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The Effect of Modification on the Structural, Acidic, and Catalytic Properties of a Layered Aluminosilicate

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Abstract—The effect of modification on the structural, acidic, and catalytic properties of a natural layered aluminosilicate containing 90% montmorillonite was studied. With the use of low-temperature nitrogen adsorption and XRD analysis, it was found that the addition of hydroxo complexes of aluminum prevents the silicate layers of the layered aluminosilicate from closing upon heating and results both in the formation of stable micropores and in a considerable increase in the specific surface area. The acidic properties of the H, Na, and Al forms of the layered aluminosilicate were studied by IR spectroscopy of adsorbed CO molecules and by the indicator method. After modification with hydroxo complexes of aluminum, the number of Lewis acid sites and the accessibility of acidic OH groups to CO adsorption increased. The total number and strength of acid sites increased as the calcination temperature of the layered aluminosilicate was increased. A correlation between catalytic activity in the reaction of acetone dimerization and the number of acid sites in different forms of the layered aluminosilicate was obtained.

INTRODUCTION

Recently, considerable attention has been given to the development of new functionally active sorbents, supports, and a new class of catalysts based on layered aluminosilicates modified by the introduction of the hydroxo complexes of polyvalent metals into the interlayer space [1–6]. These materials possess unique structural and catalytic properties, which depend on both the chemical properties of the introduced compounds and modification procedures and conditions [5–7]. Thus, because of pore structure peculiarities and the occurrence of Brønsted and Lewis acid sites, they are selective catalysts for many acid-type reactions [1–4, 7]. The effect of modification on the acidic and catalytic properties of these materials is as yet imperfectly understood [8].

In this work, based on a natural layered aluminosilicate and Al_{13}^{7+} polyhydroxo cations, we synthesized an Al-modified layered aluminosilicate (Al_{13}-LA) and studied its structural, acidic, and catalytic properties.

EXPERIMENTAL

Reagents. Montmorillonite clay from the Mukhortalinsk field (Buryat Republic), with the following chemical composition (wt %), was used as a modified material: SiO_2, 65.50; Al_2O_3, 14.30; Fe_2O_3, 1.78; MgO, 1.42; CaO, 1.08; K_2O, 0.20; Na_2O, 0.10; FeO, 0.22; MnO, 0.02; TiO_2, 0.19; P_2O_5, 0.03; and H_2O, 15.16. The clay mineral was additionally purified by elutriation, in accordance with a published procedure [9]. The total concentration of exchange cations (mainly Ca^{2+} and Mg^{2+} cations) in the natural layered aluminosilicate was 0.68 mg-equiv/g.

Acetone of chemically pure grade was used in this study. Toluene and benzene of chemically pure grade were additionally purified with NaX molecular sieves.

Synthesis of Al_{13}-LA. The H form of the layered aluminosilicate was prepared in accordance with a published procedure [10] by the treatment of the natural layered aluminosilicate with 1 N HCl in a ratio of 1 : 5 (S/L, by weight) between solid and liquid phases upon heating at 80°C for 2 h. The Na form of the layered aluminosilicate (Na-LA) was prepared by an analogous procedure with the use of 1 M NaCl at S/L = 1 : 100.

For the synthesis of Al_{13}-LA, the exchange cations of the layered aluminosilicate were replaced by the polyhydroxo cations of aluminum. A pillaring solution was prepared by the hydrolysis of a 0.2 M $AlCl_3$ solution with a 0.2 M NaOH solution (the ratio $[OH^-]/[Al^{3+}] = 2.0$; pH 4.5) at room temperature. According to published data [1, 2], $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ tridecamers with the Keggin structure are primarily formed under these conditions. The solution was aged at 50°C for 24 h. To prepare Al_{13}-LA, the pillaring solution was slowly added to a suspension of Na-LA (S/L = 1 : 100) with stirring at 80°C in a ratio of 3 mmol of Al^{3+} per gram of clay; the pillared clay suspension was allowed to stand and coagulate for 10–12 h. The resulting Al_{13}-LA was washed to remove the chloride ions, dried in air at room temperature, and calcined at 400 or 500°C (T_{calcin}) for

3 h [8]. Table 1 summarizes the main characteristics of the natural layered aluminosilicate, Na-LA, and of Al_{13}-LA.

