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Influence of Hydrocarbon Radicals on the Structure of Layered Double Hydroxides

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Abstract Mg-Al-LDHs with different Mg/Al mol ratio were studied. Adsorption of different organic substances on the layered double hydroxides (LDHs) of different composition was studied. Fatty alcohols, phenols and naphthalene derivatives were used as a sorbates. The structure changes, taking place because of this process, was explored by X-ray method. It has been found, that at the adsorption of such substances as alcohol and phenols the anion exchange take place. After the sorption the specific surface and inner distance of LDHs were measured. The mechanism of structure change was proposed.

Keywords: *layered double hydroxides, sorption, structure*

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1. Introduction

Synthetic layered double hydroxide (LDH) compounds are important industrial materials used as absorbents, base catalysts, catalysts precursor, acid neutralizing agents, and precursors in the formation of spinel ceramics [1,2]. Represented by the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A^{m-}_{x/m}\,nH_2O]$ (abbreviated notation $M^{II}{}_{R}M^{III}/A$ with R = (1-x)/x) where M^{II} and M^{III} represent metallic cations and A^{m-} the interlayer anion, the layered structure of an LDH is built by the periodical stacking of positively charged $(M^{II}, M^{III})(OH)_6$ octahedral layers related to brucite and negatively charged inter-layers consisting of anions and water molecules. Owing to the highly tunable LDH intra-layer composition coupled with the wide possible choice of anionic organic moiety, a large variety of LDH hybrid materials has been reported, and several review articles and chapters are devoted to the intercalation chemistry of LDHs and their application [2,3].

Most synthetic LDHs resemble the naturally-occurring hydrotalcite $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$. They grow as hexagonal crystals, the structure being derived from that of brucite. Each cation is octahedral surrounded by hydroxide groups, the octahedral sharing edges forming two-dimensional sheets. These sheets carry an excess positive charge due to the presence of triply charged cations and this is balanced by interlayer anions that bind the sheets together. Most LDHs are binary systems, i.e. with two kinds of metal cations within the hydroxide layers, but ternary LDHs have also been reported. A wide variety of cations can be incorporated into the hydroxide layers of the LDH as well as inorganic or organic anions into the interlayer space either by direct synthesis or ion exchange, and this has resulted in substantial academic and industrial interest, which is discussed below in a non-exhaustive manner. Directly related to the trivalent cation content, the anionic exchange capacity may vary in a large range between 0.1 and 5 meq/g. Even for the lower value, it corresponds to twice the layer charge density of smectite materials, resulting in layers tightly stacked via the attractive forces with the interlayer anions filling the gallery. Vacancies in the inter-sheet domains are not great taking into account the high packing of anions balancing the layer charge. Basal distance in LDHs can vary over a very wide range, from 1 to 50 A. The size of the inter layer space (as well as anion exchange capacity) depends on the cationic composition of the matrix, the degree of isomorphous replacement, the solvatation degree, but most of all on the size of the anions and molecules in the inter-layer space [2]. LDHs are manufactured on an industrial scale with a manufacturing capacity that increased by at least 20,000 metric tons [4].

The heat treating or calcining caused the destruction of LDHs structure. The thermal treatment of LDHs up to about 200°C induces dehydration. Treatment up to 500 °C induces dehydroxylation and loss of vaporizable anions such as carbonate, nitrate, oxalate, and acetate. Heating at up to 900°C leads to the formation of mixed metal oxides and, in many cases, spinels. These calcined LDHs possess a "structural memory effect" [5,6,7]. Remarkably, the partially or fully dehydrated mixed metal oxides produced from LDH precursors will rehydrate by water contact, take up anions, and reform the original LDH structure with great fidelity.

Another "structural memory effect" is in effect on the structure of LDHs the anions that were present in solution during synthesis. The size of the basal spacing strongly correlated with size of anions in the mother liquor [1,3,8,9]. Using this "memory effect", it makes possible to control the structure of LDHs, making adsorbents and catalysts beforehand given sieve properties. This feature makes LDHs exceptionally promising substances as catalysts and sorbents [10-16].

2. Experimental Section

2.1. Synthesis of LHDs Samples

Samples were kindly provided by SASOL. The nature of the LDHs is shown in Table 1.

