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Cu hydrotalcite-like compounds: Morphological, structural and microstructural properties

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Abstract

Copper containing mixed oxides are widely employed as catalysts for the synthesis of methanol, higher alcohol, hydrocarbons from syngas at low temperature and pressure, and for NiO_x reduction. In this work, a series of Mg–Al–Cu, as hydrotalcite-like compounds (Cu-HTlcs) precursors of mixed oxides were synthesized by direct coprecipitation. The effect of pH, Cu content and mechanical milling on the structure and texture of these materials was investigated. The obtained materials were characterized by X-ray diffraction, differential scanning calorimetry, scanning and transmission electron microscopy and BET surface area measurements. The results showed that the materials were nanocrystalline powders. The Cu-HTlcs has a hexagonal unit cell. The *a* and *c* parameters increased as a function of the Cu content in both milled and non-milled samples. Crystallite size also increased with Cu content in both cases and smaller for non-milled samples. In contrast, microstrain values were greater for milled samples. BET area decreased with Cu content and showed that materials synthesized were mesoporous type. Mechanical milling did not destroy the morphology of the samples.

Keywords: Hydrotalcite-like compounds; Layered double hydroxides; Crystallite size; Microstrain; Mixed oxides

1. Introduction

Layered double hydroxides, also known as anionic clays, are a family of compounds which has captured considerable attention in recent years [1–3]. The structure of most of them corresponds to hydrotalcite with formula is $Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$, and occurs in nature in foliated and/or fibrous masses. Hydrotalcite is structurally formed by brucite-like [$Mg(OH)_2$] sheets where partial isomorphous substitution of Mg^{2+} by a trivalent cation like Al^{3+} occurs and the resulting excess positive charge of the layer is compensated by anions which occupy the interlayer space along with water molecules.

The nature of both the layer cations and the interlayer anions can be changed and when it occurs, the compounds are known as hydrotalcite-like compounds (HTlcs). They have the general molecular formula $[M_{1-x}{}^{II}M_x{}^{III}(OH)_2]^{x+}[A^{n-}]_{x/n}{}^{x-}\cdot mH_2O$, where M^{II} and M^{III} are divalent and trivalent metal ions, respectively, A^{n-} the interlayer charge-compensating *n*-valent anion, *x* is the molar ratio of $M^{III}/(M^{II}+M^{III})$ and can take values from 0.1 to 0.5 [4,5].

The facility of the HTlcs to incorporate a variety of metals and anions has increased the interest in these materials. The conditions of synthesis, i.e., temperature, pH, metal composition and ageing time of the gels are associated to the physicochemical properties of these materials. HTlcs can be converted by thermal decomposition into stable non-stoichiometric mixed metal oxides, which possess homogenous dispersion of the elements, high specific surface areas and strong basic properties [6–8]. Interest in HTlcs and derived materials arises from their relative ease of preparation and broad uses as adsorbents, anion exchangers, catalysts and catalyst supports. Most of the applications of these materials are in the field of heterogeneous catalysis due to the production of different layer cations and interlayer anions by synthesis chemistry. It is also possible to produce a fine modulation of chemical composition and hence catalytic properties [9].

In the present work a series of Cu-HTlcs was prepared. The Cu content and milling effects on the crystalline structure, surface properties and morphology were studied. Both milling and

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Table 1
Nomenclature and composition of the prepared samples at pH of 10

Sample	Mg/Al (molar ratio)	Cu/Mg (molar ratio)	Milled sample
HT	1.5	0.0	HTM
HT-Cu1	1.5	0.3	HTM-Cu1
HT-Cu2	1.5	0.6	HTM-Cu2
HT-Cu3	1.5	1.3	HTM-Cu3

substitution of Mg by Cu are expected to generate higher density of lattice defects by plastic deformations or local atomic displacements and may enhance catalytic reactivity of these nanocrystalline materials.

