



CuNi/Al hydrotalcites synthesized in presence of microwave irradiation

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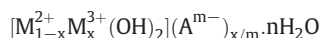
ABSTRACT

To enhance the electronic properties of nanoparticles, functional clusters are usually supported on metal oxides as alumina. Copper and nickel clusters supported on magnesia or alumina are promising materials to catalyze the decomposition of methane to produce hydrogen. A mixed support of alumina and magnesia can be proposed in the form of a hydrotalcite. In this work, the synthesis of hydrotalcites containing Cu, Ni, Mg and Al in the presence of microwave irradiation is studied. Cu/Al hydrotalcite which is hardly synthesized through conventional methods was easily prepared in the presence of microwaves.

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1. Introduction

Hydrotalcites are anionic clay-like compounds with chemical formula:



where x, di-valent cations M^{2+} , may be replaced by tri-valent M^{3+} cations, which produce positively charged layers. This charge is neutralized by x/m anions A^{m-} as CO_3^{2-} . The most frequent divalent metals are those whose ionic radii vary from 65 pm (Mg) to 80 pm (Mn) whereas the radii of the trivalent metal has to be comprised between 50 pm (Al) and 69 pm (Cr) [1].

Cu/Al- CO_3 -hydrotalcite has been synthesized crystallizing the gel at a relatively high temperature. Still, copper may be incorporated, in more friendly conditions, in the presence of another M^{2+} metal to constitute a three metallic hydrotalcite. The ratio between Cu^{2+} and the second metal M^{2+} must be equal or lower than 1. Indeed, the distortion of the octahedron coordination structure leads to a gain in energy [2]. When the ratio Cu^{2+}/M^{2+} is lower or equal to 1, copper atoms are far from each other and, then, they are arranged in undistorted octahedral coordination. Clusters of nickel or copper have been useful in a wide range of technological applications which

include solar cells, conducting polymers, superconductors, microelectronic devices and catalysts.

In a previous work [3], layered double hydroxides with the hydrotalcite-type structure containing Cu^{2+} , Ni^{2+} and Al^{3+} have been already synthesized by a conventional coprecipitation method. Still, microwave irradiation can be used to prepare original materials [4]. In Mg/Al-hydrotalcite synthesis the irradiated materials present a concentration gradient where the core is aluminum enriched [5]. This result may be interpreted in terms of the competitive diffusion determined by charge, weight and ion size. In NiMg/Al-hydrotalcites synthesized in the presence of microwaves, we have found that magnesium and aluminum are not homogeneously distributed: aluminum and nickel are selectively retained in the hydrotalcite particle core [6].

In this work, to favour the formation of new poly-metallic catalytically active sites on the hydrotalcite layers, magnesium is partially substituted by copper and nickel. These cations have ionic radii, 69 and 72 pm respectively [1]. The corresponding electronegativities are 1.8 (Cu), 1.8 (Ni) and 1.2 (Mg). Therefore, the replacement of Mg^{2+} by Cu^{2+} or Ni^{2+} should lead to an electron transfer from Al^{3+} to M^{2+} , the resulting hydrotalcites should, then, present a poorer basicity than Mg–Al hydrotalcites. However, depending on the microwave irradiation treatment the distribution of the metals should vary generating zones more basic than others.

On the one hand, di-metallic Mg/Al, Cu/Al and Ni/Al-hydrotalcites and, on the other, CuNi/Al, were studied. The di-metallic samples

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Table 1Elemental composition (weight percentage) obtained by ICP-OES and BET surface area in m^2/g .

Sample	% Al	% Cu	% Ni	% Mg	% Na	Surface area
Cu/Al	4.91	47.13	–	–	–	111
Ni/Al	5.07	–	46.08	–	0.24	3
Mg/Al	6.90	–	–	24.84	0.51	73
CuNi/Al:131	4.72	11.59	33.29	–	0.96	38
CuNi/Al:441	2.70	26.17	24.47	–	–	77

correspond to the classical 4:1 molar ratio. The molar ratios of the trimetallic samples were 1:3:1 and 4:4:1. Hydrotalcites with a low content of copper are easily formed by conventional synthesis procedures, no reports are found on high copper containing trimetallic hydrotalcites.

2. Experimental

The CuNi/Al-hydrotalcite samples were synthesized from water solutions, 2.5 M of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, 99%, Aldrich 99% and 98%, respectively). A second aqueous solution, 1.86 M, was prepared with NaOH (Aldrich). The precipitation was carried out adjusting the flow of each solution to maintain the pH constant at 9. The solution amounts were adjusted to correspond to a $(\text{Cu} + \text{Ni})/\text{Al}$ molar ratio of 4, where the Cu:Ni molar proportions were 4:4 and 1:3 (samples labeled CuNi/Al:441 and CuNi/Al:131, respectively). The resulting gels were treated in a microwave autoclave (MIC-I, Sistemas y Equipos de Vidrio S.A. de C.V.) for 10 min operating at 2.45 GHz. The microwave irradiation power was 200 W and the temperature was fixed at 80 °C. The solids were recovered by decantation and washed several times with distilled water until the residual solution reached a pH value of 8. The solids were, then, dried in an oven at 60 °C for 24 h. The Cu/Al, Ni/Al and Mg/Al-hydrotalcite-like samples were prepared as described previously, the volume of the solutions was adjusted to correspond to the molar ratio M^{2+}/Al of 4 (samples Cu/Al, Ni/Al and Mg/Al).