Structure of LDHs was studied by X-ray diffraction. The X-ray diffraction experiments were performed using a SIEMENS D-500 diffractometer with Co K_α - radiation. Special computer programs were used for smoothing, background correction and decomposition of overlapped diffraction peaks.

X-ray fluorescence spectroscopy (XRF), Shimadzu XRF-1700 sequential XRF spectrometer was used to determine the Mg/Al atomic ratios of the samples.

The nitrogen adsorption–desorption isotherms were recorded at 77 K on a Coulter SA 3100 automated gas adsorption system on samples previously degassed at 383 K for 7 h under vacuum. Specific surface areas (*S*BET) were determined using the Brunauer–Emmett Teller (BET) method on the basis of adsorption data. The pore volume (*V*p) values were determined by using the t-plot method of De Boer.

Thermal behavior was studied by thermo-analytical methods, the samples calcined under air (the temperature was raised with 10 K/min to 1273 K).

The basicity and acidity of synthesized LDHs were determined by Hammett indicators method [18].

The concentration of phenols was determined photometrical by the reaction of formation of the colored compound with 4-aminoantipyrine in an alkaline medium (pH = 10) in the presence of ammonium persulfate. The concentration of alcohol, naphthalene and β-naphthol was determined by chromatography on a chromatograph HP 5890.

Sorption studies were performed in periodic conditions, loading the sorbent in a solution containing sorbed substances (alcohols, phenols, naphthalene derivatives), and samples were taken after vigorous mixing for some time. Standard concentrations of sorbates were as follows: alcohol = $1{,}0 \cdot 10^{-5}$ mol/l, PhOH = $1{,}0 \cdot 10^{-4}$ mol/l, naphthalene and β-naphthol = $1{,}0 \cdot 10^{-6}$ mol/l.

3. Results and Discussion

The properties of LDHs samples are shown in Table 1.

Table 1. The properties of synthesized Mg-Al-LDHs

Mg/Mg+Al, mol/mol	0.52	0.72	0.81	0.86
d, Å	3.038	3.036	3.045	3.058
c, Å	22.62	22.67	22.81	23.40
Specific surface, m^2/g	250	200	192	180
Pore volume, ml/g	0.5	0.2	0.2	0.2
Acidity, meq/g	0.41	0.32	0.21	0.06
Basicity, meq/g	0.73	0.54	0.63	0.85
$E_{din.}$, meq/g	0.075	0.081	0.041	0.036
$E_{stat.}$, meq/g	0.38	0.41	0.10	0.08

Results of the thermal analysis of LDHs are shown on the Figure 1. The first basic peak corresponds to the loss of crystallization water, the following – to transition from the hydroxide form into oxide one.

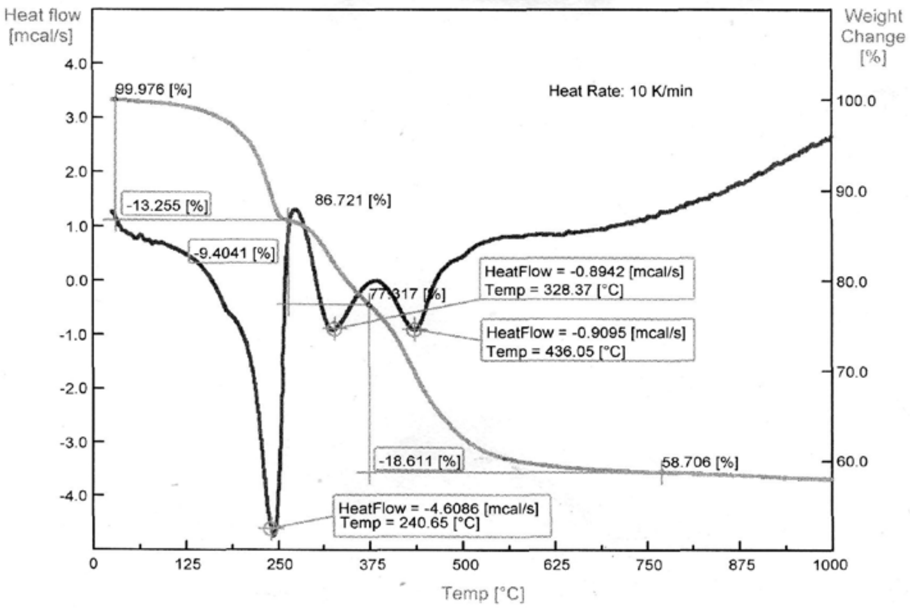
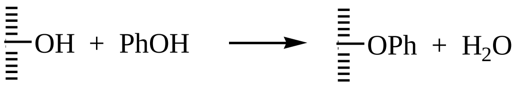


