Thermal stability of monometallic Co-hydrotalcite

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Abstract

Monometallic $Co_6^{2+} Co_2^{3+} (OH)_{16}^{-}(NO_3)_2^{-} \cdot nH_2O$ hydrotalcite-like compound was prepared by a careful precipitation from an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ in air atmosphere, followed by microwave irradiation. As comparison, an additional sample was prepared without microwave irradiation, employing aging in the crystallization step. Thermal evolution was studied by X-ray diffraction (XRD), FTIR, DTA/TGA and nitrogen physisorption. The microwaved sample (monometallic hydrotalcite) was stable up to 200 °C. The nonirradiated sample only showed the Co_3O_4 spinel phase.
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1. Introduction

Anionic clays or double layered hydroxides or hydrotalcite-like compounds are represented by the general formula: $[M(II)_{1-x}M(III)_x(OH)_2][A^{n-}]_{x/n} \cdot mH_2O$, where M(II) and M(III) are metal cations and A^{n-} denotes anions. Their structure consists of brucite-like layers, $Mg(OH)_2$, with a partial M(II) substitution by M(III), resulting in a net positive charge balanced by interlayer anions associated with variable amounts of water molecules [1]. The main applications of anionic clays are as catalysts, catalyst supports, flame retardants, ion exchangers and antiacids, among others [2]. In general, the conventional M(II)–M(III)–hydrotalcite decomposes through two endothermic transitions: the first one, at low temperature, corresponds to the loss of interlayer water without collapse of the structure and the second one at higher temperature is due to the loss of hydroxyl groups from the brucite-type layer and loss of the anions [3]. The early work devoted to monometallic hydrotalcite-like compounds [4,5], i.e. one transition metal used with both valences, M(II) and M(III), in the same network, was first reported by Taylor [6] in 1980. Zeng et al. in 1998 [4] synthesized $Mg^{2+}Co^{2+}Co^{3+}$ hydroxynitrates. They found that the thermal stability of hydrotalcites is proportional to the Mg content. The thermal evolution of cobalt hydroxide has also been reported [7].

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Three major stages of the decomposition of Co hydroxides were observed: from 149 to 164 °C for dehydration of interlayer water, from 185 to 197 and 219 to 222 °C for dehydroxylation of hidrotalcite and brucite-like phases, respectively.

Hence, although we synthesized using microwave irradiation the Co-MHLC (cobalt monometallic hydrotalcite-like compound) in a previous work [8], the resulting compound was not compared to the corresponding conventionally prepared hydrotalcite nor discussed in terms of the effect of microwave irradiation treatment.

2. Experimental

The samples were synthesized in a three-necked round-bottom flask equipped with magnetic stirring and a pH meter. The cobalt precursor solution (1 M) was prepared using $Co(NO_3)_2 \cdot 6H_2O$ (Baker, 99% purity). Initially, an ammoniacal solution (Baker, 0.5 M) was poured into the flask and a stream of air (40 ml/min) was continuously fed. The metallic solution was added dropwise by means of a micro-valve (clinical use) to have a flow of 20 drops/min; typically, all the Co solution reacted in 48–51 min. All samples were synthesized at room temperature and pH was monitored during the precipitation. After precipitation, one sample was irradiated (code M.W.) for 1 min in a domestic microwave oven (Philco) operating at 90 W and a frequency of 4.75 MHz. For comparison purposes, an additional sample was prepared without microwave irradiation, but was aged for 2 h (code N.I., meaning nonirradiated). After the precipitation reaction, both samples were washed with 1 l of deionized water and the solids were recovered by centrifugation. Both samples were dried in a vacuum oven at room temperature for 18 h and then treated at 100 °C in air flow for 4 h. Calcinations were carried out for 4 h at 400 °C in flowing air, using a heating rate of 10 °C/min. $Co(NO_3)_2$ was thermally decomposed under similar conditions as the prepared hydrotalcites in order to compare thermal properties.

X-ray diffraction (XRD) patterns were obtained with a Siemens D-500 diffractometer coupled to a copper anode X-ray tube. The Kα radiation was selected with a diffracted beam monochromator.