The samples were dissolved in a HNO_3/HCl (1:3 vol.) solution before to be analyzed in a Varian 715-ES ICP-Optical Emission Spectrometer. X-ray diffraction patterns were obtained with a Bruker-axs D8-advance diffractometer coupled to a copper anode X-ray tube. A scanning electron microscope LEICA, Stereoscan 440 was used. FTIR spectra in the region $4000\text{--}400\text{ cm}^{-1}$ were obtained with a Magna-IR Spectrometer 550 Nicolet, using the KBr pellet technique. The BET surface area was obtained with a Micromeritics ASAP 2020. The samples were pretreated at 200 °C for 5 h at a high vacuum.

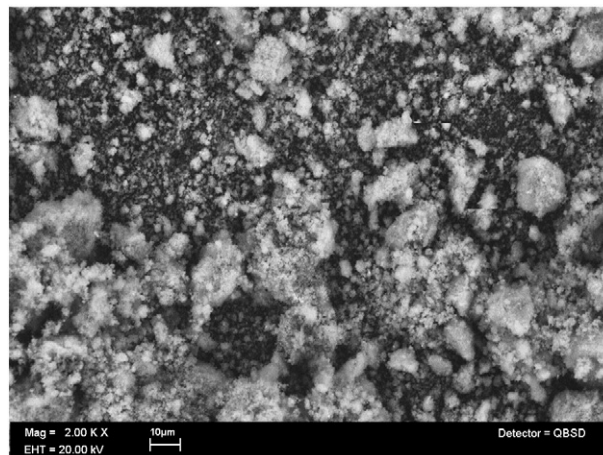


Fig. 2. Micrograph of the CuNi/Al:441 sample.

3. Results and discussion

The experimental elemental composition determined by ICP-OES reproduces the nominal values (Table 1). The conventional Mg/Al preparation was hydrotalcite with a well defined 001 X-ray diffraction peak corresponding to an interlayer distance typical of a nitrated hydrotalcite, $d = 0.879\text{ nm}$ (Fig. 1). No other crystalline compounds were present. The Ni/Al sample reproduces the main features of the previous diffractogram, only the crystallinity seems to be lower. As copper is incorporated into the mixture (sample CuNi/Al:131) the crystallinity diminishes although the main product is a hydrotalcite similar to the previous ones. Such modification of the peak broadening may be attributed either to a small particle size or to strain between the crystalline planes. The second option has to be retained as copper introduces serious deformations in the octahedron coordination structure. As the amount of copper was increased (samples CuNi/Al:441 and Cu/Al) peaks at 10.4° and 12.5° appear; the first one is attributed to a nitrate exchanged hydrotalcite whereas the second one corresponds to a hydroxylated one. Furthermore, the sample color turns out to be black indicating the presence of CuO. As the peaks at 35.55° and 38.75° , typical of copper oxide, were not observed, the copper particles must be beyond the detection limit of X-ray diffraction, i.e., either smaller than 3 nm or in a content lower than ca. 3%.

Shen *et al.* [7] reported that the crystallinity of the CuMg/Al hydrotalcites increases with a copper content. Nickel induces a definitely different behavior in the tri-metallic hydrotalcite. Indeed,

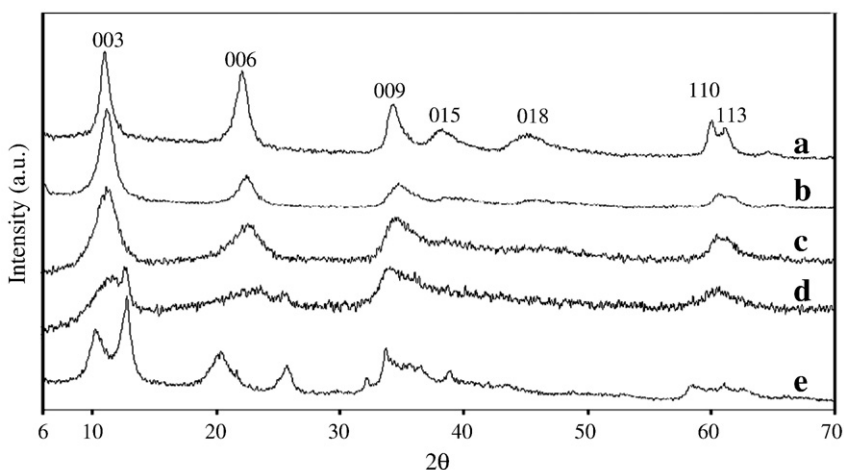


Fig. 1. X-ray diffraction patterns of the samples: a) Mg/Al, b) Ni/Al, c) CuNi/Al:131, d) CuNi/Al:441 and e) Cu/Al.

