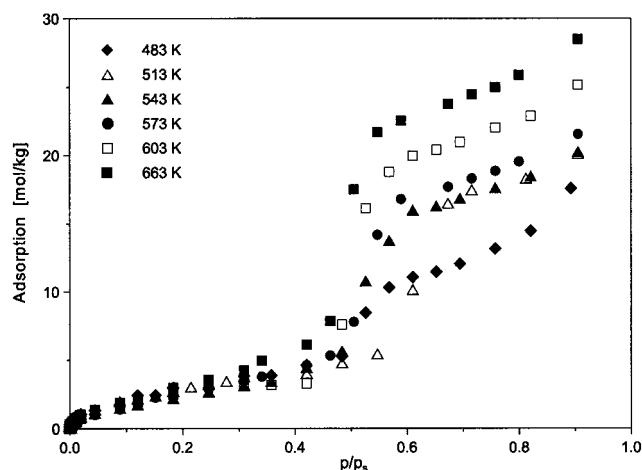(30) Jaroniec, M.; Kruk, M.; Sayari, A. *Stud. Surf. Sci. Catal.* **1998**, *117*, 325.

Figure 1. Isotherms of water adsorption on the parent (open symbols) and coked at 573 K (filled symbols) samples of Al-MCM-41(15) (squares), Al-MCM-41(30) (circles), and Al-MCM-41(60) (diamonds).

ingly, the decrease in the total pore volume is mostly due to the lowering of the primary mesopore volume. A surprising coincidence can be observed (Table 1) for the Al-MCM-41(15) material: the decrease in the total pore volume of the coked samples, relative to that of the parent one (ΔV_t), is roughly equal to the content of coke (C.c.). This is not the case for the materials with lower Al content and, thus, with a lower content of coke. In these materials, the fraction of the deposits located on the external surface is probably higher than that in Al-MCM-41(15).

The decrease in the mesopore volume upon coking of the samples agrees with the observed changes in the values of the surface area. For Al-MCM-41(30) and Al-MCM-41(60), the total surface area decreases due to lowering of the surface area of the primary mesopores, while in the case of Al-MCM-41(15), the decrease in S_p is accompanied by the diminution of S_{ext} that depends slightly on the reaction temperature. The general correspondence between the values of S_t and S_{BET} is satisfactory. From the above findings, it can be concluded that the coke formation proceeds primarily in the pores and is connected with the aluminum centers. Due to the coking, the pores become narrower and smaller.[15]

Adsorption of Water. The adsorption isotherms of water (Figures 1 and 2) are of type IV or V (according to the IUPAC classification);[14] i.e., they proceed with a distinct step. These types of isotherms usually correspond to the adsorption mechanism containing formation of multilayers of adsorbate molecules at the initial stage of the adsorption and capillary condensation of the adsorbate

Figure 2. Isotherms of water adsorption on Al-MCM-41(15) coked at temperatures indicated.

Figure 3. Isotherms of benzene adsorption on the parent (open symbols) and coked at 573 K (filled symbols) samples of Al-MCM-41(15) (squares), Al-MCM-41(30) (circles), and Al-MCM-41(60) (diamonds).

Figure 4. Isotherms of benzene adsorption on Al-MCM-41(15) coked at temperatures indicated.

that starts at the relative pressure at which the isotherm step begins.

The isotherm for each sample reveals a steep step at a relative pressure within the range of 0.5−0.6. The steps differ for particular samples in their height and position. For the noncoked samples, the decrease in the Al content (increase in the Si/Al ratio) is associated with an increase in the height of the step and its shift to a higher relative pressure (Figure 1). This indicates that water is adsorbed during the initial stage (i.e., at lower relative pressures) more easily and in higher amounts on the samples with a higher Al content and that the capillary condensation occurs earlier. In other words, the Al atoms are adsorption centers distributed on the surface of amorphous pore walls constituted of clearly less hydrophilic silica. This picture is partially inverted after coking. The changes in the height of the steps reveal the same tendency, but the positions of the steps shift to lower relative pressures (Figure 1). This indicates that the samples containing more coke become more hydrophobic than those with less coke, independently of the Al content. This can be explained, assuming that coke is formed primarily on the Al centers that become covered and inactive in the adsorption of water. Thus, the aluminum-rich pores are strongly diminished or clogged and, consequently, the access of water molecules to those pores is limited or not possible.