Vibrational spectra (FTIR) were obtained with a Nicolet 170sx FTIR, equipped with a Pyrex cell, using KBr pellets. Spectra were obtained at room temperature after 32 scans and with a resolution of 4 cm^{-1}. DTA and TGA analyses were performed in a Setaram-92 apparatus using a heating rate of 10°/min in air atmosphere. BET surface area, pore volume and pore size distribution were determined by adsorption/desorption isotherms with nitrogen at 77 K in an ASAP-2000 apparatus.

3. Results and discussion

As reported in our previous work [8], the cobalt monometallic hydrotalcite-like compound (Co-MHLC) was formed using microwave irradiation. In the nonirradiated sample, small crystallites of the Co_3O_4 spinel were detected. This means that microwave irradiation controls the extent of Co oxidation, favoring the Co-MHLC formation. Fig. 1 shows the X-ray diffractograms of the microwave-irradiated sample, nonirradiated sample and decomposed cobalt nitrate (II), all thermally treated at 400 °C. In all cases, only the Co_3O_4 spinel was observed; nevertheless, due to the broadness of the diffraction peaks in microwave-irradiated and nonirradiated samples, a lower crystallite size was obtained in comparison with the sharp peaks of the $Co(NO_3)_2$ sample.

Fig. 2 shows the FTIR spectra of $Co(NO_3)_2$ and microwave samples thermally treated at 100 °C. The signal corresponding to the NO_3^- appears at 1387 and 826 cm^{-1} as can be noted in $Co(NO_3)_2$ sample. A careful analysis of the FTIR spectrum of the microwave-irradiated sample shows that it presents vibration bands (3422, 1607, 1383 and 830 cm^{-1}) that correspond to hydrotalcite-like structure [7]. Nevertheless, as the peaks at 576 and 662 cm^{-1} are well defined, in contrast to that of the pure hydrotalcite, the presence of Co_3O_4 phase is confirmed [9]. This sample also showed small peaks in the region of 1050–1200 cm^{-1}, which were found in our previous work to correspond to several Co–ammonia complexes [8].

Fig. 3 presents the FTIR spectra of samples calcined at 400 °C. As can be seen, in all samples, the absorption bands at 388, 569 and 664 cm^{-1} attributed
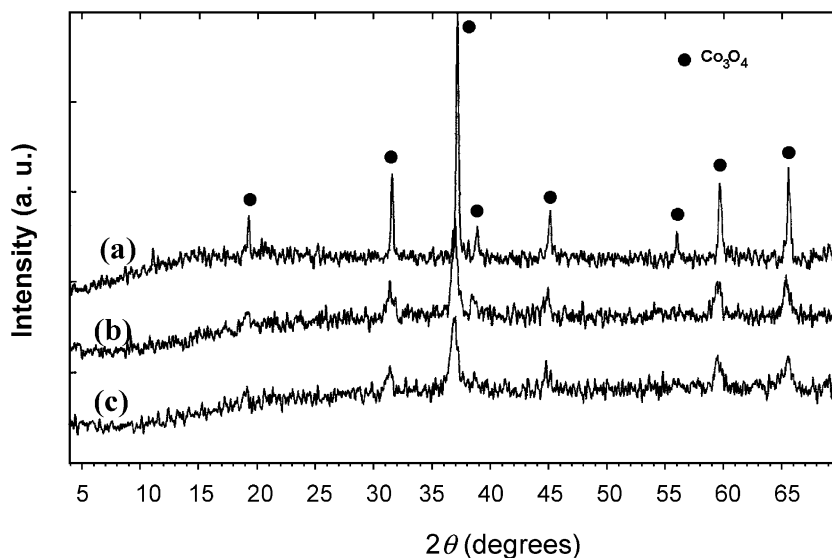
Fig. 1. X-ray diffractograms of (a) Co(NO$_3$)$_2$, (b) microwave-irradiated (M.W.) and (c) nonirradiated (N.I.) samples calcined at 400 °C.

to Co–O vibration for the Co$_3$O$_4$ spinel phase are clearly noted. The Co(NO$_3$)$_2$ precursor also presented an additional shoulder at 510 cm^{-1}, which could be assigned to another Co–O oxide type vibration [10]. In the microwave sample, it was not possible to eliminate completely all NO$_3$$^-$ and OH$^-$ (note bands at 1383 and 1618 cm^{-1}). Our results agree with those

reported by Xu and Zeng [5,7]; however, a shoulder between 800 and 835 cm^{-1} did not disappear, which can be interpreted as residual nitrate in the Co$_3$O$_4$ network.

