

Synthesis and structural transformations of hydrotalcite-like materials Mg-Al and Zn-Al

Citation for published version (APA):

Prihod'ko, R. V., Sychev, M. V., Astrelin, I. M., Erdmann, K., Mangel, A., & Santen, van, R. A. (2001). Synthesis and structural transformations of hydrotalcite-like materials Mg-Al and Zn-Al. *Russian Journal of Applied Chemistry*, 74(10), 1621-1626. <https://doi.org/10.1023/A:1014832530184>

DOI:

[10.1023/A:1014832530184](https://doi.org/10.1023/A:1014832530184)

Document status and date:

Published: 01/01/2001

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

INORGANIC SYNTHESIS
AND INDUSTRIAL INORGANIC CHEMISTRY

Synthesis and Structural Transformations
of Hydrotalcite-like Materials Mg–Al and Zn–Al

R. V. Prikhod'ko, M. V. Sychev, I. M. Astrelin, K. Erdmann,
A. Mangel', and R. A. van Santen

Kievskii politekhnicheskii institut National Technical University, Kiev, Ukraine

Kopernik University, Torun, Poland

CI Electronics, Salisbury, UK

Technical University, Eindhoven, the Netherlands

Received January 16, 2001

Abstract—Mg–Al and Zn–Al hydrotalcite-like layered double hydroxides of various compositions were synthesized and characterized. A detailed comparative analysis of the structure and composition of starting and reconstructed layered double hydroxides was made.

Synthetic layered double hydroxides (LDHs), or so-called hydrotalcite-like materials, arouse increased interest as sorbents [1, 2], anion exchangers [3, 4], catalysts [5, 6], and catalyst precursors [7, 8]. The idealized LDH formula is as follows: $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}A_{x/z}^{z-} \cdot m\text{H}_2\text{O}$, where M^{2+} is Mg^{2+} , Ni^{2+} , Zn^{2+} , ...; M^{3+} is Al^{3+} , Fe^{3+} , Ga^{3+} , ...; and A^{z-} is CO_3^{2-} , NO_3^- , Cl^- , ... [8]. The unit cell is formed by brucite-like layers separated by interlayer gaps. The doubly charged cations, M^{2+} , bound to six oxygen atoms, form primary octahedral fragments joint to form networks [5]. These networks are mutually superimposed in the form of H-bound brucite-like layers. Isomorphic replacement of M^{2+} by differently charged cations, e.g., by Al^{3+} , results in the appearance of a positive charge, which is compensated by the anions localized in the interlayer gaps [5].

Layered double hydroxides are solid bases, which predetermines their use in basic catalysis [4–8]. In most cases, LDHs are used in calcined form [8]. Recently, the feasibility has been shown, however, of using uncalcined LDH catalysts in a number of organic syntheses [4, 6, 7]. At the same time, there is increased interest in materials with reconstructed structure, obtained using the so-called memory effect [4], i.e., the ability of heat-treated LDH to recover the initial hydrotalcite-like structure upon rehydration [5]. In this case, the degree of recovery of the LDH structure depends on the temperature of preliminary heating and the chemical composition of LDH [5]. Despite the

fact that the memory effect has been known for more than 20 years and its importance for preparing new catalysts grows [4], the number of works concerned with fundamental aspects of this phenomenon is insufficient [7, 9–12].

In this study, LDHs of different compositions were synthesized and a comparative analysis of their structure before and after transformation was made.

EXPERIMENTAL

As objects of study served Mg–Al and Zn–Al LDHs. Synthesis of these materials with atomic ratios M^{2+}/Al^{3+} of 2, 3, and 5 was described in [7, 13]. The materials prepared are designated as Mg2Al, Mg3Al, and Mg5Al, or Zn2Al, Zn3Al, and Zn5Al, where the digit stands for the atomic ratio Mg/Al or Zn/Al. The residual anions (NO_3^-) were removed by ion exchange for CO_3^{2-} [14].