The changes in the height of the steps are directly connected to the sorption capacities and their variations, which are described below in a separate section.

The isotherms for Al-MCM-41(15) coked at different temperatures (Figure 2) show a strong increase in both the height of the adsorption step and the sorption capacity with the reaction temperature, i.e., with a decrease in the amount of coke. This points out, among other things, an expected increase in hydrophobicity with growing amount of coke. In accordance to this, the steps of the isotherms shift to lower relative pressures with the increasing reaction temperature (i.e., decreasing amount of coke), which supports the mentioned tendency in the changes of hydrophilic/hydrophobic properties.

The above findings indicate that the amount of aluminum in the materials is the factor controlling the adsorption of water in two aspects: (i) directly as adsorption centers in the noncoked materials, and (ii) indirectly via influence on the amount of deposits in the coked materials. As the steps on the isotherms generally shift to lower relative pressures with increase in the reaction temperature, the latter is an additional factor,
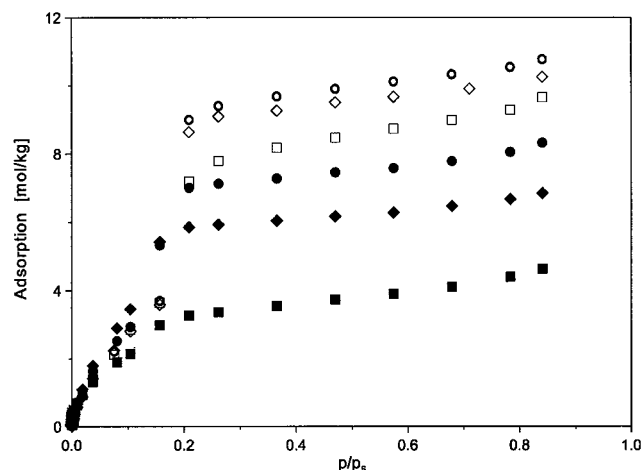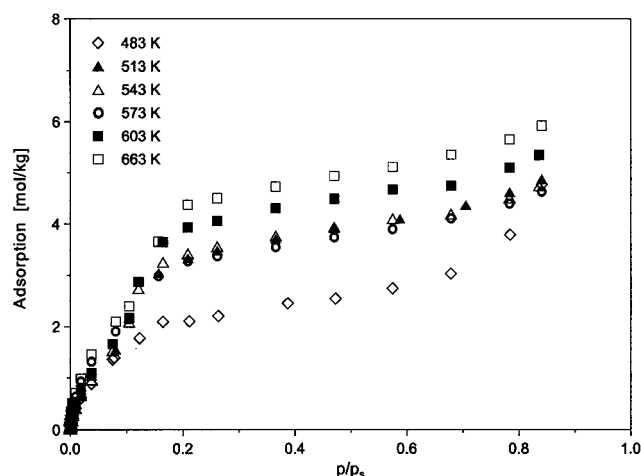
acting also indirectly, since it controls the amount of carbonaceous deposits.

The described effects of the contents of Al and/or coke on adsorption, reflected by the shape and position of the isotherm step, are similar to those found previously for metal-substituted aluminophosphate molecular sieves.[31,32] For these materials, increase in the content of the framework metal atoms, i.e., in content of the adsorption centers, results in a higher adsorption during the initial stage (at lower relative pressures) and, consequently, in an earlier start of capillary condensation of water.

