Adsorption Properties of Lamellar Silica

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Abstract—Isotherms and heats of adsorption of water, n-heptane, trimethylamine, and methanol (at 303 K) vapors and isotherms of adsorption of nitrogen (at 77 K) on the lamellar silica prepared by removing metals from natural mineral vermiculate were measured. The surface concentration of adsorption sites and their energetic characteristics were found to be similar to those of ordinary silicas. The distinction of the lamellar silica from ordinary silicas manifests itself through extended desorption branches, a feature that makes it possible to classify the lamellar silica under study as a limitedly swellable sorbent.

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Lamellar silicates belonging to the group of hydroxymicas, in particular, vermiculite, which are widely used in the building industry production of thermoinsulating materials, have been thoroughly studied by the adsorption [1], adsorption-induced deformation [2], calorimetric [3, 4], and XRD [5, 6] methods. The properties of these material have been examined in a number of review, see, e.g., [7, 8]. It was demonstrated that the removal of metal cations from vermiculite by treatment with acids makes it possible to obtain a unique material with a relatively high specific surface area and composed of virtually pure silica; in contrast to traditional silicas, it has metastable lamellar structure [9, 10].

Although lamellar silica is of considerable interest as a sorbent and catalyst support, its sorption properties have been studied insufficiently: only the differential heats of adsorption of C₃–C₄ alkanes were obtained [10]. In the present work, the adsorption properties of lamellar silica were studied by adsorption calorimetry, which makes it possible to concurrently determine the concentration and energetic characteristics of adsorption sites, using a single sample.

EXPERIMENTAL

The isotherms and differential heats of adsorption of vapors of water, n-heptane, triethylamine, and methanol were measured at 303 K on an adsorption vacuum setup that included a capillary microburette for dosing volatile liquids (sorbates) and a DAK-1-1 differential calorimeter (Experimental Factory of Scientific Instrumentation, Chernogolovka). The integrator of the calorimeter was replaced by an analogue-to-digital converter card installed into a PC and controlled by the MultiCrom version 1.52m software for acquisition and processing chromatographic data. The adsorption isotherms for nitrogen on lamellar silica samples were measured at 77 K using an electromagnetic microbalance, as described in [11].

The samples were prepared from demetallized vermiculite of two types. The first one was lamellar silica obtained by washing expanded natural vermiculate from metals. The washing was performed as described in [12], first with an excess amount of 5% hydrochloric acid and then with a 40 + 40% mixture of sulfuric and nitric acids. The sorbent obtained was a loose powder with a pour density of 0.15 g/cm³ and a specific surface area of 320 ± 30 m²/g. For the adsorption experiments and for the preparation of the granulated sorbent sample (second type), a 0.05–0.20 mm fraction was used. The vermiculate powder was granulated by extrusion. The powder was mixed with a binder, triturated in a mortar until the plastic state was attained, and squeezed through an extrusion nozzle. The granules were dried at room temperature for 24 h in a drying box at 100°C for 1 h and calcined in air at 300, 350, and 450°C for 1 h. The binder was a 4 wt % starch solution. In the course of drying the content of water plus starch decreases from 48–50 to 10–11 wt % at room temperature, to 5–7 wt % at 100°C, and to 1.0–1.5 wt % at 300°C—only at 450°C, the starch was completely burnt out. The specific surface area S_{sp} of the calcined samples differed insignificantly from that of the initial powder, 340 m²/g on the average. Before adsorption measurements, both types of samples were thermoevacuated at 473 K and 0.003 mmHg for 40 h. The regeneration was performed under the same conditions. These samples will be referred to as powdery and granulated, respectively. The adsorbates, bidistilled water, freshly distilled triethylamine and methanol, and for-chromatography-grade n-heptane, were purified from dissolved gases by repeated evacuation at liquid nitrogen temperature.
(77 K) with subsequent heating to room temperature (~20°C) and dosed from a capillary microburette. The heats of condensation were calculated by the Clausius–Clapeyron equation. The saturation vapor pressures were determined using the Antoine equation.

