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Adsorption Properties of Alumina Modified by Stearic and Oleic Acids

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Abstract—Two sets of alumina samples were prepared, one chemically modified by stearic acid and the other by oleic acid, with modifier concentrations within 0.1–4.0 groups/nm^2. The adsorption of nitrogen, water, and benzene vapors, as well as Acid Orange dye (from aqueous solution), was studied as a function of modifier concentration. In the highest concentration (2.7 groups/nm^2), stearate generates a dense surface monolayer, which is hardly accessible to the penetration of molecules of the test compounds. Alumina with stearate concentrations of about one-half the monolayer coverage is the most active adsorbent of organic ions from aqueous solutions. Alumina with the limiting oleate concentration adsorbs a large benzene volume (three times the specific pore volume of the support), because oleate exists on the surface in a liquid state.

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Acids containing long-chain hydrocarbon radicals are chemisorbed on alumina [1] and can generate oriented self-organized monolayers [2–4]. Modification with oleic acid makes alumina an active adsorbent of organic ions [5].

Here, we compare the adsorption properties of alumina modified by long-chain carboxylic acids with equal numbers of carbon atoms: stearic (octadecanoic) aliphatic acid and oleic (9-*cis*-octadecenoic) acid, which contains a double bond in the middle of the hydrocarbon radical. We consider the adsorption of nitrogen, water, and benzene vapors, as well as Acid Orange (an ionic dye) from aqueous solution, as a function of stearate or oleate concentration on alumina surfaces.

EXPERIMENTAL

Alumina for chromatography was used. Its specific surface area determined by thermal desorption of nitrogen was 93 m^2/g; the specific pore volume determined from benzene and water condensation was 0.23 cm^3/g; and the average pore diameter was 10 nm.

Before modifying, alumina was washed with distilled water until pH was 7 and dried at 140°C. Solutions of stearic and oleic acids of various concentrations were prepared in isooctane. Alumina samples were exposed to acid solutions at room temperature for 24 h, filtered on a Buchner funnel, and dried at 120°C to constant weight. The modifier surface concentration on alumina was determined as weight loss on ignition at 600°C. Sets of five samples with different modifier concentrations were prepared.

Specific surface areas of modified samples were determined by thermal desorption of nitrogen. The adsorbed water or benzene volume was measured after the sample was exposed to the relevant saturated vapor until a constant weight was achieved.

Water adsorption isotherms at 23°C were measured on unmodified alumina and on samples with the highest modifier concentrations. Adsorption was carried out in a desiccator for 3 months. Aqueous sulfuric acid of known strengths was used to vary the water vapor pressure.

Acid Orange dye was used to determine the adsorption properties of the modified samples in aqueous solutions.

The dye adsorption from water was measured as follows. Adsorbent samples, each weighing 20 mg, were each exposed to 5 mL of an aqueous solution containing 10 mg/L dye for 5 days. The dye concentration in the solution after adsorption was determined on a spectrophotometer at 400 nm.

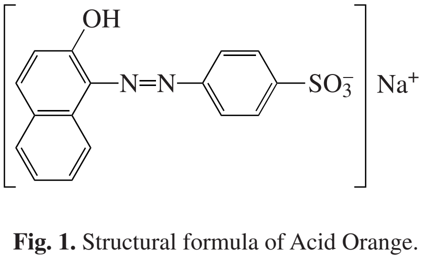

Fig. 1. Structural formula of Acid Orange.

Modifier concentrations m (wt %) and N (groups/nm^2) and molecular surface areas ω (nm^2) on alumina

	Stearic acid						Oleic acid					
m, wt %	0.5	1.5	3.0	5.0	7.5	11	0.5	2.0	5.0	7.5	12	15
N, groups/nm^2	0.11	0.33	0.68	1.30	1.90	2.70	0.11	0.45	1.20	1.80	3.20	3.90
ω, nm^2	9.00	3.00	1.50	0.78	0.53	0.37	9.00	2.20	0.86	0.56	0.32	0.26

RESULTS AND DISCUSSION

The table displays the surface modifier concentrations on alumina. The minimal and maximal stearate concentrations differ 20-fold, while those of oleate differ 30-fold. The maximal surface concentration of oleate is 1.4 times that of stearate. The surface occupied by one oleate and stearate group with the maximal surface coverage, ω, is 0.26 and 0.37 nm^2, respectively.

