



Structure of oxides prepared by decomposition of layered double Mg–Al and Ni–Al hydroxides



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ABSTRACTS

Thermal decomposition of Mg–Al and Ni–Al layered double hydroxides LDH at temperatures lower than 800 °C leads to the formation of oxides with different structures. Mg–Al oxide has a very defective structure and consists of octahedral layers as in periclase MgO and mixed octahedral–tetrahedral layers as in spinel MgAl₂O₄. Mixed Ni–Al oxide has a sandwich-like structure, consisting of a core with Al-doped NiO-like structure and some surface layers with spinel NiAl₂O₄ structure epitaxial connected with the core. Suggested models were verified by simulation of X-ray diffraction patterns using DIFFaX code, as well as HRTEM, IR-, UV-spectroscopies, and XPS.

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1. Introduction

Layered double hydroxides (LDH) which are also known as anionic clays are a group of materials having hydroxalite-like structure and common formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} [A^{n-}]_{x/n} \cdot yH_2O$, where M^{2+} and M^{3+} are bivalent and trivalent cations, A^{n-} are interlayer anions. Sequence of brucite-like layers corresponds to the three-layer rhombohedral 3R₁ polytype (...AC=CB=BA=AC...). Each layer consists of two layers of hydroxyl anions that are close-packed relative to each other and create interstitial octahedral holes which are occupied by M^{2+} and M^{3+} cations. Trivalent ions create positive charge that is compensated by interlayer anions A^{n-} . Cationic and anionic composition of LDH can be modified. The traditional method of synthesis is the coprecipitation from appropriate metal salts. LDH can be formed in the range $0.20 < x < 0.33$, where $x = M^{3+} / (M^{3+} + M^{2+})$ [1] that corresponds to $M^{2+} / M^{3+} = 2-4$.

Thermal decomposition of LDH at the temperatures of 350–700 °C leads to the formation of mixed oxides. Some of them are capable of recovering the hydroxalite structure upon contact with water. In the literature this property has been referred to as the “memory effect” [1]. “Memory effect” is widely used in different applications for intercalation of anions with various natures and sizes into the interlayer spaces. However, there is no single answer on the question: “why the “memory effect” does not work for all known cation compositions?”

In our previous work the “memory effect” has been studied for carbonate-based Mg–Al and Ni–Al LDHs. It was shown that the degree of layered structure recovery for Mg–Al LDH depends on Mg²⁺ content [2]. Substitution of Mg²⁺ by Ni²⁺ leads to the loss of “memory effect”. The Ni–Al oxide remains after contact with water and additional bayerite [3] or boehmite phases [4] are formed depending on hydration conditions. Partial Ni–Al LDH reconstruction is possible only at hydrothermal conditions or increased pressure [4,5]. Besides the nature and quantity of cations, the calcination temperature also influences the degree of reconstruction. For Mg–Al LDH the temperature range 450–600 °C is mostly used for hydroxalite reconstruction [6,7].

Let us consider some different opinions about Mg–Al and Ni–Al oxides structure represented in the literature. XRD pattern of Mg–Al oxide

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calcined at 450–700 °C contains peaks of periclase-like phase with smaller interplanar spacings compared to MgO and broad additional peak with maximum corresponding to interplanar distance in the range of 2.53–2.56 Å. In most of the works description of the oxide structure is nothing more than either MgO (periclase, NaCl structure type, space group $Fm\bar{3}m$) or periclase-like structure modified by Al^{3+} [8,9]. For example, with use of Rietveld refinement authors [10] determined that the structure is periclase-like with substitution of Mg^{2+} by Al^{3+} ions. The authors related the low values of goodness of fit to poor crystallinity. In [11] with use of EXAFS it was supposed that oxide is the solid solution $Mg_{1-x}Al_{2x/3}\square_{x/3}O$, where Mg^{2+} ions are in octahedrons (as in periclase structure) and Al^{3+} ones are in tetrahedrons. Both models contain cation vacancies for charge balance. Model containing excess oxygen atoms in the interstitial positions $Mg_{1-x}Al_xO_{1+x/2}$ has been suggested in [12]. However the authors [12] did not exclude the model with cationic vacancies $Mg_{(1-x)/(2+x)}Al_{2x/(2+x)}\square_{x/(2+x)}O$ as in [10]. Besides the single phase composition of calcination products there were suggestions that Mg - Al ($Mg:Al=3:1$, $T=500$ °C) LDH is decomposed on MgO and amorphous Al_2O_3 [13], but the authors have not provided the detailed analysis of XRD patterns.

The main divergence of opinion concerns the broad non-periclase peak with interplanar distance $d=2.53-2.56$ Å. This peak was related to the presence of a residual hydrotalcite phase [14] or it was considered as the 311 diffraction peak of $MgAl_2O_4$ [15] despite this peak corresponding to interplanar spacing $d=2.437$ Å. It was suggested that enlarged spacing is related to the inversion of Mg - Al spinel. The first attempt to assign all peaks including a broad additional one to the single phase was made in [4]. The authors suggested that Mg - Al oxide has a spinel-like structure and performed Rietveld refinement in the $Fd\bar{3}m$ space group. The same model was considered for Mg - Al oxide by authors [16] using neutron diffraction experiment, but they did not find Al^{3+} ions in tetrahedral positions. It is significant that many authors registered tetrahedral coordination of Al^{3+} ions by ^{27}Al NMR. Johnsen et al. [17] suggested a new model for Mg - Al oxide calcinated at 890 °C. By means of DIFFaX+ simulation and refinement code they demonstrated that cations are distributed over octahedral and tetrahedral positions determined by cubic close packing of oxygen in such a way that two types of layers can be distinguished in the [111] direction. One of them is periclase-like where only octahedral sites are occupied. The second layer is spinel-like containing octahedral and tetrahedral coordinated cations.