A part of the LDHs prepared was calcined in thin bed at 673 or 773 K (heating rate 180 deg h^{-1}) for 16 h in a flow of N_2 , cooled, and stored in sealed ampules in argon. These materials are designated by index C. The reconstruction of LDHs was performed as described in [15], i.e., 1 g of calcined LDHs was suspended in 100 ml of deionized water, heated to 373 K, kept there for 40 min with stirring, cooled, filtered, and dried at 383 K for 12 h. The materials thus prepared are denoted by index R.

Table 1. Chemical formula, M^{2+}/Al^{3+} atomic ratio, structural parameter a , and crystallite size ε of the synthesized LDHs

Sample	Formula	M^{2+}/Al^{3+}	a	
			nm	
Mg2Al	$[Mg_{0.668}Al_{0.332}(OH)_2](CO_3)_{0.166} \cdot 0.56H_2O$	2.01	0.3042	18.5
Mg3Al	$[Mg_{0.751}Al_{0.249}(OH)_2](CO_3)_{0.125} \cdot 0.62H_2O$	3.02	0.3061	19.9
Mg5Al	$[Mg_{0.833}Al_{0.167}(OH)_2](CO_3)_{0.084} \cdot 0.64H_2O$	4.98	0.3086	20.7
Zn2Al	$[Zn_{0.669}Al_{0.331}(OH)_2](CO_3)_{0.166} \cdot 0.46H_2O$	2.02	0.3071	44.8
Zn3Al	$[Zn_{0.748}Al_{0.252}(OH)_2](CO_3)_{0.126} \cdot 0.45H_2O$	2.97	0.3080	40.3
Zn5Al	$[Zn_{0.837}Al_{0.163}(OH)_2](CO_3)_{0.081} \cdot 0.43H_2O$	5.13	0.3088	47.0

X-ray diffraction analysis (XDA) of the materials studied was done on DRON-3 and Philips 1170 diffractometers ($Cu_{K\alpha}$ radiation, $\lambda = 0.154178$ nm, Ni-filter) with oriented samples. The size of the LDH crystallites along the a axis was determined using the Scherrer equation [7], high-purity grade α - SiO_2 served as standard. IR spectra were recorded with a FTIR Perkin-Elmer 2000 spectrophotometer, using samples prepared by compaction of pellets of a material under study with thoroughly dried KBr (1 : 60 ratio). The ^{27}Al NMR spectra were obtained with magic angle rotation on an AMX 300 WB Bruker spectrometer ($H = 78.20$ MHz, $[Al(H_2O)_6]^{3+}$ standard).

The chemical composition of the materials studied was determined by atomic absorption spectroscopy (AAS) on a Perkin-Elmer 3030 spectrophotometer. The rehydration of calcined LDHs was studied by the method of water absorption on a CIsorp installation (C.I. Electronics Ltd).

The chemical formulas of the materials synthesized (Table 1) show good agreement between the predicted and experimentally found compositions. X-ray diffraction patterns of the obtained LDHs (Fig. 1) contain basal reflections typical of hydroxylite [5]. As known, the intensity of the (110) reflection is proportional to half the structural parameter a of the LDH unit cell, which corresponds to the spacing between the neighboring cations in the brucite-like layer [5]. For the materials studied, this parameter grows with increasing M^{2+}/Al^{3+} atomic ratio (Table 1). Such a dependence was observed on replacing Al^{3+} structural cations with cations of larger ionic radius (Mg^{2+} or Zn^{2+}) [16, 17] and, consequently, confirms their localization in the LDH structure. The crystallite size of these materials along the a axis also grows with increasing M^{2+}/Al^{3+} ratio (Table 1).

