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Studies on the Structure of Mg–Al and Ni–Al Oxide Carriers Obtained from Layered Double Hydroxides for Hydrocarbon-Processing Catalysts

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Abstract

The structure of oxides obtained by the calcination of layered Mg–Al and Ni–Al (Mg/Al = Ni/Al = 2 : 1) double hydroxides with the structure of hydrotalcite. It is demonstrated that the formation mechanisms for the oxides are different: the Mg–Al oxide retains the original cation ratio, whereas the structure of the oxide formed represents a kind of layered defective spinel. Calcining the Ni–Al hydroxide results in the fact that the majority of Al^{3+} ions reaches the surface of the oxide particles, thereby forming aluminum hydroxide with retaining the nickel oxide phase in the course of hydration. It is established that, depending on the number of aluminum atoms in the bulk of the particles there are different structures of oxides formed, those determine the oxide ability either of restoring the layered oxide structure in the case of Mg–Al hydrotalcite, or saving the structure Ni–Al oxide in the course of hydration.

Key words: double layered hydroxides, mixed oxides, structure modelling, defective spinel

INTRODUCTION

Layered double hydroxides are known to be hydrotalcite-like compounds (hydrotalcites), with the following general formula:

$$[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot yH_2O$$

(M^{2+} and M^{3+} are divalent and trivalent metal cations, A^{n-} is an interlayer anion) are widely studied as promising anion exchangers, nanocomposites, precursors of oxide catalysts for hydrocarbon processing, and others [1, 2]. The structure of hydrotalcite is presented by brucite-like layers formed by the groups of OH^-, those are arranged with respect to each other in a closest packing manner. The hydroxide ions form a system of octahedral voids randomly filled by di- and trivalent cations. The latter cause an excess positive charge to form in the layers, which is compensated by anions located in the interlayer spaces, where there are water molecules present, too. Owing to the diversity of possible polytypes [3, 4] the hydrotalcites tend to contain stacking faults.

Before a certain temperature of calcinations, the hydrotalcites exhibit some "memory effect" [5], *i. e.* the layered structure thereof could be restored from the oxide after hydration. This property represents a basis of one of methods for the activation carbonate-containing Mg–Al hydrotalcites, which consists in a complete or partial replacement of the interlayer anions CO_3^{2-} by OH^- groups. Hydrotalcites containing interlayer hydroxide ions exhibit a better anion exchange capacity being more readily inclined to intercalation with various metal complexes.

The calcination of the Mg–Al hydrotalcites at 550–600 °C results in the formation of a mixed oxide. The nature thereof has been still not established unequivocally, because alongside with the peaks of periclase-like phase (with smaller interplanar distances, as compared to MgO) the diffraction patterns contain a wide additional peak with $d = 2.53–2.56$ Å. The authors of [6], referring to the EXAFS data, suggest that the decrease in the lattice parameters could be connected with the formation of solid solution $Mg_{1-x}Al_{2x/3}O$, wherein Mg^{2+} ions are located in octahedra (as in periclase) and Al^{3+} ions occupy tetrahedral positions. The authors of [7, 8] identified an additional peak ($d = 2.56$ Å), not inherent in the structure of MgO to be a peak 311 inherent in spinel $MgAl_2O_4$, although the peak corresponds to the interplanar spacing $d = 2.437$ Å.

To all appearance, the increase in the interplanar spacing could be caused by the fact that the Mg–Al spinel obtained is inverse [9]. Also, it is believed that a broad halo within the region of $2\theta = 35.5°$ ($d = 2.53$ Å) corresponds to the residues of the hydrotalcite [10]. The authors of [11], basing on data obtained by means of ^{27}Al NMR those confirm the presence of small amounts of Al^{3+} in the tetrahedrons and with taking into account the additional peak $d = 2.56$ Å in the XRD patterns, suggested that the calcined Mg–Al hydrotalcite exhibits spinel-like structure. The authors of [12, 13] expressed a similar idea that all the peaks belong to the same phase that represents defective (layered) spinel.

The model which describes the structure of the calcined Ni–Al hydrotalcite was first presented by the authors of [14]. This is a two-phase system consisting of NiO doped with Al^{3+} ions, and the individual particles of nickel oxide. Later the authors of [15] considered a single-phase metastable model of the NiO structure, doped with aluminum. The authors of [16] considered calcined Ni–Al hydrotalcite to be a three-phase system consisting of NiO, Al_2O_3 doped with nickel, and a spinel-like structure. The latter determines the thermal stability and either decorates NiO particles, or serves as a support thereof. The subsequent paper by these authors [17] presented the hypothesis concerning the existence of the three-phase system to be further developed: there are the phase of NiO which, to all appearance, contains a small fraction of Al^{3+}; nickel-doped alumina which is grafted onto a spinel-like phase and a quasi-amorphous spinel-like phase which decorates the surface of NiO particles and/or serves as a substrate thereof.