Adsorption of Benzene. The adsorption isotherms of benzene (Figures 3 and 4) for the parent samples show a slight step, which means that these isotherms can be thought as being of type IV.[14] This type of isotherm indicates that the adsorption of benzene proceeds via the multilayer adsorption at lower relative pressures followed by capillary condensation, i.e., similarly to the mechanism found for water (polar molecules). However, as seen from Figure 3, the shape and position of the step on the isotherms do not depend on the aluminum content of the

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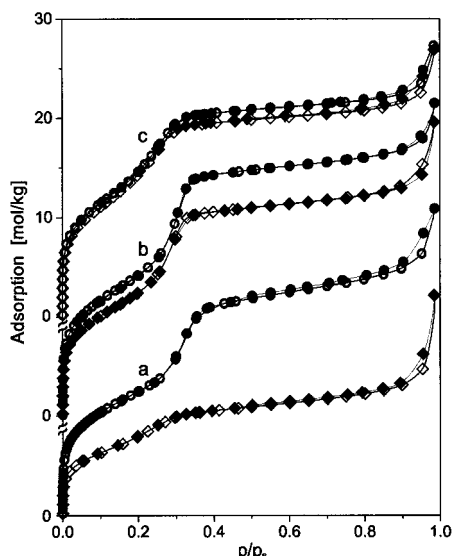
Figure 5. Isotherms of nitrogen adsorption on the parent (circles) and coked at 573 K (diamonds) samples of Al-MCM-41(15) (a), Al-MCM-41(30) (b), and Al-MCM-41(60) (c). Open and filled symbols correspond to adsorption and desorption, respectively.

Figure 6. Isotherms of nitrogen adsorption (open symbols) and desorption (filled symbols) on Al-MCM-41(15) coked at temperatures indicated.

samples. The only difference between the samples deals with the height of the steps which increases with decrease in the content of Al. The step height, being connected directly with the sorption capacity, is discussed below separately. The steps occur within the relative pressure range of ca. 0.15−0.2 (Figure 3). Such a narrow range indicates that the aluminum centers do not substantially influence the lyophilic character of the surface in relation to benzene.

For the coked samples, the steps almost vanish (Figures 3 and 4) and the shape of the isotherms is somewhere between those of types I and II. The "smoothing" of the isotherms and transformation from type IV or V into the shape close to type I has already been observed for the adsorption of water on the aluminophosphate molecular sieves as a consequence of growing content of metals substituted into the framework.[31,32] That transformation of the isotherm shape indicates that the adsorption is more rapid and that the capillary condensation starts earlier than in the case of the isotherms of type IV or V. Thus, the coked samples show a higher affinity toward benzene than the parent materials do, despite the drastically decreased sorption capacity. This could be expected, taking into account possible interactions between carbonaceous deposits and benzene due to its π electrons. Noteworthy is that the above statements hold true for all the coked samples independently of the amounts of Al and/or coke (Figure 4). That fact supports the conclusion on an "inert" character of the Al centers in relation to the adsorption of benzene.

Adsorption of Nitrogen. Similarly to the adsorption isotherms of water, those of nitrogen (Figures 5 and 6) are mostly of type IV, as are also those of benzene on the parent samples. Consequently, the mechanisms of the adsorption are similar as well. A distinct step associated with condensation of nitrogen occurs on the isotherms for all noncoked samples and some coked ones. The position of the steps is constant, which indicates, as in the case of benzene, an inert character of the Al centers toward nitrogen. However, unlike for benzene, the sample with the lowest content of Al exhibits the lowest height of the step.
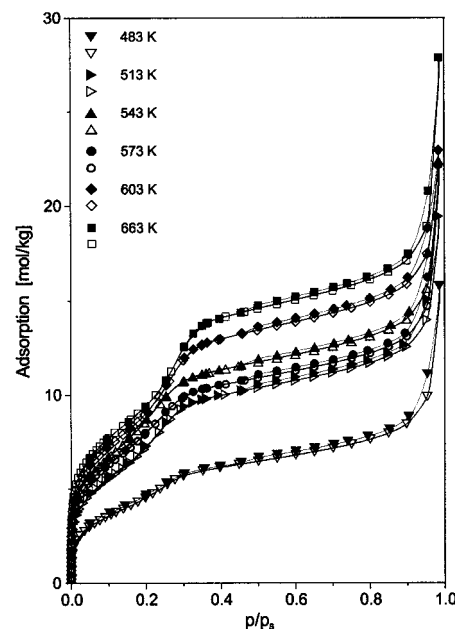
Each of the isotherms shows another step at the relative pressure approaching 1. These steps indicate the existence of some macropores that are almost independent of the Al content of the parent samples and slightly increase with the growing content of deposits for the coked samples (Figure 5). This may suggest formation of additional macropores during the deposition of coke.

