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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Nitrate-Citrate Sol-Gel Synthesis of Hydrated Calcium Aluminate and Sorption Materials on Its Basis

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Abstract—Sol-gel technique was used to develop a method for synthesis of hydrated tricalcium aluminate $\text{Ca}_3[\text{Al}(\text{OH})_6]_2$ and surface-layered gas-chromatographic sorbents on its basis. The materials obtained were examined by X-ray diffraction analysis, scanning electron microscopy, X-ray fluorescence microanalysis, adsorption porosimetry, and gas chromatography. It was found that cubic $\text{Ca}_3[\text{Al}(\text{OH})_6]_2$ is the main phase in the surface layer of the sorption materials. The Hammett indicator method was used to examine the acid-base properties and the variation of the content of active centers between sorbents obtained in different ways. The chromatographic retention parameters were determined for test compounds, and the polarity and selectivity of the sorbents under study was evaluated. It was shown that Chromaton N-AW modified with hydrated calcium aluminate can be used, with addition of SE-30 stationary liquid phase, to separate complex mixtures of organic compounds.

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It is known that three main types of calcium aluminates are formed in the $\text{CaO}-\text{Al}_2\text{O}_3$ system. These are calcium meta-aluminate CaAl_2O_4 , calcium ortho-aluminate $\text{Ca}_3\text{Al}_2\text{O}_6$, and calcium diortho-aluminate $\text{Ca}_2\text{Al}_2\text{O}_5$, with other kinds of calcium aluminate of varied composition possibly formed in addition to the above compounds [1]. It has been found that the interaction with water at high temperatures yields hydrated forms of aluminates [2]. Owing to their high thermal stability, mechanical strength, resistance to corrosive media, and ecological safety, calcium aluminates attract researchers' attention in development of materials with various functional properties. These compounds are widely used as a component of portland cement [3], exhibit a catalytic activity due to the large number of active centers on the surface [4], and exhibit luminescent properties upon activation with ions of rare-earth elements [5–8].

The main factors affecting the service characteristics of a material are the phase composition, dispersity, specific surface area of the final product, content of acid-base centers, and their distribution over values of the ionization constant, which are directly associated with its preparation method. At present, calcium aluminates of varied composition are, as a rule, produced by the

conventional ceramic technology [9, 10], with the use of mechanical activation [11], precipitation method [12], classical sol-gel technology [13, 14], and nitrate-citrate method [15–18]. The use of the sol-gel method in its classical and modified forms makes it possible to obtain compounds with new properties and to substantially expand the application fields of the materials.

The goal of our study was to examine the structural and acid-base surface characteristics of hydrated calcium aluminate synthesized by the nitrate-citrate sol-gel method and assess the possibility of obtaining surface-layered sorbents on the basis of Chromaton N-AW modified with hydrated calcium aluminate and applying these sorbents for a gas-chromatographic separation of organic compounds.

EXPERIMENTAL

Hydrated tricalcium aluminate $\text{Ca}_3[\text{Al}(\text{OH})_6]_2$ was synthesized by the sol-gel method, with calcium nitrate tetrahydrate (Ca^{2+}), aluminum nitrate nonahydrate (Al^{3+}), and citric acid monohydrate (H_3Cit) as the starting components. The amount of the reagents was calculated on the basis of the $\text{Ca}^{2+} : \text{Al}^{3+} : \text{H}_3\text{Cit}$ molar ratio of 3 :

2 : 5 (all the reagents were of chemically pure grade). The starting substances were separately dissolved in the minimum amount of distilled water, the solutions were combined, and the mixture was agitated for 1.5 h for the complexation reactions to be complete. The resulting sol was heated until a gel was formed. The gel was thermally treated at 130°C (SNOL 58/350 drying box) to remove the liquid phase and obtain a xerogel. In the final stage of synthesis, the resulting precursor was calcined in a SNOL 6/1300 muffle furnace at temperatures of 1000–1200°C for 1 h, with the heating rate being 5 deg min⁻¹. To form a developed surface of the synthesis product, an annealed sample was cooled with distilled water at 0°C [19].

Gas-chromatographic surface-layered materials were produced with Chromaton N-AW diatomic support (0.14–0.25 mm) with specific surface area of less than 1 m² g⁻¹, which is tetragonal silicon dioxide (space group P4₁2₁2) with insignificant admixture of iron oxide. Hydrated tricalcium aluminate was deposited onto Chromaton N-AW in two ways: mechanically and with the use of stationary liquid phase (SLP) SE-30, which is a methyl silicone elastomer. In the case of the mechanical deposition, a sieved fraction (0.16–0.20 μm) of calcium aluminate synthesized in the study was mixed, in amount of 10% relative to the mass of the starting sorbent, with Chromaton N-AW under shaking for 10 min (sorbent I), with Ca₃[Al(OH)₆]₂ retained on the support surface by adhesion forces [20].