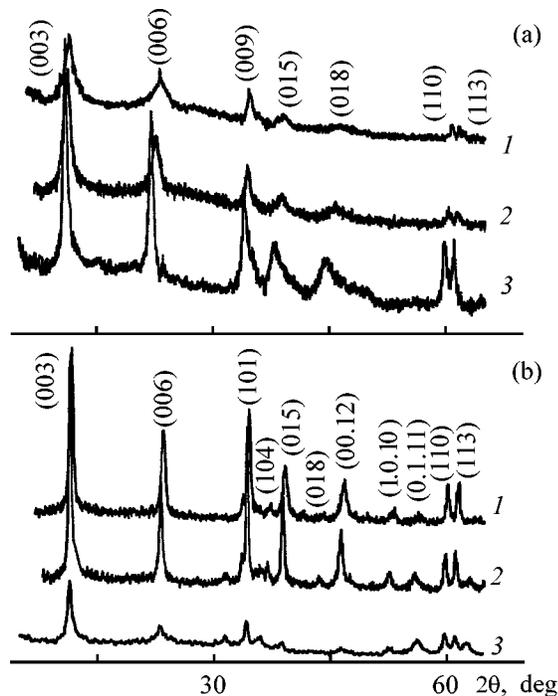


Fig. 1. Diffraction patterns of LDHs synthesized. (2θ) Bragg angle; the same for Figs. 3, 5. (a) (1) Mg2Al, (2) Mg3Al, and (3) Mg5Al; (b) (1) Zn2Al, (2) Zn3Al, and (3) Zn5Al; the same for Figs. 2, 3.

The IR spectra of the synthesized LDHs in the wave number range 4000 – 2000 cm^{-1} contain a broad absorption band (AB) peaked at 3600 – 3650 cm^{-1} , related to OH vibrations in the brucite-like layer [5]. With increasing M^{2+}/Al^{3+} ratio, the position of the band maximum shifts steadily to higher frequencies for Mg–Al and to lower frequencies for Zn–Al. This is reasonable, since a similar absorption band was noted at 3700 and 3620 cm^{-1} for magnesium and zinc hydroxides, respectively. As known, the narrower the full width at half-maximum (FWHM), $I_{1/2}$, of a band, the more ordered is the cation distribution in the LDH structure [5, 18]. For the materials studied, the $I_{1/2}$ parameter grows with increasing Mg^{2+} and Zn^{2+} content. As a result, the distribution of structural cations becomes less ordered. It should be noted that the ab-

sorption band related to $\text{Mg}(\text{OH})_2$ impurity is absent. Unfortunately, the similarity of the vibration frequencies of $\text{Zn}(\text{OH})_2$ and Zn–Al LDHs makes identification of the zinc hydroxide phase impossible.

In the range $1400\text{--}200\text{ cm}^{-1}$, the IR spectra of LDHs contain a strong band at around $1368\text{--}1376\text{ cm}^{-1}$ (Fig. 2), attributed to ν_3 bending vibrations of CO_3^{2-} anions [14, 19]. Weakly resolved shoulders at 1090 , $1050\text{--}1056$, and $860\text{--}880\text{ cm}^{-1}$, attributable to ν_1 and ν_2 vibrations of CO_3^{2-} [12, 19], are also present. The shoulder at 790 cm^{-1} (Al–O– bond vibrations [12]) was noted solely for the Mg2Al sample, evidently indicating the presence of a certain amount of the $\text{Al}(\text{OH})_3$ impurity. The absorption band at $760\text{--}765\text{ cm}^{-1}$, attributable to Zn–Al–O vibrations inside the brucite-like layer, is also present in the Zn–Al LDHs IR spectra. In addition, the IR spectra contain absorption bands at $668\text{--}624\text{ cm}^{-1}$ (Mg–Al LDH), $612\text{--}620\text{ cm}^{-1}$ (Zn–Al LDH; ν_4 , bending vibrations of the carbonate bond), and $580\text{--}560\text{ cm}^{-1}$. The last absorption bands are typical of brucite-like layer (stretching and bending vibrations of M–O, M–O–M, and O–M–O bonds) [20]. With increasing content of the M^{2+} cations in LDH, the positions of the $428\text{--}396\text{ cm}^{-1}$ bands (vibrations of hydrotalcite octahedral networks [19, 20]) steadily shift to lower frequencies, approaching the value found for brucite (364 cm^{-1}).

The ^{27}Al NMR spectra of the materials studied are similar to those obtained previously for synthetic hydrotalcite [17, 21]. They contain only one strong resonance related to Al^{3+} octahedrons with chemical shift of 7.9 and 14.0 ppm for Mg–Al and Zn–Al, respectively. This implies that, in the LDHs studied, aluminum(III) atoms are localized in octahedral positions of brucite-like layers.

