Calorimetric and IR-spectroscopic study of adsorption of methanol on zeolite-like aluminophosphates

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Electrostatic properties of zeolite-like aluminophosphates are intermediate between those of zeolites and zeolite-like silica modifications. The adsorption measurements and IR spectroscopic investigations of the framework vibrations demonstrate that the number of the adsorption complexes of CH_3OH with Al atoms increases in the following order: $AlPO_4$-5 < $AlPO_4$-17 ≪ $AlPO_4$-18.

The OH vibrations of methanol molecules in the first coordination sphere of the Al atoms are reflected in the IR spectra as an absorption band at 3200 cm^{-1}, which is not observed for the adsorption of CH_3OH on zeolites.

Key words: zeolite-like aluminophosphates, adsorption, methanol, IR spectra.

In zeolites, ion-exchange cations usually behave as active adsorption centers. The surface of zeolite-like aluminophosphates ($AlPO_4$) is electroneutral, whereas the formation of adsorption complexes involving Al atoms can result in significant structural changes in the $AlPO_4$ lattices. Previously[1] it was shown that the hydration of some aluminophosphates leads to Al atoms with a coordination number higher than 4.

Possible participation of Al atoms in interaction with adsorbed molecules depends both on the nature of the adsorbate and on the specific features of the structure of $AlPO_4$. The adsorption of ammonia on $AlPO_4$-5 results in adsorption complexes containing Al atoms, whereas during the adsorption of MeOH all Al atoms remain tetrahedral.[2] On the other hand, in $AlPO_4$-18, the Al atoms directly interact with MeOH molecules.[3]

Although several dozens of modifications of zeolite-like phosphates are known,[4] there are only a few reports on the thermodynamics of adsorption of different types of molecules.[5—9] Among these data there are the heats of adsorption of *n*-alkanes, benzene, and several low-boiling gases, *i.e.*, of the substances whose adsorption can hardly cause any structural changes in the lattices of $AlPO_4$.

Recently[3] the results of the investigations of the adsorption and the adsorption heats of methanol on $AlPO_4$-5 and $AlPO_4$-18 have been published. These results virtually coincide with the data obtained previously by us[10] for the same $AlPO_4$. The purpose of the present work is to compare the heats of adsorption of MeOH on $AlPO_4$-17 with the IR spectra of aluminophosphates and adsorbed molecules.

Experimental

Zeolite-like aluminophosphates $AlPO_4$-5, -17, and -18 were synthesized, where the P_2O_5/Al_2O_3 ratios were 0.92, 0.93, and 0.74, respectively. One can believe[11] that the excessive Al in $AlPO_4$-18 is not an admixture. In order to remove the organic impurities, the samples were heated in air for 5 h at 773 K. Prior to measurements, dehydration was carried out *in vacuo* for 6 h at 673 K.

The heats of adsorption were measured at 303 K on a Setaram microcalorimeter of the Calve type. To determine the heats of adsorption in the calorimetric experiments, a vacuum volumetric device was used. The isotherms of adsorption at different temperatures were measured using a vacuum balance instrument.

The IR spectra were recorded on an UR-20 spectrophotometer. The samples for recording the spectra in the region of stretching vibrations were pressed without binding additives. Their density was 7—12 mg cm^{-2}. The spectra of the frameworks were recorded for the samples supported onto a KBr plate from a isopropanol solution. The density of these samples was 1.0—1.5 mg cm^{-2}.

Results and Discussion

According to the data given in Fig. 1, the starting heats of adsorption of MeOH on $AlPO_4$, which are close to 100 kJ mol^{-1}, rapidly decrease at the coverages lower than 0.5—1.0 mmol g^{-1}. Such a drop in the high starting heats is often observed for the adsorption of small polar molecules on different zeolites and zeolite-like materials. For example, during the adsorption of MeOH on silicalite[12] and on highly dealuminated faujasite,[13] the region of high heats corresponds to the coverages up to

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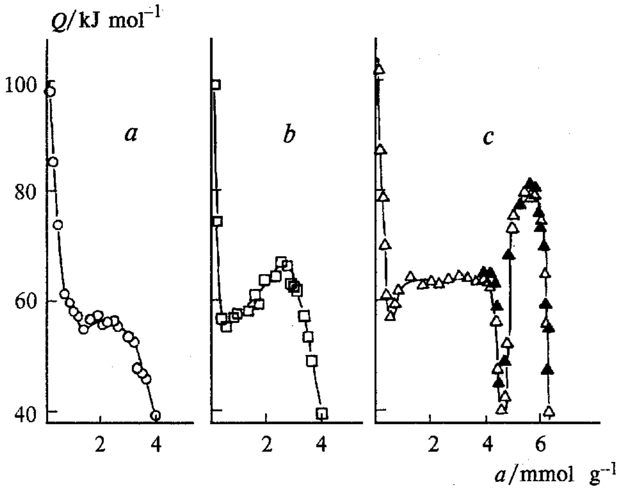

Fig. 1. The heats of adsorption of MeOH on zeolite-like aluminophosphates: $AlPO_4$-5 (*a*), $AlPO_4$-17 (*b*), $AlPO_4$-18 (*c*).