Chromaton N-AW was modified with calcium aluminate (10 wt %) in the presence of SLF SE-30

(0.5 wt %) dissolved in chloroform under permanent agitation of the reagents for 20 min, with the subsequent removal of the solvent (sorbent II). The surface layer of calcium aluminate is fixed on a solid support due to the surface-tension forces of the liquid phase [21] (see the scheme).

The phase composition of the samples was determined by X-ray diffraction (XRD) analysis. XRD patterns were measured on a Rigaku MiniFlex 600 diffractometer (CuK_α radiation, 2θ = 3–80°, scanning rate 2 deg min⁻¹). The synthesis products were identified with a PDF-2 database.

The surface morphology of the samples was examined by scanning electron microscopy (SEM) on a Hitachi TM-3000 microscope at accelerating voltage of 15 kV in the mode of charge removal from a sample (electron beam: 5 × 10⁻² Pa; sample chamber: 30–50 Pa). The element distribution over the surface of the sorbents was determined with a Quantax 70 attachment for energy-dispersive analysis.

The specific surface area of the sorbents was determined by multiple-point BET measurements from the low-temperature adsorption of N₂ on a Tristar 3020 automated gas-adsorption analyzer.

The nature and strength of acid-base centers was judged from data furnished by the method of adsorption of Hammet indicators from an aqueous medium [22]. The set of the indicators being used made it possible to record acid-base surface centers in the pK_a range from –0.29 to +16.8. The optical density of indicator solutions before and after the adsorption was determined with PE-5400UV spectrofluorimeter at a wavelength corresponding to the maximum absorption by each indicator.

Chromatographic studies of the sorbents were carried out on a Chrom 5 chromatograph with a flame-ionization detector in the isothermal mode and in the programmed-temperature mode in the range 150–250°C at a heating rate of 10 deg min⁻¹. Packed glass chromatographic columns with inner diameter of 3 mm and length of 1.2 m were used. The flow rate of the carrier-gas (helium) was 30 cm³ min⁻¹.

RESULTS AND DISCUSSION

An XRD analysis of the phase composition of samples annealed at temperatures of 1000, 1110, and 1200°C and cooled with distilled water at 0°C (Fig. 1) demonstrated that the synthesis products are a mixture of substances of various compositions. The main phase is