Figure 1. LHD Calcining

The kinetics of ion-exchange sorption of phenol on LDHs of different composition was studied. The anion-exchange reaction for phenol on LDHs proceeds as follows:



$$\equiv OH + PhOH \longrightarrow \equiv OPh + H_2O$$

Since phenol is an acid, so the represented reaction is an anion exchange reaction of neutralization occurs rather quickly and irreversibly.

Investigation of the kinetics of the reaction showed that the rate of sorption depends on the concentration of phenol and amount of LDH. To replace the mass of the sorbent on the concentration of active sites (C_{as}) in a volume of solution used the values of the dynamic capacity of LDHs, defined in dynamic conditions (Table 2).

Table 2. The dynamic capacity of LDHs (phenol)

Mg/(Mg+Al), mol/mol	0.52	0.72	0.81	0.86
E, meq/g	0.18	0.31	0.36	0.46

The kinetic equation of sorption of phenol is as follows:

$$\vartheta = k \cdot C_{PhOH} \cdot C_{as}$$

The rate constants of phenol sorption for sorbents with different molar ratio of Mg/(Mg + Al) have been calculated. The obtained values of the constants are presented in Table 3.

Table 3. Second order constants of sorption

Mg/(Mg+Al), моль/моль	0.52	0.72	0.81	0.86
$k \cdot 10^3$, l/mol·s	0.83	1.29	1.67	1.70

(Studies of sorption of alcohols, naphthalene, beta-naphthol and other compounds have been carried out. Kinetics of sorption are similar. Studies have shown that the rate of sorption increases with the acidity of the adsorbate).

The reaction with phenol proceeds rapidly (Figure 2), and after 15-20 minutes the dynamic equilibrium set.

