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MgCoAl and NiCoAl LDHs synthesized by the hydrothermal urea hydrolysis method: Structural characterization and thermal decomposition

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ABSTRACT

Layered double hydroxides (LDHs) with Mg/Co/Al and Ni/Co/Al were synthesized for the first time by the urea hydrolysis method. The experimental conditions promoted aluminum rich and crystalline materials. The formation of LDHs was investigated by powder X-ray diffraction (XRD), chemical analysis, solid state nuclear magnetic resonance with magic angle spinning (^{27}Al-MAS-NMR), simultaneous thermogravimetric/differential thermal analysis (TGA/DTA), FTIR spectroscopy, scanning electron microscopy (SEM), and N_2 adsorption–desorption experiments. A single phase corresponding to LDH could be obtained in all the investigated compositions. Thermal calcination of these LDHs at 500 °C resulted in the formation of solid solutions in which Al^{3+} was dissolved. All the calcined materials have rock-salt like structures and high surface areas.

1. Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are inorganic materials extensively studied as catalysts, precursors and supports of catalysts, anionic exchangers, sorbents, etc. [1,2]. The LDHs are represented by the general formula $[M^{2+}{}_{(1-x)}M^{3+}{}_{x}(OH)_2]^{x+}(A_{x/n})^{n-}\cdot nH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively, and $A^{n}-$ is a charge compensation anion. Their structure consists of brucite-type layers, where the substitution of divalent with trivalent cations results into a net positive charge, compensated by interlayer anions. There is also crystallization of water into the interlayer region [3].

Coprecipitation is the usual method utilized for synthesis of hydrotalcite-like compounds [3,4]. In this case, precipitation of the hydroxide crystallites starts immediately once the first drops of the basic solution are added to the mixed solution of the cations (or vice versa), and thus nucleation and particle growth overlap, resulting in a low crystallinity and broad distribution of particle size [5]. On the other hand, urea hydrolysis method is used to promote homogeneous precipitation and morphological control of crystallite size, leading to a substantial improvement of product crystallinity [1,6]. The slow decomposition of urea produces an alkaline pH, which is a prerequisite for LDH precipitation, besides generating the lamellar hydroxyls and the interlayer carbonate anions.

Cobalt-containing LDHs have been used for several catalytic applications such as hydroxylation of phenol, Fischer–Trops catalysts and steam reform of methanol [7,8]. Additionally, aluminum and cobalt based materials find their applications in catalysis mainly in hydrocracking processes [9]. For this application, a good dispersion of the cations is needed and can be achieved introducing magnesium in the catalyst composition [10]. Likewise, nickel-containing LDHs are used as catalyst precursors in hydrogenation reactions [11]. These materials are not very commonly found in nature, but they are easily synthesized [4].

Mixed oxides containing high surface area find a number of industrial applications (i.e, in catalysis, adsorption, sensor, and magnetic technologies). These powders usually occur by the

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thermal decomposition of mixed hydroxides, hydroxy carbonates or hydroxy nitrates, although frequently polyphasic materials are obtained [12]. However, an alternative is the thermal decomposition of LDHs, which gives rise at materials with chemical homogeneity and good thermal stability [13–15].

In this work, we report on the synthesis by urea hydrolysis method and thermal decomposition of layered double hydroxides containing Mg^{2+}, Co^{2+} and Al^{3+} or Ni^{2+}, Co^{2+} and Al^{3+} as layer cations. The LDHs were used as precursors of mixed oxides. The precursors and the mixed oxides have been characterized by different physical–chemical methods, such as, powder X-ray diffraction (XRD), solid state nuclear magnetic resonance with magic angle spinning (^{27}Al-MAS-NMR), Fourier-transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), differential thermal analysis (DTA), scanning electron microscopy (SEM), and N_2 adsorption for the determination of the surface area.

2. Experimental

2.1. LDHs preparation

MgCoAl and NiCoAl LDHs with molar ratios M^{2+}/M^{3+} of 2 ($x = 1/3$) were prepared by urea hydrolysis method similarly as described in the literature [1]. The general procedure consisted in preparing a solution with the amounts of metal salts required to obtain a 0.625 mol L^{-1} total concentration in 100 mL of de-ionized water. This solution was added to 300 mL of an aqueous solution containing urea (6.25 mol L^{-1}). The total volume (400 mL) containing the required amounts of reactants ($Co(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_2 \cdot 9H_2O$, urea and $Mg(NO_3)_2 \cdot 6H_2O$ or $Ni(NO3)_2 \cdot 6H_2O$) was placed in a Teflon-lined autoclave under autogenous pressure at 120 °C over 24 h. After cooling, the resultant solids were filtered and washed with distilled water to obtain a neutral pH, and finally, the solids were dried at 120 °C over 20 h. The samples were designated as MgCo3, MgCo5, NiCo3 and NiCo5, where the numbers indicate the mass percentage of cobalt related to other M^{2+} cation. All chemicals were obtained from Vetec (Brazil), and were used without any purification. In all the procedures, the urea was added to reach a urea/metal ions molar ratio of 10. Calcination of all the samples was carried out at 500 °C for 3 h (soak time) and at a heating rate of 20 °C min^{-1} (ramp time). The calcined samples received the letter *c* in the nomenclature (e.g. the calcined MgCo3 was named MgCo3c).