Unlike calcined Mg–Al hydrotalcites those can be readily hydrated in contact with the water and even in the air even with restoring the layered structure, the hydration of calcined Ni–Al hydrotalcites is rather complicated. The authors of [18] demonstrated that the calcined Ni–Al hydrotalcites couldn't exhibit restoring the layered structure after 22 h contacting with water vapour. A partial restoring can be achieved via hydrothermal treatment either in an aqueous solution of NH_4OH [19] or at elevated temperature (160 °C) and pressure values ($6 \cdot 10^5$ Pa) [20].

The aim of this work consisted in studying the influence of the cation nature upon the structure of the original carbonate Mg–Al (Mg/Al = 2 : 1) and Ni–Al (Ni/Al = 2 : 1) hydrotalcites, the phase composition and structure of the products of the thermal decomposition and rehydration thereof within the framework of different approaches of XRD structural analysis.

EXPERIMENTAL

Synthesis of the double hydroxides and mixed oxides

Synthesis of the starting layered double hydroxides containing di- and trivalent cations of different nature metals was carried out by means of co-precipitation, described in detail by the authors of [21]. For this purpose we prepared the mixtures of the aqueous solutions of magnesium and aluminum nitrates, as well as of nickel and aluminum nitrates, with an atomic ratio $M^{2+}/M^{3+} = 2$. The total concentration of di- and trivalent cations in each of the solutions was constant amounting to 3 mol/L. The solutions obtained were added drop-wise with vigorous stirring to a solution of Na_2CO_3 (1 mol/L). In the course of the synthesis we maintained constant pH 10.0 *via* adding NaOH solution (1 mol/L). The synthesis temperature was equal to (60±3) °C. For monitoring the pH and temperature values, we used a Mettler Toledo electrode with an integrated thermal sensor.

After adding the entire salt solution, the suspension was stirred for 1 h at the temperature of synthesis. Aging the precipitate (to increase its crystallinity) was performed at 60 °C for 18 h. The double hydroxides obtained were washed with distilled water until a neutral pH of wash water, filtered and dried during 16 h at 80 °C. The hydrotalcites synthesized in such a way contained carbonate anions between brucite-like layers.

The formation of the oxide phase occurred in the course of calcining the Mg–Al and Ni–Al hydrotalcites at 600 °C in air.

The hydration of calcined samples was performed using distilled water for 8 h at a room temperature followed by drying at 80 °C. The concentration of magnesium, nickel and aluminum in solutions and solid samples was determined by means of atomic emission spectroscopy.

The XRD investigation was performed by means of a Bruker D8 Advance diffractometer using monochromatic CuK_α radiation in the range of diffraction angles 2θ = 5–80 deg.

The lattice parameters and crystallite sizes of the Mg–Al and Ni–Al hydrotalcites were determined from the position and the half-widths of peaks, respectively 003, 006 and 110. The correction of the crystal structure of Mg–Al and Ni–Al oxides was performed by means of the Rietveld method using a TOPAS 3.0 software package, the calculation of the diffraction patterns was carried out basing on a model of one-dimensional disordered crystal for hydroxide and oxide forms using a DIFFaX package [22].

The ^{27}Al NMR spectra of oxide samples were obtained with the use of a Bruker Avance 400 (9.4T) NMR spectrometer with a multi-nucleus sensor SB4 in the mode of magic angle spinning (54°44′). The external standard was presented by solid $AlCl_3 \cdot 6H_2O$.

RESULTS AND DISCUSSION

Studying the original hydrotalcites

The XRD patterns of original Mg–Al and Ni–Al hydrotalcites (Fig. 1, *a*) do not correspond to pure polytypes $3R_1$ (AC=CB=BA= ...) and $2H_1$ (AC=CA= ...) (see Fig. 1, *b*) because there is a pronounced asymmetry in the medium diffraction angles 2θ = 30–55 deg (peaks 012, 015, 018). The investigation of the effect of different defect types on the hydrotalcite structure using the DIFFaX software demonstrated that such a distortion of the diffraction peaks could be caused by inclusion of $2H_1$ polytype fragments in the structure of $3R_1$ polytype. In the course of modelling, in order to describe the layer of hydrotalcite, we used data from ICSD No. 62-96 database. The broadening of the peaks associated with a small size of the crystallites in the plane of the layers was taken into account by using the Lorentz function with a half-width equal to the half-width of 110 peak not affected by structural disorder. According to the results of modelling, the fraction of packing defects was equal to 40 % for the Mg–Al hydrotalcite, and 50 % for the Ni–Al hydrotalcite. Consequently, the structure of original Mg–Al and Ni–Al hydrotalcites almost identical.