0.5 mmol g^{-1}. If it is believed that these heats indicate the interaction of the adsorbed molecules with the highly active adsorption centers at a 1:1 molar ratio, not more than one such a center should be accounted for 15—20 tetrahedrons T(Al, P, Si)O_4.

Earlier[14] it was shown that the number of these centers determined from q_{H_2O} on $AlPO_4$-5 corresponds to the number of the crystal lattice defects found by study of the isotopic exchange of oxygen. At the same time,[15] high values of q_{H_2O} on $AlPO_4$ are attributed to the interaction of the adsorbed molecules and Al atoms, whose tetrahedral coordination is changed to the octahedral coordination during the hydration. The data obtained by us support the hypothesis of the defect nature of the highly active centers, because the high heats of adsorption at low coverages are observed not only when the Al atoms do change their coordination ($AlPO_4$-18) during the adsorption of MeOH,[3] but also when this does not occur ($AlPO_4$-5).[2]

The minima on the heat curves at the ~0.5—1.0 mmol g^{-1} coverages correspond to the adsorption of MeOH, in which Al atoms do not participate and the molecules of adsorbate remote from each other do not interact. The values of heats in this region are 10—15 kJ mol^{-1} higher than those for the zeolite-like modifications of silica,[12,13] which also exhibit the minima at the ~0.5 mmol g^{-1} coverages, but these minima are not so distinct as in the case of $AlPO_4$. One could suggest that the relatively high values of q_{MeOH} for $AlPO_4$ are caused by the particular features of the lattice structures. For example, the heats of adsorption of alkanes and benzene on $AlPO_4$-5 are higher than those on faujasite-like silica,[5] while they are lower in the case of broad-pored $AlPO_4$-5 (VPI-5).[8]

However, in the region of low coverages the values of q_{MeOH}, measured for the adsorbents close in chemical composition and not containing very strong adsorption centers, are almost independent of structure. Figure 1 shows that, for all of the samples of aluminophosphates, the heats of adsorption determined at minimum points at the ~0.5—1.0 mmol g^{-1} coverages are virtually the same (55—57 kJ mol^{-1}). On the other hand, q_{MeOH} for silicalite and faujasite-like silica[12,13] are also very close at similar points (42—45 kJ mol^{-1}).

The minimal values of q_{MeOH} for $AlPO_4$ at small coverages are only ~15 kJ mol^{-1} lower than those for zeolite Na—Y,[13] in which cations Na^+ act as adsorption centers. The relatively high q_{MeOH} values in the points of minimum for $AlPO_4$ can not be explained by the participation of Al atoms in the formation of adsorption complexes, because, according to the results of the ^{27}Al NMR investigations, during the adsorption of MeOH the Al atoms with >4 coordination are observed only in the coverages region >1.0 mmol g^{-1} (*cf.* Ref. 3).

Thus, the experimental data indicate that the electrostatic properties of aluminophosphates occupy an intermediate position between those of zeolites and zeolite-like modifications of SiO_2, though, according to the theoretical calculations,[16,17] silicas of a zeolite structure should be not less polar than aluminophosphates.

The isotherms of adsorption for three samples of $AlPO_4$ are convex with respect to the pressure axis in the region of the lowest pressures, *i.e.*, below the coverages corresponding to the minimal points on the heat curves (Fig. 2). In the region of higher relative pressures, the shape of the isotherm of adsorption of $AlPO_4$-18 changes, and in the interval from ~1 to ~4 mmol g^{-1} a vertical segment appears. An increase in adsorption occurs virtually without changing a pressure; in each point, the time for the equilibrium to be achieved is up to 12 h, although the process is quite reversible. The adsorption of MeOH leads to the transformation of a part of Al atoms from the tetrahedral coordination to the state with coordination number 5 (*cf.* Ref. 3). At the coverages ~4 mmol g^{-1} one MeOH molecule is due to 2 Al atoms, and the oxygen atoms of the adsorbed methanol molecules can be assumed to form bridges between the