The whole set of the obtained results characterizes the synthesized materials as LDHs with hydrotalcite structure.

As expected, calcination at $T > 573\text{ K}$ results in amorphization of the LDH crystalline structure. The diffraction patterns of calcined samples contain reflections that can be assigned to MgO or ZnO (Fig. 3). It is quite reasonable that their intensity grows with increasing $\text{M}^{2+}/\text{Al}^{3+}$ ratio (Fig. 3).

The calcination of Mg–Al and Zn–Al LDHs at $600\text{--}773\text{ K}$ yields double oxides, $\text{Mg}(\text{Al})\text{O}$ or $\text{Zn}(\text{Al})\text{O}$, nearly isostructural to MgO or ZnO [7, 12, 21, 22]. Degradation of the Zn–Al LDHs is observed at 573 K , irrespective of the Zn/Al ratio [12]. The presence of the amorphous Al_2O_3 phase or zinc aluminate on the surface of ZnO particles is possible.

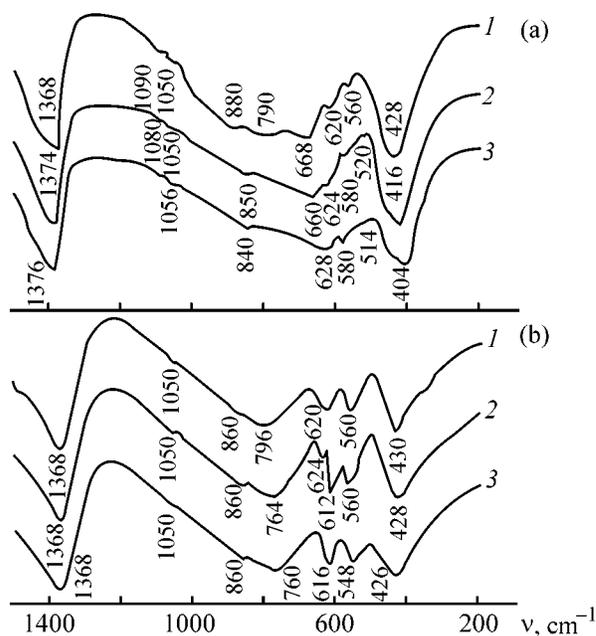


Fig. 2. LDHs IR spectra. (ν) wave number.

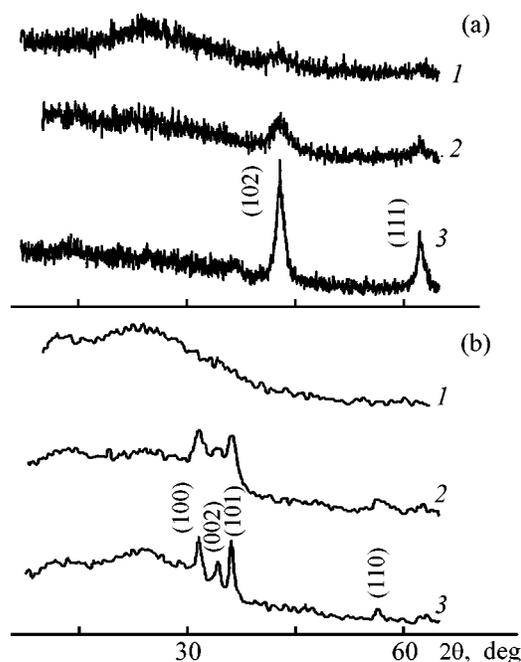


Fig. 3. Diffraction patterns of LDHs calcined at 773 K .

The IR spectra of LDH(C) contain absorption bands characteristic of double oxides [23]. The CO_3^{2-} vibrational bands disappear nearly completely, whereas the weak band around 1370 cm^{-1} is present. This indicates incomplete removal of carbonate anions, which can be occluded in the mixed oxide lattice [24].