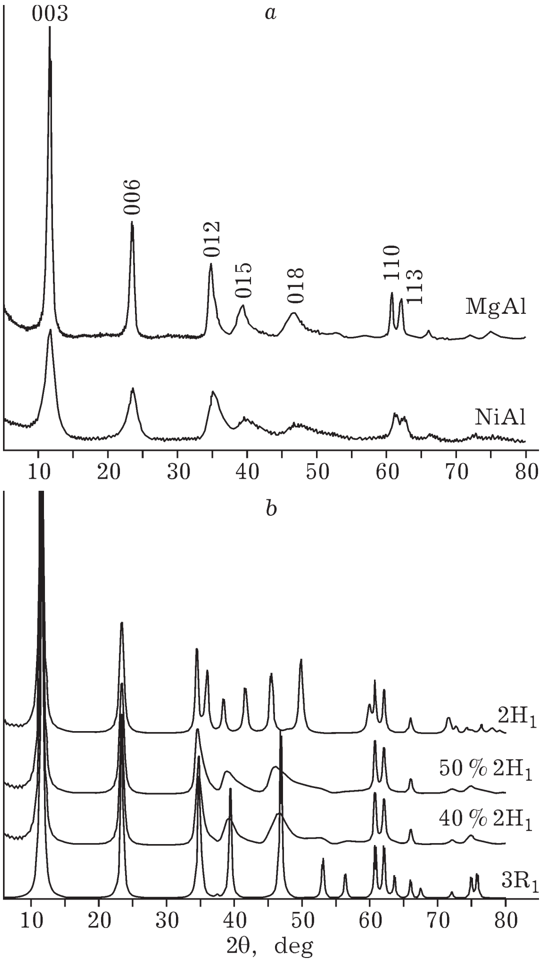

Fig. 1. XRD patterns of the original hydrotalcites (*a*) and model XRD patterns for polytypes $3R_1$, 2H1 and defective structures containing polytype $2H_1$ included in polytype $3R_1$ (*b*).

In the case of replacing Mg^{2+} by Ni^{2+}, there is a slight decrease observed in the lattice parameters *a* and *c* (Table 1), which is associated with a smaller ionic radius of Ni^{2+}, as to compared to the radius of Mg^{2+} (0.68 and 0.72 Å,

TABLE 1

Structural characteristics of original of carbonate-containing hydrotalcites

Cationic composition	d_{003}, Å	c, Å	a, Å	L_c, nm	L_a, nm	$3R_1/2H_1$
Mg–Al	7.62	22.79	3.044	15	28	60 : 40
Ni–Al	7.60	22.75	3.021	5	9	50 : 50

TABLE 2

Structural characteristics of rehydrated samples

Cationic composition	Phase composition	Mass fraction, %	d_{003}, Å	c, Å	a, Å	L_c, nm	L_a, nm
Mg–Al	Hydrotalcite	100	7.62	22.85	3.048	17	26
Ni–Al	$Ni_{1-x}Al_{2x/3}O$	87	–	–	4.166(1)	–	–
	Bayerite $Al(OH)_3$	13	–	–	–	–	–

respectively), as well as one could observe an approximately three-fold decrease in the size of the crystallites in the directions c (L_c) and a (L_a). The results obtained are in good agreement with the literature data [19, 23].

Investigation of rehydrated form

After the calcination at 600 °C and the subsequent hydration of the resulting oxide in water, one can observe recovering the layered structure of the Mg–Al hydrotalcite. The X-ray peak asymmetry disappears within the region of middle diffraction angles, which indicates the packing defects to disappear (Fig. 2). The structure corresponds to pure $3R_1$ polytype.

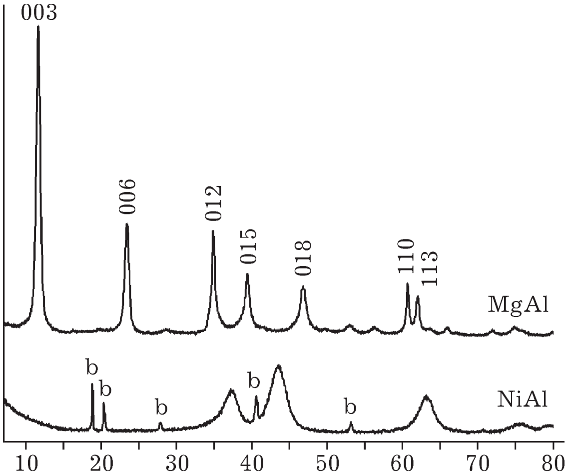

Fig. 2. XRD patterns of rehydrated samples. b – bayerite $Al(OH)_3$.