2. Experimental

In a first step, Cu-HTlcs were synthesized by coprecipitation technique at room temperature and continuous stirring, from $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Cu(NO_3)_2{\cdot}6H_2O$, using NaOH and Na_2CO_3 as the precipitant agent. The materials were prepared, weighting the salts and fitting the constant molar ratios of $Mg/Al = 2.0$ and $Cu/Mg = 1.3$ and using a variable pH from 7 to 12, at room temperature and continuous stirring. In a second step, Cu-HTlcs were prepared with the same ternary system (Cu–Mg–Al) but now varying the molar ratio Cu/Mg and controlling the pH at 10 ± 0.2 with the best condition established in the first step. After the addition process, the slurry was continuously stirred during 1 h with the purpose of maintaining the homogeneity of the sample. The suspension was aged about 24 h at room temperature. The samples were named as HT, HTCu1, HTCu2 and HTCu3. Then, 50% of each sample was milled, whereas the other 50% was directly washed, filtered and dried during 24 h at 80 °C. The milling was performed in an attritionator in an aqueous media, using steel balls of 3.8 mm in diameter for 44 h and the weight ratio of balls/sample was 30/1. Table 1 lists the as-prepared samples.

All the samples were characterized by X ray powder diffraction analysis using a D5000 Siemens diffractometer and Cu Kα radiation ($\lambda = 0.1542$ nm, 35 kV and 25 mA). A 2θ range from 5° to 80° was investigated at a scanning speed of $60^\circ\ h^{-1}$. TG-DSC studies were carried out using a Seysts Evolution 1750 Setaram calorimeter, from room temperature to 900 °C at a heating rate of $10\ ^\circ C\ min^{-1}$ in air. Morphology was observed in a 6300 JEOL scanning electron microscope. The analysis of metals and distribution of elements were performed by a 2380 Perkin-Elmer atomic absorption spectrometer and energy dispersive spectroscopy Noran system. A 2000FXII JEOL transmission electron microscope was used to examine the size of the crystals. Surface area measurements, using BET method of adsorption of N_2, were carried out in an ASAP-2405 Micrometrics Digisorb.

3. Results and discussion

Figs. 1 and 2 show the effect of pH on the precipitation of the Cu-HTlcs of the first experimental step.

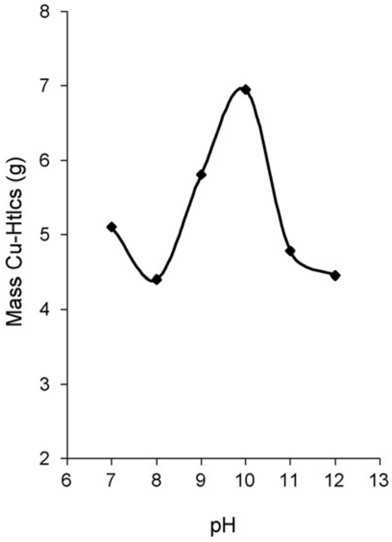

Fig. 1. Mass of Cu-HTlcs obtained as function of pH.

No byproduct or secondary phase was formed. Only Cu-HTlcs was observed by XRD in all the samples prepared at different pH values. The highest amount of Cu-HTlcs was obtained with pH 10.

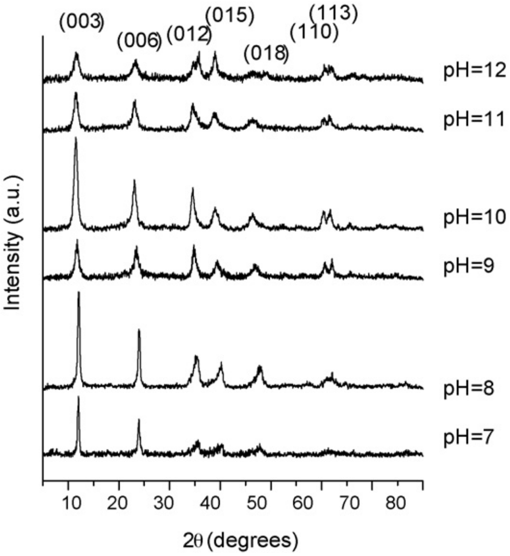

Fig. 2. XRD of the Cu-HTlcs as pH function at constant $Mg/Al = 2$ and $Cu/Mg = 1.3$.