Figure 2 shows the specific surface areas of unmodified and modified aluminas determined from thermal desorption of nitrogen (per gram of the support). These values decrease considerably with increasing modifier concentration (roughly to the same extent for both modifiers). In the samples with the maximal modifier concentration, the specific surface area is about one order of magnitude smaller than the specific surface area of unmodified alumina. This signifies that the part of the inner pore surface occupied by modifier molecules is inaccessible to nitrogen molecules.

Figure 3 illustrates the pore volumes determined from water capillary condensation as a function of modifier concentration (the adsorbed water volume per gram of the support). These volumes decrease considerably with increasing concentration of either modifier. Differences in water adsorption become noticeable only in the samples with the highest modifier concentrations. The sample with the highest oleate concentration adsorbs more water than the sample with the highest stearate concentration.

Figure 4 shows the water adsorption and desorption isotherms measured on unmodified alumina and on the samples with the highest stearate or oleate concentrations. On unmodified alumina, considerable adsorption and desorption hysteresis is observed. Upon desorption, some water (~2 molecules/nm^2) is not removed from the surface at $p/p_s = 0$, probably, because of chemisorption. The small slope of the desorption branch of the isotherm indicates a rather wide pore-size distribution.

Water adsorption on the modified samples is far lower than on unmodified alumina. In the initial range of relative pressures, the water adsorption isotherms on both modified samples approximately coincide. Differences become noticeable only at high relative water vapor pressures. The overall water volume adsorbed at

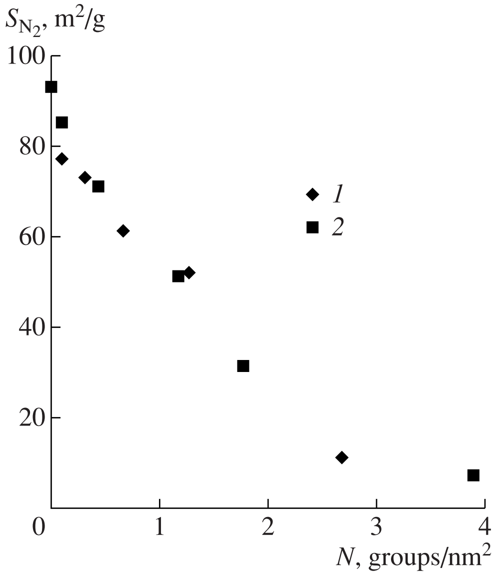

Fig. 2. Specific surface area S_{N_2}, m^2/g, of alumina modified by (*1*) stearic acid and (*2*) oleic acid vs. modifier surface concentration N, groups/nm^2.

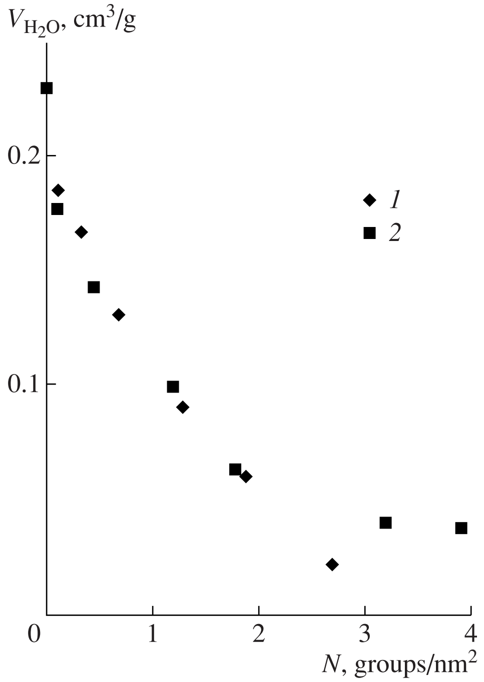

Fig. 3. Saturated water vapor adsorption V_{H_2O}, cm^3/g, on alumina modified by (*1*) stearic acid and (*2*) oleic acid vs. modifier surface concentration N, groups/nm^2.