Similar values of the parameters inherent in the original and rehydrated forms of Mg–Al hydrotalcite (see Tables 1, 2) indicate the fact that the retention of cationic composition after rehydration is observed.

At the same time, the structure of calcined Ni–Al hydrotalcite after the hydration in water is not recovered. The XRD patterns of hydrated Ni–Al samples, alongside with relatively broad of nickel oxide peaks exhibit fairly narrow peaks corresponding to bayerite $Al(OH)_3$, whose amount is equal to about 13 % (see Fig. 2).

The calculated lattice parameter a for the obtained nickel oxide is lower as to compare with that inherent in pure NiO (4.177 Å), which may indicate the presence of Al^{3+} in the structure of NiO (see Table 2). The formation of aluminum hydroxide occurs to all appearance *via* involving Al atoms contained on the surface of $Ni_{1-x}Al_{2x/3}O$ particles. The formation of hydroxide having just the structure of bayerite could be associated with certain conditions those are realized in the process of hydration. The authors of [24] demonstrated that the formation of bayerite needs contacting between γ-Al_2O_3 and an aqueous solution at pH 8–9.

Summarizing the results concerning the hydration of oxide phases obtained *via* calcining the hydrotalcites with the different nature of divalent cations at 600 °C, one could assume that the ability to recover the layered structure of hydrotalcite depends mainly on the arrangement of the oxide structure formed.

XRD investigation of the structure of the calcined hydrotalcites

The XRD patterns of the calcined Mg–Al hydroxide are characterized by a diffuse peak within the region $2\theta = 35.2$ deg ($d = 2.55$ Å) and two broad peaks at 2θ equal to 43.36 and 62.88 deg. The latter are close in position to the peaks inherent in MgO (periclase) having the structure of NaCl type, wherein the anion sublattice represents a cubic closest packing, whereas the cations occupy all the octahedral cavities. The calculated cell parameter $a = 4.177(1)$ Å is smaller as compared to that inherent in pure periclase ($d = 4.211$ Å). In the literature there are different opinions regarding the reduced cell parameter and an additional diffuse peak. As mentioned earlier, there is still no consensus concerning the real structure of the resulting oxide.

At the first stage we considered two models based on a periclase-like structure with the statistical distribution of the Mg^{2+} and Al^{3+} ions throughout octahedra (model 1) and with the transition of a part of the Al^{3+} ions into the tetrahedra (model 2). The correction of the populations in the respective positions was performed by means of Rietveld method using TOPAS software. X-ray diffraction patterns for the models corrected are presented in Fig. 3.

For the model 1, the correction of the population of the octahedral positions in the periclase structure ($R_{wp} = 10.8$ %) revealed the presence of cation vacancies $(Mg,Al)_{0.94\ 0.06}O$. The model 2 with the correction of Mg^{2+} population in octahedral and Al^{3+} population in tetrahedral positions demonstrated the best value of reliability factor $R_{wp} = 10.2$ %. According to the corrected data, the population of the tetrahedral positions by Al^{3+} cations amounted to 0.04.

The high values of the R_{wp} parameter, not sufficiently good description of the intensity ratio for the peaks $2\theta = 43.36$ and 62.88 deg, the presence of an additional peak at $2\theta = 35.2$ deg within the framework of the models considered (see Fig. 3) indicate a completely different arrangement of the structure. For this reason,