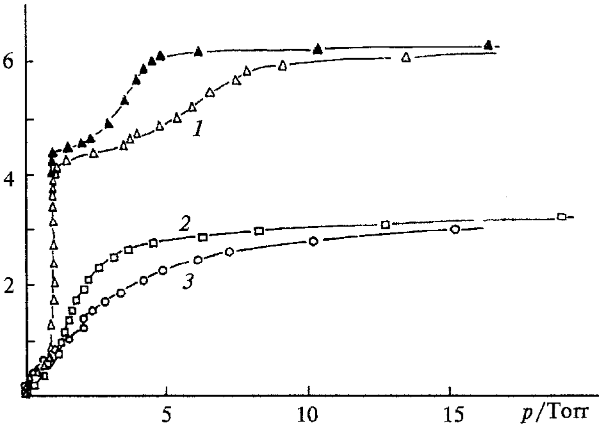

Fig. 2. Isotherms of adsorption of MeOH at 298 K on zeolite-like aluminophosphates: $AlPO_4$-18 (*1*), $AlPO_4$-17 (*2*), $AlPO_4$-5 (*3*) (dark points correspond to desorption).

adjacent Al atoms. The heat of adsorption in this segment of the curve is almost constant and equals to 63.5±0.5 kJ mol^{-1}.

This value is only 7—9 kJ mol^{-1} higher than the minima on the calorimetric curves obtained for all of the aluminophosphates studied. These values of the adsorption heats reflect the interaction of the adsorbed molecules with the oxygen atoms of the lattice. Probably, a portion of heat eliminated during the formation of the adsorption complexes with the participation of aluminum is consumed for the process of changing the coordination of the Al atoms. As a result, the heat of adsorption in this region is still lower than that for zeolite Na—Y (*cf.* Ref. 13).

Figure 2 shows that the isotherms of adsorption of MeOH on $AlPO_4$-5 and $AlPO_4$-17 in the coverages region of ~1 mmol g^{-1} are rather close, although the difference in adsorption is beyond the experimental error. In this case, the time for establishing the equilibrium is not longer than 2 h. Apparently, only a small part of the Al atoms directly interact with the methanol molecules in these cases. Especially distinctive are the differences in the mechanisms of adsorption on the samples of $AlPO_4$ when comparing the data obtained at different temperatures. For $AlPO_4$-5 and $AlPO_4$-17, the character of the temperature dependence of the isotherms of adsorption is the same as that for zeolites. In the case of $AlPO_4$-18, the dependence is of another character: with increasing temperature the starting segment of the isotherm shifts toward higher pressures (Fig. 3).

A similar temperature dependence of the adsorption of cyclopentane on the crystalline mesopore molecular sieves with the pore sizes from 14 to 100 Å was explained by the other authors[18] from the point of view of the theory of capillary condensation. Previously the isotherms of adsorption of H_2O on $AlPO_4$-5 were regarded in the frames of the same theory.[15] However, if one takes into account the facts that the sizes of pores and adsorbed molecules are not significantly different, the vertical segments of the isotherms are observed at rather low pressures, and the values of the heats of adsorption are much higher than the heats of condensation, it is possible to conclude that the existing notions of the capillary-condensation phenomena are not in agreement with the experimental data. On the basis of these notions, the drastic differences in the character of adsorption of MeOH on $AlPO_4$-18, from one side, and on $AlPO_4$-5 and $AlPO_4$-17, from another side, can not be explained either, because all these adsorbents have rather close pore sizes (5—8 Å).

At the same time, the features noted above do not refuge the proposal about the formation of adsorption complexes involving Al atoms within the segments of isotherms in question. If it is believed that the shape of an isotherm of adsorption in the region of low pressures is indicative of the intensity of complex formation in different $AlPO_4$, the intensity should increase in the following order: $AlPO_4$-5 < $AlPO_4$-17 ≪ $AlPO_4$-18.

