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Influence of the Mg^{2+} or Mn^{2+} contents on the structure of NiMnAl and CoMgAl hydrotalcite materials with high aluminum contents

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ABSTRACT

In this work, layered double hydroxides with high aluminum content (aluminum atom fractions 0.3 and 0.5, relative to total metal cations) were successfully synthesized in the systems Co—Al, Co—Mg—Al, Ni—Al and Ni—Mn—Al, using a co-precipitation method with controlled pH. Terephthalate was used as the charge compensation anion. Different characterization techniques (XRD, FTIR, ICP, AAS, TGA, CHN and EXAFS) showed that for these high-aluminum LDHs, the terephthalate ions are vertically placed within the interlayer galleries and the cations were effectively included in the layers. The unusually large limiting value for the intralayer aluminum proportion is possibly associated with the larger length and polarizability of the terephthalate anion as compared to the usual small inorganic anions (as carbonate, nitrate or hydroxyl). However, in the trimetallic samples (Co—Mg—Al and Ni—Mn—Al) a segregated aluminum phase was found for higher Mg or Mn contents. With high Mn content a manganese terephthalate phase was also observed.

1. Introduction

Layered double hydroxides (LDHs) with the hydrotalcite structure have the general formula $M_{1-x}{}^{2+}M_x{}^{3+}(OH^-)_2A_{x/n}{}^{n-}\cdot mH_2O$, and consist of brucite-like layers where a partial divalent (M^{2+})/trivalent (M^{3+}) substitution has taken place, thus providing a positive charge to the layers, which is balanced by anions (A^{n-}) located, together with water molecules, in the interlayer space. The anions can be easily replaced by ion exchange. Many ternary LDHs involving mixtures of different M^{2+} and/or M^{3+} cations can also be prepared [1].

Terephthalate LDHs are useful as catalyst precursors, as the terephthalate anion (TA) provides a larger expansion of the interlayer galleries, being effective for the incorporation of oxometalates by ion-exchange [2]. The corresponding mixed oxides may be obtained by calcining the exchanged LDHs, and they can be used as precursors for several catalysts, such as the ones used in the hydrotreating of petroleum fractions (NiMo [3], CoMo and NiW mixed-sulphides) or in propane oxidative dehydrogenation (VMg mixed-oxides [4]).

It is often said that pure LDH phases can only be formed with aluminum atom fractions in the range $0.20 < x < 0.33$. It has been argued that for $x > 0.33$, the presence of M^{3+}—O—M^{3+} linkages would be required and these are unfavorable from the point of view of charge repulsion (the so-called cation avoidance rule) [1]. In our previous work with the NiAl-TA system [5], we found that the x values within the brucite layers increase with increasing overall aluminum content up to a limiting value in the range 0.5–0.6, significantly higher than predicted by the cation avoidance rule. The proportion of a segregated aluminum tri-hydroxide phase increased continuously with increasing overall aluminum content, but only became significant for overall aluminum atom fractions equal to or higher than 0.6.

This naturally raises the question as to whether it is possible to prepare terephthalate LDHs with x values above the one predicted by the cation avoidance rule where the divalent cation is other than Ni^{2+} (Co^{2+}, Mg^{2+} and Mn^{2+} in the present case). The possibility of preparing trimetallic LDHs with high aluminum atom fraction is also interesting, from the standpoint of compositional flexibility of these materials. These systems are important from the catalytic standpoint, as catalysts containing Co, Mg and Al have been studied, for example, in the selective oxidation of styrene [6], reforming and decomposition of methane [7,8], gasification of biomass [9], partial oxidation of methane to syngas [10],

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transesterification for biodiesel production [11] and hydrodesulfurization of FCC gasoline [12]. Catalysts based on Ni, Mn and Al have been evaluated in oxidative processes (including conversion of hydrocarbons and the oxidative coupling of methane) and in reductive catalysis, as a promoter in combination with other transition metals [13], in N_2O decomposition [14] and water–gas shift reaction [15].

In attempting to tackle the preceding points, in this work we synthesized LDHs in the CoMgAl-TA and NiMnAl-TA systems, and compared them with the ones obtained in the NiAl-TA system previously reported by us [5].

The relative proportion between the divalent cations was varied from 0 to 100%, therefore bimetallic (extreme values in the range) and trimetallic (internal values in the range) materials were prepared. In all cases, overall aluminum atom fractions ≥0.5 were used and, for comparison, in the case of the CoMgAl-TA system, a series of materials with x values within the accepted range (0.3) was also prepared. The materials were characterized by powder X-ray diffraction, Fourier-transform infrared spectroscopy, elemental analysis and, in some cases, X-ray absorption spectroscopy.

2. Experimental

2.1. Preparation of the materials

Three different series of LDH materials with terephthalate as the charge compensation anion were prepared. The first and second comprised the CoMgAl-TA system, one with nominal aluminum atom fraction equals 0.3 and the other with aluminum atom fraction equals 0.5, both with respect to total metal cations (CoMgAl30 series and CoMgAl50 series, respectively). The Co atom fraction with respect to total divalent cations was varied from 0.0 to 1.0 with 0.2 steps between the values. The third one is the NiMnAl-TA system, with nominal aluminum atom fraction value equals 0.6 (NiMnAl60 series) and Ni atom fraction relative to total divalent cations varying in the same range as in the first two series. A co-precipitation method with controlled pH was used, similar to what was described by Arias et al. [5]. The samples were identified according to the following nomenclature: in the CoMgAl-TA system, the materials were named Co*Y*Mg*Z*Al*X*, where *Y*, *Z* and *X* are, respectively, the nominal molar percentages of Co, Mg and Al with respect to total metal cations. In the case of the NiMnAl-TA system, an analogous nomenclature was used, replacing Co by Ni and Mg by Mn.