Determination of acidity. To evaluate acid–base surface properties, the Hammett method was applied with the use of the following indicators: methyl red ($pK_a = 4.8$), methyl orange ($pK_a = 3.3$), dicinnamalacetone ($pK_a = -3.0$), and benzalacetophenone ($pK_a = -5.6$) [11]. The measurement of H_0 was performed by nonaqueous titration with *n*-butylamine solutions in benzene at 20°C. Test samples (0.15–0.2 g), which were preheated at 400 or 500°C in a flow of air for 4 h, were placed in weighed test tubes filled with toluene (5 ml), and 0.05–5 ml of an *n*-butylamine solution in benzene (0.058 mol/l) was added. After 2 h (after equilibration), the suspensions were divided into several portions to which three or four drops of 0.1% solutions of each of the indicators in benzene were added. The amount of *n*-butylamine required to attain an equivalence point in the presence of a particular indicator corresponded to the total acidity of the sample in the test range of pK_a.

The low-temperature adsorption of the probe molecule of CO on the surface of Na-LA and Al_{13}-LA was studied by IR spectroscopy. The samples were pressed into pellets weighing 11–14 mg/cm^2. Before adsorption, each pellet was evacuated at 450°C for 1.5 h and then cooled to 100 K; small portions of CO were added to the cuvette with the use of a metering valve. The IR spectra were measured on a Shimadzu FTIR-8300 Fourier spectrometer with a resolution of 4 cm^{-1}; the number of scans was 50. The difference spectra of adsorbed CO, which were obtained after subtracting sample absorption before the addition of CO, are given in this paper. Normalized absorption was calculated as the ratio of the absorbance to the pellet density.

Determination of structure characteristics. The adsorption of nitrogen at 77 K was measured on an ASAP-2400 Micrometrics unit after evacuation at 200°CC for 12–16 h. The specific surface area (S_{sp}) was determined by the BET method. The average pore size was calculated from the equation $D_{av} = 4V_{pore}/S_{sp}$ [12].

The powder diffraction patterns were measured on an STAD/P diffractometer from STOE with a Ge monochromator and a coordinate detector and in an FR-552 Guinier camera (CuK_{α_1} radiation).

Catalytic experiments. Acetone condensation was performed at 50°C in a glass reactor that was equipped with a magnetic stirrer and a reflux condenser. The reactor was loaded with 10 ml (0.78 mmol) of acetone, 0.5 ml (0.039 mmol) of toluene (internal standard), and 0.8 g of a catalyst (particle size of 0.1–0.2 mm). At regular intervals, the reaction mixture was sampled and analyzed by GLC. A Tsvet-500 chromatograph with a metal column (2 m × 3 mm) that was packed with 5% XE-60 on Chromosorb W (0.16–0.25 mm) was used; nitrogen was a carrier gas (30 ml/min). The column temperature was 60°C, and a flame-ionization detector was used [13].

Table 1. Main characteristics of layered aluminosilicates

Sample	T_{calcin}, °C	S_{sp}, m^2/g	ΣV_{pore}, cm^3/g	D_{pore}, Å	d_{001}, Å	S_μ, m^2/g	ΣV_μ, cm^3/g
Natural layered aluminosilicate	400	113	0.27	97	11.36	–	–
	500	109	0.25	93	10.98	–	–
Na-LA	400	144	0.29	82	14.21	–	–
	500	141	0.30	84	15.38	–	–
Al_{13}-LA	400	203	0.31	65	18.02	56.1	0.03
	500	179	0.30	68	17.46	33.0	0.02

Note: T_{calcin} is the treatment temperature; d_{001} is the interplanar spacing; V_μ is the micropore volume; and S_μ is the specific surface area of the micropores.

RESULTS AND DISCUSSION

We found that both temperature treatment and the replacement of Ca^{2+} and Mg^{2+} exchange cations in the layered aluminosilicate by H^+, Na^+, or Al_{13}^{7+} significantly affected the texture characteristics of the resulting samples (Table 1).