RESULTS AND DISCUSSION

Nitrogen adsorption. The adsorption isotherms for nitrogen on the powdery and granular lamellar silicas at 77 K are displayed in Fig. 1; the inset shows the initial segments ($p = 0–30$ mmHg) of the isotherms in the BET equation coordinates. As can be seen from Fig. 1, the isotherms are straightened in the BET coordinates only within a narrow interval of relative pressures, $p/p_s = 0.015–0.095$. The equations of the isotherms displayed in Fig. 1,

\[
\frac{(p/p_s)(a(1 - p/p_s))}{(a(1 - p/p_s))} = 0.3206(p/p_s) + 0.0049, \\
\frac{(p/p_s)(a(1 - p/p_s))}{(a(1 - p/p_s))} = 0.3083(p/p_s) + 0.0033
\]

where $a$ is the specific amount of nitrogen adsorbed, mmol/g; $p/p_s$ is the relative nitrogen pressure, is the saturation pressure of nitrogen vapor (at the measurement temperature), mmHg) allowed us to determine the specific surface area by the equation

\[
S_{sp} = a_mN_A\omega_m,
\]

where $a_m$ is the monolayer capacity, mol/g; $N_A$ is the Avogadro number, mol$^{-1}$; and $\omega_m$ is the surface area occupied by a molecule in a complete monolayer, m$^2$. The value of $a_m$ is calculated from the coefficients of Eqs. (1) and (2). For the powdery and granulated samples, $S_{sp} = 315$ and $300$ m$^2$/g, respectively. Thus, the granulation produced little effect on $S_{sp}$.

Water adsorption. Figure 2 shows the adsorption isotherm for water on the powdery lamellar silica and compares it with analogous isotherms for KSK-2-150 and KSK-2-900 silica gels preliminary thermoevacuated at 423 and 1173 K and characterized by a specific surface area (measured with nitrogen) of 330 and 275 m$^2$/g, respectively. We chose these types of silica gels for comparison because their nature and structural characteristics are similar to those of lamellar silicas and because the structure of the surface of these silica gels was studied in detail by A.V. Kiselev and coworkers [15–17]. The initial segment of the adsorption isotherm for water (till $p/p_s = 0.3$) on the powdery sorbent lies in between the isotherms for the adsorption of
water on the silica gels. The shape of isotherms for adsorption on silica gels is known to be strongly affected by the conditions of preliminary thermoevacuation (thermal dehydroxylation), that is, on the number of hydroxyl group per unit surface area $\alpha_{OH}$ [18].

The authors of [18] suggested to estimate the concentration of free hydroxyl groups on the surface of a sorbent by comparing the amounts of triethylamine adsorbed on it and on a reference sorbent with known surface concentration of free hydroxyl groups $\alpha_{OH}$. According to [18], the concentration of free hydroxyl groups on the surface of KSK-2-150 silica gel thermoevacuated at 423 K is 3.4 $\mu$mol/m$^2$. If water molecules form hydrogen bonds only with free hydroxyl groups, then the ratio of the amounts adsorbed (at $p/p_s = 0.02$) on KSK-2-150, powdery lamellar silica, and KSK-2-900 can be estimated as 3.4, 1.3, and 0.6 $\mu$mol/m$^2$, respectively. This means that, at the initial stage of the adsorption of water on the lamellar silica, 40% of the free hydroxyl groups can adsorb water molecules. As can be seen, however, the isotherm for the adsorption of water onto the lamellar silica has a stepwise shape (Fig. 2). Starting from $p/p_s = 0.28$, the amount adsorbed begins to increase sharply, with the adsorption isotherm for water on the lamellar silica approaching the adsorption isotherm for water on KSK-2-150, an adsorbent characterized by the maximum possible surface concentration of hydroxyl groups, already at $p/p_s = 0.33$. As the adsorption isotherm ascends steeply at $p/p_s > 0.28$ (Fig. 3a), the differential heat of adsorption as a function of the amount $\alpha$ of water adsorbed (Fig. 3b) first decreases to $\alpha = 5$ $\mu$mol/m$^2$ and then increases. That the differential heat of adsorption changes sharply is indicative of the different types of adsorption sites being involved in the formation of adsorption complex. We believe that the initial decrease in the heat of adsorption is associated with the energy being spent on the transport of first water molecules into the interlayer space, in which the liquid phase is formed thereafter. Within this region, the isotherm rises sharply, while the adsorption heat curve shows a diffuse maximum with an amplitude close to the heat of condensation of water ($L = 44.1$ kJ/mol). An important feature of the adsorption process under study is that the time it takes to attain the equilibrium state increases with the amount adsorbed of water adsorbed on the lamellar silica. At relative pressures $p/p_s > 0.7$, the time required for the attainment of adsorption equilibrium (a quasi-equilibrium state) is 4.5–5.0 h, while at the relative pressures corresponding to the initial portion of the adsorption isotherm, it takes only 1.5–2.0 h. The mechanism of the penetration of water into the interlayer space of vermiculate containing sodium, potassium, and barium exchangeable cations proposed in [2] involves the deformation of the sorbent. There is good reason to believe that, in our case, the penetration of water into the interlayer space is accompanied by the gradual increase of the adsorbent volume (swelling).

