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Adsorption isotherms of water as a tool for characterization of metal substituted aluminophosphate molecular sieves

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Abstract

A summarizing overview is presented for our investigations of water adsorption on aluminophosphate molecular sieves of AFI structure type. The mechanism of water adsorption is mainly controlled by the amount and not the kind of the substituted heterometal. The initial stage of the process consists of a layer-like adsorption. This is followed by (*i*) a phase transition to liquid-like water at a definite relative pressure dependent on a substitution level and (*ii*) final volume filling of micropores. Adsorbed water forms islands around the metal centers, especially under low relative pressures. This leads to an apparent effect of averaging the adsorption between the layer-like one and the volume filling of micropores, being more pronounced with higher metal contents of the crystals. The effect is reflected in a gradual transition of the isotherms from type IV or V to type I. Neutral molecular sieves with Me^{3+} centers substituted for Al^{3+}, e.g. Cr^{3+} or Fe^{3+}, exhibit no significant differences in adsorption of water as compared to the charged materials with Me^{2+} or Me^{4+} centers substituted into the framework. The regular changes of adsorption isotherms of water, following variation in the heterometal content, can be used as evidence for framework incorporation of the heterometals. ***To cite this article: J. Kornatowski C. R. Chimie 8 (2005).***

Résumé

Nous présentons un récapitulatif de nos travaux relatifs à l'adsorption d'eau dans des tamis moléculaires aluminophosphates de type structural AFI. Le mécanisme d'adsorption d'eau est principalement contrôlé par la quantité, et non pas par la nature de l'hétéroélément métallique de substitution. L'étape initiale du processus consiste en une adsorption de type couche. Ceci est suivi par (*i*) une transition de phase vers de l'eau de type *liquide* à une pression relative définie qui dépend du taux de substitution puis (*ii*) par le remplissage final du volume microporeux. L'eau adsorbée forme des îlots autour des centres métalliques, en particulier aux faibles pressions relatives. Ceci a pour effet apparent de moyenner l'adsorption entre celle de type couche et celle liée au remplissage du volume microporeux, cet effet étant d'autant plus prononcé que les teneurs en élément métallique dans les cristaux sont plus élevées. L'effet est visualisé par la transition progressive des isothermes du type IV ou V vers le type I. Les tamis moléculaires neutres, avec des centres métalliques Me^{3+} substituant Al^{3+}, comme Cr^{3+} ou Fe^{3+}, ne montrent aucune différence significative du point de vue de l'adsorption d'eau en comparaison des matériaux chargés, pour lesquels des centres métalliques Me^{2+} ou Me^{4+} sont présents dans la charpente minérale. Les évolutions régulières des isothermes d'adsorption

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d'eau, en fonction de la teneur en hétéroélément métallique, peuvent être utilisées comme preuve de l'incorporation des ces hétéroéléments dans la charpente minérale. ***Pour citer cet article : J. Kornatowski C. R. Chimie 8 (2005).***

Keywords: Water isotherms; Adsorption mechanism; Sorption capacity; Aluminophosphates; Metal substitution

Mots clés : Isothermes d'adsorption d'eau ; Mécanisme d'adsorption ; Capacité d'adsorption ; Aluminophosphates ; Substitution par des hétéroéléments métalliques

1. Introduction

Aluminophosphate molecular sieves [1] are unique materials with respect to their adsorption properties. Their frameworks as a whole are neutral and should exhibit lyophobic character [2]. However, a specific structure of the aluminophosphate molecular sieves, composed of charged tetrahedra of $[AlO_{4/2}]^-$ and $[PO_{4/2}]^+$ alternatively ordered in the crystalline framework, causes reversed, i.e. lyophilic properties. This is especially significant for such species as water in which the molecules have a very large dipole moment, small molecular dimensions, and high ability to form hydrogen bonds. The local discontinuity of the charge distribution within the framework of aluminophosphates results in a strong hydrophilicity of these materials, which is independent of the other structure features to a high extent [2].