2.2. Characterization

The chemical compositions of the hydrotalcite-like samples were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) after dissolution of the samples with hydrochloric and nitric acids (1:1 v) at 80 °C. Moreover, CHN analyses were performed for determination of carbon and hydrogen amounts.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) experiments were performed on Shimadzu TG-60 equipment, using 1.0 mg packed in platinum crucible, a heating rate of 10 °C min^{-1} from room temperature to 750 °C, and a dynamic nitrogen atmosphere (flow rate = 50 mL min^{-1}).

The X-ray powder diffraction experiments (XRD) were recorded for the precursors and calcined samples at room temperature using a Bruker D8 Advance instrument (Cu Kα radiation, 1.5406 Å). Typical measurement conditions were 2θ range 5–80°, step size 0.02° 2θ, and step counting time 10 s for the LDHs samples. For the calcined samples the counting time was 1 s.

The ^{27}Al-MAS-NMR spectra were made to investigate the Al coordination in precursors and calcined samples. A Bruker DRX 300 spectrometer with a nominal field of 7.05 T was used for MgCoAl samples. A rotation frequency of 10 kHz and Larmor frequency of 78 MHz were applied. For NiCoAl samples, a Bruker Advance III 400 spectrometer was used in a nominal field of 9.4 T. The measurements were made with a rotation frequency of 12 kHz and Larmor frequency of 100 MHz. For all samples a MAS probe with rotors of 4 mm was used, and a solid sample of $AlCl_3 \cdot 6H_2O$ (^{27}Al, $\delta = 0.0$ ppm) was used as reference.

Fourier-transform infrared (FTIR) spectra were recorded on a BOMEN MB-102 spectrometer using pressed KBr pellets to verify the vibrational modes present in the precursors and calcined samples.

Scanning electron micrographs (SEM) were taken with a Quanta 200 microscopy (FEI Company, Eindhoven, Netherlands). Additionally, the energy-dispersive X-ray spectroscopy (EDS) was used to determine the elemental composition (EDAX Inc., Mahwah, NJ), using an accelerating voltage of 20 kV.

Surface area and pore diameters were determined by N_2 adsorption–desorption in a Micromeritics Tristar 3000 equipment using the BET equation for surface area and BJH for pore distribution calculations. Prior to the measurements, LDH samples were dried at 150 °C for 2 h and then degassed at 200 °C under vacuum for 2 h, in order to remove physisorbed water. In the case of calcined samples, the temperatures were 250 and 300 °C, respectively.

3. Results and discussion

Elemental chemical analysis results for the LDHs samples are given in Table 1. It should be noted that the M^{2+}/Al^{3+} ratios calculated using ICP are different of starting solutions. So, while the expected values for M^{2+}/Al^{3+} ratios would be 2.0 for MgCo3 and MgCo5, values obtained are 1.30 and 1.24, respectively. This effect is expected when the synthesis are performed under high pressure and temperatures above 60 °C [16,17]. In other words, the solid is enriched in aluminum when compared with the composition of the starting nitrate solutions. Furthermore, the samples contain higher cobalt amounts than expected. The results indicate that a complete precipitation of magnesium is difficult due to the experimental conditions used such as urea/($M^{2+} + Al^{3+}$) molar ratio, high temperature and pressure [1,5]. In the case of nickel-containing LDHs, the M^{2+}/Al^{3+} ratios are close to expected, probably due to the smaller size of Ni^{2+} cations. Nevertheless, the formation of co-precipitated $Al(OH)_3$ in the samples can be ruled out due to the CO_3^{2-}/Al^{3+} molar ratios in the solids were

Table 1
Elemental chemical analysis results of the LDHs samples.

Sample	Proposed formula	C[a]	H[a]	Mg[a]	Co[a]	Al[a]	Ni[a]	M^{2+}/Al3+[b]	CO_3^{2-}/Al3+[b]
MgCo3	$[Mg_{3.06}Co_{0.14}Al_{2.46}(OH)_{11.42}](CO_3)_{1.18} \cdot 3H_2O$	3.0	3.7	15.7	1.8	14.0	–	1.30	0.48
MgCo5	$[Mg_{2.94}Co_{0.25}Al_{2.58}(OH)_{12.14}](CO_3)_{0.99} \cdot 3H_2O$	2.5	3.6	15.0	3.1	14.6	–	1.24	0.38
NiCo3	$[Ni_{3.61}Co_{0.11}Al_{1.98}(OH)_{11.86}](CO_3)_{0.76} \cdot 3H_2O$	1.5	3.5	–	1.1	8.8	34.9	1.88	0.38
NiCo5	$[Ni_{3.38}Co_{0.19}Al_{1.89}(OH)_{10.99}](CO_3)_{0.91} \cdot 3H_2O$	1.8	2.8	–	1.8	8.4	32.7	1.89	0.48

[a] Mass percentage.
[b] Molar ratio.