As for Ni - Al oxide, to our knowledge for the first time a model describing its structure was suggested in [18] where Ni - Al oxide was considered as solid solution of Al_2O_3 in NiO . The authors [16] considered some different models: (1) NiO (bunsenite, NaCl structure type, $Fm\bar{3}m$ space group); (2) biphasic model consisting of NiO and $NiAl_2O_4$; (3) hexagonal distorted NiO and (4) single phase model with spinel-like $NiAl_2O_4$ structure ($Fd\bar{3}m$ space group). The authors performed the Rietveld refinement for all models and the best correspondence was for model (4) and refinement showed the presence of vacancies in 16d sites along with full filling of 16c sites by Ni^{2+} and partial filling of 8a sites by Al^{3+} ions. In [19] calcined Ni - Al LDH was considered as composed of NiO ; Al_2O_3 doped by Ni^{2+} ions and spinel-like phase. The latter was examined as playing the main role in oxide thermostability and represented as shell of the NiO particles or playing the role of the substrate.

Since there are many different opinions concerning the structure of the oxides prepared by the thermal decomposition of the Mg - Al and Ni - Al LDH at moderate temperatures, we made our own investigation that was supported mainly by X-ray diffraction (XRD) using Rietveld refinement and DIFFaX simulation of XRD patterns based on models for one-dimensionally (1D) disordered crystals. Some methods, such as HRTEM, XPS, IR- and UV- spectroscopies, were used for model confirmation. Two different structural models proposed for the Mg - Al and Ni - Al oxides allow us to explain different ability for LDH reconstruction.

2. Experimental

2.1. Samples and treatments

Synthesis of Mg - Al and Ni - Al LDHs with various mole fractions of M^{2+} was performed by means of coprecipitation of double hydroxides from nitrate solutions of Mg^{2+} , Ni^{2+} and Al^{3+} [2]. Total concentration of metals was 3 mol L^{-1} . The prepared solutions were added dropwise to a solution of Na_2CO_3 (1 mol L^{-1}) at vigorous stirring. During the synthesis at 60 °C the pH values were maintained constant, optimal for precipitation of the corresponding double hydroxides (pH=10 for Mg - Al LDH, pH=9 for Ni - Al LDH) by adding NaOH (1 mol L^{-1}). After the addition of the entire volume of the solutions of nitrates, the suspension was stirred at 60 °C for 1 h and then aged for 18 h at the same temperature. The resulting precipitates were washed with distilled water up to neutral value pH of scourage, filtered, and dried for 16 h at 80 °C. Synthesized LDH contained carbonate interlayer anions.

Oxide products were obtained after calcination of Mg - Al and Ni - Al LDH at 600 °C for 2 h in air environment. Hydration of oxides was performed in distilled water for 2 h in air environment at room temperature with subsequent drying at 80 °C.

2.2. Characterization

Concentrations of Mg^{2+} , Ni^{2+} and Al^{3+} ions in the solutions and in the solid samples were determined by atomic absorption spectroscopy (AAS) with inductively coupled plasma using Varian 710-ES spectrometer. X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer ($CuK\alpha$ radiation, $\lambda=1.5418$ Å) by scanning with step of 0.05° and accumulation time of 5 s/step. Lattice constants were refined by least-squares method employed in POLYCRYSTALL [20] and TOPAS 3.0 (Bruker) with use of the internal standard Si SRM 640d. Rietveld refinement was performed using TOPAS 3.0 software. Simulation of XRD patterns was carried out using DIFFaX [21] and Defect [22] programs. TG-DTG-DTA studies were carried out using a Netzsch STA-449C Jupiter system. Measurements were performed in Al_2O_3 crucibles under an argon atmosphere at a heating rate of 10°/min. High resolution transmission electron microscopy (HRTEM) studies were carried out in a JEOL JEM 2010 operated at 200 kV. Energy dispersive X-ray (EDX) analysis was performed on EDAX spectrometer using Si/Li-EDX detector. X-ray photoelectron spectrums (XPS) were recorded on a SPECS XR-50 X-ray photoelectron spectrometer using $AlK\alpha$ radiation ($h\nu=1486.61$ eV). IR spectrums were recorded using a NICOLET 5700 FTIR spectrometer (400–4000 cm^{-1} , resolution 4 cm^{-1} , KBr pellet). Diffuse reflectance UV-vis absorption spectra were obtained using a Shimadzu ISR-240A UV-2501 spectrophotometer (190–900 nm, step 1 nm).

3. Results and discussion

3.1. Thermal decomposition of LDH

Thermal decomposition of carbonate consisting LDH is commonly divided into 4 stages: (1) removal of physically adsorbed water; (2) removal of interlayer water; (3) dehydroxilation of brucite-like layers; and (4) decarbonation of interlayers [23]. Temperatures of dehydroxilation and decarbonation as well as the rate of thermal decomposition depend on the mole fraction of M^{2+} .

From the weight loss on the second stage the amount of interlayer water y in $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot yH_2O$ was calculated. Thus, for Mg - Al LDH with Mg^{2+} mole fraction 0.67 the interlayer water content $y=0.57$ and it has lower $y=0.39$ at

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