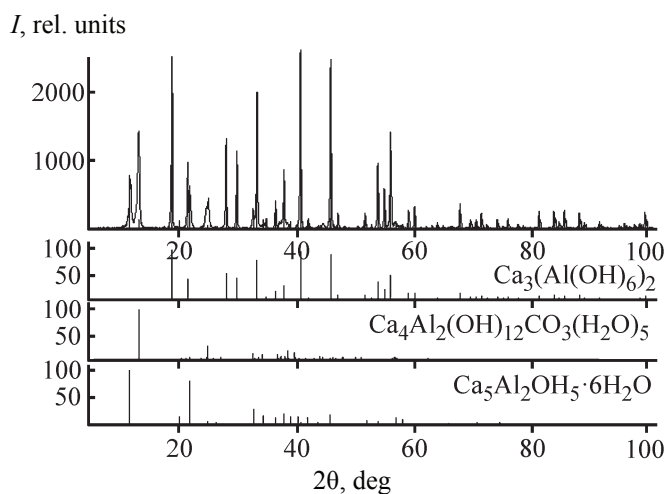
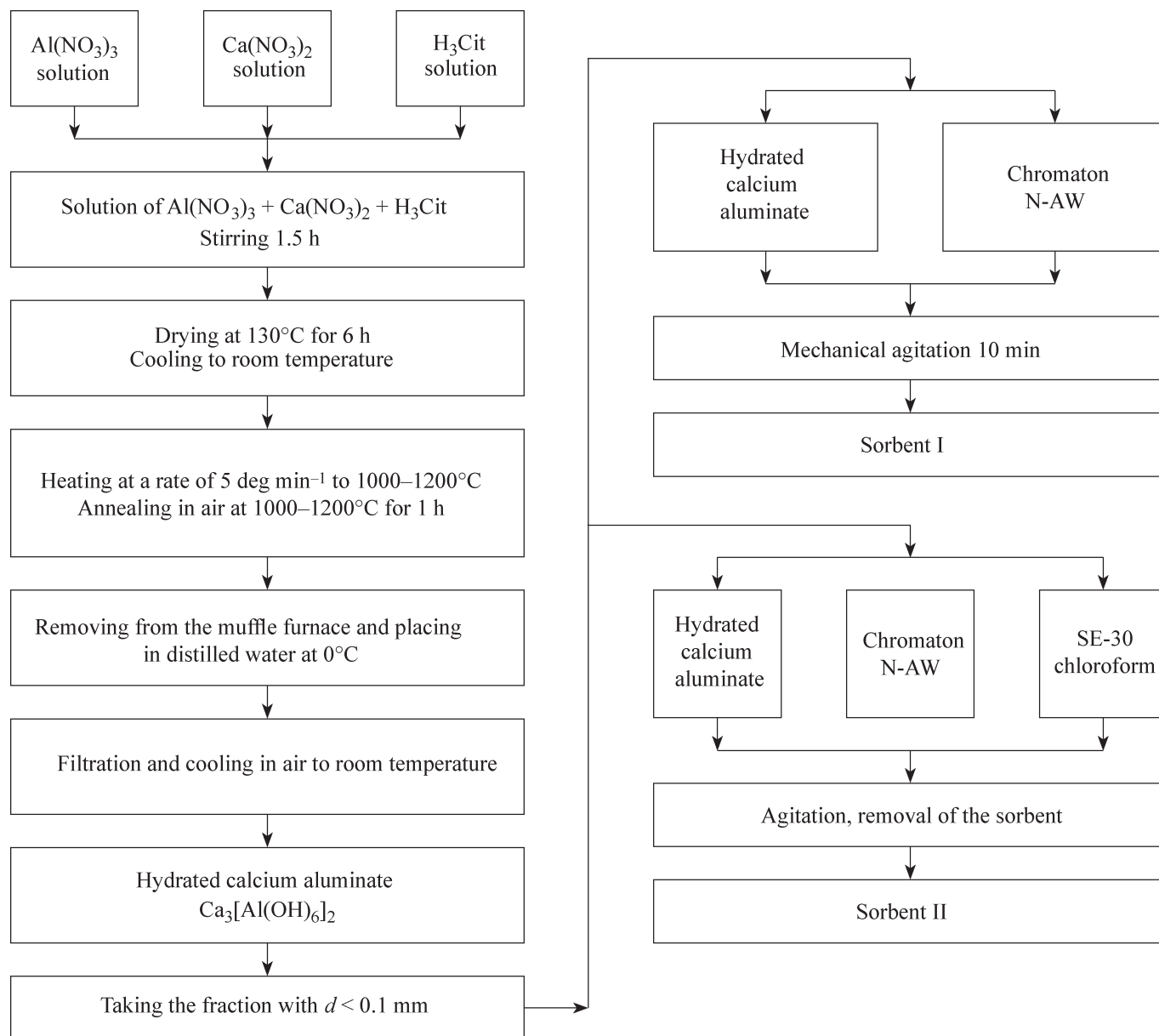


Fig. 1. Results of an XRD analysis of the synthesis product. (I) Intensity and (2θ) Bragg angle; the same for Fig. 3.

Scheme 1. Obtaining hydrated calcium aluminate and preparing gas-chromatographic sorbents.

cubic hydrated calcium aluminate $\text{Ca}_3[\text{Al}(\text{OH})_6]_2$ (space group $\text{Ia}\bar{3}\text{d}$, $a = 12.57 \text{ \AA}$). The identification was based on the correspondence of the general diffraction pattern of the aluminate synthesized in the study to that of the reference sample (PDF-2 database, 01-078-1532 file). $\text{Ca}_4\text{Al}_2(\text{OH})_2\text{CO}_3(\text{H}_2\text{O})_5$ (PDF-2 database, file 01-087-0493) and $\text{Ca}_2\text{Al}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ (PDF-2 database, file 00-012-0008) are present as impurity phases. The presence of hydrated forms of calcium aluminate is due to the specific feature of the synthesis: cooling of a calcined hot product with distilled water at 0°C . This cooling method

not only favors formation of hydrated phases, but also yields a developed surface of the synthesis product due to the interaction of a hot aluminate with water molecules. Raising the calcination temperature does not strongly affect the phase composition of the samples because their X-ray diffraction patterns are identical.

According to SEM data (Fig. 2a), calcination of samples results in that, irrespective of the synthesis temperature, calcium aluminate has the form of spherical particles with distinct boundaries and sizes of 400 to 1000 nm. According to the results of a low-temperature