For the Al-MCM-41(15) samples coked at various temperatures, the low-pressure steps gradually vanish as the coke content increases (Figure 6). However, the isotherms transform into type II, and not I, due to another step at p/p_s approaching 1. This step is very strong and there is no apparent correlation between its height and temperature of the coking reaction. This implies that macropores corresponding to the high-pressure step are formed randomly.

Sorption Capacity and Mechanism of Adsorption. The total sorption capacities and the heights of the isotherm steps, compared between the particular samples and/or between the examined adsorbates, yield interesting results.

Apparently, the most unexpected facts are observed for water. The sorption capacities of the parent samples follow the sequence Al-MCM-41(15) < Al-MCM-41(60) ≤ Al-MCM-41(30); i.e., the lowest value was found for the sample with the highest amount of Al centers (Figure 1, Table 2). It might be expected that adsorption of water should proceed more easily with a rising amount of Al centers within the much less hydrophilic silica walls of MCM-41.[10−12] In parallel, the heights of the isotherm steps grow in the same sequence, which means that the lowest amount of condensed water occurs in the sample with the highest content of Al. The same dependences are observed for the coked samples with various contents of Al (Figure 1, Table 2). This unexpected behavior cannot originate from clogging the pores with some extraframework Al species since, in such a case, the sorption capacity for benzene and nitrogen could not be higher than that for water (see below). This is also supported by the ^{27}Al NMR results (Figure 7), indicating that a fraction of octahedral (extraframework) Al species is small (10−20%). Only the picture of the Al-MCM-41(15) samples coked at various

Table 2. Sorption Capacities of the Parent and Coked Al-MCM-41 Materials ($p/p_s = 0.85$)

sample	H_2O (298.2 K) (cm^3/g)	C_6H_6 (298.2 K) (cm^3/g)	N_2 (77 K) (cm^3/g)
Al-MCM-41(15)	0.771	0.864	0.850
Al-MCM-41(15)+C483	0.290	0.426	0.278
Al-MCM-41(15)+C513	0.348	0.433	0.423
Al-MCM-41(15)+C543	0.350	0.424	0.473
Al-MCM-41(15)+C573	0.372	0.414	0.441
Al-MCM-41(15)+C603	0.435	0.478	0.537
Al-MCM-41(15)+C663	0.492	0.529	0.580
Al-MCM-41(30)	0.845	0.963	0.922
Al-MCM-41(30)+C573	0.650	0.744	0.788
Al-MCM-41(60)	0.835	0.917	0.771
Al-MCM-41(60)+C573	0.562	0.612	0.737
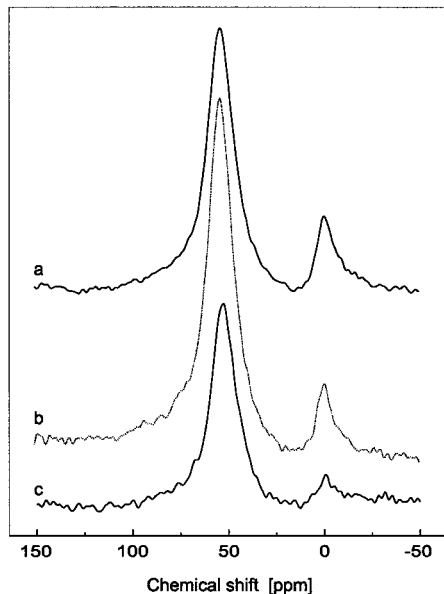
Figure 7. ^{27}Al NMR spectra of Al-MCM-41(15) (a), Al-MCM-41(30) (b), and Al-MCM-41(60) (c).