According to XRD data, the values of the first basal reflection d_{001} decreased upon heating because of the dehydration and dehydroxylation of the samples (Fig. 1). It is evident that low-intensity and diffuse peaks at small angles at 300°C are due to partial degradation of the layered structure of the layered aluminosilicate, although the specific surface area and the average pore diameter of different forms of the layered aluminosilicate changed insignificantly. IR-spectroscopic data are also indicative of the degradation of the layered aluminosilicate structure. The spectrum of the natural layered aluminosilicate exhibited the entire set of absorption bands, which is typical of the structure of montmorillonite (Fig. 2, spectrum *1*). Upon the replacement of exchange cations by sodium cations, the relative intensities of absorption bands at 1090 and 1044 cm^{-1}, which correspond to the stretching vibrations of a layer of silicon–oxygen tetrahedrons, significantly changed (Fig. 2, spectrum *2*). In the region of the deformation vibrations of silicon–oxygen tetrahedrons and aluminum–oxygen octahedrons, absorption bands at 580, 425, and 340 cm^{-1} disappeared or their intensity significantly decreased. This change in the IR spectrum was due to the degradation of the tetrahedral and octahedral layers of montmorillonite. The degradation of the montmorillonite structure upon the introduction of the hydroxo complexes of aluminum into the layered aluminosilicate structure (Fig. 2, spectrum *3*) can also be judged from the shift of an effective absorption band maximum at 1044 to 1097 cm^{-1} and from a noticeable change in the relative intensities of absorption bands, which is due to deformation vibrations.

Not only temperature but also the nature of the introduced cation affected the texture characteristics of the