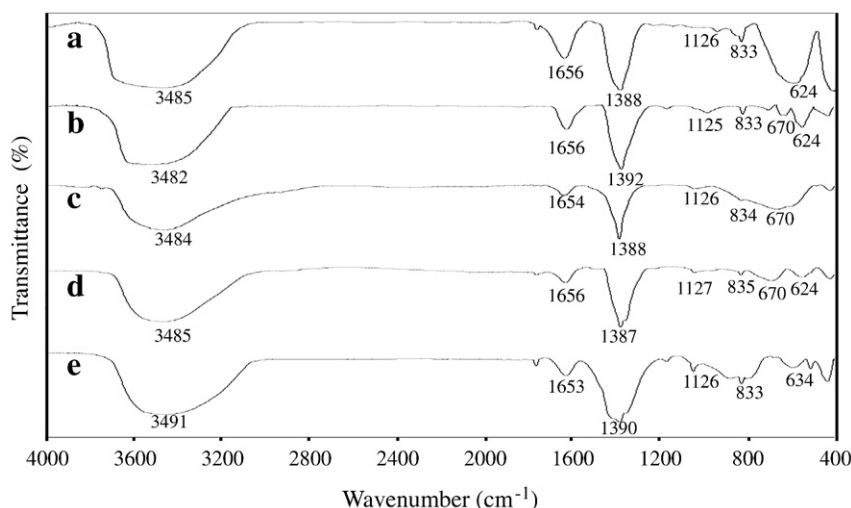


Fig. 3. Infrared spectra of the samples: a) Mg/Al, b) Ni/Al, c) CuNi/Al:131, d) CuNi/Al:441 and e) Cu/Al.

nickel is smaller and more electronegative (1.94) than magnesium (1.32). In conventional Mg/Al hydrotalcite the electron transfer is from magnesium to aluminum (electronegativity of 1.74) via an oxygen bridge. In Ni/Al preparations, such transfer is much higher. Note that transfer from copper (electronegativity 1.98) should be very similar. The lower electronegativity value for magnesium induces the OH groups to be more strongly bound to magnesium, resulting in the stabilization of the layers and the other way round for nickel [8].

As shown by the XRD peak positions, in sample Ni/Al, the anions are nitrates. The Cu/Al sample is not fully crystalline and presents the two interlayer spaces, nitrate and hydroxyl. In sample CuNi/Al:441 the obtained material is inhomogeneous due to an irregular distribution of copper and nickel in the hydrotalcite layers, on the one hand, the nickel enriched core (as nickel diffuses better than copper) is nitrated, the periphery is then copper enriched and it is highly hydroxylated. The copper that cannot diffuse into the hydrotalcite particle forms CuO nanoparticles. The heterogeneity of the sample is confirmed by the micrograph of Fig. 2.

The infrared spectra shown in Fig. 3 are all similar. The broad band at 3454 cm^{-1} corresponds to an elongation vibration of structural hydroxyl groups. The band at 1640 cm^{-1} is due to OH groups from water molecules, and the interlayered nitrates appear at 1386 cm^{-1} . The bands between 500 and 900 cm^{-1} can be attributed to the metal-oxygen vibrations, where the vibration of Mg–O appears at 670 cm^{-1} [9]. These results are compatible with the model presented in the X-ray diffraction section as the detected species are the same in all samples; the only difference is their distribution.

Specific surface areas are reported in Table 1. The Mg/Al sample value does not reproduce the value found in our previous work [10], $110\text{ m}^2/\text{g}$, as synthesis pH was 13 instead of 9. Sample Ni/Al exhibits a much smaller surface area ($3\text{ m}^2/\text{g}$), this value has to be attributed to intercalated nitrates avoiding nitrogen penetration [11]. These two materials, being Mg/Al and Ni/Al, are similar in their structure but not in their texture. The value of surface area for Cu/Al is the highest ($111\text{ m}^2/\text{g}$); such value has to be attributed to the presence of a large amount of CuO nanoparticles as shown by the sample color. The poly-

metallic samples reveal a saturation effect due to the dilution rule, which predicts that if the ratio Cu:Ni is higher than or equal to 1, the octahedron coordination structure is distorted favoring the segregation of copper as CuO nanoparticles. As the number of CuO nanoparticles increases the surface area increases.

4. Conclusion

In copper and nickel containing hydrotalcites synthesized in the presence of microwave irradiation, two interlayer distances were determined, corresponding to hydroxyl and to nitrate compensating anions. Nickel diffuses to the particle core. Copper, due to its high oxidation ability, generates a high stress in the lattice, and it remains in the outer part of the particles. Copper excess constitutes small CuO nanoparticles easily detected by the sample color. Cu/Al hydrotalcite, which is hardly synthesized through conventional methods, was easily prepared in the presence of microwave irradiation.

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