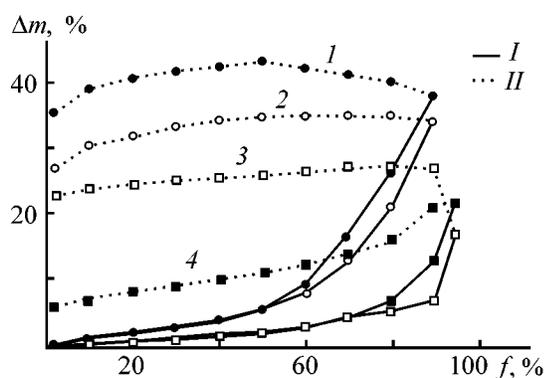


Fig. 4. Adsorption-desorption isotherms of water. (Δm) Change in sample mass and (f) relative humidity. (I) Adsorption and (II) desorption. (1) Mg₂Al, (2) Mg₅Al, (3) Zn₂Al, and (4) Zn₅Al, all calcined at 773 K.

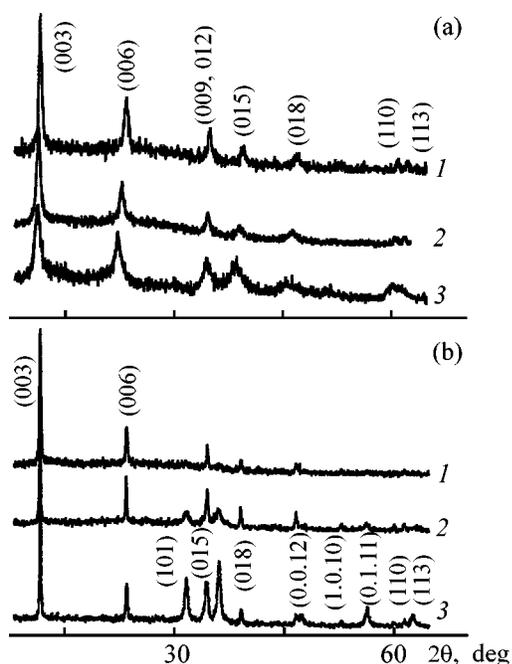


Fig. 5. Diffraction patterns of reconstructed LDHs. (a) (1) Mg₂Al(R), (2) Mg₃Al(R), and (3) Mg₅Al(R); (b) (1) Zn₂Al(R), (2) Zn₃Al(R), and (3) Zn₅Al(R).

The NMR revealed tetrahedrally coordinated Al³⁺ cations, Al³⁺(tet), in the Mg–Al and Zn–Al LDHs calcined at 673–923 K [7, 17, 22]. For Zn-containing materials, the intensity of the Al³⁺(tet) resonance is considerably higher than that for Mg–Al LDHs [7]. Double oxides prepared by calcination of Zn–Al LDHs contain Al³⁺ ions mostly in tetrahedral positions [25]. The change in partial coordination of Al³⁺ ions is caused by dehydroxylation of LDHs [17, 21]. With increasing temperature, the coordination environment of Al³⁺(oct) cations becomes more distorted. This affects neighboring Mg²⁺ or Zn²⁺ ions [7, 21],

capable of forming corresponding oxides. An analysis of the parameters of the ²⁷Al NMR line showed that the lowest ordering of Al³⁺ ions and, consequently, the most significant degradation of LDHs occur in the temperature range 723–773 K [7].

The aforesaid suggests that the Mg–Al and Zn–Al LDHs calcined at $T > 923$ K are predominantly the double oxides Mg(O)Al or Zn(O)Al. The most essential disordering of the LDH crystalline structure is observed at 723–773 K. For this reason, materials calcined at 773 K were used to study the structural reconstruction

Hydration is the driving force of the structural reconstruction of calcined LDHs [5]. This process was studied by the method of adsorption-desorption of water vapor. As expected, it is fundamentally different from physical adsorption. Water absorption is observed even at moderate humidity (less than 40%) (Fig. 4). In the Mg–Al LDHs, the amount of sorbed water grows with increasing M²⁺/Al³⁺ atomic ratio, whereas for Zn-containing materials, the opposite tendency is observed. The sample mass does not recover to the initial value upon water desorption (Fig. 4), i.e., the hydration is irreversible. The data obtained are consistent with the results of thermogravimetric analysis [5, 18] and show that the amount of water bound with calcined LDHs depends on the origin and concentration of a doubly charged cation. The Zn–Al samples possess lower hydrophilicity.