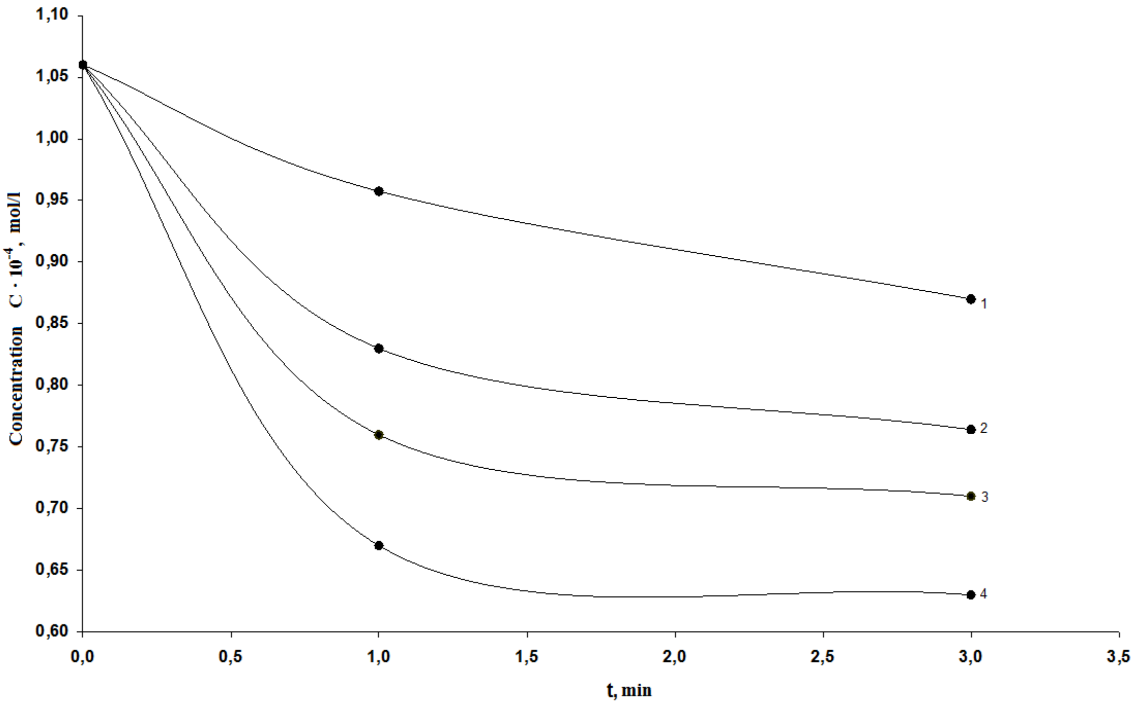


Figure 2. Change of phenol concentration at different temperature; 1 – 21°C, 2 – 40°C, 3 – 60°C, 4 – 75°C

However, if at the end of the sorption to leave the LDHs in a solution of phenol in a long time (48 hours), the degree of adsorption increases, a simultaneous increase the inter-planar distance from 3.03 to 5.76 Å. By our assumption, this is due to the reorientation of the aromatic rings in the inner space of LDHs (Figure 3), with increased availability of active sites.

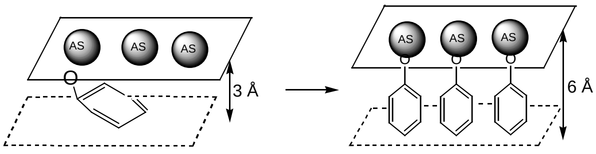
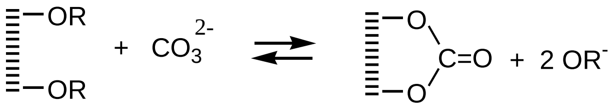


Figure 3. – Reorientation of phenol molecules if LDHs inner space

To test this hypothesis, studies on the sorption of alkoxides were conducted. Experiments have shown that the sorption of alcohols also occurs through a mechanism of anion exchange. To prove this, the LDH was placed into alkoxide solution and left for 48 hours. Sorbents after adsorption was washed with ethanol and ether up to the absence of alcohol traces, and then washed with an aqueous solution containing carbonate ions. In the washing solution by gas-liquid chromatography established the presence of alcohol, indicating that the reverse reaction of anion exchange:



$$\equiv OR,\ \equiv OR + CO_3^{2-} \rightleftharpoons \equiv O,\ \equiv O > C{=}O + 2\,OR^-$$

(The same phenomena are observed for phenol, and β-naphthol, but not for naphthalene. In the case of naphthalene, a complete removal during washing with ethanol and ether take place). We can assume that after a long stay in alcohol solution the hydrocarbon radicals are arranged perpendicular to the main plane of LDHs (Figure 4).

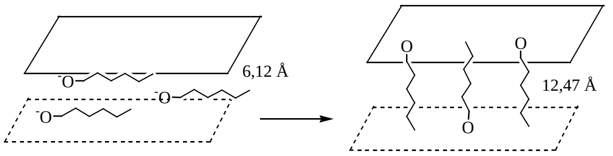


Figure 4. Change of interlayered distance after the sorption of heptanol

It is interestingly to trace the change of inter-layer distances at sorption of alcohols with the different length of hydrocarbon radical (Figure 5) [19,20]. These results well correlate with the changes of interlayer distances in case of adsorption of alkylsulfates.

In the linear approximation of the results, shown in Figure 5, described by the following dependencies:

For alcohol:

$$d(A) = 2,43 + 1,45\ C$$

For alkylsulfates:

$$d(A) = 5,41 + 1,35\ C$$

5,41 – the contribution of sulfonic group, 2,43 – the contribution of the hydroxyl group, 1,35-1,45 – the contribution of each $–CH_2–$ group.