Aluminophosphates containing unidimensional pore systems [3] are especially interesting as simple model materials for studying adsorption properties of molecular sieves. The framework of $AlPO_4$-5 consists of the building units composed of 12-, 6- and 4-membered rings. They form a system of straight tubular pores arranged in parallel arrays characteristic of AFI type structure [2,3]: large pores of 12-membered rings of the 7.3 Å diameter and small pores of 6-membered rings with the 3.0 Å diameter. Adsorption in these pore systems obviously depends on the dimensions of adsorptive molecules.

Adsorption properties of porous solids result from a heterogeneity of both the surface and the inner structure [2]. The surface heterogeneity of aluminophosphate molecular sieves is created by the charge discontinuity described above and by surface imperfections occurring in the pores and on the external surface of the crystals. Isomorphous substitution of various metals into the framework [4] yields a compositional heterogeneity and considerably influences the adsorption properties [2]. Such modification is mostly connected with formation of a negative framework charge [4] in effect of the substitution of divalent metal cations for Al^{3+}. The formally 4+ and 5+ ions of, e.g. Si, Ge, Sn, Ti, Zr, As, Sb or V can either be substituted for P (e.g. SAPO-*n* family [4]) or introduced into the Al positions as oxy-cations (e.g. VO^{2+}) of a lower effective valence [5–8] and form a negative framework charge similar to the divalent metals. Additionally, the double bonding of oxygen and the distorted coordination of such centers create small structural defects in the framework. Materials with the Me^{3+} ions substituted for Al as stable framework centers have not been reported extensively in the literature. The Fe^{3+} containing materials [9] easily undergo redox reactions ($Fe^{3+} \rightleftharpoons Fe^{2+}$) and CoAPO-5 is even more problematic as the oxidation to Co^{3+} after calcination is more and more doubtful [10,11]. Our synthesis of CrAPO-5 [12,13] has yielded the first substituted zeolitic aluminophosphate material with no framework charge. Its stable compositional heterogeneity is created by the Cr^{3+} heterocenters [2].

Adsorption measurements on molecular sieves are mainly used to examine accessibility of the pores to adsorptive molecules by determination of sorption capacity [14–16]. The adsorption abilities point out whether the pore system is open or closed/clogged, which cannot be seen from XRD or other spectroscopic measurements. The adsorptives most useful for that purpose are those with dimensions of the molecules close to the pores dimensions. Smaller molecules like water can overcome potential hindrances and fill the pores despite a partial clogging. A much more significant feature is that the water molecules are small enough to pass the 6-membered ring windows of the structure. For $AlPO_4$-5 this means that the water molecules can penetrate the crystals not only along both the large and the small channels, but also in any other direction, seemingly 'through the walls' of the crystals and channels [2,13]. This eliminates application of water as a probe molecule for examination of the accessibility to the channel system and its open or closed state. For the same reason, measurements of the sorption capacity for water are almost meaningless. The full sorption capacity hardly depends on modification by the isomorphous substitution. It also cannot manifest a reduction in the sorption volume due to usually small volume of species potentially deposited in the pores. On the other hand, it has unexpectedly been stated that the course of the process of water adsorption (the isotherm shape) is very sensitive to the isomorphous substitution of heterometals into the framework. The response of the adsorption isotherms to the substitution is so characteristic that it can be accepted as qualitative and even semi-quantitative proof for the framework incorporation of the metals. The possible characterization of molecular sieves comes from interactions of water with the framework. Here, it is shown with the example of AFI type materials what is reflected in the isotherms of water adsorption with respect to the framework structure, its chemical composition, pore structure, and mechanisms of adsorption. The present study is focused only on the adsorption effects. Characterization of the investigated materials, together with the indications for framework incorporation of the metals, has been presented in our other cited papers.