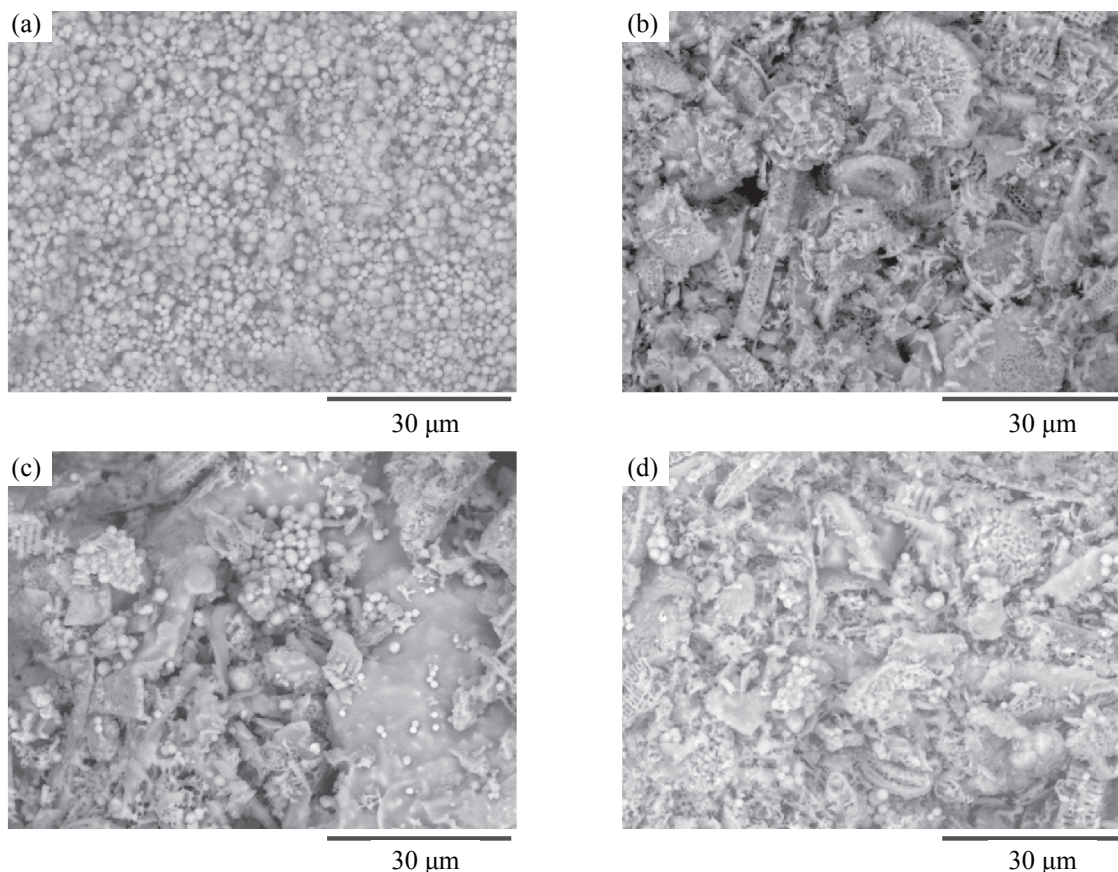


Fig. 2. SEM micrographs of the surface of the samples. (a) Hydrated calcium aluminate, (b) Chromaton N-AW, (c) sorbent I, and (d) sorbent II.

adsorption of nitrogen, the aluminate obtained at 1000°C has larger specific surface area and total pore volume, compared with other samples (Table 1). Therefore, it was used to prepare sorbents.

When hydrated calcium aluminate is deposited onto the surface of Chromaton N-AW in two above ways, the phase composition of the samples remains unchanged. Lines corresponding to the main phase of Chromaton N-AW, tetragonal modification of silicon dioxide (Fig. 3a), and those inherent in cubic hydrated calcium aluminate, $\text{Ca}_3[\text{Al}(\text{OH})_6]_2$, which is the main phase of the aluminate we synthesized (Figs. 3b and 3c), are present in the X-ray diffraction patterns of the sorbents. Mechanical mixing of the substances without a chemical interaction in preparation of the sorption materials is also confirmed by microscopic measurements. The surface of the starting SiO_2 (Fig. 2b) shows well discernible aluminate particles (Figs. 2b and 2c), with the use of SLP in the course of modification resulting in a more uniform distribution of $\text{Ca}_3[\text{Al}(\text{OH})_6]_2$. The energy-dispersive microanalysis demonstrated that silicon, calcium, and aluminum are

present at each point examined in a sample. This is also indicative of the uniform distribution of calcium aluminate over the surface of Chromaton N-AW. The values of the specific surface area, total pore volume, and pore size for the sorbents under study are listed in Table 1.