Table 2
Chemistry analysis results for the Cu-HTlcs samples without milling

Sample	Mg/Al (molar ratio)		Cu/Mg (molar ratio)		Composition (wt.%)					
	Prep[a]	Mea[b]	Prep[a]	Mea[b]	As-prepared			Measured		
					Mg	Al	Cu	Mg	Al	Cu
HT	1.5	1.22	0.00	0.00	66.74	33.26	0.00	55.00	45.00	0.00
HTCu1	1.5	1.58	0.30	0.46	55.13	27.48	17.39	47.71	30.28	22.02
HTCu2	1.5	1.72	0.60	0.72	46.96	23.41	29.63	43.41	25.21	31.39
HTCu3	1.5	1.39	1.3	1.63	36.23	18.05	45.72	29.83	21.54	48.63

[a] As-prepared (weighted before synthesis).

[b] Measured after synthesis (atomic absorption).

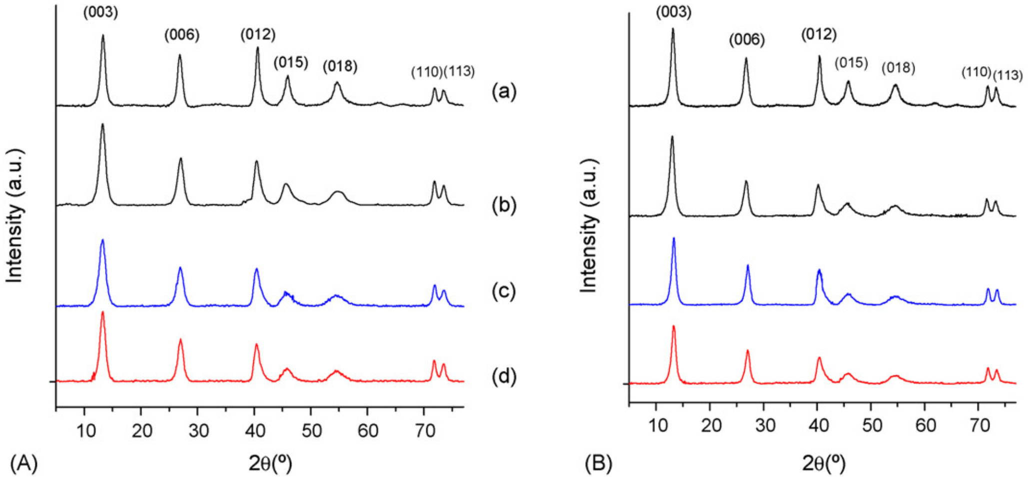

Fig. 3. X-ray powder diffraction patterns of the Cu-HTlcs as a function of Cu content. (A) Unmilled samples: (a) HT, (b) HTCu1, (c) HTCu2 and (d) HTCu3. (B) Milled samples: (a) HTM, (b) HTMCu1, (c) HTMCu2 and (d) HTMCu3.

Table 2 shows the Cu, Al and Mg contents for the second experimental step. The Mg/Al molar ratios are lower in the measured samples than in the as-prepared samples, when weighted. Besides, the Cu/Mg ratios are higher in the measured samples than those found in the as-prepared ones, indicating that Cu incorporation was favored over Mg to form the Cu-HTlcs, under the experimental conditions.

The diffraction patterns of all the samples are typical of the hydrotalcite-like structure. Fig. 3 shows the XRD patterns of the milled and unmilled samples. The reflections obtained from randomly oriented powders are sharp and intense at low values of 2θ angle, and less intense, broad and asymmetric lines at higher angular values, due to their poor crystallization, attributed to the non-stoichiometric nature and partially disordered structure. When Cu content increases, the crystalline perfection slightly decreases, but it does considerably when the materials are milled.

Table 3 shows the lattice parameters and values of crystallite sizes and strain (microstructural parameters), for the unmilled and milled HTlcs. Lattice values were calculated by the Winplotr Software [10]; crystallite sizes and strain were calculated by the Williamson–Hall plot and the Two Stages Approach [11–13]. The values of the *a* and *c* parameters and crystallite sizes and strain increase as the Cu content increases in the two series of prepared samples; however, *a* and *c* are smaller for the milled samples. In contrast, the strains are greater for the milled samples.

Figs. 4 and 5 show the thermal decomposition of unmilled and milled samples obtained by DSC.