The results of the thermogravimetric analysis of the samples are summarized in Table 1. The first weight loss (25–130 °C) was attributed to the dehydration of
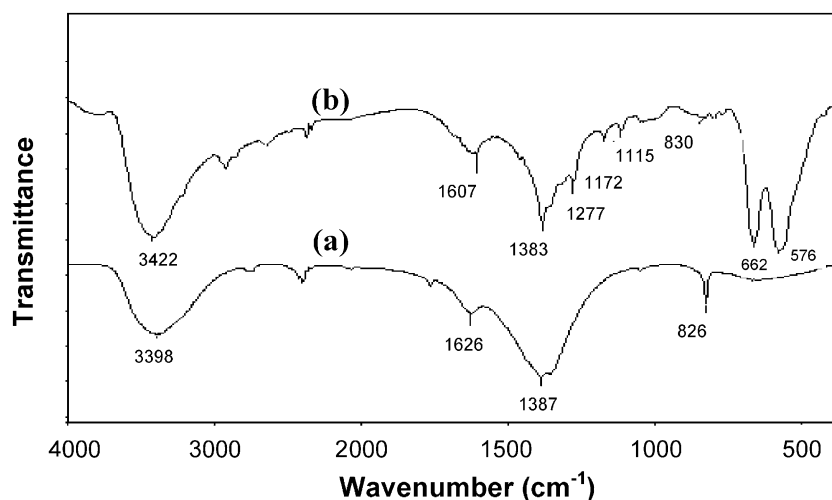

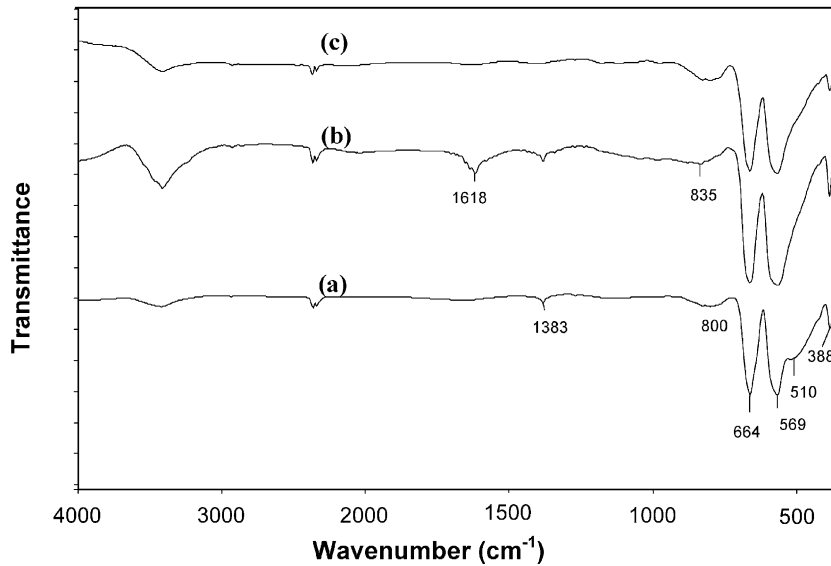Fig. 2. FTIR spectra of (a) Co(NO$_3$)$_2$ and (b) microwave-irradiated sample (M.W.) thermally treated at 100 °C.

Fig. 3. FTIR spectra of (a) Co(NO$_3$)$_2$, (b) microwave-irradiated (M.W.) and (c) nonirradiated (N.I.) samples calcined at 400 °C.

the samples. The second major weight loss, occurring between 130 and 275 °C, was due to a decomposition of nitrates and a dehydroxylation process. In this case, the nonirradiated sample lost less weight than the other samples. Furthermore, this sample exhibited the highest amount of Co$_3$O$_4$. It seems that the weight loss only represents the dehydroxylation to improve the crystallization to Co$_3$O$_4$. The DTA results (not shown here) presented endothermic peaks and were similar to those reported by Xu and Zeng [7] obtained in air atmosphere, the Co-MHLC presented a clear endothermic transition, corresponding to the loss of interlayer water and NO$_3^-$ with collapse of the structure. The third weight loss at 850–910 °C has to be attributed to the presence of CoO [3,11].