2. Experimental

The samples of $AlPO_4$-5 and its derivatives substituted with Si, Mg, Co, V, Zr, Mo, Fe, V + Mo, Cd, Cu, and Ni were synthesized hydrothermally following our procedure [17,18] for growing large crystals. The formal molar ratios (given as oxides) in the reaction gels were: a Al_2O_3: b P_2O_5: c Me_2O_n: d R: e H_2O, where R = triethylamine, $a = 1$ for Si, V, Zr and Mo and $a = 0.9–0.915$ for the other metals, $b = 1$ or $b = 0.9–0.915$ (always $a + c/2 = b$ or $b + c/2 = a$), $c = 0.17–0.2$, $d = 1.35–1.55$ and $e = 270–300$. The metals were used mostly in the form of sulfate salts except Si used as SiO_2 and Mo used as sodium molybdate. Additionally, series of samples with various contents of Mg, Zr, V, and Si were prepared in a similar way [17,18]. The CrAPO-5 samples were synthesized with use of co-templates and various amounts of Cr as described elsewhere [2,12,13]. All the materials were thoroughly calcined under slow streams of air and oxygen at 763 and 793 K, respectively, each for at least 48 h, until full removal of the organic templates was achieved. The products were characterized by XRD, SEM and ICP or AAS analysis. Before the adsorption measurements, the samples were activated in situ at 673 K under vacuum of 10^{-4} bar for at least 8 h. The adsorption was measured in a vacuum device equipped with a McBain balance and MKS Baratron gauges at 298.2 K. Each experimental point of the isotherms was recorded after equilibrium state at a given relative pressure had been achieved, i.e. when mass increase Δm under constant pressure was lower than 10^{-5} g after 12 h. Water was degassed with a freeze-and-thaw technique.

3. Results and discussion

3.1. Materials

The large AFI type crystals studied were within the dimension range of 150–500 × 40–80 µm while the smallest ones were 70 × 25 µm (SEM). They showed the morphology of elongated hexagonal prisms typical of the AFI type. The CrAPO-5 crystals were 50–100 µm wide and below 20 µm long [12,13], i.e. had the form of flat hexagonal plates. The XRD patterns were characteristic of the AFI type structure and indicated high crystallinity as well as a lack of impurities or by-products. The metal contents (ICP or AAS analyses) were 0.4–4.4 atom%, i.e. ca. 0.1–1.1 Me/u.c., except ca. 0.1% Ni and Mo in traces (cf. Fig. 1) [2,5a,13].

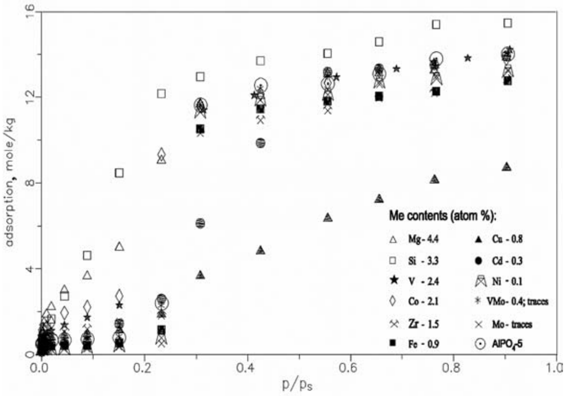

Fig. 1. Isotherms of water adsorption on various MeAPO-5 samples (298.2 K).

3.2. Adsorption

3.2.1. Sorption capacity (Me^{II}- and Me^{III}APO-5)

Adsorption of water in the AFI type materials follows a complex mechanism reflected in type IV or V isotherms (the IUPAC classification). The literature data, e.g. [19,20], present considerable discrepancies in the sorption capacities related most likely to imperfect structures of powder preparations investigated (see below and [2]).