temperatures seems to be as expected: the sorption capacities and the heights of the isotherm steps grow with the decreasing coke content (Figure 2, Tables 1 and 2).

At the relative pressures above the condensation step, adsorption of water rises relatively little and the isotherms are parallel to one another (Figure 1). The samples become nearly saturated with water at $p/p_s \cong 0.6$. The same applies to the coked samples with various Al content (Figure 1). The samples of Al-MCM-41(15) coked at different temperatures show an increase in adsorption also after the condensation step (Figure 2). The latter suggests a clearly higher contribution of the macropores and/or external surface in the total adsorption than in the case of the parent samples or those with a lower content of Al, i.e., with a lower content of coke.

The benzene sorption capacities of all the parent and coked samples are higher than in the case of water (Table 2). Their dependences on both the Al content and the reaction temperature are similar to those for water, which is rather surprising when one considers the nonpolar character of benzene molecules in comparison to polar water molecules.

The sorption capacities for nitrogen are generally close to those for benzene, i.e., also higher than those for water. The only difference is that the capacity of Al-MCM-41(60) is lower than not only that of Al-MCM-41(30) but also that of Al-MCM-41(15). This is accompanied by the lowest height of the isotherm step for that sample. The other features and dependences are the same as those for benzene and water.

The above experimental findings can be explained assuming the following mechanism of adsorption. The polar water molecules are strongly bonded at the Al centers on the surface of the pores. That strong bonding and subsequent association of water lead to formation of clusters of liquidlike water around the Al centers and to clogging of the pores. Thus, the diffusion of water is hindered and, consequently, water fills the pores only partially, i.e., only the pore sections near the Al centers. Obviously, this effect should increase with a growing number of Al centers and with a decreasing distance between the centers as the water clusters could grow larger and be anchored on more Al centers commonly. Such clusters should be more strongly localized and would probably require a higher activation energy for a re-arrangement. Thus, even larger regions unavailable to water can be left than in the case of the Al centers separated with longer distances. Such a picture agrees well with the observation that the sorption capacities for nitrogen and benzene are higher than that for water.

The lack of correlation between the Al content and the sorption capacity could result from two reasons. One is connected with the adsorption mechanism described above. It might indicate the existence of an optimum Al content that could yield the maximum sorption capacity. This agrees with the presented observations: the sorption capacity of Al-MCM-41(30) is a little higher than that of Al-MCM-41(60) and clearly higher than that of Al-MCM-41(15). On the other hand, the variations of the capacity can result from the changes in the volume of the primary mesopores with the content of Al (Table 1). However, the results most likely reflect a combined effect of both factors.

Strong support for the above considerations comes from the fact that adsorption processes for all three examined adsorbates proceeded similarly despite different physicochemical properties of the compounds as well as different adsorbate−adsorbent interactions. Nitrogen and benzene fill the pores to a higher extent relative to water. The polar water molecules cannot extensively fill the pores of the low-hydrophilic materials. The Al centers strongly increase this feature. One should also take into account a possibly important role of distribution of the Al centers in the pores.

A series of Al-MCM-41(15) samples coked at various temperatures gives further support for the above conclusions. In contrast to the hardly expected effects observed for the materials of various compositions, coking of one material of defined stable properties results in regular changes corresponding to the effects expected.