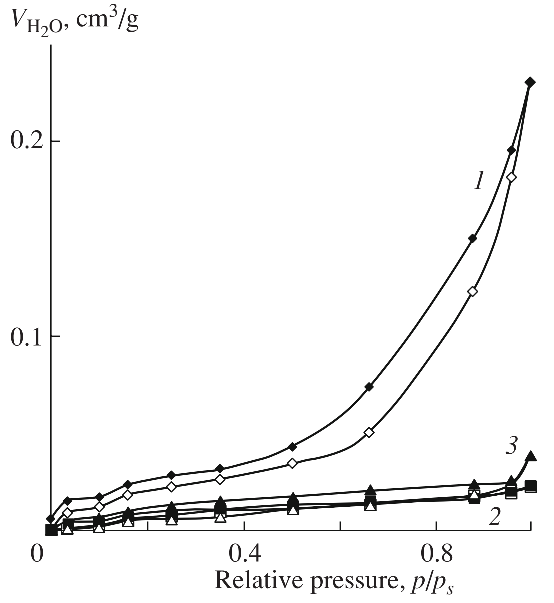

Fig. 4. Water vapor adsorption isotherms at 23°C on (*1*) unmodified alumina, (*2*) alumina modified with 2.7 groups/nm^2 of stearate, and (*3*) modified with 3.9 groups/nm^2 of oleate. Light symbols pertain to adsorption; dark symbols to desorption.

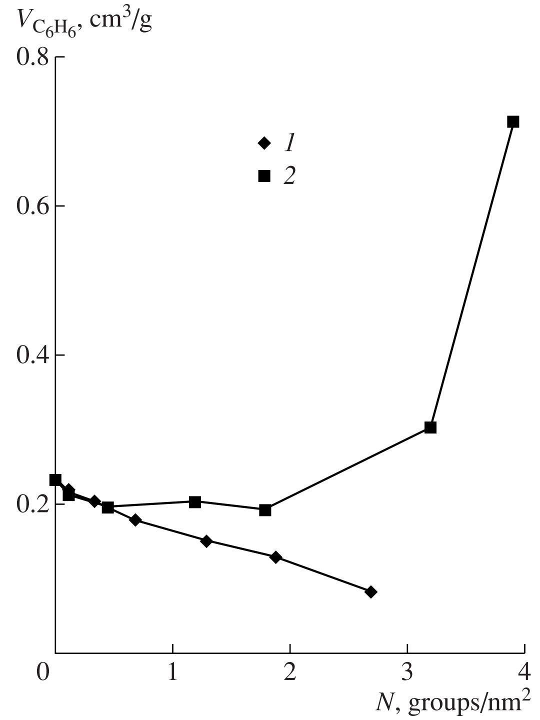

Fig. 5. Saturated benzene vapor adsorption $V_{C_6H_6}$, cm^3/g, on alumina modified with (*1*) stearic acid and (*2*) oleic acid vs. modifier surface concentration N, groups/nm^2.

$p/p_s = 1$ on stearic acid-modified alumina is one order of magnitude lower than on the unmodified sample. The oleic acid-modified sample adsorbs the overall water volume almost twice that adsorbed on the stearic acid-modified sample. Adsorption–desorption hysteresis is observed for both modified samples, very insignificant on the stearic acid-modified alumina sample but more noticeable on the oleic acid-modified sample. Presumably, the oleate monolayer is less ordered and more penetrable by water molecules than the stearate monolayer. In addition, adsorption interactions between water molecules and the oleate olefinic group are made possible by the double bond. Water is desorbed completely from both modified samples at $p/p_s = 0$, unlike from the unmodified sample.

Very considerable differences between the absorption properties of the two sets of modified samples are observed in comparison of benzene condensation. Figure 5 plots the adsorbed benzene volume (per gram of the support) as a function of modifier concentration. On stearic acid-modified alumina, the adsorbed benzene volume drops linearly with rising modifier concentration. It approximately corresponds to the difference between the pore volume of the unmodified sample and the volume occupied by the modifier. On the oleic acid-modified samples with modifier surface densities of 0.11–1.8 groups/nm^2, benzene adsorption first changes insignificantly, then increases in the sample with the highest modifier surface coverage (3.9 groups/nm^2) to reach the value three times the adsorption on unmodified alumina. The sample with the highest oleate surface coverage looses friability after exposure to benzene vapor; that is, oleate adsorbs benzene like a liquid. At lower oleate surface coverages, the hydrocarbon radicals containing a double bond, likely, prefer to interact with the surface active sites of alumina rather than with benzene molecules. These data on benzene adsorption on aluminas modified with the two acids agree with benzene absorption by these acids themselves (after 7 days of exposure to saturated benzene vapor). Oleic acid absorbs 4.1 cm^3/g benzene, which is almost 20 times benzene absorption by stearic acid (0.23 cm^3/g).