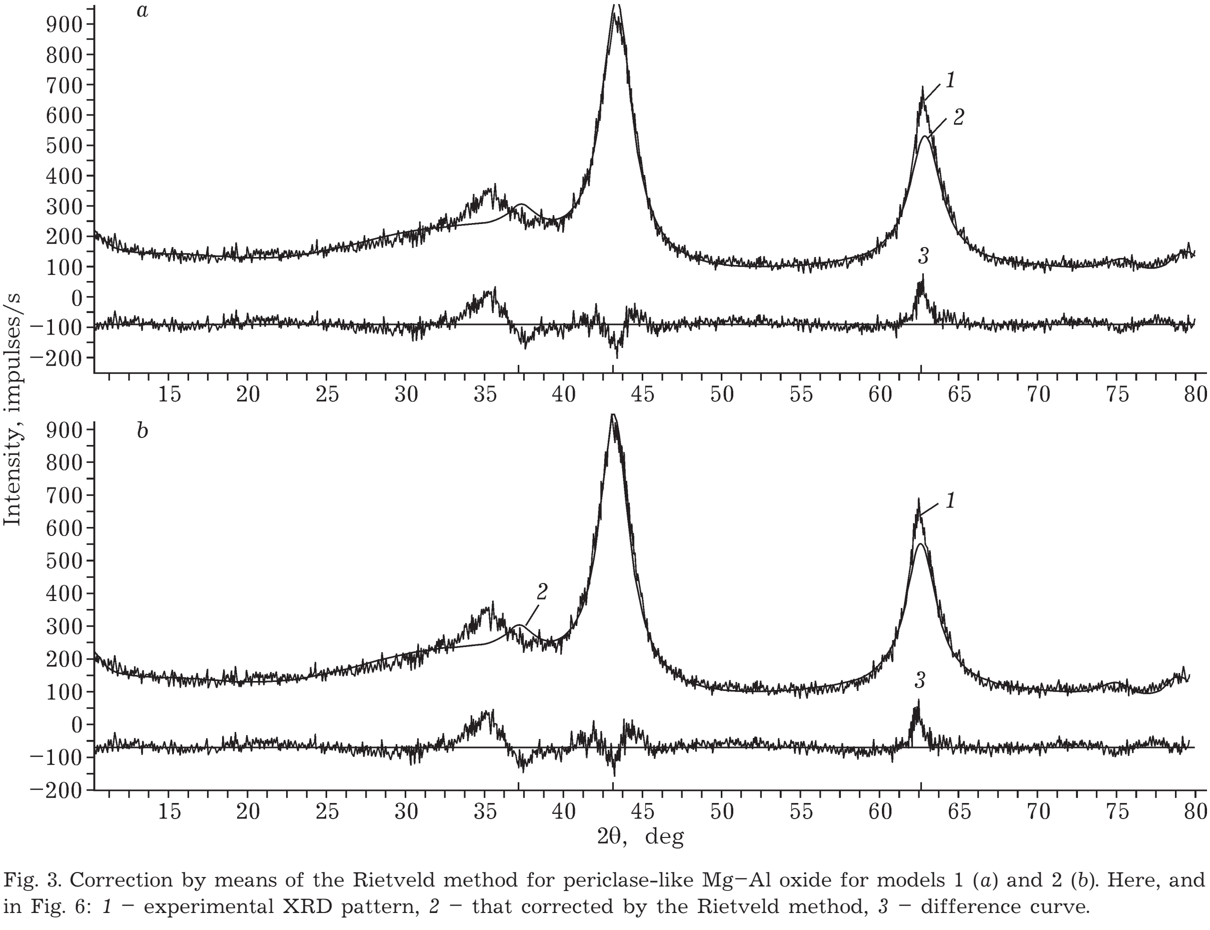

Fig. 3. Correction by means of the Rietveld method for periclase-like Mg–Al oxide for models 1 (*a*) and 2 (*b*). Here, and in Fig. 6: *1* – experimental XRD pattern, *2* – that corrected by the Rietveld method, *3* – difference curve.

we attempted to simulate the diffraction pattern, considering Mg–Al mixed oxide as a defective spinel containing the elements periclase-like structure.

It is known that the spinel structure just as the structure of periclase have the oxygen sublattice that represents a cubic close packing. The periclase in the direction of the closest packing could be presented as a sequence of octahedral layers, wherein all the octahedral voids are occupied. In the spinel there are alternating octahedral layers with an occupancy of 0.75 (three octahedral from the four being occupied) and mixed octahedral-tetrahedral layers.

The authors of [12] *via* the simulation diffraction patterns using a DIFFaX+ software demonstrated that the Mg–Al oxide obtained by means of calcining the Mg–Al hydrotalcite with nitrate anions in the interlayer space, exhibits a defective spinel structure consisting of periclase-like octahedral layers filled with Mg, and spinel mixed octahedral-tetrahedral layers filled with the statistical occupation of 0.25 of octahedra and tetrahedra by Al ions. In the course of creating the spinel layers they based on the structure of MgO (model 3). The model we proposed, unlike the model 3 comprises a mixed layer consisting of a spinel structure, filled with aluminum ions (model 4). We carried out a comparative analysis of these models in order to describe the XRD patterns of the samples under investigation.