Note that the isotherms for water adsorption on vermiculate containing metal ions clearly show step over a relative pressure range of 0.1 to 0.9 [3]. Within the same range, the dependence of the differential heat of adsorption on the amount of water adsorbed exhibits two or three maxima [3]. The heat of adsorption corresponding to the first maximum was found to be ~200 kJ/mol for vermiculate containing sodium cations and 120 kJ/mol for vermiculate containing barium cations, with these maxima being observed at specific amounts of water adsorbed of 0.12 and 0.7 mmol/g, respectively. We observed (Fig. 3b) two moderate-amplitude maxima (~50 kJ/mol), the positions of which in the dependence of the differential heat of adsorption on the amount of water adsorbed are not too different from the positions of the above-indicated maxima (0.3 and 0.95 mmol/g or 1 and 3 $\mu$mol/m$^2$, respectively). We believe that these maxima reflect the interaction of

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![Graph](image-url)  
**Fig. 3.** (a) Adsorption isotherm and (b) the dependence of the heat of adsorption on the amount adsorbed for water on the powdery lamellar silica. The dashed horizontal line represents the heat of condensation of the sorbate at 303 K.
water with trace amounts of metal ions. The presence of maxima in the dependence of the differential heat of adsorption on the amount of water adsorbed and the low initial heat of adsorption (only 27 kJ/mol) are indicative of the localization of impurity ions in the interlayer space. Such dependences of differential heats of adsorption on the adsorbed amount of water were observed for potassium forms of zeolite X [19]. The authors of [19] explained the wavelike character of the curves by the displacement of exchangeable cations. The displacement of cations from some cavities to others was also observed in [19, 20] during the dehydration of zeolite X samples. It seems probable that such a displacement occurs in the system under study.

Triethylamine adsorption. The dependence of the differential heat of adsorption of triethylamine on the powdery lamellar silica on the amount adsorbed of triethylamine nearly coincides with the analogous dependence for the adsorption of triethylamine on KSK-2-200 silica gel [16]. This means that the concentrations of free hydroxyl groups involved in the adsorption of triethylamine on the surfaces of the silica gel and lamellar silica are the same, ~3 µmol OH/m² at the inflection point of segment ab of the dependences [18]. The energy of adsorption of triethylamine on such sites was found to be 80 kJ/mol. The surface concentration of adsorption sites on the granulated sorbent is about 13% lower than those on the silica gel and powdery silica.

When plotted in the amount adsorbed versus relative pressure coordinates, the isotherms for the adsorption of triethylamine on the lamellar silicas and on KSK-2-200 silica gel differ from one another by no more than 10% up to \( p/p_s = 0.4 \). For the granulated lamellar silica gel, this deviation is negative (Fig. 5). The desorption and adsorption branches of the isotherm for the powdery silica coincide at high relative pressures but show a small hysteresis in the range intermediate pressures. Such a behavior is typical of adsorbents containing micropores, in contrast to macroporous KSK-2-200 silica gel. According to [10], the volume of the micropores in the lamellar silica prepared as described above is ~0.1 cm³/g or 30% of the total pore volume. Therefore, the results obtained are quite explicable.

Adsorption of \( n \)-heptane. The isotherms for the adsorption of \( n \)-heptane on the powdery and granulated samples are nearly linear up to \( p/p_s = 0.6 \). After the first series of measurements, the granulated sample can be readily regenerated by thermoevacuation at 473 K, so that the adsorption branches virtually coincide (Fig. 6, branches 2A and 3A). After a long-term treatment (for more than 100 h) with \( n \)-heptane vapor at a near-saturation pressure, the relative pressure of \( n \)-heptane decreases to \( p/p_s = 0.8 \), after which the ultimate amount adsorbed increases from 9 to 11.5 µmol/m², i.e., by about 30%. A similar effect was observed in [21] for the adsorption of water on precipitated soot aerosols: after
the sample was seasoned in saturated vapors for ~120 h, the adsorption capacity of the sample increased by a factor of 3.5. We believe that this effect is associated with swelling. Since the overcoming of the interaction between layers of mica-like silica requires energy expenditures, a substantial part of the dependence of the differential heat of adsorption of \( n \)-heptane on its amount adsorbed lies below the level corresponding to its heat of condensation, 36.9 kJ/mol at 303 K (Fig. 7). The same behavior was observed for the adsorption of water on this sorbent (Fig. 3b). This is the main distinction of the lamellar silica from the silica gels. The adsorption isotherm for \( n \)-heptane onto KSK-2 silica gel [22] (Fig. 6) ascends sharply starting from \( p/p_s = 0.5 \), a behavior typical of capillary condensation. In comparison with the lamellar silica, the pores of which exhibit no propensity for capillary condensation, the maximum adsorption capacity of the silica gel is higher by a factor of 1.8 to 2.3 (Figs. 6, 7; table). The lamellar silica behaves as a swellable sorbent with labile inter-layer spaces, which cannot provide fixation for menisci, in contrast to ordinary silica with a rigid skeleton.