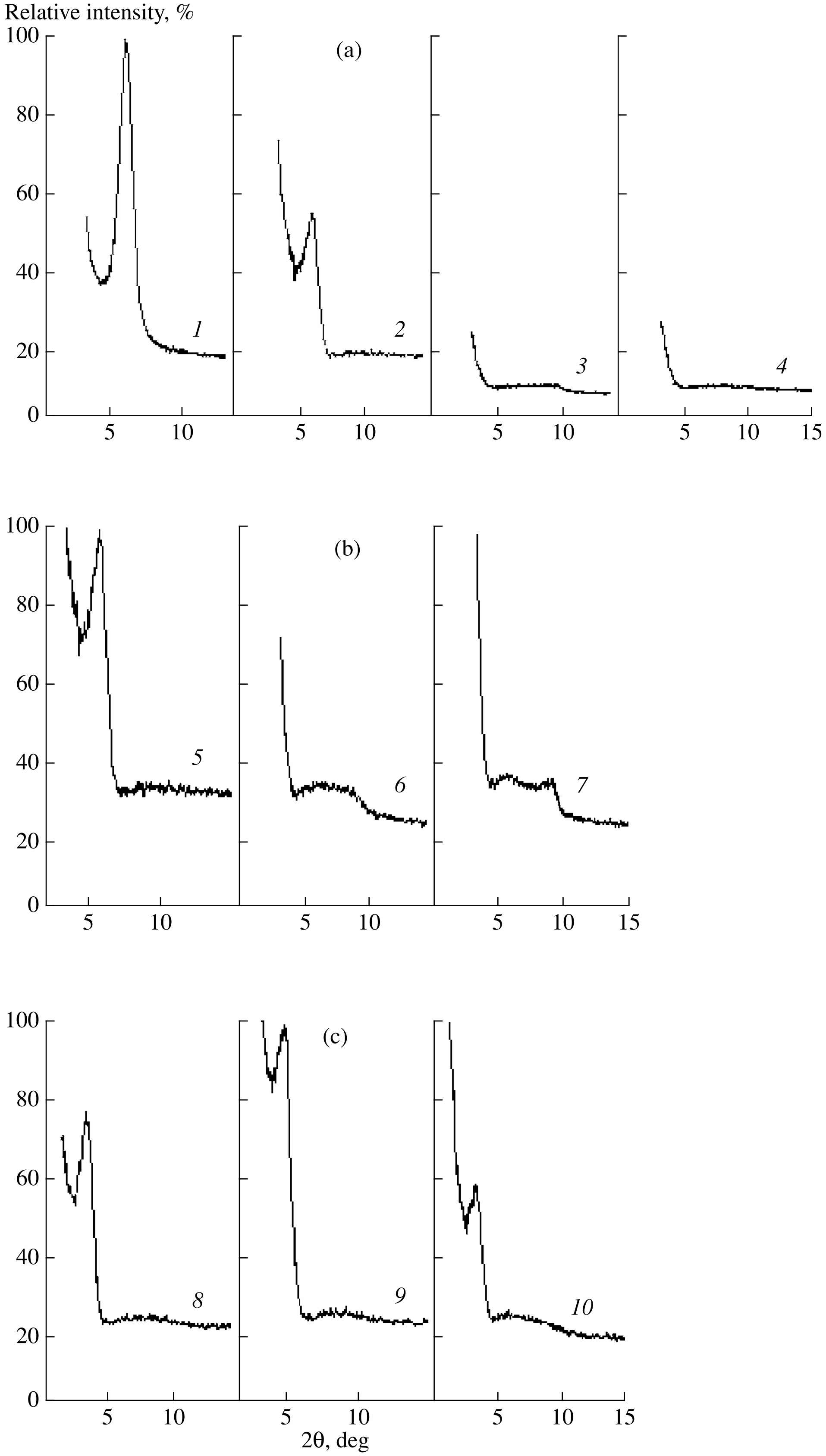

Fig. 1. Small-angle diffraction patterns of (a) natural layered aluminosilicate, (b) Na-LA, and (c) Al_{13}-LA at the following temperatures (°C): (*1*) 25, (*2*, *5*, *8*) 300, (*3*, *6*, *9*) 400, and (*4*, *7*, *10*) 500.

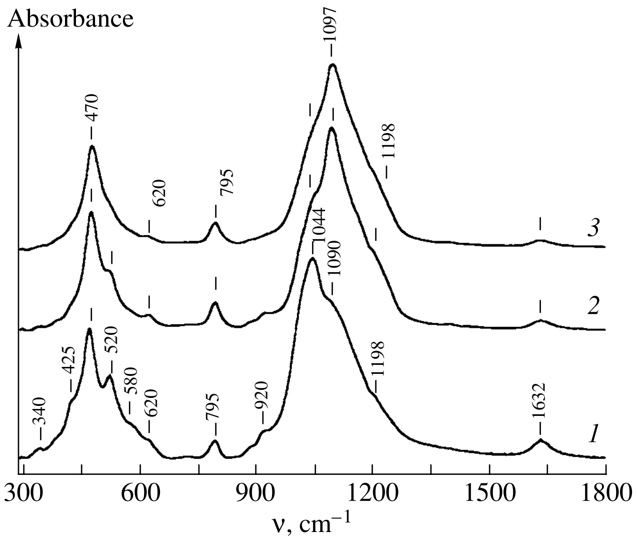

Fig. 2. IR spectra of layered aluminosilicates: (*1*) natural layered aluminosilicate, (*2*) Na-LA, and (*3*) Al_{13}-LA.

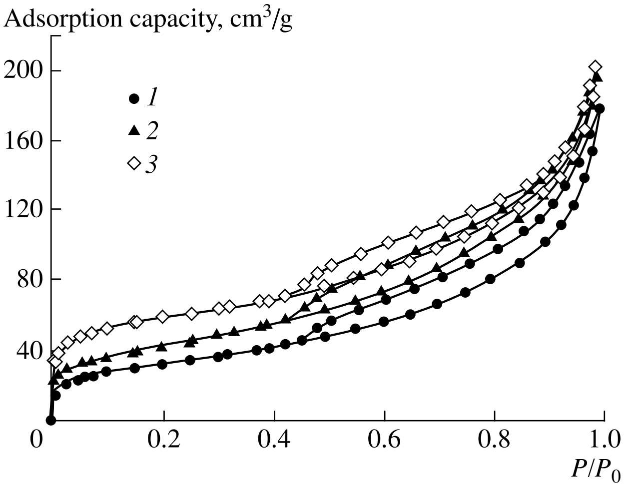

Fig. 3. Isotherms of N_2 adsorption on (*1*) natural layered aluminosilicate, (*2*) Na-LA, and (*3*) Al_{13}-LA, which were calcined at 400°C.