According to X-ray diffraction analysis, the basal reflections, typical of hydroxycalcite, recover after rehydration of these materials (Fig. 5). Except in the case of the Mg₅Al(R) sample, the obtained reflections are stronger and narrower than those for unheated LDHs. This result, also obtained by Prinetto *et al.* [4], can be accounted for by the increased crystallinity and (or) a more ordered orientation of LDH(R) crystallites. In the case of Mg₅Al(R), in which the Mg²⁺ concentration is the highest, the lower reflection intensities indicate a lower degree of crystallinity and, probably, the presence of the oxide phase, which could not be transformed into LDH completely.

For Mg–Al(R) samples, the structural parameter a increases only slightly, compared with uncalcined LDHs (Table 2). In this case, the relation between the parameter a and the Mg²⁺/Al³⁺ ratio is virtually similar to that for the starting materials. For Zn–Al(R) LDHs, the effect of the Zn²⁺/Al³⁺ ratio on a is less pronounced. This may indicate that part of Zn²⁺ cations are not incorporated in brucite-like layers in reconstruction. For Zn–Al(R), the ratio Zn²⁺/Al³⁺ approaches two, irrespective of the Zn²⁺ content in the

starting LDHs [12]. The validity of this conclusion can be confirmed by the similarity of the average a values for Zn–Al(R) and Zn₂Al samples (Table 2). The increase in the Zn²⁺/Al³⁺ ratio differently affects the size of LDH(R) crystallites along the a axis. It decreases for Mg–Al(R) and grows somewhat for Zn–Al(R) (Table 2). This indicates that the morphologies of the reconstructed and starting LDHs are different and are affected by the type of a doubly charged cation.

The ²⁷Al NMR spectra of the reconstructed Mg–Al and Zn–Al LDHs show only a single resonance at 7.8–8.0 ppm, attributable to octahedrally coordinated Al³⁺. The parameters of this resonance, W and $W_{0.1}$ (FWHM and width at one tenth of maximum, respectively), are virtually similar to those of unheated LDHs. For Zn–Al(R) LDHs, the Al^{3+(oct)} resonance is narrower and stronger than that for uncalcined materials. Apparently, in this case, reconstruction facilitates the ordering of the octahedral environment of Al³⁺ cations. It is not improbable that this results from the formation of the Al(OH)₃ phase characterized by the most ordered environment of Al³⁺ cations.

As in the case of unheated LDHs, the IR spectra of reconstructed materials contain a strong absorption band at 3650–3500 cm⁻¹, related to OH vibrations of the brucite-like layer [15, 18, 19]. As also in the case of the starting LDHs, the band peak shifts with growing M²⁺/Al³⁺ ratio.

The FWHM, $I_{1/2}$, of the band in question yields information about the uniformity of the cation distribution in the brucite-like layer of LDHs [18, 19]. The additional absorption bands at around 3700 cm⁻¹ indicate the presence of an oxide (hydroxide) impurity. A comparison of the starting and reconstructed LDHs shows that for Mg–Al(R) the $I_{1/2}$ parameter decreases considerably with increasing Mg²⁺/Al³⁺ atomic ratio (Fig. 6a). Hence follows that reconstruction leads to a more uniform distribution of Mg²⁺ and Al³⁺ ions inside the brucite-like layer. At the same time, the IR spectra of these samples contain a shoulder at 3700 cm⁻¹, whose intensity grows with increasing Mg²⁺ content. Consequently, a part of these cations are not incorporated into brucite-like layers in the course of reconstruction, but form the Mg(OH)₂ phase instead. For this reason, Mg–Al(R) LDHs can be regarded as hydrotalcite-like materials with highly ordered structure containing an admixture of brucite.