The nature, strength, and concentration of acid and base centers were determined by the method of adsorption of Hammett indicators. The strength of surface acid-base centers is determined by the $\text{p}K_a$ of an indicator adsorbed in the conjugated form, and the amount of the indicator reflects the surface content of centers with a given strength. Figure 4 shows distribution spectra of adsorption centers for the acid-base indicators, $q_{\text{p}K_a} - f(\text{p}K_a)$, on the surface of the hydrated aluminate (a), sorbent I (b), and sorbent II (c). Analysis of the spectra suggests that the surface states of the samples under study are different. The surface of hydrated calcium aluminate is represented by a set of a large number of various centers, the predominant of which are the basic $\text{Ca}-(\text{OH})^{\delta-}$, $\text{Al}-(\text{OH})^{\delta-}$ ($\text{p}K_a$ 9.45) and acid $\text{Ca}-(\text{OH})^{\delta+}$, $\text{Al}-(\text{OH})^{\delta+}$ ($\text{p}K_a$ 5) Brønsted centers and also acid ($\text{p}K_a$ 13.7) Lewis centers associated with the presence

Table 1. Data on low-temperature adsorption of BET samples

| Sample | S_{sp} , $m^2 g^{-1}$ | Total pore volume, $cm^3 g^{-1}$ | Pore size, nm |
|-----------------------------|-------------------------|----------------------------------|---------------|
| $Ca_3[Al(OH)_6]_2$, 1000°C | 19 | 0.041 | 8.6 |
| $Ca_3[Al(OH)_6]_2$, 1100°C | 11 | 0.034 | 12.5 |
| $Ca_3[Al(OH)_6]_2$, 1200°C | 8 | 0.027 | 13.9 |
| Chromaton N-AW | <1 | – | – |
| Sorbent I | 2.0 | 0.003 | 7.2 |
| Sorbent II | 7.0 | 0.028 | 15.8 |

of Ca^{2+} and Al^{3+} surface cations, which are coordination-unsaturated surface centers. Also present are the neutral $Ca-(OH)^{\delta 0}$, $Al-(OH)^{\delta 0}$ (pK_a 6.4), acid (pK_a 2.5, 3.64), and less pronounced basic (pK_a 12, 12.8) Brønsted centers and basic Lewis centers (pK_a -0.29) due to the presence of O^{2-} centers [22]. The acidity function of the surface, H_0 , is nearly neutral and equal to 9.7 units, which is due to the presence of nearly all possible adsorption centers on the sample surface. When Chromaton N-AW, whose surface is mostly represented by neutral Brønsted centers $Si(OH)^{\delta 0}$ with pK_a 6.4, is modified with the resulting calcium aluminate, the number of acid-base centers on the sorbent surface changes significantly. Acid Lewis centers (pK_a 13.7) are predominant for sorbent I, and basic (pK_a 9.46) Brønsted centers and acid (pK_a 13.7) Lewis centers, for sorbent II. The share of the rest of the centers is insignificant. This change of the surface leads to an increase in the acidity function to 10.2 units for sorbent I and 9.9 units for sorbent II.

To analyze the chromatographic properties of modified sorbents based on calcium aluminate, we examined the retention parameters of various classes of organic compounds. The values obtained for the retention time (Table 2) indicate that addition of SE-30 to the Chromaton N-AW + $Ca_3[Al(OH)_6]_2$ system results in that t for organic substances on a sorbent under study decreases, which is due to the change in the number of surface active centers upon modification.

Comparison of the data on the acid-base properties and distribution of adsorption centers with the gas-chromatographic data on the retention of the test compounds indicates the following. Upon modification of Chromaton N-AW with calcium aluminate (sorbent I), the substantial content of Lewis acid centers results in that large values are observed for retention parameters of aromatic hydrocarbons. The retention of methyl ethyl

ketone, pyridine, and nitropropane is due to the proton-donor-acceptor complexation. It is also indicative of the presence and strength of Lewis adsorption centers. In this case, metal ions on the surface of the sorbents serve as electron-density acceptors, and ketones and nitrogen-containing substances, as donors. As a result of screening of the Lewis adsorption centers, the retention

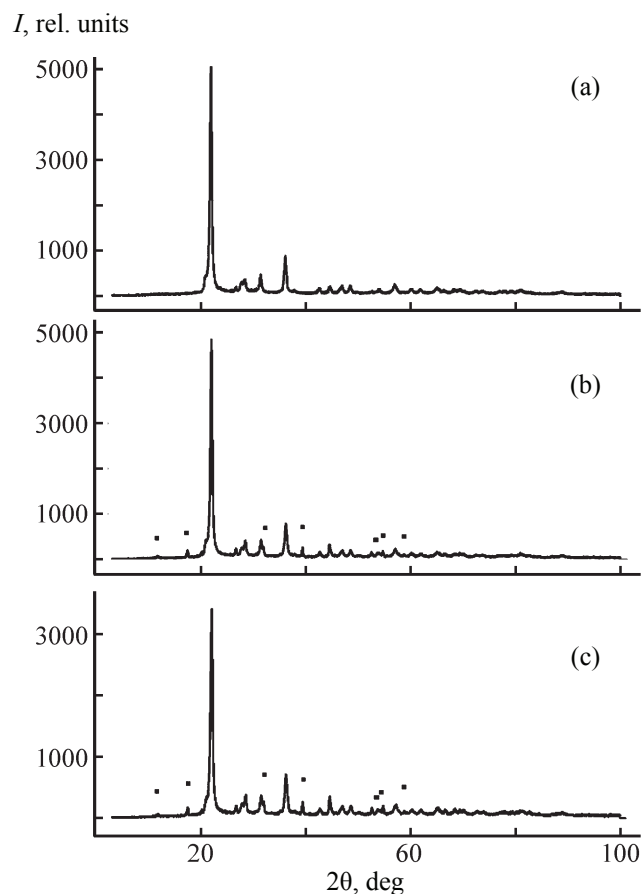
**Fig. 3.** XRD data for the samples. (a) Chromaton N-AW, (b) sorbent I, and (c) sorbent II.