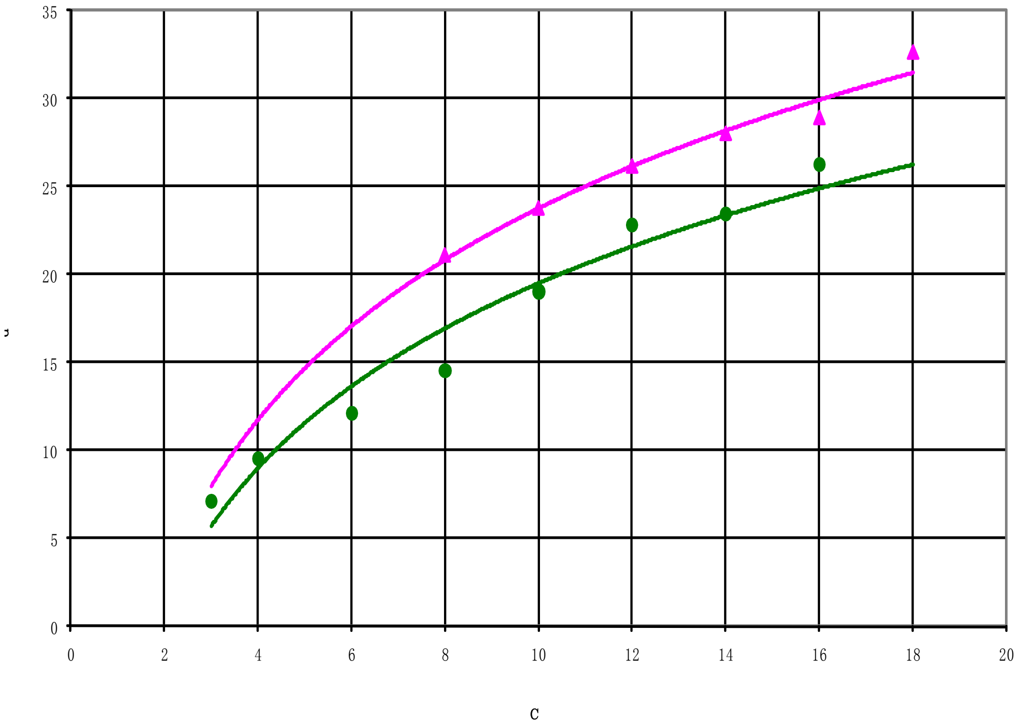


Figure 5. Change of interlayer distances of LDHs at sorption of alcohols (1) and alkylsulfates (2) [21]

Table 4. Basicity of LDH after the sorption of alkoxides (E_0 = 0.85 meq/g)

Alkoxide	Amount of sorbed alcohol, mmol/g	Non-active sites, meq/g
CH_3O^-	0.86	-
$C_2H_5O^-$	0.51	0.34
n-$C_3H_7O^-$	0.36	0.49
i-$C_3H_7O^-$	0.32	0.53
i-$C_4H_9O^-$	0.31	0.54
n-$C_4H_9O^-$	0.27	0.58
n-$C_5H_{11}O^-$	0.11	0.74
i-$C_5H_{11}O^-$	0.09	0.76

Such patterns suggest a perpendicular arrangement of hydrocarbon radicals of alcohols relative to the layers of inorganic matrix. Similar patterns were observed for dicarboxylic acids, which bind two oxide layers to each other, while the inter-planar distance is proportional to the length of the hydrocarbon radical [23]. For ethoxylated products [21] radicals initially arranged in a plane perpendicular to the layers of monomolecular hydroxide, and after drying the angle is 56 degrees. Alcohols with long hydrocarbon radicals, settling initially parallel to the layers of the matrix in the inner space of LDH, should to block the active sites. To test this hypothesis, we determined the concentration of the basic sites remaining in the LDH after 15 minutes of sorption (Table 4).

At short adsorption time the increase of interlayered distance does not take place and the hydrocarbon radicals blocking the access to the basic sites, the degree of block is proportional to the length of the hydrocarbon radical. At long stay of LDHs in the alkoxides solution it will be the radical reorientation, accompanied by an increase in the interlayered distances.

Enthalpy of moving apart the layers were determined from kinetic experiments. LDH was placed in a solution containing ions $C_7H_{15}O^-$ and kept some time at various temperatures, and then the ethoxylation in the presence of LDH as basic heterogeneous catalyst was carried out. The reaction rate increased with an increase in the interlayer distances, respectively with the increasing availability of basic sites (Figure 6). The obtained value of the enthalpy is $_{\Delta}H$ = 2 kcal/mol.