For Zn–Al(R) samples, raising the Zn²⁺/Al³⁺ ratio leads to a pronounced increase in the $I_{1/2}$ parameter (Fig. 6b). This indicates the less ordered distribution of Zn²⁺ and Al³⁺ structural cations in the brucite-like layer of reconstructed materials. We cannot ex-

Table 2. Structural parameter a and crystallite size ε of reconstructed LDHs

Sample	a	ε
	nm	
Mg ₂ Al(R)	0.3046	34.6
Mg ₃ Al(R)	0.3063	22.7
Mg ₅ Al(R)	0.3088	18.4
Zn ₂ Al(R)	0.3069	21.6
Zn ₃ Al(R)	0.3072	28.9
Zn ₅ Al(R)	0.3075	29.7

clude that part of them form single phases [Zn(OH)₂, Al(OH)₃, or oxides], as also indicated by the NMR data.

In the wave number range 1400–200 cm⁻¹, the LDHs(R) IR spectra contain a strong absorption band near 1360 cm⁻¹, which can be attributed to bending vibrations of interlayer OH⁻ ions. Weakly resolved shoulders due to ν_1 and ν_2 vibrations of CO₃²⁻ are absent or shifted owing to the replacement of this ion by the hydroxide ion. For the Zn–Al (R) LDHs, the shift to higher wave numbers was observed for the 765–760 cm⁻¹ absorption bands (Zn–Al–O vibrations). This can be accounted for by a change in the Zn²⁺/Al³⁺ ratio in the brucite-like layer. Owing to the exchange

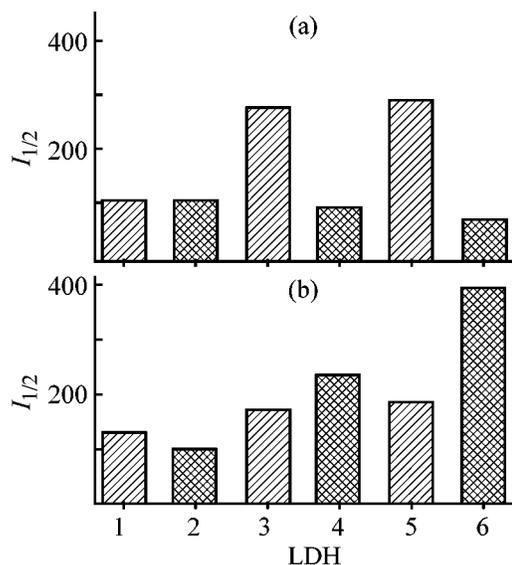


Fig. 6. The FWHM $I_{1/2}$ of the IR band related to OH vibrations (3650–3500 cm⁻¹) in a brucite-like layer for starting and reconstructed LDHs. (a) (1) Mg₂Al, (2) Mg₂Al(R), (3) Mg₃Al; (4) Mg₃Al(R), (5) Mg₅Al, and (6) Mg₅Al(R). (b) (1) Zn₂Al, (2) Zn₂Al(R), (3) Zn₃Al, (4) Zn₃Al(R), (5) Zn₅Al, and (6) Zn₅Al(R).

of CO_3^{2-} ions for OH^- ions, the intensities of the 688–620 cm^{-1} bands also change as compared with the starting LDHs. The IR spectra of LDH(R) show absorption bands characteristic of brucite layer vibrations at 580–560 cm^{-1} (M–O and M–O–M bonds), which indicates at least a partial reconstruction of the starting hydroxalite structure.

CONCLUSIONS

(1) Reconstruction of calcined double layered hydroxides by hydration is a complex process resulting in a significant transformation of their structural properties, compared with the starting materials.

(2) The type of doubly charged cation and the $\text{M}^{2+}/\text{Al}^{3+}$ atomic ratio exert the strongest influence on the extent of reconstruction of layered double hydroxides. The Mg–Al materials possess higher structural reversibility than their Zn–Al analogues.

(3) Full reconstruction of layered microstructure of the Mg–Al and Zn–Al double hydroxides is possible at calcination temperatures not exceeding 723 and 573–623 K, respectively.