**Methanol adsorption.** Figure 8a shows the adsorption isotherm for methanol on the granulated silica. As can be seen, the isotherm has a hysteresis loop characteristic of swellable sorbents [23], while a substantially part of the differential heat of adsorption versus amount adsorbed curve lies below the level corresponding to the heat of condensation (Fig. 8b), as in the case of the adsorption of \( n \)-heptane and water. As discussed above, the adsorption of various compounds on the powdery and granulated lamellar silicas and the heats of condensation of these compounds at 303 K

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>( L ), kJ/mol</th>
<th>( a )</th>
<th>( \alpha )</th>
<th>( V )</th>
<th>( a )</th>
<th>( \alpha )</th>
<th>( V )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Powdery ((S = 315 \text{ m}^2/\text{g}))</td>
<td>Granulated ((S = 300 \text{ m}^2/\text{g}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>44.1</td>
<td>19.2</td>
<td>60.9</td>
<td>0.35</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Methanol</td>
<td>38.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>10.9</td>
<td>32.7</td>
<td>0.45</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>34.7</td>
<td>2.8</td>
<td>9.0</td>
<td>0.40</td>
<td>3.2</td>
<td>9.6</td>
<td>0.45</td>
</tr>
<tr>
<td>( n )-Heptane</td>
<td>36.9</td>
<td>2.8</td>
<td>8.8</td>
<td>–</td>
<td>2.7 (3.5)</td>
<td>9.0 (10.5)</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Note: \( L \) is the heat of condensation; \( a \) and \( \alpha \) are the limiting amounts adsorbed, in mmol/g and \( \mu \text{mol/m}^2 \), respectively; \( V \) is the specific adsorption volume, cm\(^3\)/g; the parenthesized values refer to the samples seasoned in saturated vapors for more than 100 h.
this behavior is indicative of adsorbent swelling. The data from [24] on the adsorption of methanol onto aerosils with specific surface areas of 45 and 136 m$^2$/g and white soot ($s = 30$ m$^2$/g) are also presented. At relative pressures below 0.4, the adsorption isotherms for methanol on these silicas are reversible and virtually coincide with the adsorption branch of the isotherm for the adsorption of methanol on the lamellar silica. Note, however, that the differential heat of adsorption versus amount adsorbed curve for the aerosils and white soot lies about 10 kJ/mol higher than that for the lamellar silica. In our opinion, in the latter case, as for $n$-heptane, the energy spent by methanol molecules to penetrate into the space sorbent layers causes a decrease in the total heat of adsorption already at the beginning of the process of filling.

The results obtained show that the lamellar silica, being similar to the silica gels in energy of adsorption sites, belongs the class of limitedly swellable sorbents. The effect of swelling are especially pronounced for the granulated sorbent, as can be clearly seen from the adsorption isotherms for $n$-heptane and methanol and from the differential heat of adsorption versus amount adsorbed curves. The values of the limiting amount adsorbed (at $p/p_s = 1$) for various compounds are presented in the table. These data support the assumption that the test lamellar silicas swell in the adsorption systems studied.

The table shows that the limiting adsorption capacity of the granulated sample for $n$-heptane and triethylamine is higher than that of the powdery sample; it increases markedly upon treatment the sample in saturated $n$-heptane vapors.

The results obtained suggest that the adsorption characteristics of lamellar silicas are as good as those of silica gels. Given the specifics of this adsorbent, in particular, the propensity for a strong retention of the ions of some transition metals [3], lamellar silicas is, in our opinion, of considerable interest as a sorbent and carrier for heterogeneous catalysts and for the development of nanoreactors on the basis of interplanar spaces in lamellar matrices [25–27]. When dealing with systems containing such silica, it is necessary to take into account its properties as a swellable sorbent.

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