Table 2. Reduced retention time t , retention indices I , and polarity coefficients y, x, z, u, s of tyer test compounds for the sorbents under study, 150°C

| Test compounds | Sorbent I | | | Sorbent II | | |
|-----------------------------|-----------|-----|----------------------|------------|-----|----------------------|
| | t , min | I | polarity coefficient | t , min | I | polarity coefficient |
| Ethanol (y) | 0.67 | 652 | 3.56 | 0.32 | 663 | 3.67 |
| Benzene (x) | 0.86 | 676 | 1.15 | 0.28 | 636 | 0.75 |
| Methyl ethyl ketone (z) | 0.87 | 686 | 2.10 | 0.30 | 659 | 1.83 |
| Nitropropane (u) | 1.32 | 926 | 5.68 | 1.03 | 907 | 5.49 |
| Pyridine (s) | 1.14 | 823 | 2.76 | 0.43 | 812 | 2.65 |
| $\Sigma y, x, z, u, s$ | – | – | 15.25 | – | – | 14.39 |

Table 3. Differential molar free adsorption energy ΔG and partial molar enthalpy of adsorption, ΔH , of the test compounds on the sorbents under study

| Test compound | $-\Delta G$, kJ mol ⁻¹ | | ΔH , kJ mol ⁻¹ | |
|---------------------|------------------------------------|------------|-----------------------------------|------------|
| | sorbent I | sorbent II | sorbent I | sorbent II |
| Ethanol | 14.13 | 9.48 | 33.16 | 32.19 |
| Benzene | 16.21 | 14.15 | 35.57 | 33.49 |
| Methyl ethyl ketone | 18.15 | 16.21 | 58.11 | 55.15 |
| Nitropropane | 23.17 | 19.12 | 63.15 | 61.44 |
| Pyridine | 19.37 | 18.39 | 60.51 | 58.87 |
| –CH ₂ – | 0.35 | 0.29 | – | – |

parameters of the test compounds decrease upon addition of the modifying methyl silicone elastomer SE-30. In this case, sorbent II characterized by the substantial content of basic Brønsted centers exhibits and increased capacity for retention of alcohols (Table 2).

One of the key factors in choosing a sorbent is the chromatographic polarity evaluated by Kovats retention indices and Rohrschneider polarity coefficients relative to Carboxpack B [23] against the standard compounds, each of which characterizes a certain kind of specific intermolecular interaction in the sorbate–sorbent system. In addition, we used the overall polarity index, defined as the sum of coefficients y, x, z, u, s . According to the results obtained (Table 2), a general tendency is observed toward a decrease in the chromatographic polarity when sorbents are obtained with addition of SE-30 SLP (overall polarity decreases from 15.25 to 14.39).

The surface-layered sorbent I possesses an increased capacity x for a π – π interaction with aromatic hydrocarbons and donor–acceptor complexation (z, u, s). The largest value of Rohrschneider polarity coefficients was observed for nitropropane. For sorbent II, the contribution to polarity becomes more pronounced because of the ability of basic Brønsted centers to form hydrogen bonds with electrophilic molecules (y).

The values of the differential free molar adsorption energy $-\Delta G$ (kJ mol⁻¹), listed in Table 2, also make it possible, together with the above-presented Rohrschneider constants, to evaluate the polarity of the sorbents and their capacity for various kinds of intermolecular sorbents.