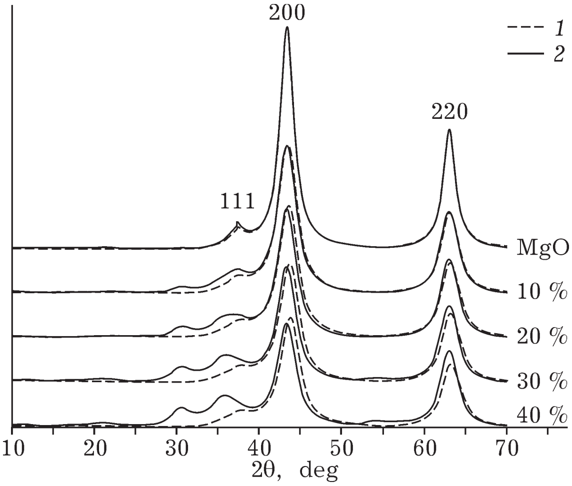

Fig. 4. Simulation of progressively introducing the mixed spinel-like layers into the structure of periclase: *1*, *2* – models 3 and 4, respectively.

In the absence of spinel mixed layers the diffraction pattern corresponds to scattering on a periclase-like structure (Fig. 4). Increasing the fraction of spinel layers leads to the intensity redistribution and to appearing a diffuse scattering within the region of lower (with respect to the location of 111 periclase peak) angles. However, for the model 4 the redistribution of intensities is more significant.

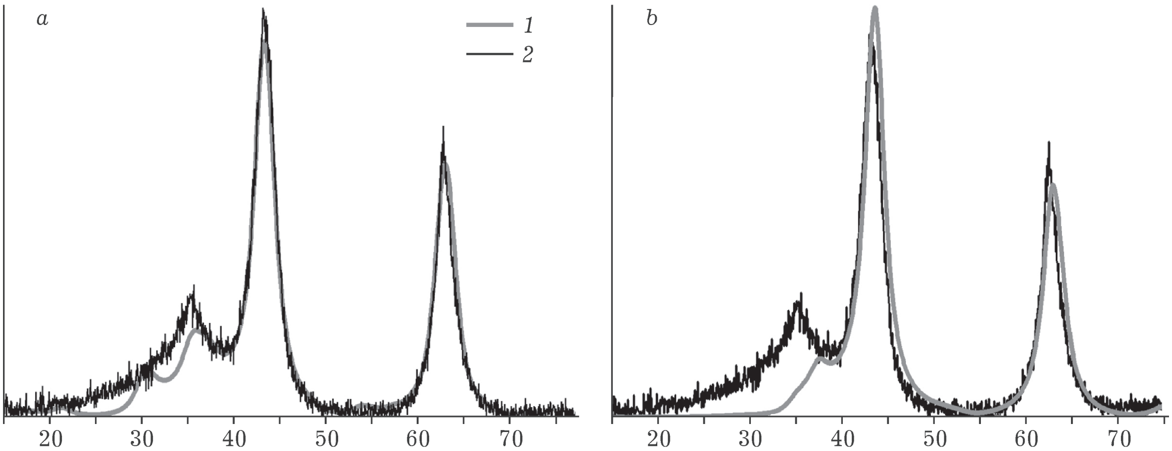

Fig. 5. Experimental XRD patterns for Mg–Al oxide (*1*) and model diffraction patterns (*2*) calculated for the layered defect spinel, consisting of 70 % periclase-like layers and 30 % of spinel-like layers: *a*, *b* – models 4 and 3, respectively.

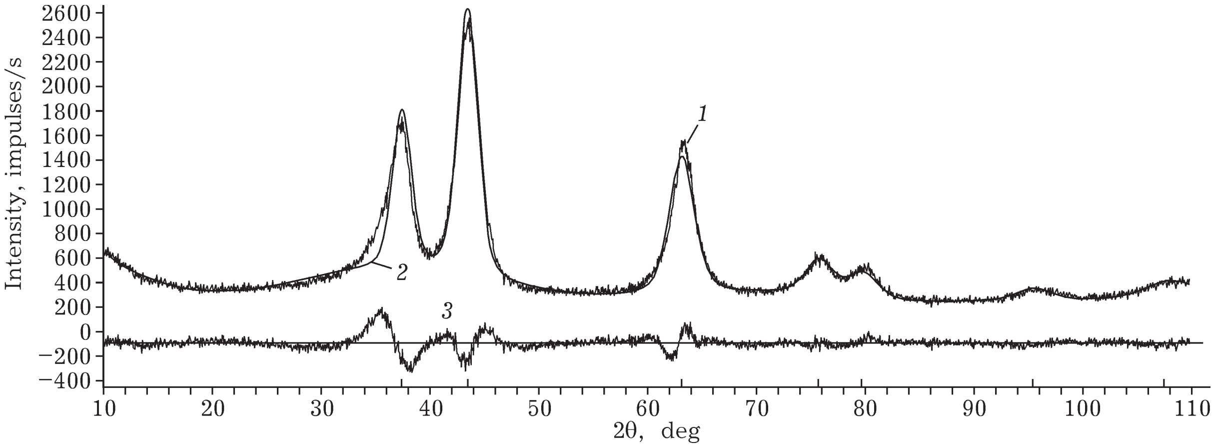

Fig. 6. Rietveld correction for bunsenite-like Ni–Al oxide. For designations, see Fig. 3.