Figs. 4 and 5 show the typical endothermic stages of the HTlcs in the thermal decomposition; the first two-stage peak corresponds to elimination of physically adsorbed and interlayer water molecules, the second peak corresponds to removal of hydroxyl groups from the brucite network and carbonate anions from the interlayer anion.

The milling does not destroy the structure of the Cu-HTlcs. Figs. 6 and 7 show the morphological features of these compounds, studied by SEM and TEM, respectively.

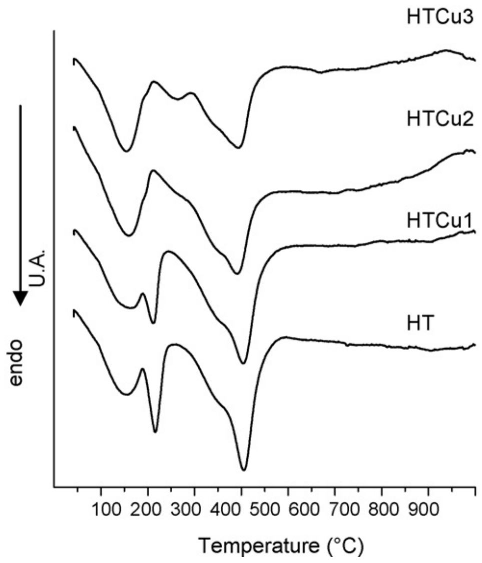

Fig. 4. DSC thermal decomposition of unmilled Cu-HTlcs (endothermic peaks).

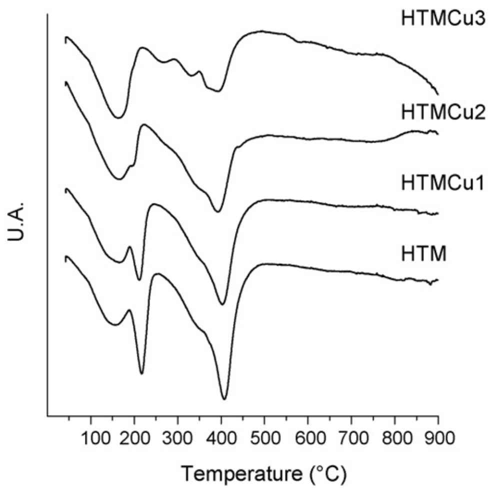

Fig. 5. Thermal decomposition of milled Cu-HTlcs (endothermic peaks).

Table 3
Lattice (*a* and *c* in Å) and microstructural (crystallite size in Å and strain) parameters of the unmilled and milled samples

Sample	*a*	*c*	Size	Strain	Sample	*a*	*c*	Size	Strain
HT	3.043	22.924	96	0.0064	HTM	3.040	22.738	85	0.0098
HTCu1	3.047	22.972	120	0.0074	HTMCu1	3.044	22.796	86	0.0102
HTCu2	3.057	23.020	132	0.0077	HTMCu2	3.055	22.856	94	0.0108
HTCu3	3.061	23.031	150	0.0094	HTMCu3	3.056	22.950	102	0.0123