The values of ΔG point to an enhanced tendency of the sorption materials toward electrostatic interactions with compounds having an excess of electron density: nitropropane, pyridine, methyl ethyl ketone. The change

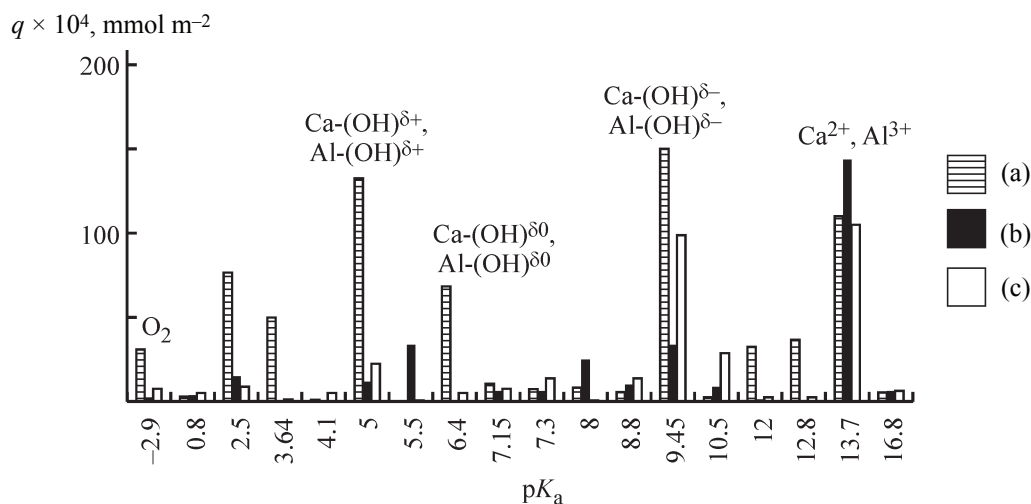


Fig. 4. Distribution q of centers for adsorption of Hammett indicators on the sample surface. (a) Hydrated calcium aluminate, (b) sorbent I, and (c) sorbent II.

in the chromatographic polarity is affected to a lesser extent by the ability to exhibit dispersion interactions, $-\Delta G(-CH_2-)$.

The average values of the partial molar enthalpy of dissolution, ΔH , are 30–62 kJ mol⁻¹ (Table 3). This is indicative of a physical adsorption of the test compounds

due to van der Waals interactions and possibility of formation of a hydrogen bond in the sorbate–sorbent system.

Table 4 presents values of the selectivity coefficients for the materials based on calcium aluminate with respect to model mixtures of *n*-alkanes (C₆–C₁₀), arenes