We also compared the modifying effect of the two acids on the adsorption of organic dye ions from water. Figure 6 displays the Acid Orange partition factor (K, L/g) as a function of the surface coverage by the modifier.

$$K = A/c,$$

where A is adsorption, mg/g; and c is equilibrium dye concentration, mg/L.

Unmodified alumina almost does not adsorb Acid Orange. On the stearic acid-modified samples, the partition factor rises almost linearly with modifier surface coverage to reach a peak on the sample bearing 1.3 groups/nm^2 of stearate. This modifier coverage density is one-half the ultimate coverage. With stearate surface coverage density increasing further, dye adsorption drops linearly, becoming on the sample with the highest surface coverage density (2.7 groups/nm^2) almost as low as on unmodified alumina. Therefore, in the last case, stearate hydrocarbon radicals on the alumina surface form a dense ordered monolayer, which cannot be penetrated by dye ions for adsorption. In the case of oleic acid modification, the Acid Orange partition factor first rises as the modifier surface coverage increases to 0.45 groups/nm^2, then changing only insignificantly until the maximal modifier surface coverage is reached (3.9 groups/nm^2). The maximal partition factor for the oleic acid-modified samples ($K \approx 1$ L/g) is noticeably lower than for the stearic acid-modified samples ($K = 2.5$ L/g). Presumably, oleic acid, unlike stearic acid, does not generate a dye-ion-impenetrable, ordered surface monolayer on alumina. Likely, the appearance of a dense monolayer is inhibited by the kink in the middle of the hydrocarbon chain in the region of the double bond in an oleic acid molecule.

Oleic acid dramatically increases the adsorption of organic dye cations and anions from water onto alumina as a result of surface modification [5]. The adsorption of organic ions is strongly affected by pH, ionic strength, and organic solvent additives. From the above data, we can infer that the identical mechanism operates in the interaction between organic ions and the alumina surfaces modified by stearic or oleic acid. In both cases, adsorption is due to a combination of ionic and hydrophobic interactions. The differences in organic ion adsorption likely arise from the different structures of the modifier layers of these acids. These differences must be taken into account in choosing the adsorbent for organic ions. Thus, the maximal partition factor was observed for stearic acid-modified alumina with the surface coverage $\theta \approx 0.5$ (modifier surface density of 1.3 groups/nm^2). In oleic acid-modified alumina chosen as an adsorbent, the modifier surface density can vary as considerably as approximately by one order of magnitude, from 0.4 to 4 groups/nm^2, without considerable changes in partition factor.

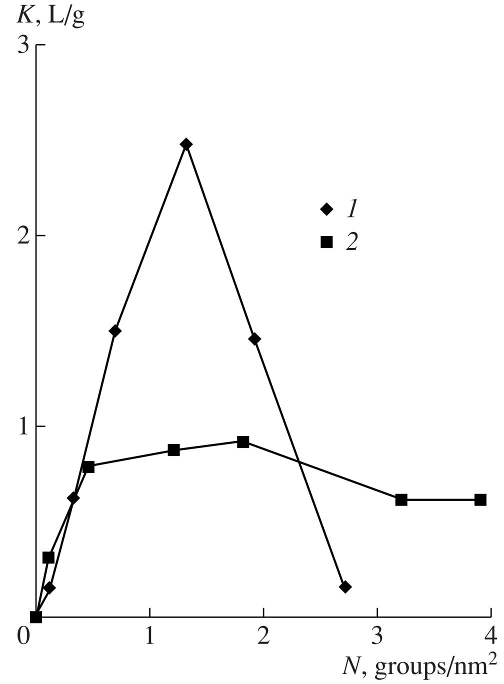

Fig. 6. Acid Orange partition factor K, L/g, on alumina modified with (*1*) stearic acid and (*2*) oleic acid vs. surface modifier concentration N, groups/nm^2.

In summary, the existence or nonexistence of a double bond in the hydrocarbon chain of a long-chain carboxylic acid (modifier) gives rise to considerable differences in surface-grafted layers, which affects the adsorption properties of modified aluminas.

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