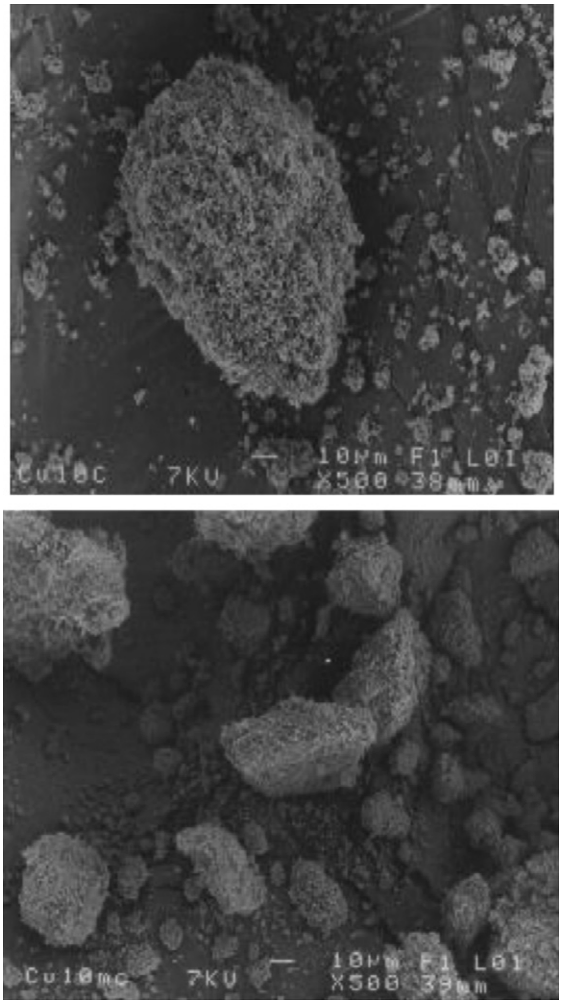

Fig. 6. SEM micrographs of HTlcs. Up: HT and down: HTM.

Table 4 shows the specific surface area and pore radius values of selected samples. Specific surface area values decrease as Cu content increases in the two series of samples, but they are greater for the milled HTlcs. The materials are mesoporous solids and the pore sizes increase as Cu content increases.

Table 4
Specific surface areas and pore radius values of selected samples.

Sample	BET area (m^2/g)	Pore radius (Å)	Sample	BET area (m^2/g)	Pore radius (Å)
HT	94	110	HTM	108	98
HTCu1	88	127	HTMCu1	98	112
HTCu3	68	141	HTMCu3	84	133

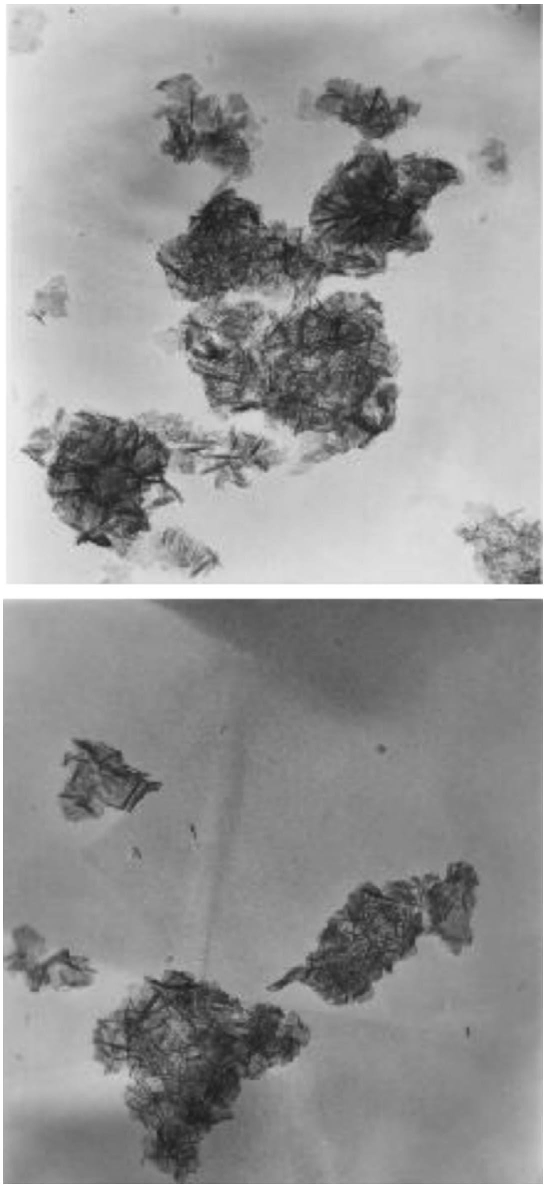

Fig. 7. TEM micrographs of HTlcs. Up: HT and down: HTM.

4. Conclusions

Pure hydrotalcite phase was obtained in all samples and the pH of 10 was the best condition of the coprecipitation. X-ray diffraction analysis showed that when Cu content increases, the crystalline perfection slightly decreases, but it does considerably when the materials were milled. Also, the values of the *a* and *c* parameters, crystallite sizes and strain increased in the two series of the prepared samples as function of Cu content; however, *a* and *c* are smaller and the strains are greater for the milled samples, which implies a higher density of lattice defects due to plastic deformations. The milling did not destroy neither the structure nor the morphology of the Cu-HTlcs.

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