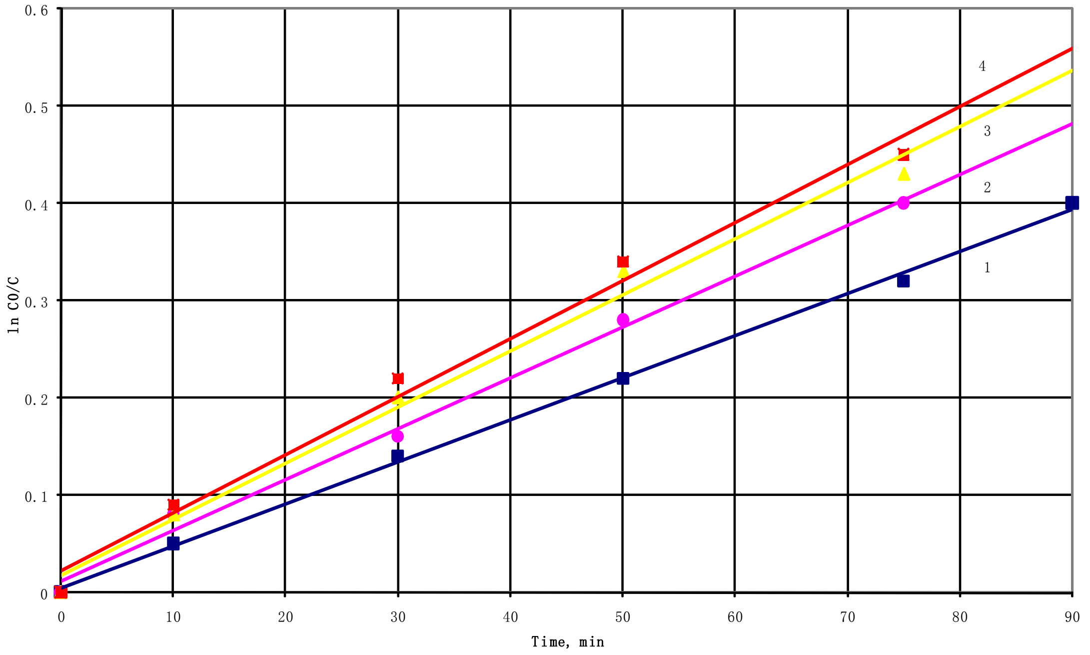


Figure 6. Changing of the reaction rate after LDH heating(1 – original LDH, 2 – 110°C, 3 – 130 °C, 4 – 150°C)

Similar experiments we carried out, examining the sorption of naphthalene and β-naphthol. These substances were chosen for study because of the sorption of these substances occurs by different mechanisms: physical sorption for naphthalene, ion exchange – for b-naphthol). After completion of the sorption process the specific surface area was measured and interlayer distances was determined. Measuring the size of internal space was performed using X-ray diffraction analysis. The experimental results are shown in Figure 7.

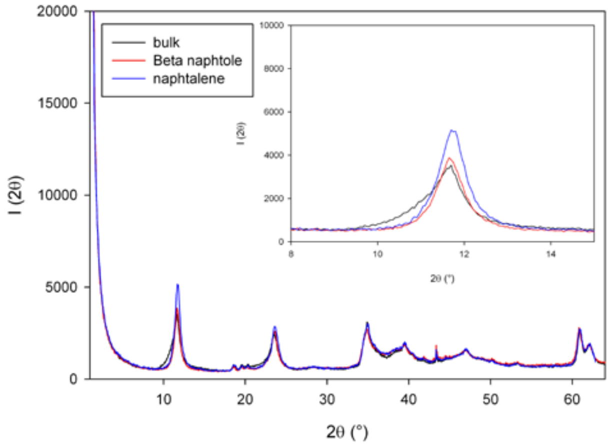


Figure 7. XRD patterns of LDH Mg/(Mg+Al) = 0.72 mol/mol (as-prepared, with naphthalene, with β-naphthol)

The X-ray diffraction patterns shown in Figure 7 are very similar that indicates a minor change of the structure. The insert shows that intensity decreases and a reflection corresponding to 11,8° diffraction angle shifts to smaller angle. This means increasing interplanar distance resulted from penetration of organic substances inside the lattice (see also shifts of the reflection at 43, 61 and 62°). The shift of some reflections, appearance and increase of new reflections with unchangeable other reflections indicate a change of the structure. The structure evolution occurs in a row: as-prepared – with naphthalene – with β-naphthol.

