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Reconstitution effect of Mg/Ni/Al layered double hydroxide

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ABSTRACT

Layered double hydroxide (LDH) having a different cation (Mg, Ni, Al) composition was successfully synthesized by the low supersaturation method. The sample was thermally decomposed and reconstituted in water and nitrate media at different temperatures. X-ray powder diffraction and X-ray fluorescence were used to investigate the differences between the obtained layered materials and those after the reconstitution process. To the best of our knowledge, there are only few studies where the influence of the third metal cation on the reconstitution process was analyzed.

1. Introduction

Layered double hydroxides (LDH) or hydrotalcite (HT) type materials are widely applied in catalysis, ion-exchange, adsorption and pharmaceutics [1]. The general formula for the LDH materials is $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{m-}_{x/m}]\cdot nH_2O$, where M are bivalent or trivalent cations with similar radii, and A is an interlayer anion, usually CO_3^{2-}. The nature of the layer cations can be changed using a wide range of main group (e.g., Mg, Al) or transition metal (e.g., V, Cr, Mn, Fe, Co, and Ni) cations [2]. All these materials having various compositions share typical common characteristics: layered structure and the formation of mixed-metal oxides. When a LDH is calcined, it progressively loses physico-sorbed water, then interlamellar water molecules, and finally water from the dehydroxylation of the layers, along with the charge compensating anions, leading to the collapse of the layered structure. The temperature at which these phenomena occur depends on the chemical composition. However, already above 400 °C a mixed-metal oxide usually is forming [3,4]. The calcination sometimes could be used as an intermediate treatment to functionalize the clay by intercalation of anions in the interlayer. Such functionalization makes the memory effect especially useful. The memory effect is a unique property by which the oxide is retrotopotactically transformed into the original hydrotalcite structure in aqueous solutions or humid air atmosphere [5]. This reconstitution effect has been applied for the removal of anions [6] and to improve the catalytic properties of the specimens [7]. Detailed reconstitution effect was investigated only for classical Mg/Al systems [8], although other compositions of LDH exhibit the property to reconstruct, but not always recover the original structure [9,10]. The aim of the present work was to study the influence of a reconstitution medium for the memory effect of the ternary Mg/Ni/Al system. The important task was to investigate the change of the cationic composition of LDH when in reconstitution media the magnesium cation is used.

2. Experimental

LDH was prepared by the coprecipitation under a low supersaturation method from the solution of the appropriate metal nitrates with a molar ratio of (Mg + Ni):Al = 3:1 and a solution of $NaHCO_3$: NaOH with a molar ratio of 1:2. During the preparation the 15% of the 1 M $Mg(NO_3)_2$ solution was replaced by a 1 M $Ni(NO_3)_2$ solution. The solution of metal nitrates was added to the solution of $NaHCO_3$ + NaOH (pH ≈ 12) very slowly and under vigorous stirring. After mixing the obtained gel was aged at 353 K for 6 h. The slurry was filtered and washed with distilled water and the resulting powder was indicated as Mg/Ni/Al. The mixed-metal oxide obtained by heating at 923 K for 3 h was labeled as $Mg/Ni/Al_{cal}$. The regeneration of the mixed-metal oxide was carried out at room temperature (293 K) for 6 h with continuous stirring in deionized water (the sample denoted as $Mg/Ni/Al_{W20}$). The regeneration in 1 M $Mg(NO_3)_2$ solution performed under the same conditions and sample was denoted as $Mg/Ni/Al_{N20}$. The higher temperature of 353 K was used to investigate the influence of the temperature on the regeneration of LDH ceramics. The experiment was performed in the same solutions for 6 h. The sample reconstituted in water denoted as $Mg/Ni/Al_{W80}$ and in the solution of $Mg(NO_3)_2$ — $Mg/Ni/Al_{N80}$. Schematic presentation of synthesis and post-synthesis modifications of LDH samples is shown in Fig. 1.

The influence of the reconstitution conditions on the specific surface area of the formed mixed-metal oxide was investigated after repeated thermal treatment at 923 K. The X-ray powder diffraction (XRD) patterns of the synthesized, calcined and regenerated LDH samples were recorded with a conventional Bragg–Brentano

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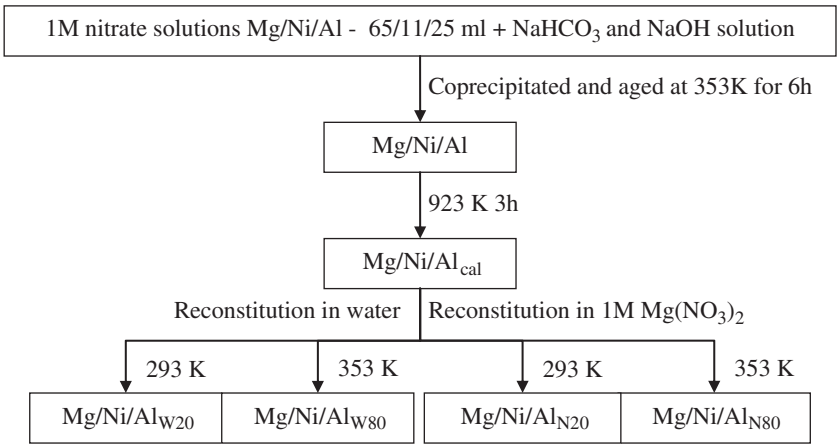

Fig. 1. Chart of synthesis and post-synthesis modifications of LDH samples.