layered aluminosilicates (Table 1). The average pore diameter decreased in the order layered aluminosilicate > Na-LA > Al_{13}-LA. According to the data on the low-temperature adsorption of nitrogen, a capillary-condensation hysteresis loop, which is characteristic of mesoporous sorbents, was observed in the isotherms of the natural layered aluminosilicate and Na-LA (Fig. 3). At the same time, the isotherm of nitrogen adsorption on Al_{13}-LA exhibited an abrupt increase, which is characteristic of sorbents the have micropores, in the low pressure region. In contrast to the natural layered aluminosilicate and Na-LA, the sample of Al_{13}-LA contained a considerable number of micropores, the specific surface area of which was as high as 56 m^2/g (that is, it amounted to 27.7% of the total specific surface area of the aluminosilicate). The introduction of bulky polynuclear hydroxo cations into the interlayer spaces of a layered aluminosilicate prevents its silicate layers from closing upon heating and results in the appearance of systems of stable slitlike micropores that are 8 Å wide [4, 7]. As a result, a pillared layer structure of layered aluminosilicates is formed, which is resistant to heat, a fact that is supported by the XRD data (Fig. 1) and high values of S_{sp} (Table 1).

Table 2 summarizes the results of the determination of the total number of acid sites on the surface of layered aluminosilicates by nonaqueous titration with *n*-butylamine. It was found that temperature treatment and the nature of the cation introduced into layered aluminosilicates affect the acidity of aluminosilicates. Thus, as the sample dehydration temperature was increased, the number and strength of acid sites increased. After the treatment of layered aluminosilicates with hot HCl, the number of acid sites increased, because the ionic character of the system increased as a consequence of the replacement of calcium and magnesium exchange cations by aluminum and hydroxonium cations [14]. In this case, acid sites with $pK_a = -5.6$ appeared on the surface of H-LA. Note that the total number of sites increased insignificantly upon the introduction of aluminum cations, as compared with

Table 2. Acid characteristics of layered aluminosilicates and their catalytic activity in acetone dimerization

Sample	T_{calcin}, °C	$k_{eff} \times 10^4$*, s^{-1}	[L]**	Amount of acid sites***, mmol/g			
				$H_0 = -5.6$	$H_0 = -3.0$	$H_0 = +3.3$	$H_0 = +4.8$
Na-LA	400	0.1	–	–	0.02	0.18	0.32
	500	2.1	0.03	0.01	0.04	0.30	0.42
H-LA	400	1.8	–	0.08	0.13	0.20	0.25
	500	4.7	0.04	0.10	0.20	0.28	0.41
Al_{13}-LA	500	9.3	0.06	0.10	0.24	0.32	0.43

* Effective reaction rate constant of acetone dimerization at 50°C (catalyst loading of 10 wt %).

** Total amount of Lewis sites determined from CO adsorption.

*** Amount of acid sites determined by titration with *n*-butylamine.

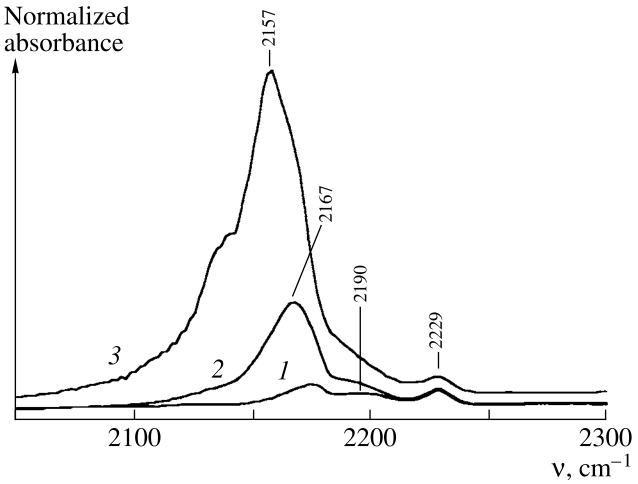

Fig. 4. IR spectra of CO adsorbed on Al_{13}-LA: (*1*) 0.1, (*2*) 0.9, and (*3*) 10 Torr.