Analytical Approach. From the tested isotherm equations (cf. Experimental Section), the DRSI equation yielded the best fit of the calculated isotherms to the experimental ones, based on the values of the determination coefficient (DC). As seen from Table 3, the description of the experimental data can be considered as satisfactory.

According to the Dubinin's model,[21] the W_0 parameter corresponds to the total pore volume of microporous adsorbents. Application of this model to mesoporous adsorbents results in the W_0 values lower than the geometric volume of the pores (Tables 2 and 3). This fact indicates that the W_0 parameter for Al-MCM-41 is associated with the pore volume actually engaged in the adsorption process and not with the total pore volume. The same has already been found for ZSM-5 zeolites[33] and AFI type materials.[34]

The total heterogeneity of a porous solid is a sum of the structural and surface heterogeneities. It is characterized

Table 3. Parameters of the DRSI Equation for the Isotherms of Benzene Adsorption on the Parent and Coked Al-MCM-41 Materials (298.2 K)[a]

sample	W_0 (cm^3 g^{-1})	DC	$10^3 X_{max}$ (mol cm^3 kJ^{-1} kg^{-1})	$A(X_{max})$ (kJ mol^{-1})	Δ (kJ mol^{-1})
Al-MCM-41(15)	0.508	0.9929	66.32	3.571	6.516
Al-MCM-41(15)+C483	0.278	0.9988	32.56	4.303	7.531
Al-MCM-41(15)+C513	0.222	0.9948	21.96	5.656	9.463
Al-MCM-41(15)+C543	0.230	0.9978	23.06	5.592	9.389
Al-MCM-41(15)+C573	0.253	0.9970	22.56	6.080	10.34
Al-MCM-41(15)+C603	0.296	0.9968	31.75	4.928	8.488
Al-MCM-41(15)+C663	0.269	0.9970	23.05	6.352	10.73
Al-MCM-41(30)	0.681	0.9988	101.4	3.291	5.844
Al-MCM-41(30)+C573	0.537	0.9922	65.78	4.184	7.326
Al-MCM-41(60)	0.480	0.9995	58.58	4.337	7.438
Al-MCM-41(60)+C573	0.397	0.9956	39.57	5.752	9.558

[a] W_0 is the volume of pores; DC, determination coefficient; X_{max}, maximum value of the adsorption potential distribution function; $A(X_{max})$, value of the adsorption potential at X_{max}; and Δ, half-width of the distribution function.
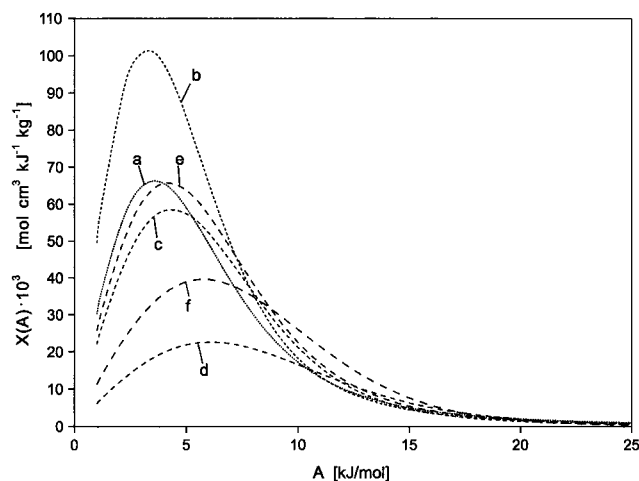

Figure 8. Functions of the adsorption potential distribution calculated with use of the DRSI equation for benzene adsorbed on Al-MCM-41(15) (a), Al-MCM-41(30) (b), Al-MCM-41(60) (c), Al-MCM-41(15)+C573 (d), Al-MCM-41(30)+C573 (e), and Al-MCM-41(60)+C573 (f).