A good enough agreement with the experiment (Fig. 5, *a*) is achieved for the model 4 at 70 % of periclase octahedral layers and 30 % of spinel octahedral-tetrahedral layers.

Besides the presence of diffuse scattering, within the angular range of 25–40 deg, there is the best ratio between 200 and 220 periclase peak intensities. The incomplete agreement with the experiment, to all appearance, could be caused by unaccounted defects in this model. For the model 3, the correspondence with the experimental data is much worse.

The diffraction pattern for the calcined Ni–Al hydrotalcite corresponds to bunsenite with the lattice parameter a = 4.162(1) Å decreases as to compare with pure NiO (a = 4.177 Å), which confirms the presence of Al^{3+} ions in the structure of NiO. The bunsenite structure, just as the structure of periclase, belongs to NaCl type. To establish the true structural model we performed Rietveld correction, considering the bunsenite-like mixed oxide wherein the ions of Ni^{2+} and Al^{3+} are distributed throughout octahedral and tetrahedral positions, respectively. The best value of the R factor (8.4 %) is achieved when the level of occupancy for tetrahedra is equal to 0.85 and that for octahedra is equal to 0.06 (Fig. 6). The R factor increases up to 9 % in the case of correcting the occupancy level only for octahedral positions. It is seen that the asymmetry of peak 111 cannot be described within the framework bunsenite-like Ni–Al oxide.

Under the assumption of the diffuse scattering within the region of a small angle slope of the peak 111, by analogy with the Mg–Al oxide system, we tested the model of defective spinel with the content of spinel octahedral-tetrahedral layers equal to 5 and 10 % (Fig. 7). It can be seen that introducing the small amounts of spinel layers promotes appearing an asymmetry of the 111 bunsenite peak. It could not be excluded that the Ni–Al oxide contains a small amount of spinel octahedral-tetrahedral layers.

It should be noted that in the course of Ni–Al oxide hydration, besides appearing the peaks of aluminum hydroxide, a slight decrease is observed in the 111 peak asymmetry in the bunsenite-like structure (arrow in Fig. 8). At the same time, the lattice parameter increases from 4.162(1) to 4.166(1) Å approaching the lattice

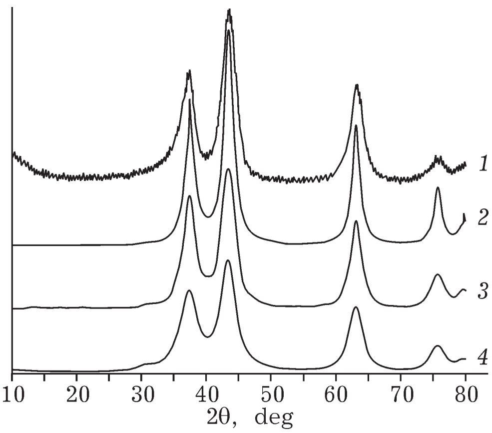

Fig. 7. Diffraction patterns: experimental (*1*) and calculated for Ni–Al oxide (*2–4*) basing on the model of bunsenite-like structure (*2*) and the model defective spinel consisting of bunsenite-like octahedral layers and octahedral-tetrahedral spinel layers at a ratio of 95 : 5 (*3*) and at a ratio of 90 : 10 (*4*).

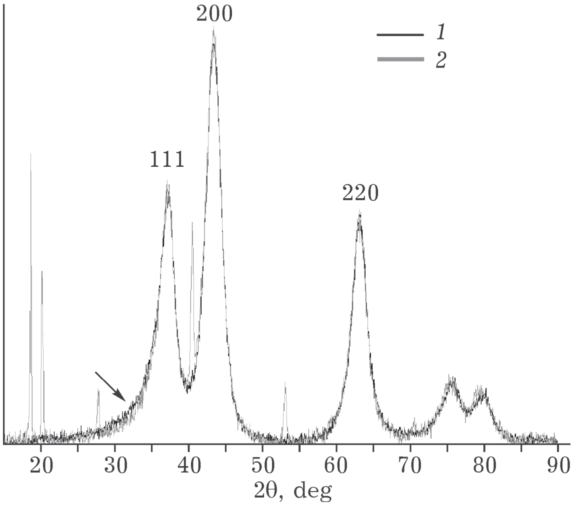

Fig. 8. Comparison of the diffraction patterns in the system of Ni–Al for calcined (*1*) and rehydrated (*2*) samples.

parameter of NiO (4.177 Å). Perhaps, in the course of contacting with water, the aluminum ions additionally leave the oxide particles.