All the investigated samples except CuAPO-5 (where XRD shows relevant structure problems) exhibit a high sorption capacity of 13.5 ± 0.6 mmol/g at $p/p_s = 0.9$, which is close to that for pure $AlPO_4$-5 (Fig. 1). This value is clearly lower than those commonly reported in the literature, the latter being up to ca. 24 mmol/g [15,21,22]. A geometrical calculation of the pore volume and the sorption capacity for liquid water give values of 0.17 cm^3/g or ca. 16 water molecules per unit cell [23]. The experimental values of this study fit the calculated data very well, which indicates that the sorption capacities determined for the large crystals are correct. For a better comparison with the powder preparations, the adsorption isotherm has also been measured for a ground sample of pure $AlPO_4$-5 (particle mean size of ca. 1–3 μm). It reveals a capacity of ca. 23 mmol/g, which suggests a very high contribution of adsorption on the external surface of the crystals and/or in the intercrystalline space. The former might result from adsorption on the OH-group nests formed on the surface defects created by the grinding. This effect implies that the commonly reported data for powder preparations reflect such an influence of numerous surface defects and OH group nests of that type.

In any case, the ease of obtaining considerable discrepancies in sorption capacities strongly implies that a reliable interpretation of the effects is difficult.

3.2.2. Shape and changes of the isotherms (Me^{II}- and Me^{III}APO-5)

The isotherms are of type IV and V (S-form) with a steep step characteristic of all the materials investigated (Figs. 1–4). For the parent $AlPO_4$-5, the middle of the step corresponds to the relative pressure of about 0.28 (Figs. 1,2 and 4). After substitution of smaller amounts of metals, the amount of water adsorbed before the step decreases considerably compared to the parent $AlPO_4$-5. Next, it increases quickly with the growing metal content and exceeds even the value for $AlPO_4$-5 (Figs. 1–4) [2,12,13]. The other common tendency, seen in the series of the isotherms (Figs. 1,2 and 4), is that

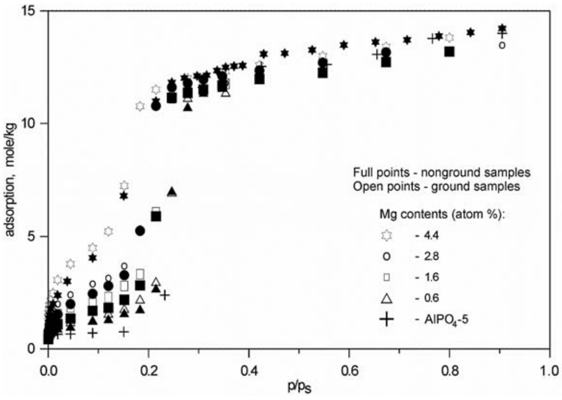

Fig. 2. Isotherms of water adsorption on non-ground and ground MgAPO-5 with various Mg contents.

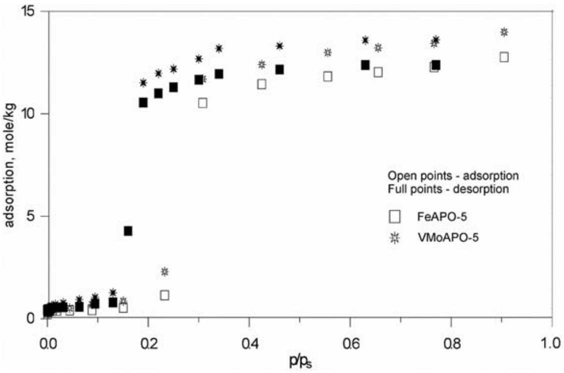

Fig. 3. Hysteresis for water desorption from FeAPO-5 and VMoAPO-5.