Anion exchange with β-naphthol leads not only to change the distance between layers, but also to a change in specific surface area. The specific surface areas of sorbents with absorbed organic compounds were determined by the BET method. The results are presented in Table 5.

Table 5. The value of specific surface area (S, m^2/g) for different LDHs

(Mg/(Al+Mg), mol/mol	As-prepared	with β-naphtol	with naphthalene
0.52	162.4	155.7	156
0.72	14.4	14.4	14.4
0.81	9.2	12.0	19.59
0.86	22.0	28.0	34.7

Presented in Table 5 data shows that at low ratios of Mg/Al + Mg the sorption of naphthalene and β-naphthol has virtually no effect on the value of specific surface, but at high ratios of Mg/Al + Mg – changes much more.

Aromatic rings of adsorbed naphthalene are arranged in parallel position to inorganic layers, regardless of the concentration of active sites. The interlayer distance in LGHs is about 7 Å. The effective area for β-naphthol is 9.89 Å2. This value is comparable to the "thickness" of the aromatic ring, constituting ~ 3.5 Å, whereas the diameter of the benzene molecule is 7.1 Å. For β-naphthol plane-parallel arrangement is observed only in the initial stage of ion exchange (Figure 8).

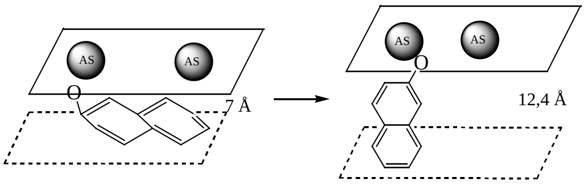


Figure 8. Change the location of β-naphthol molecule in LDH inner space during the ion-exchange process

After then the equilibrium, accompanied by an increase in the inter-planar spacing and increasing the number of active sites available for the following molecules β-naphthol take place. This process is accompanied by an increase in specific surface area of LDHs.

Dependence of the specific surface after sorption of naphthalene and β-naphthol, depending on the composition of layered double hydroxides are shown in Figure 9. It is seen that with increasing of degree of isomorphic substitution, and sorption of organic compounds leads to large changes in specific surface area.

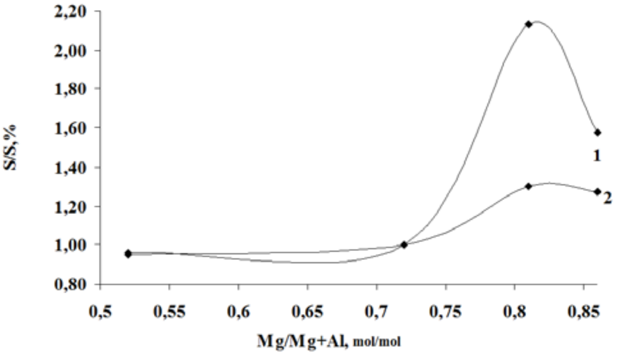


Figure 9. The relative change in specific surface, depending on the composition of LDHs; 1 - with naphthalene, 2 - with β-naphthol

Thus, our work revealed a difference in the behavior of LDHs during the sorption of organic compounds by ion-exchange mechanism and by physical sorption. As well patterns, confirming the assumption that changes in the structure of LDHs in the process of sorption of compounds having dimensions that exceed the size of the interlayer space of LDHs was established.

Calcining of LDHs containing various organic compounds leads to the formation of porous solids. The size of the cavities is determined by the size of removed molecules [1,2]. This phenomenon can create sorbents and catalysts with beforehand set structure of internal cavities, making LDHs even more attractive precursors of catalysts and sorbents.

4. Conclusions

We investigated the structure, morphology and anion-exchange capacities of Mg-Al layered double hydroxides with varying Mg/Al+Mg molar ratio and inner space composition.

It has been founded that the size of internal cavities is determined by the size of the molecules and anions presented in the inner space of LDHs. The kinetics of sorption of organic anions has been studied. It is shown that it depends on the concentration of active centers, which, in turn, blocking by radicals in the process of adsorption. It is proved that molecules with long hydrocarbon radicals change their configuration at the end of the sorption process, which leads to a change in the inter-planar spacing and physical-chemical properties of the studied LDHs.

Acknowledgments

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