The general procedure consisted in preparing a solution with the amounts of metal salts required to obtain a 0.5 mol L^{-1} total concentration in 100 cm^3 of de-ionized water. A 100 cm^3 volume of another solution was prepared containing the precipitating agent (NaOH) with 1.0 mol L^{-1} total concentration and terephthalic acid in 10% excess relative to the stoichiometric one. All amounts were calculated taking into account the theoretical formula for the LDHs: $(M_yL_{1-y})_{(1-x)}Al_x(OH)_2(C_8H_4O_4)_{x/2}\cdot nH_2O$, where M is Co or Ni and L is Mg or Mn.

Both solutions were added dropwise to 400 cm^3 of previously boiled de-ionized water, with continuous nitrogen bubbling in order to avoid the formation of the carbonate LDH, under vigorous stirring while controlling the pH in the 6.5 ± 0.3 range, in all cases. The precipitation temperature was 333 K for the CoMgAl-TA systems and 323 K for NiMnAl-TA. After completing the addition of the solutions, the temperature was kept constant for 4 h. Next, the suspension was aged for 16 h under stirring and nitrogen bubbling at room temperature. In the case of the CoMgAl30 series, however, it was necessary to keep the heating for 48 h under nitrogen in order to obtain a crystalline hydrotalcite structure, instead of the room-temperature aging.

In all the cases, the resulting solid was recovered by vacuum filtration, abundantly washed with previously boiled de-ionized water until neutral pH and finally dried in an oven at 373 K for 4 h.

2.2. Characterization

X-ray diffraction profiles were obtained in a Rigaku Ultima IV apparatus using CuKα radiation (λ = 0.15418 nm), operated at 40 kV and 20 mA. Scans were performed at 2° min^{-1} in the 3°–70° range (2θ values).

FTIR spectra were obtained in a Spectrum One Perkin Elmer instrument with the samples dispersed in ca. 1% proportion in potassium bromide and pressed as wafers. Scans were performed between 4000 and 400 cm^{-1}; 30 scans for the samples and 30 scans for background recording.

Thermogravimetric analysis (TGA) was carried-out in a TA Instruments model SDT Q600 apparatus. About 10 mg of each sample were placed on a platinum sample holder and heated from 308 to 1073 K at 10 K min^{-1} under a 30 cm^3 min^{-1} nitrogen flow.

The elemental analyses for Co, Mg and Al for the CoMgAl-TA systems were carried-out by ICP-AES (inductively coupled plasma optical emission spectroscopy) in an Arcos Spectro equipment. The samples were analyzed after calcination at 823 K. It was assumed that, after this calcination, only metal oxides remained in the samples. For the NiMnAl-TA system, the measurements for Ni, Mn and Al were carried out by atomic absorption spectroscopy (AAS) in a Thermo Scientific iCE 3000 Series equipment. For quantification of the amount of terephthalate in the LDH's, CHN elemental analyses were performed using a Perkin Elmer 2400CHN, with acetanilide as a calibration standard.

The X-ray absorption spectra at the Co K-edge were obtained at the XAFS1 line at the Laboratório Nacional de Luz Síncrotron – LNLS, Campinas, Brazil, with a storage ring operated at 1.37 GeV and 250 mA maximum current. Calibration of the beam energy was done using a cobalt metal foil. The intensities of the incident and transmitted beams were monitored using ionization chambers filled with argon, nitrogen and air. Energy scans were performed from 7610 to 8690 eV. The samples were mounted as a thin layer on filter paper and all spectra were obtained in transmission mode. The Athena program, from the IFEFFIT software package [16] was used to extract the EXAFS oscillations in k space, in terms of $k^3\chi(k)$, where $\chi(k)$ is the EXAFS function, in the k range 0–15 Å^{-1}. Simulations of the EXAFS spectra were performed in R-space using the Artemis program of the IFEFFIT software package [16] where the reported crystal structure of a MgAl carbonate LDH (ICSD-81963) was entered as starting reference for the LDH intralamellar simulation. The Mg atoms in this structure were then replaced by Co atoms. The same crystal structure was used to obtain the passive electron reduction factor $S_0{}^2$ for the Co absorber from ab initio calculation using the FEFF 8.2 code [17]. Fitting parameters are reported here as they are given by the program.

3. Results and discussion

3.1. CoMgAl-TA system

X-ray diffraction patterns for the CoMgAl30 and CoMgAl50 series are exhibited in Fig. 1. It is possible to observe the characteristic LDH peaks, corresponding to the (003), (006), (009), (0012), (012) and (110) reflections. In general, as the nominal cobalt content decreases, i.e., the nominal Mg content increases, an increase in the intensities is observed in the CoMgAl30 series. This behavior was not the same for the CoMgAl50 series, in which the intensities did not vary nearly as much as in the other series. In the CoMgAl30