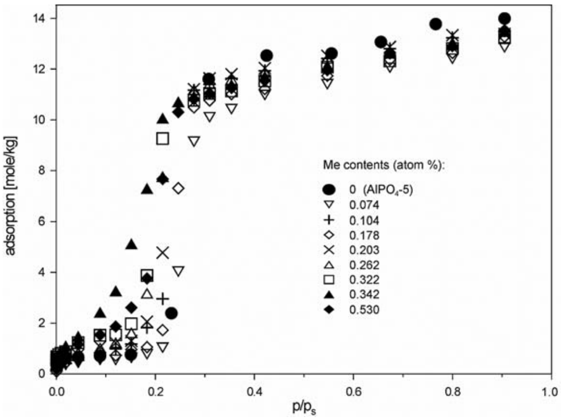

Fig. 4. Isotherms of water adsorption on CrAPO-5 samples with various Cr contents.

the step shifts to lower relative pressures as compared to parent $AlPO_4$-5 in parallel to the increase in the water amount adsorbed before the step. These changes lead together to a gradual "smoothing" of the isotherms and, when the step corresponds to the relative pressure of ca. 0.15, the "smoothing" means an almost complete transition to a type I isotherm. This is seen especially well for MgAPO-5 and SAPO-5, i.e. the samples with the highest substitution level (Figs. 1 and 2). These clear changes of the isotherm shape regularly follow the metal contents of the samples. The adsorption isotherms determined for a series of the samples with different contents of Mg (Fig. 2) give decisive evidence that the amount of the substituted metal, and not its type, is the factor controlling the adsorption process. The common regularity of the changes and the straight influence of the growing metal contents cannot origin from any effects caused by a random deposition or distribution of metal species in the pore system, especially since the sorption capacity remains unchanged for all the materials. Thus, the regular shift of the isotherm steps in relation to the non-substituted $AlPO_4$-5 material offers the evidence for framework incorporation of the heterometal ions.

3.2.3. Adsorption mechanism

The above observations may reflect several various possible mechanisms:

- the complete filling of the small (6-membered ring) channels with water adsorbed during the initial stage before the isotherm step and then filling of the large channels after the step;
- covering of the adsorption surface with a (mono)-layer of water molecules before the step, then condensation (the step), and volume filling of micropores with liquid-like adsorbate;
- initial filling of the pore openings with water adsorbate resulting in an apparent clogging of the pores by water itself due to its strong clustering (e.g. around the Me centers or OH group nests), then breaking of this hindrance at a sufficiently high pressure (the step), and filling of micropores with the liquid-like adsorbate.

The first mechanism is an over-sophisticated theoretical possibility. Practically, there is no reason or driving force that could control and direct the water molecules exclusively to the small pores at the beginning of adsorption at low relative pressures. Thus, it is improbable. The third mechanism might well be probable. However, it should not exhibit any regular dependence on the amount of substituted metals and, quite opposite, some irregularities should be observed as the result of varying distributions of the heterocenters [2,24].

The experimental data fit best to the second adsorption mechanism, which is supported by the desorption measurements (Fig. 3). The upright directed large hysteresis loop at low relative pressures (0.17–0.27) is an evidence for a phase transition of the adsorbate. This corresponds to the postulated transition to a liquid-like water phase in the pores of the AFI type materials.

A potential influence of the crystal morphology on the adsorption [25] may include the effect of crystal dimensions and internal structure of the crystals, since possible overgrowing or twinning might significantly hinder the adsorption. This is especially important in the case of large crystals that commonly form twins [5,18]. A grinding treatment should open for adsorption the crystal regions formerly inaccessible to water. As the adsorption isotherms for the ground MgAPO-5 samples (Fig. 2) are almost identical with those for the large crystals, it indicates that both the sorption capacity for water and the adsorption mechanism are not influenced by the morphological factors [25]. This seems to be justified by the fact that water can freely diffuse via 6-membered rings and overcome possible hindrances inside the pores.

The isotherms for CrAPO-5 with a neutral framework are, of course, also of type IV or V (Fig. 4). This shape suggests, similarly as mentioned above, that the adsorption mechanism comprises most probably a layer-like adsorption at the initial stage, then a phase transition to a liquid-like water, and volume filling of micropores at higher relative pressures [24]. The influence of the neutral Cr heterocenters does not differ from that of Me^{2+} and Si^{4+} [2,24].