During the adsorption of MeOH some changes in the IR spectra of the $AlPO_4$ framework are observed. These changes apparently reflect distortions of the crystal lattices that arise when increasing the coordination number of Al atoms. For $AlPO_4$-5 the changes in the IR spectra are insignificant, and at a pressure of MeOH of

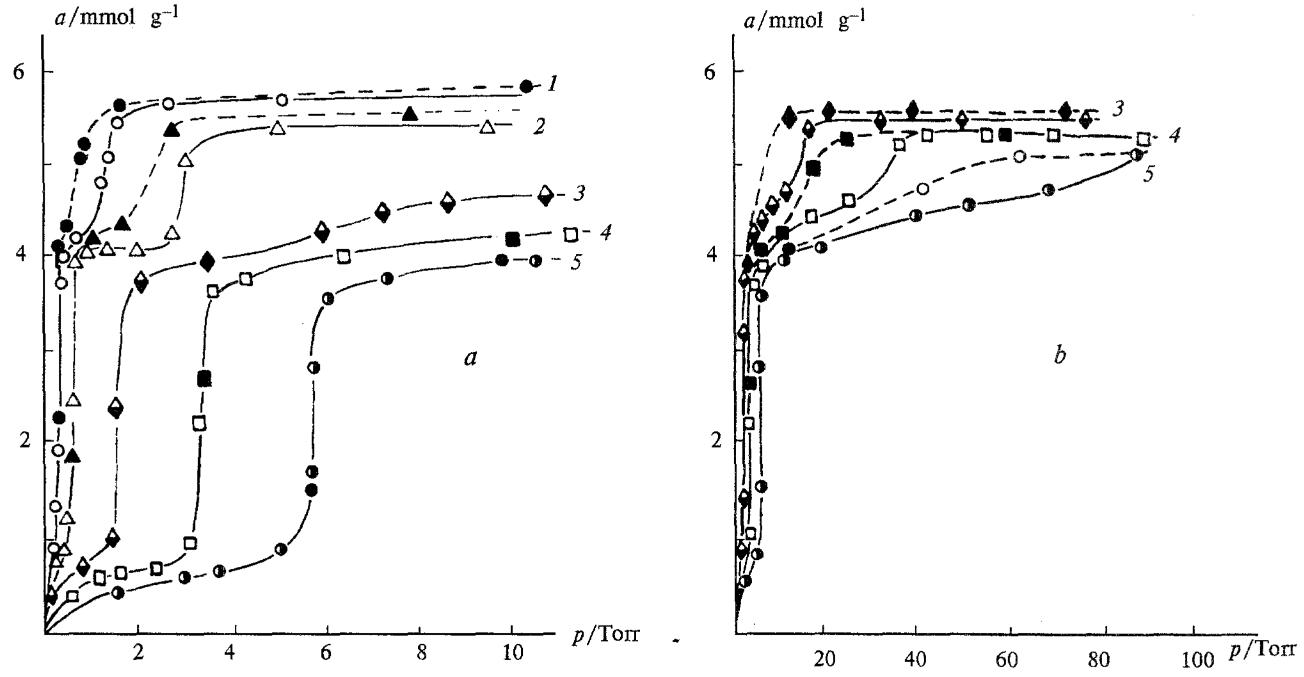

Fig. 3. Temperature dependence of adsorption of MeOH on $AlPO_4$-18: 283 K (*1*); 293 K (*2*); 303 K (*3*); 313 K (*4*); 323 K (*5*) (dark points reflect desorption); *a*, at pressures up to 10 Torr; *b*, at pressures up to 100 Torr.

~80 Torr only some broadening of the absorption band at 712 cm^{-1} is observed. In the case of $AlPO_4$-17, the adsorption of MeOH leads to more notable changes in the IR spectrum. At a pressure of ~6 Torr, the band at 520 cm^{-1}, which was observed in the spectrum of the starting sample as a shoulder, is resolved; the band at 456 cm^{-1} moves to 457 cm^{-1}, and the band at 638 cm^{-1} moves to 645 cm^{-1}. Besides, the intensities of the adjacent bands at 701 and 738 cm^{-1} are reversed. However, in general the main spectral characteristics do not change during adsorption. In contrast to the experiments with $AlPO_4$-5, the evacuation of the sample of $AlPO_4$-17 at room temperature does not result in complete restoration of the spectrum.

In the experiments with $AlPO_4$-18, the intensities and half-widths of the most of the bands in the IR spectrum are significantly changed already at p ~2 Torr, whereas the band at 538 cm^{-1} disappears almost completely. The bands at 460, 490, and 542 cm^{-1} are shifted upfield, whereas the bands at 625, 660, 704, and 755 cm^{-1} exhibit downfield shifts. Similarly to the case of $AlPO_4$-17, the initial spectrum is restored only after evacuation at high temperature. Thus, the IR spectra support the suggestion about different stabilities of the crystal lattices of $AlPO_4$ toward MeOH, as was found by the adsorption measurements.