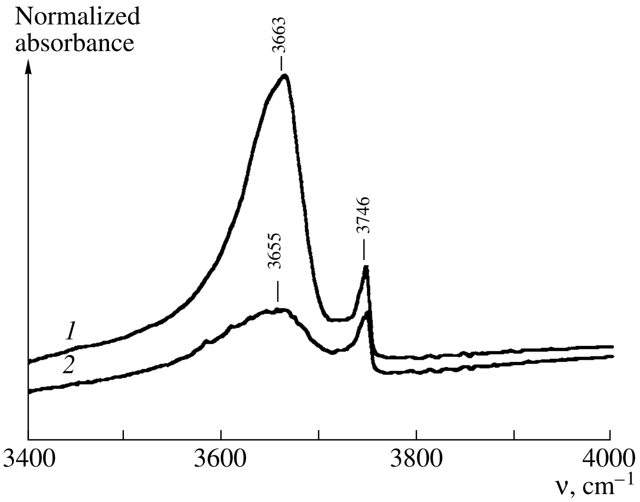

Fig. 5. IR spectra of hydroxyl groups in (*1*) Na-LA and (*2*) Al_{13}-LA.

the proton form of the layered aluminosilicate. It is believed that, in the Al_{13}-LA system, aluminum cations are chaotically distributed and inaccessible to *n*-butylamine molecules; this is consistent with the data on CO adsorption.

Figure 4 demonstrates the difference spectrum of CO adsorbed on the surface of Al_{13}-LA. The sample contained Lewis acid sites of two types, which are characterized by absorption bands at 2229 cm^{-1} and in the range 2195–2185 cm^{-1}. The latter type of acid sites is typical of aluminum oxide [15]. An absorption band at 2175–2160 cm^{-1} characterizes the complexes of CO with acidic OH groups. An intense absorption band at 2167 cm^{-1}, which was observed in the spectrum at a CO pressure of 10 Torr, belongs to weak H-bonded CO complexes with Si–OH groups (3745 cm^{-1}).

The IR spectra of OH groups in Na-LA and Al_{13}-LA samples (Fig. 5) consist of an intense wide absorption band at 3660 cm^{-1}, which likely corresponds to interlayer hydroxyl groups, and a narrow absorption band at 3745 cm^{-1}, which belongs to terminal Si–OH groups. It is likely that a considerable decrease in the intensity of the band at 3660 cm^{-1} in the Al_{13}-LA sample was due to a change in the concentration of hydroxyl groups; this decrease was also due to the structural environment of these groups, which affected the accessibility of CO adsorption.

Consequently, upon replacement of sodium cations by Al_{13}^{7+} cations, both the number and strength of Lewis and Brønsted acid sites and their accessibility increased as a result of an increase in the interplanar spacing. Based on experimental data, we can expect that the activity of Al_{13}-LA in acid-catalyzed reactions will be close to or even higher than the activity of H-LA due to a greater accessibility of sites.

The catalytic properties of layered aluminosilicates with various cations were compared with the use of the dimerization reaction of acetone as an example (Table 2). The reaction was heterogeneous under conditions of catalytic experiments because of the following reasons: (1) visually, the catalyst was a separate solid phase, which can be readily separated from the reaction mass; (2) the reaction did not occur in the reaction mixture with the catalyst filtered off. It was found that both temperature treatment and chemical treatment of layered aluminosilicates significantly affected their catalytic properties. As can be seen in Table 2, the activity of layered aluminosilicates increased with increasing temperature of calcination. This result correlates with data on indicator titration with *n*-butylamine and with data on CO adsorption, according to which the number of acid sites increases with calcination temperature.

The nature of the introduced cation also affected the catalytic activity of layered aluminosilicates. However, it should be noted that the dependence of the activity on the number of acid sites exhibited a complex character. Thus, at equal numbers of acid sites with the strength $H_0 = +4.8$, the Al_{13}-LA and H-LA systems, which contain sites with $H_0 = -5.6$, exhibited the highest activity. At the same time, at equal numbers of acid sites with $H_0 = -5.6$, Al_{13}-LA was more active than H-LA by a factor of ~2; this was likely due to different amounts of Lewis acid sites in the samples. With the use of CO adsorption, it was found that the amounts of these sites in H-LA and Al_{13}-LA were equal to 0.04 and 0.06 mmol/g, respectively. Previously [3, 16], with the use of layered double hydroxides as an example, it was found that catalytic activity depends not only on the number of Lewis acid sites but also on their accessibility. It is likely that the accessibility of active sites also plays an important role in our case; however, the degree of its effect remains unclear. Thus, both the results of this work and previously published data [1, 3, 16] demonstrate that the catalytic activity of various layered aluminosilicates in acetone dimerization can be predicted based on their acid and texture properties, which depend on both the chemical properties of introduced compounds and the procedure and conditions of modification.

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