3.2.4. General considerations

An almost identical sorption capacity is observed for all the studied samples with various metals or various amounts of one metal [2,24]. Therefore, the sorption capacity for water depends neither on the kind nor on the amount of the introduced metals, i.e. on the substitution of $AlPO_4$-5 with a metal [24]. This can only be an apparent effect as we deal with the volume filling of micropores, i.e. full 'saturation' of the adsorption volume with liquid-like water. The adsorption mechanism, however, is controlled by the amount of the substituted metal while the type of the metal plays a secondary role [24]. The same tendencies are also observed for CrAPO-5 [2,24,25] and FeAPO-5 [2,24]. Similar features have at least been implied for the MeAPO-11 [26] and MeAPO-31 [27] materials. Analogous conclusions can also be drawn from the IR spectroscopy studies [28] and investigations with various microscopy techniques [29–31]. Thus, the occurrence of any heterocenters in the structure, not necessarily the charged ones, accelerates the transformation into the liquid-like water and volume filling of micropores, likely via formation of water clusters around the metal centers of the framework. Such transformation of the adsorption mechanism occurs gradually and is reflected by a fluent transition of the isotherms from type IV or V towards type I with the rising content of heterometals [12,24]. The effect is independent of the metal type, i.e. of the fact whether the heterocenters formed by the isomorphous substitution are charged or neutral.

3.2.5. Materials substituted with higher charged metal ions

The water sorption capacity is similar to that of the parent AlPO$_4$-5 for all Zr and three of five V samples (Figs. 5 and 6). A very low sorption capacity of two VAPO-5 samples results from a thermal collapse (at least partial) of the structure during calcination (XRD). As the other sample with a similar content of V is thermally stable, these observations support the conclusion that V can enter various coordinations in the framework, depending on the synthesis route and V source [5a,32]. The stepwise shape and changes in the VAPO-5 isotherms indicate the same adsorption mechanism and dependence on the substitution level as in the case of the other metals. Such changes are not observed for the ZrAPO-5 series (Fig. 5). This implies either a considerably weaker influence of the Zr centers than that of the other metals or, much more likely, formation of Zr species inactive in adsorption. A distinctly higher adsorption observed during the initial period of the process for the two highest substituted ZrAPO-5 samples after grinding seems to support the latter possibility. The grinding may result in formation of defects in those species and, thus, in an increase in their adsorption affinity to water. Then, the above observations suggest that Zr occurs in the highly substituted samples simultaneously in two forms: (*i*) as species inactive in adsorption of water in prevailing amounts and (*ii*) as isolated Zr heterocenters of the framework in lower amounts. A possibility that Zr occurs as an extraframework species occluded in the pores is contradicted by the adsorption results for benzene and nitrogen [18].