There are great variety of the structures of $AlPO_4$, and it could be hardly possible to follow a direct correlation between the stability of the coordination condition of the Al atoms and dimensions or configuration of the intracrystalline cavities and channels. In general the stability of the Al atoms in the tetrahedra should be determined by the Al—O bond lengths and by the valent angles O—Al—O and P—O—Al.

In the structure $AlPO_4$-5, all of the Al atoms are crystalographically equivalent. The mean length of the Al—O bond in $AlPO_4$ containing tetrapropylammonium hydroxide is 1.71 Å (see Ref. 19). This value is notably lower than the mean Al—O bond length in $AlPO_4$-18, which does not contain any organic components (1.74 Å).[20] In the lattice of $AlPO_4$-18, the Al atoms occupy three crystallographically different positions. In the presence of tetraethylammonium hydroxide, the mean Al—O bond lengths for two of these positions attain 1.76—1.77 Å, and only for the third position the bond length remains within the 1.72—1.73 Å limits. Therefore, the Al atoms in $AlPO_4$-18 are bonded to the oxygen atoms of the lattice noticeably weaker than to $AlPO_4$-5, and they can participate in the formation of adsorption complexes.

$AlPO_4$-17 occupies an intermediate position between $AlPO_4$-5 and $AlPO_4$-18. The available X-ray structural data[21] were obtained for sample containing a different organic base, *viz.*, piperidine. In some of the tetrahedra, the mean Al—O bond length is 1.72 Å, and in the other tetrahedra three oxygen atoms are located at 1.73—1.74 Å distances, while with the fourth oxygen atom this bond is longer, *viz.*, 1.81 Å.

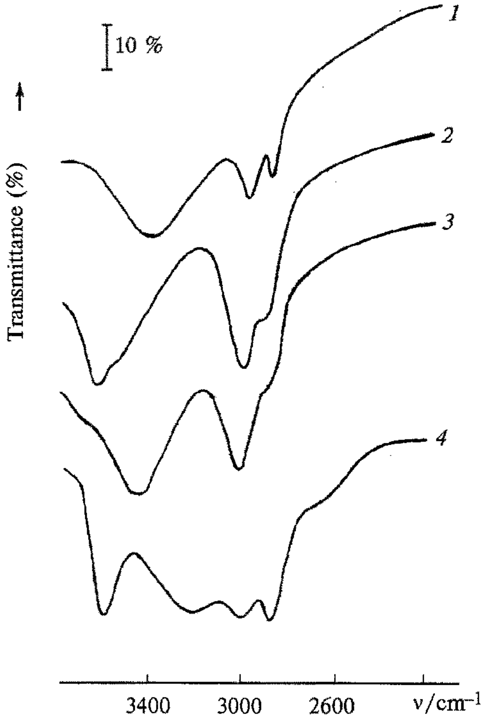

Fig. 4. IR spectra of MeOH adsorbed on zeolites Na—X (*1*), Na—Y (*2*), properly de-aluminated faujasite (*3*), and zeolite-like aluminophosphate $AlPO_4$-18 (*4*).

When the oxygen atoms of MeOH penetrate the first coordination sphere of the Al atoms, the condition of the adsorbed MeOH molecules dramatically changes. In Fig. 4 the IR spectra of MeOH adsorbed on $AlPO_4$-18 and on faujasites with different contents of Na^+ ions are shown. The positions of the bands of the symmetrical and asymmetrical vibrations of the Me-groups in the 2800—3000 cm^{-1} region is almost independent of the nature of adsorbent. The frequencies of the stretching vibrations of the OH groups of methanol adsorbed on different zeolites differ significantly, but they remain in the region restricted by the frequencies of the gaseous (3687 cm^{-1}) and liquid (3337 cm^{-1}) phases.[13]

In the spectrum of MeOH adsorbed on $AlPO_4$-18 two absorption bands are observed, which can be assigned to the stretching vibrations of OH groups. One of these bands (3600 cm^{-1}) is close in position to the corresponding band found for MeOH adsorbed on dealuminated faujasite (DNa—Y) and corresponds apparently to the molecules of MeOH that are not bounded to Al atoms and virtually inert. In the 3700—3300 cm^{-1} region of the spectra of MeOH adsorbed on zeolites, broad badly resolved absorption bands are observed, whereas for the more homogeneous surface of $AlPO_4$-18 one rather sharp band is characteristic. The other band in the spectrum of MeOH on $AlPO_4$-18 has no analogs in the methanol—water system. It is close in frequency to the absorption band of OH groups of crystalline methanol

(3235 cm^{-1}) and probably reflects the vibrations of the OH groups of the methanol molecules incorporated into the first coordination sphere of the Al atoms.