geometry (θ–2θ scans) on a DRON-6 automated diffractometer, equipped with a secondary graphite monochromator. Cu K_α radiation (λ = 1.541838 Å) was used as a primary beam. The patterns were recorded from 5 to 70° 2θ in steps of 0.02° 2θ, with a measuring time of 0.5 s per step. Silicon was used as a reference sample. The average crystallite size of the layered double hydroxides was calculated by the X-Fit program. Thermogravimetric (TG) analysis of Mg/Ni/Al samples was carried out with a Netzsch instrument "STA 409 PC Luxx" using a heating rate of 10 K/min in air atmosphere. The LDH samples were also analyzed with X-ray fluorescence (XRF) technique on a Spectro Analytical Instruments GmbH&Co.KG. The surface morphology of the synthesized and regenerated at room temperature samples was a studied by scanning electron microscope (SEM) EVO 50 EP, Carl Zeiss SMT AG, Germany. The surface area was estimated using the Brunauer–Emmet–Teller (BET) equation. Prior to analysis the calcined samples were outgassed at 673 K overnight. The measurements were carried out on a Micromeritics ASAP 2010 instrument by nitrogen adsorption at 77 K.

3. Results and discussion

The characteristic hydrotalcite type structure of the synthesized sample was confirmed by the XRD analysis data (Fig. 2) [2]. It was previously shown that Mg/Al hydrotalcite decomposes in three steps. Firstly, evaporation of adsorbed water occurs. Secondly, the elimination of the interlayer structural water (up to 523 K) proceeds. Finally, dehydroxylation and decarbonation (up to 873 K) take place [11]. In this study, TG analysis was used to investigate thermal stability of the Mg/Ni/Al sample (see Fig. 3). The mass loss due to the removal of water persists till 520 K and two minima at 360 K and 493 K on the differential thermogravimetric (DTG) curve are seen. Evidently, our synthesized sample with nickel Mg/Ni/Al shows a very similar thermal behaviour as Mg/Al hydrotalcite. Therefore we can conclude that this low content of transition metal (Ni) has a negligible effect on the thermal stability of LDH. The temperature of 923 K was chosen for full decomposition of the layered structure.

The calcined Mg/Ni/Al samples treated in water or magnesium nitrate solution at room and 353 K temperatures show a reconstitution of the layered double hydroxide, as could be easily determined from their XRD patterns (see Fig. 2). The sharp reflections of the (003) and (006) planes at low 2θ values (11–23 °) and broad asymmetric reflections at higher 2θ values (34–66 °) can be observed in the XRD patterns of synthesized and reconstituted LDH. The lattice parameters a and c cell corresponding to the rhombohedral structure were determined from the position of the (003), (006) and (110) diffraction lines, assuming a 3R stacking of the layers (Table 1).

The published interlayer distance value of the carbonate containing Mg/Al LDH is 7.8 Å [3]. In our study, a small increase of the basal spacing is seen in the sample when nickel is introduced to the HT structure. The strongest influence on the c parameter can be seen after reconstitution in the magnesium nitrate solution. Besides, the d_{003} higher than 8.0 Å was determined, and this corresponds to the basal spacing value of the nitrate containing LDH [12]. It should be noted, that the mixed-metal oxide phase is seen in the XRD patterns of Mg/

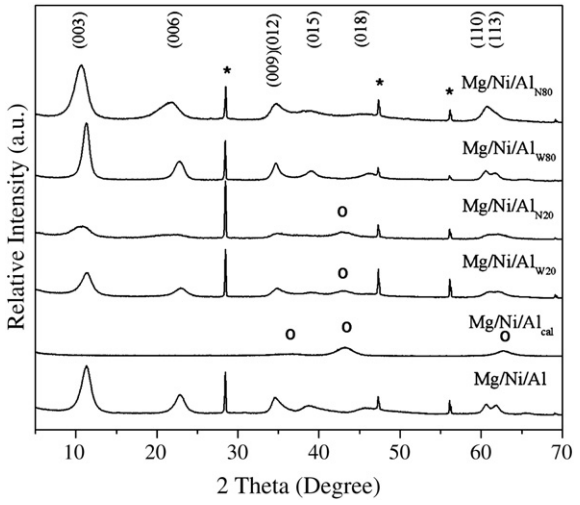

Fig. 2. XRD patterns of synthesized, decomposed and reconstituted LDH. The side phases are marked: o — MgO and * — Si used as reference.

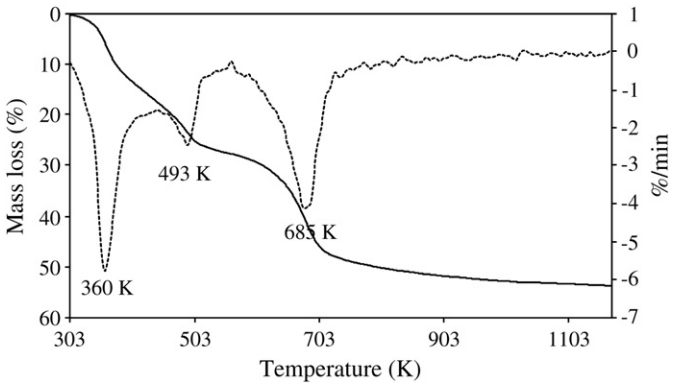

Fig. 3. Thermogravimetric (solid line) and differential thermogravimetric (dashed line) curves of the Mg/Ni/Al sample.