BET surface areas, pore volume and pore size distribution measurements for thermally treated samples (100 and 400 °C) are shown in Table 2. Co(NO$_3$)$_2$ presented the lowest surface area and pore volume, compared with nonirradiated and microwave samples. Note that the nonirradiated sample is highly stable after calcining at 400 °C; it only looses 21% of the original surface area. The microwave-irradiated sample showed the lowest stability. The surface area was reduced by 77% of the original value. Furthermore, the pore volume in the nonirradiated sample is constant, whereas the irradiated sample at 100 °C has a pore volume of 0.262 ml/g (much higher than the irradiated

Table 1
Weight loss of the samples determined by TGA

Sample	Weight loss (%) between 25 and 130 °C	Weight loss (%) between 130 and 275 °C	Weight loss (%) between 850 and 910 °C
Co(NO$_3$)$_2$	21.13	25.21	3.43
M.W.	6.11	27.89	4.08
N.I.	0.86	3.23	6.20

Table 2
Surface area (S.A.), pore volume (P.V.) and pore size distribution (P.S.D.) of thermally treated samples (100 °C) and of the resulting calcined forms (400 °C)

Sample	Temperature (°C)	S.A. (m^2/g)	P.V. (ml/g)	P.S.D. (maximum/ average, Å)
Co(NO$_3$)$_2$	100	13.2	0.092	280/189
Co(NO$_3$)$_2$	400	8.9	0.026	720/150
N.I	100	48.4	0.185	210/119
N.I.	400	37.6	0.187	220/164
M.W.	100	47.9	0.262	310/208
M.W.	400	11.0	0.073	420/222

sample, 0.185 ml/g), which turns out to be 0.073 ml/g after the thermal treatment.

4. Conclusion

The thermal behavior of the cobalt monometallic hydrotalcite-like compound, if compared to the non-irradiated sample and the cobalt precursor, shows that hydrotalcite is an intermediate to produce Co_3O_4. The resulting Co_3O_4 crystallites obtained from irradiated and nonirradiated samples are small, whereas those synthesized from the cobalt nitrate are large and well crystallized. Microwave irradiation determines the thermal stability of the sample, which presents a lower surface area and more homogeneous crystals. In non-irradiated sample, the pore volume is not modified by the thermal treatment, whereas in the microwave-irradiated sample, the pore volume initially higher (0.262 ml/g) is reduced up to 0.073 ml/g, which is in the range of the values obtained for the thermally decomposed $Co(NO_3)_2$.

References

[1] R. Allmann, Acta Crystallogr. B24 (1968) 972.
[2] A. Vaccari, Catal. Today 41 (1998) 53, and references therein.
[3] J.T. Kloprogge, R.L. Frost, Appl. Catal., A Gen. 184 (1999) 61.
[4] H.C. Zeng, Z.P. Xu, M. Qian, Chem. Mater. 10 (1998) 2277.
[5] Z.P. Xu, H.C. Zeng, Chem. Mater. 11 (1999) 67.
[6] R.M. Taylor, Clay Miner. 15 (1980) 369.
[7] Z.P. Xu, H.C. Zeng, J. Mater. Chem. 8 (1998) 2499.
[8] B. Zapata, P. Bosch, G. Fetter, M.A. Valenzuela, J. Navarrete, V.H. Lara, Int. J. Inorg. Mater. 3 (2001) 23.
[9] M. Qian, H.C. Zeng, J. Mater. Chem. 7 (1997) 493.
[10] M.W. Urban, Vibrational Spectroscopy of Molecules and Macromolecules on Surfaces, Wiley, New York, 1993.
[11] D. Barreca, C. Massignan, S. Daolio, M. Fabricio, C. Piccirillo, L. Armelao, E. Tondello, Chem. Mater. 13 (2001) 588.