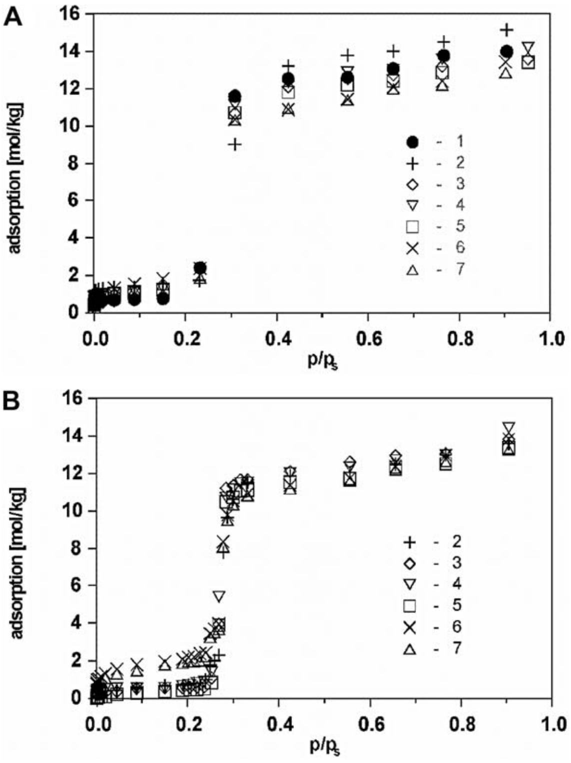

Fig. 5. Isotherms of water adsorption on non-ground (**A**) and ground (**B**) ZrAPO-5 crystals. Zr contents (wt.%): (1) 0.00 (AlPO$_4$-5), (2) 0.22, (3) 0.29, (4) 0.30, (5) 0.42, (6) 3.48, (7) 5.41.

4. Conclusions

The sorption capacity of the AFI type molecular sieves for water is constant, i.e. independent of the material modification by isomorphous substitution. Structure defects and/or large amounts of surface OH group nests can considerably increase the apparent sorption capacity. The mechanism of water adsorption comprises a layer-like adsorption at the initial stage, followed by a phase transition to liquid-like water (step of the isotherm), and volume filling of micropores with the liquid-like adsorbate. This is evidenced by the changes in both the position and the shape of the step

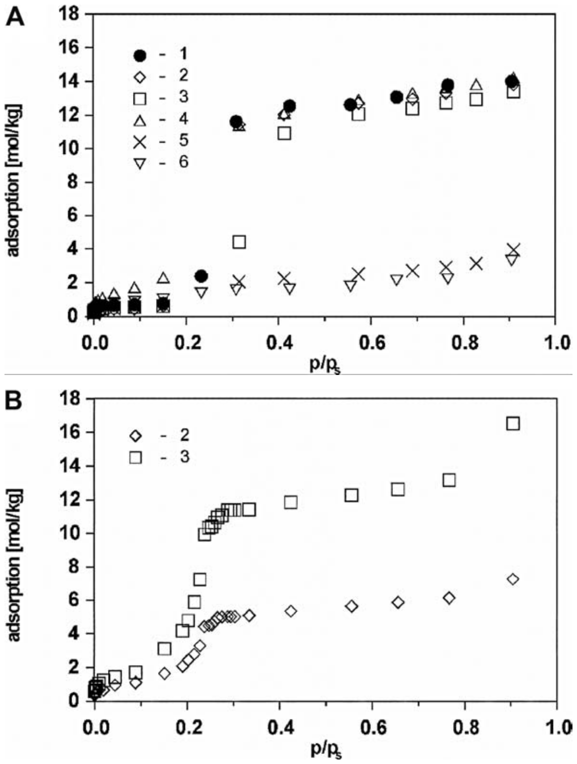

Fig. 6. Isotherms of water adsorption on non-ground (**A**) and ground (**B**) VAPO-5 crystals. V contents (wt.%): (1) 0.00 ($AlPO_4$-5), (2) 0.06, (3) 0.08, (4) 1.34, (5) 1.56, (6) 1.69.

of the isotherms as well as by the occurrence of a significant low-pressure hysteresis. The regular shift of the isotherm step to lower relative pressures and gradual transition of the water adsorption isotherm to type I (“smoothing”) with increasing metal content give a reliable evidence for framework incorporation of the heterometals. This holds under the reservation that a reasonable comparison with the isotherms for the differently substituted and non-substituted materials can be made.

No significant difference has been found between the neutral heterocenters of chromium or iron and the charged centers of the 2+, 4+ or 5+ metal ions. The main factors controlling the adsorption processes are (*i*) the content of the substituted metal, i.e. the number of the heterocenters and (*ii*) their distribution in the crystals. The kind of metal plays a secondary role. The importance of the content factor results from the fact that the number of metal centers controls the adsorption mechanism, which is reflected in a gradual transition from the type IV or V isotherm to the type I isotherm with rising levels of substitution.

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