(4) An analysis of the IR spectra of layered double hydroxides in the region of OH vibrations of the brucite-like layer (3600–3500 cm^{-1}) yields the most comprehensive information about the uniformity of distribution of the structural cations.

ACKNOWLEDGMENTS

The work was supported by the Ministry of Science and Education of the Ukraine (grant no. 0198 U 001 177), Committee of Research of Poland (KBN; grant no. 3 TO9A 04714), and NWO of the Netherlands (Spinoza grant).

REFERENCES

- Miyata, S., *Clays Clay Miner.*, 1983, vol. 31, pp. 305–311.
- Kopka, H., Beneke, K., and Lagaly, G., *J. Coll. Interface Sci.*, 1988, vol. 123, pp. 427–436.
- Rives, V., and Ulibarri, M.A., *Coord. Chem. Rev.*, 1999, vol. 181, pp. 61–120.
- Prinetto, F., Tichit, D., Teissier, R., and Coq, B., *Catal. Today*, 2000, vol. 55, pp. 103–116.
- Cavani, F., Trifiro, F., and Vaccari, A., *Catal. Today*, 1991, vol. 11, pp. 173–301.
- Choudary, B.M., Bhuma, V., and Narender, N., *Indian J. Chem.*, 1997, vol. 36B, pp. 278–280.
- Sychev, M., Prihod'ko, R., Erdmann K., *et al.*, *Appl. Clay Sci.*, 2001, vol. 18, no. 1–2, pp. 103–110.
- Sanchez V.J., Figueras, F., Gravelle, M., *et al.*, *J. Catal.*, 2000, vol. 189, pp. 370–381.
- Reihle, W.T., *CHEMTECH.*, 1986, vol. 1, pp. 58–63.
- Kelkar, C.P., and Schutz, A.A., *Microporous Mater.*, 1997, vol. 10, pp. 163–172.
- Chen, Y.Z., Hwang, C.M., and Liaw C.W., *Appl. Catal. A: Gen.*, 1998, vol. 169, pp. 207–214.
- Kooli, F., Depege, C., Ennaqadi, A., *et al.*, *Clays Clay Miner.*, 1997, vol. 45, pp. 92–98.
- Velu, S., and Swamy, C.S., *Appl. Catal. A: Gen.*, 1994, vol. 119, pp. 241–252.
- Aramendia, M.A., Aviles, Y., Benitez, J.A., *et al.*, *Microporous Mesoporous Mater.*, 1999, vol. 29, pp. 319–328.
- Watanabe, Y., and Tatsumi, T., *Microporous Mesoporous Mater.*, 1998, vol. 22, pp. 399–407.
- Di Cosimo, J.I., Diez, V.K., Xu, M., *et al.*, *J. Catal.*, 1998, vol. 178, pp. 499–510.
- Hudson, M.J., Carlino, S., and Apperley, D.C., *J. Mater. Chem.*, 1995, vol. 5, pp. 323–329.
- Narayanan, S., and Krishna, K., *Appl. Catal. A: Gen.*, 1998, vol. 174, pp. 221–229.
- Del Arco, M., Rives, V., and Trujillano, R., *Stud. Surf. Sci. Catal.*, 1994, vol. 87, pp. 507–515.
- Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 25th ed., New York: Wiley & Sons, 1997, pp. 132–138.
- MacKenzie, K.J.D., Meinhold, R.H., Sherriff, B.L., and Xu, Z., *J. Mater. Chem.*, 1993, vol. 3, no. 12, pp. 1263–1269.
- Kloprogge, J.T., and Frost, R.L., *Phys. Chem. Chem. Phys.*, 1999, vol. 1, pp. 1641–1647.
- Baird, T., Campbell, K.C., Holliman, P.J., *et al.*, *J. Chem. Soc. Faraday Trans.*, 1995, vol. 91, no. 18, pp. 3219–3230.
- Rao, K.K., Gravelle, M., Sanchez V.J., and Figueras, F., *J. Catal.*, 1998, vol. 173, pp. 115–121.
- Soled, S., Levin, D., Miseo, S., and Ying, J., *Stud. Surf. Sci. Catal.*, 1998, vol. 118, pp. 359–367.