At the coverages higher than 4 mmol g^{-1}, the isotherm of adsorption of MeOH on $AlPO_4$-18 at 293 K exhibits a narrow plateau, which is followed by a sharp increase in adsorption up to ~5.5 mmol g^{-1} at virtually constant pressure (see Fig. 3). At 283 K the plateau virtually disappears, and only an inflection point is observed in the isotherm. On the other hand, at 298 K (see Fig. 2) and higher temperatures (see Fig. 3) it is already difficult to detect the segment with a dramatic increase in adsorption, since it increases gradually, although the isotherm remains concave with respect to the pressure axis. The shape of the isotherms of adsorption at a > 4 mmol g^{-1} and a < 4 mmol g^{-1} changes with increasing temperature in almost the same mode. This fact apparently indicates that similar processes occur in these intervals of coverages .

The heats of adsorption of MeOH on $AlPO_4$-18 in the coverage range higher than 4 mmol g^{-1} change very abruptly. Figure 2 shows that at first the q values decrease to the heat of the condensation of methanol, and then they increase again to reach 80 kJ mol^{-1} at the ~6 mmol g^{-1} loading. The following drastic decrease in the adsorption heats corresponds to the saturation. It is believed that similar changes in $q_{C_6H_6}$ on silicates are caused by the rearrangement of adsorbate molecules in the intracrystalline channels.[22] The investigations of the ^{27}Al NMR spectra indicate that significant changes of the symmetry of the crystalline lattice of $AlPO_4$-18 also occur in this region (see Ref. 3).

At coverages higher than 4 mmol g^{-1}, the heats of adsorption can be considered to be reversible within the limits of experimental accuracy (see Fig. 1), whereas a hysteresis loop is observed on the isotherms of adsorption. It is clear from Figs. 1 and 3 that the hysteresis loop narrows with decreasing temperature (in Fig. 3 the desorption branch is shown only for the isotherm measured at 283 K). Since under these conditions capillary condensation does not occur, the hysteresis can be explained by the particular features of the formation and decay of the adsorption complexes including Al atoms.

The minimum on the calorimetric curve for the erionite-like aluminophosphate ($AlPO_4$-17) is observed when the coverage reaches 1 molecule per cavity. The following increase in the values of heats up to the maximum at a loading of ~3 molecules per cavity (~3 mmol g^{-1}) indicates the strengthening of the interaction between adsorbing molecules. The difference in q values between the points of the minimum and the maximum (~12 kJ mol^{-1}) is close to the energy of hydrogen bonds for the dimers of alcohols.[22]

Possible intermolecular interactions in the comparatively narrow one-dimensional channels of $AlPO_4$-5 are strongly restricted. In contrast to $AlPO_4$-17, the heat of adsorption on $AlPO_4$-5 increases insignificantly after passing the minimum point, and then it drops to the value of the heat of condensation at ~4 mmol g^{-1} coverages. Significant portion of the intracrystalline space in $AlPO_4$-5 is completely inaccessible for the methanol molecules.[10]

The maximum observed in the coverage region of ~5.5 mmol g^{-1} for chabazite-like $AlPO_4$-18 corresponds to heats close to ~80 kJ mol^{-1}. Provided that such values of q reflect the interaction of the adsorbed molecules, their packing density in $AlPO_4$-18 should be somewhat higher than that in $AlPO_4$-17. In fact, the ratio of the adsorption capacities calculated for MeOH and H_2O, based on the densities of normal liquids, is 0.75 for $AlPO_4$-17 and 0.87 for $AlPO_4$-18. This difference could be caused by differences in the mechanisms of adsorption. During the hydratation both samples of aluminophosphates form adsorption complexes involving Al atoms.[1,23] The molecules of methanol are incorporated into the first coordination sphere of the Al atoms only during adsorption on $AlPO_4$-18.[3] In the case of $AlPO_4$-17, the majority of the Al atoms do not interact with MeOH molecules. This apparently accounts for the fact that the packing of the methanol molecules in the cavities in $AlPO_4$-17 is less dense than that of $AlPO_4$-18. On the other hand, rigid localization of the adsorbed molecules at Al the atoms in $AlPO_4$-18 reduces the probability of the intermolecular interactions in the region of small coverages , and in the interval from 1 to 4 mmol g^{-1} the heats of adsorption remain constant.

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