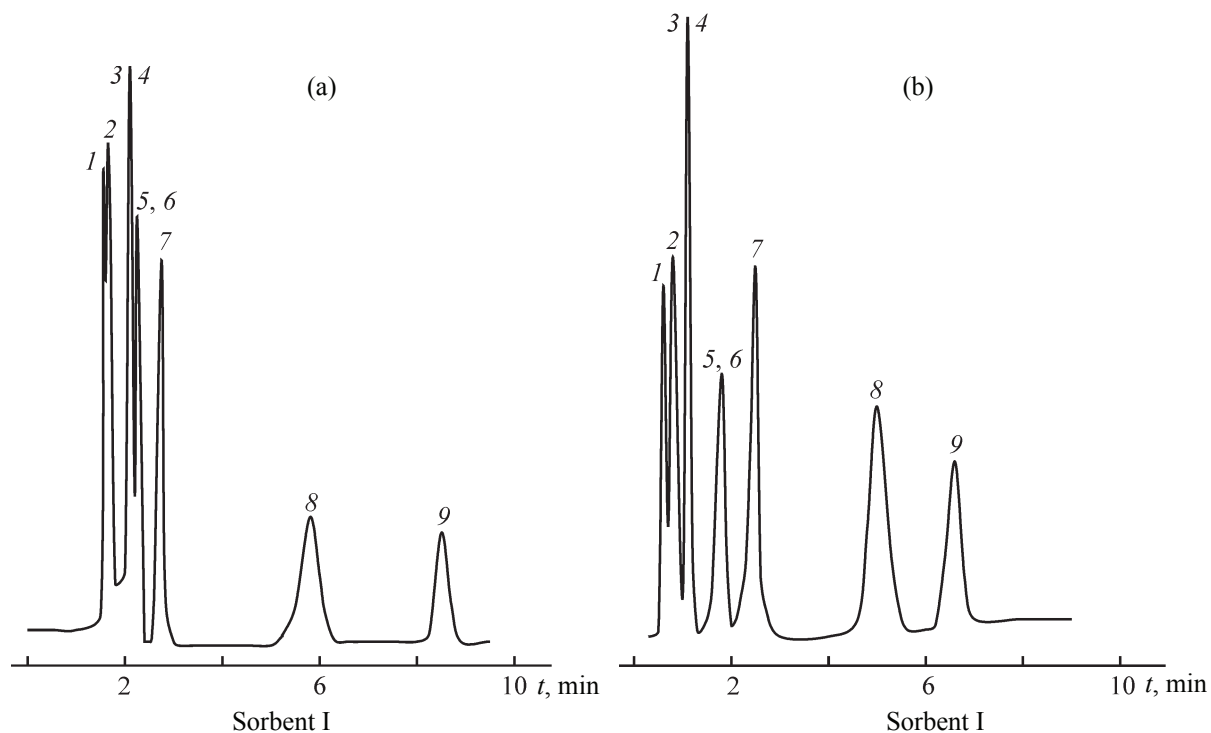


Fig. 5. Chromatograms of a mixture of alkyl-substituted and polyaromatic hydrocarbons in the programmed-temperature mode from 150 to 250°C at a rate of 10 deg min⁻¹. (*t*) Time. (1) Benzene, (2) toluene, (3, 4) ethylbenzene and *ortho*-xylene, (5, 6) mesitylene and pseudocumene, (7) naphthalene, (8) acenaphthene, (9) phenanthrene.

Table 4. Selectivity coefficients α_R and capacity coefficients k'_i of the test compounds on the sorbents under study, 150°C

| Test compound | α_R | | k'_i | |
|------------------|------------|------------|-----------|------------|
| | sorbent I | sorbent II | sorbent I | sorbent II |
| Hexane | 1.00 | 1.00 | 2.18 | 1.25 |
| Heptane | 1.63 | 1.36 | 3.56 | 1.70 |
| Octane | 1.89 | 1.60 | 4.15 | 2.00 |
| Nonane | 2.19 | 1.96 | 4.78 | 2.45 |
| Decane | 3.32 | 2.32 | 7.26 | 2.90 |
| Methanol | 1.00 | 1.00 | 1.04 | 1.25 |
| Ethanol | 1.26 | 1.28 | 2.48 | 1.60 |
| Propanol | 1.42 | 1.40 | 2.78 | 1.75 |
| Butanol | 1.74 | 1.64 | 3.41 | 2.05 |
| Benzene | 1.00 | 1.00 | 3.18 | 1.40 |
| Toluene | 1.21 | 1.28 | 3.85 | 1.80 |
| Ethylbenzene | 1.70 | 1.55 | 5.41 | 1.90 |
| α -Xylene | 1.80 | 1.64 | 6.33 | 2.05 |
| Mesitylene | 2.03 | 1.91 | 6.48 | 2.25 |

(benzene, toluene, ethylbenzene, xylene, mesitylene), and alcohols (C₁–C₄). These data point to a sufficiently high selectivity of separation of homologous series by the surface-layered sorbents obtained. It should be noted that the best separation of the mixture of alkanes is observed for sorbent I, and that of aromatic hydrocarbons, for sorbent II. Both the sorbents are distinguished by a good separating capacity for alcohols.

The values of the capacity coefficients k'_i (Table 4), which reflect the extent to which a substance interacts with a sorbent and depend on the parameters of the chromatographic system, vary from 1.04 to 7.26 for sorbent I and from 1.25 to 2.90 for sorbent II. This is indicative of a sufficiently high-quality separation of the model system components.

The surface-layered materials produced on the basis of hydrated calcium aluminate Ca₃[Al(OH)₆]₂ were used for a gas-chromatographic separation of complex multi-component mixtures of organic compounds and, in particular, alkyl-substituted benzenes and polyaromatic hydrocarbons (Fig. 5). The best results were obtained for sorbent II, which can significantly raise the separation selectivity of benzene, toluene, xylenes, ethylbenzene,

mesitylene, and polycyclic arenes and lower the time and temperature of analysis as compared with sorbent I and other known surface-layered materials. These are Chromosorb sorbents with layers of graphitized carbon black; mixture of silicone oil and bentonite [20]; porochromes modified with organic salts of alkali, alkaline-earth, and transition metals [24]; carbon-fluoroplastic sorbents [25]; and composite materials based on polytetrafluoroethylene [26]. The starting components for obtaining the suggested chromatographic materials are readily available, highly efficient, thermally stable, and have a weaker dependence of the mass-exchange diffusion on the flow rate of the carrier gas. With these and other advantages of surface-layered sorbents over ordinary chromatographic materials taken into account, it seems quite appropriate to recommend these compounds for practical application in analytical gas chromatography.

CONCLUSIONS

The nitrate-citrate sol-gel method was used to obtain hydrated calcium aluminate with specific surface area of 8–19 m² g⁻¹ and surface-layered sorbents on its basis. The phase composition, surface morphology, and acid-base

base properties of the materials were examined. The reduced retention time, Kovats indices, and Rohrschneider polarity coefficients of the test compounds were determined for the sorbents under study. It was shown that Chromaton N-AW modified with hydrated calcium aluminate can be used for gas-chromatographic separation of various classes of organic compounds.

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