NMR investigation of the structure of calcined hydrotalcites

According to NMR spectral data (Fig. 9), the Mg–Al oxide contains aluminum both in the octahedral and in the tetrahedral environment: the two distinct peaks at 14.7 (octahedra) and 82 ppm (tetrahedra) indicate this. This result confirms the conclusion derived from the data on the presence of aluminum in the tetrahedral environment as a part of the layered structure of the defective spinel in the course of simulation.

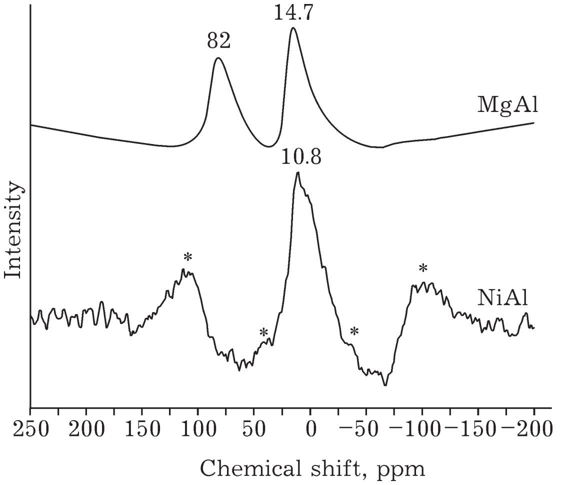

Fig. 9. ^{27}Al NMR spectra for Mg–Al and Ni–Al oxides. Asterisk indicates satellite peaks.

The spectrum of Ni–Al oxide exhibits only the peaks of aluminum in the octahedral environment with a chemical shift of 10.8 ppm. Therefore, the aluminum observed is predominantly located in the octahedra. Taking into account a low signal/noise ratio in the spectrum of Ni–Al oxide, it can be assumed that because of a low symmetry of the oxygen environment, the aluminum can be observed only partially.

CONCLUSIONS

Thus, within the framework of this paper we first proposed an approach to the consideration of the structure of calcined Mg–Al hydrotalcite like a layered defect spinel containing completely filled octahedral layers and mixed octahedral-tetrahedral layers in the [111] direction of the cubic closest packing of the spinel cell. Simulation was performed for the diffraction patterns.

It has been found that in the course of calcining the Mg–Al hydrotalcite, as anionic carbonate groups and water removed from the interlayer space, the ions of Al^{3+}, being smaller comparing to Mg^{2+}, go out of octahedral layers into the interlayer space, forming spinel-like octahedral-tetrahedral layers. The fraction of the octahedral layers, according to the simulation, is equal to 70 %, whereas the fraction of the octahedral-tetrahedral layers amounts to 30 %. The presence of Al^{3+}ions in tetrahedral environment is confirmed by means of NMR.

It is demonstrated that the calcination of Ni–Al hydrotalcite results in the fact that a part of ions remains within the bulk of oxide to form at least 10 % of the spinel layers. Accordingly, a significant part of Al atoms on the surface occurs in the form of X-ray amorphous alumina to convert into hydroxide $Al(OH)_3$ with the structure of bayerite in the course of hydration. According to NMR data, Ni–Al oxide is almost free from aluminum in the tetrahedral environment, which supports a minor amount of spinel octahedral-tetrahedral layers.

The oxides of Mg–Al and Ni–Al have been revealed to exhibit different properties under the conditions of hydration. Upon contacting with water the defective Mg−Al spinel can be readily hydrated to form hydrotalcite. To all appearance, Al^{3+} ions displaced by hydroxyl groups and water from the spinel-like come back into octahedral brucite-like layers. In this case, the lattice parameter *a* in the original and rehydrated Mg−Al hydrotalcite is almost unchanged, which indicates the cationic composition of brucite-like layers in the original and rehydrated samples of hydrotalcite to be constant. At the same time, the Ni−Al hydrotalcite system does not exhibit any recovery of the layered structure to occur. To all appearance, this fact could be connected with appearing the aluminum on the oxide surface and with the almost complete absence therein of spinel-like layers, those contain Al^{3+}ions.

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