Figure 9. Functions of the adsorption potential distribution calculated with use of the DRSI equation for benzene adsorbed on the Al-MCM-41(15) samples: parent (a), and coked at 483 (b), 513 (c), 543 (d), 573 (e), 603 (f), and 663 K (g).

by the distribution function of the adsorption potential[35,36] (for details and equations, see Rozwadowski et al.[26,27]). The plots of this function for the samples examined (Figures 8 and 9) show that the adsorption potentials of the parent samples are generally lower than those of the coked samples and that the maximum of the function shifts to higher potentials with the increasing coke content (cf. Table 3). These results suggest that the carbonaceous deposits play a role of adsorption centers that affect the adsorption potential and influence the benzene sorption capacity. The sorption capacity depends on both the amount and the distribution of the deposits (Table 2, Figures 7 and 8). Thus, the carbonaceous compounds creating centers capable of bonding benzene molecules increase heterogeneity of the examined materials.

Conclusions

The parent Al-MCM-41 samples as well as those coked at the same temperature (573 K) show a growth of the BET surface area with decreasing Al content. This effect involves an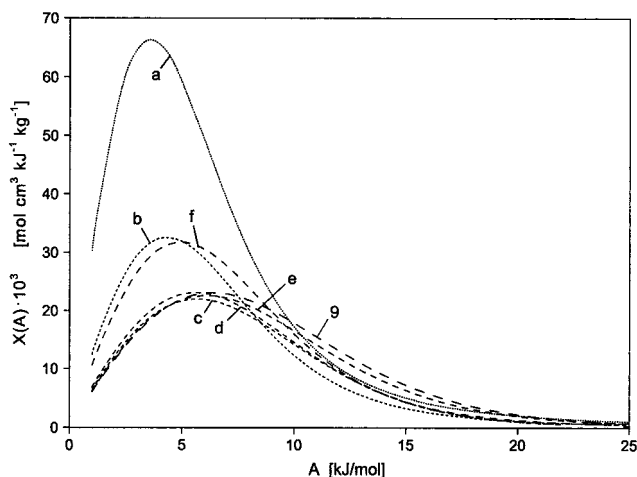 increase in the surface area of the primary mesopores and a decrease in the external surface area. It might result from a superior ordering of the materials with the lower Al content.

The samples coked at different temperatures exhibit a decrease in both the BET surface area and the total pore volume with increasing content of coke. The effects deal mostly with the primary mesopores and indicate that coke is primarily formed on the Al centers in the pores.

Processes of adsorption of water, benzene, and nitrogen conform to similar mechanisms, including multilayer adsorption at lower relative pressures followed by capillary condensation of an adsorbate.

The Al centers do not substantially influence the lyophilic character of MCM-41 in relation to benzene. Thus, the sorption capacity of the parent samples for benzene is relatively high and independent of the Al content. The coked samples show a higher affinity toward benzene (the capillary condensation starts earlier) than the noncoked ones do, likely due to interactions between carbonaceous deposits and π electrons of benzene molecules. The sorption capacity drastically decreases with the growth of coke content and the decrease in pore volume. This is supported by the changes of adsorption potentials, which also show that carbonaceous compounds both create centers capable of bonding benzene and increase the heterogeneity of the MCM-41 materials.

The Al centers are also inert in relation to nitrogen. Coke strongly decreases the sorption capacity and causes a random formation of additional macropores.

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The capillary condensation of adsorbed water occurs at low relative pressures due to interactions with the Al centers. Unexpectedly, an increase in the Al content, i.e., an increase in the number of hydrophilic centers, causes a decrease in sorption capacity. It is likely due to formation of clusters of liquid water around the Al centers and clogging of the pores. This mechanism is supported by the fact that the sorption capacities for benzene and nitrogen (nonpolar compounds) are clearly higher than that for water.

Increasing the coke content results in the condensation of water at higher relative pressures and in a decrease in the sorption capacity. The Al content is a factor controlling adsorption of water, both directly as a number of adsorption centers and indirectly via influencing the content of coke. Temperature is an accompanying factor, also acting indirectly via controlling the amount of coke.

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