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Study of the textural properties of some layered double hydroxides

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Abstract: Layered double hydroxides (LDHs) are one of the nano ordered layered compounds. The importance of layered compound is based on their ability to retain chemical species with electrical charges compatible to those of the layers. They may be used in areas such as catalysis, industry, medicine, environmental protection, construction etc. Layered double hydroxides are anionic clays comprising positively charged layers with anions and water molecules intercalated in the interlayer region. The aim of this work was to obtain Cu and/or Ni substituted layered double hydroxides with different micromorphology characteristics. The obtained results pointed out that the relationship between LDHs composition and their textural properties can be controlled. The layered double hydroxides samples were fabricated by using direct coprecipitation method. Field Emission Scanning Electron Microscope (FE-SEM) and X-Ray Diffraction (XRD) analyses were used to study the textural characteristics and the structural characteristics of the samples.

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Introduction

Layered double hydroxides (LDH) are anionic clays with positively charged layers with two kinds of metallic cations and exchangeable hydrated gallery anions. This is also referred to as anionic clays in comparison with cationic clays and also as hydrotalcite-like compounds in the name of the polytypes of the corresponding [Mg-Al] based mineral. Hydrotalcite is the first natural mineral discovered in LDHs family.

Layered double hydroxides have been studied extensively for a wide range of applications utilizing catalysts, bio-organic nanohybrids, adsorbents, ceramic precursors, and scavengers of pollutant metals and anions due to their acidic and alkaline characteristics, memory effect, large surface area, high anion exchange and good thermal stability.[1]

Recent research has shown great flexibility of the LDH-like materials in tailoring chemical and physical properties of materials to be used for specific applications. Researchers have been able to produce catalyst precursors by introducing various transition and noble metals into the sheets of the LDH structure. More recently, there have been new developments using a LDH as a matrix for storage and delivery of biomedical molecules and as a gene carrier. Many techniques are used for the preparation of LDHs. The most commonly method used is coprecipitation, but some other methods, such as rehydration, hydrothermal reaction, pre-pillaring and intercalation, were also reported.[2,3] Very important parameters in the preparation of LDH by coprecipitation are temperature in the reactor, pH, concentration of metallic salts solution and alkaline solution, flow rate of reactants, ageing time of precipitate. Parameters as geometry of the reactor including reactants injection pipes, addition rate are less important.[4,5]

In this work, the coprecipitation technique was used to prepare the LDHs. Physical characterization of the final products was investigated by X-ray Diffraction (XRD) and Field Emission Scanning Electron Microscopy (FE-SEM).

Results and discussions

The XRD difractograms of the CuLDH and NiLDH are shown in Figure 1 and Figure 2. The XRD patterns of the synthesized samples point to the diffraction reflections typical to the layered double hydroxides structure with sharp and symmetric basal reflections of (0 0 3), (0 0 6) and (0 0 9) planes.

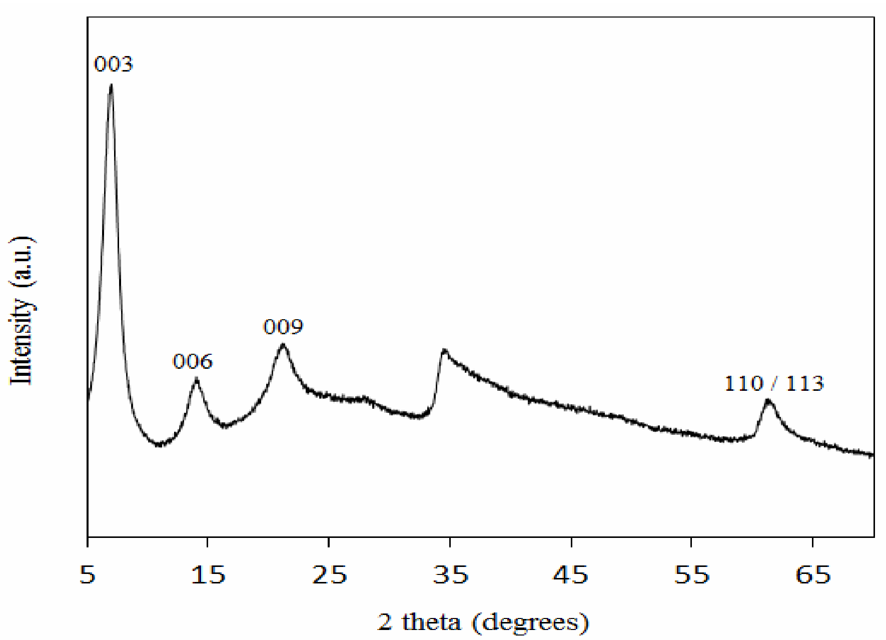

Figure 1. The XRD patterns of the as-synthesized clay CuLDH.

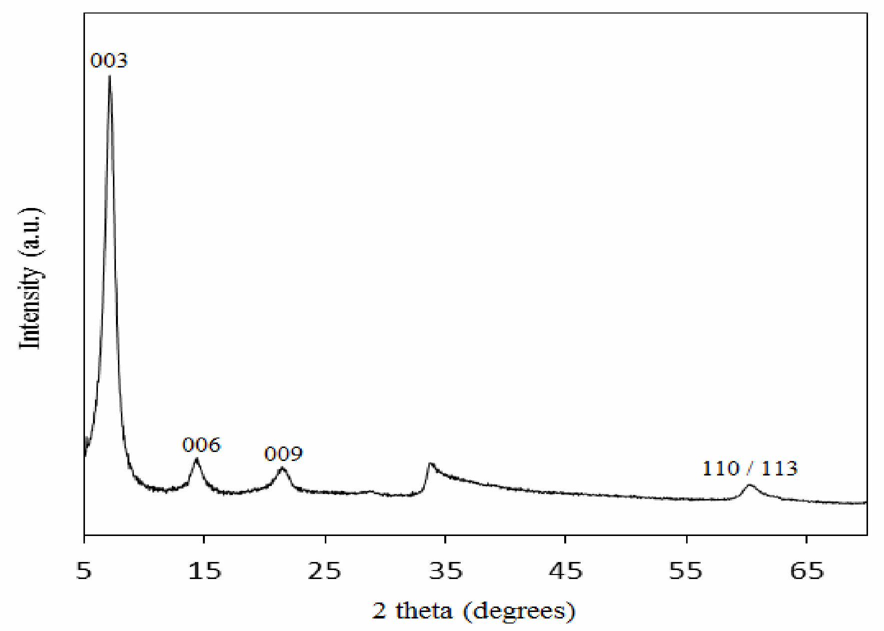

Figure 2. The XRD patterns of the as-synthesized clay NiLDH.

The XRD reflections for both samples were indexed using a hexagonal cell with rhombohedral symmetry (R-3m), commonly used as a description of the LDH structure, and the lattice XRD parameters were calculated and presented in Table 1. The parameter *a* is a function of the metal–metal distance within the layers, pointing out the cations stacking in the (0 0 3) planes, while the *c* parameter is a function of the average charge of the metal cations, the nature of the interlayer anions and the water content of the hydrotalcite-like sample.

Table 1. The structural properties of the studies samples.

Sample	Anionic clay structural parameters (Å)	
	a	*c*
CuLDH	3,07	37,2
NiLDH	3,09	26,13

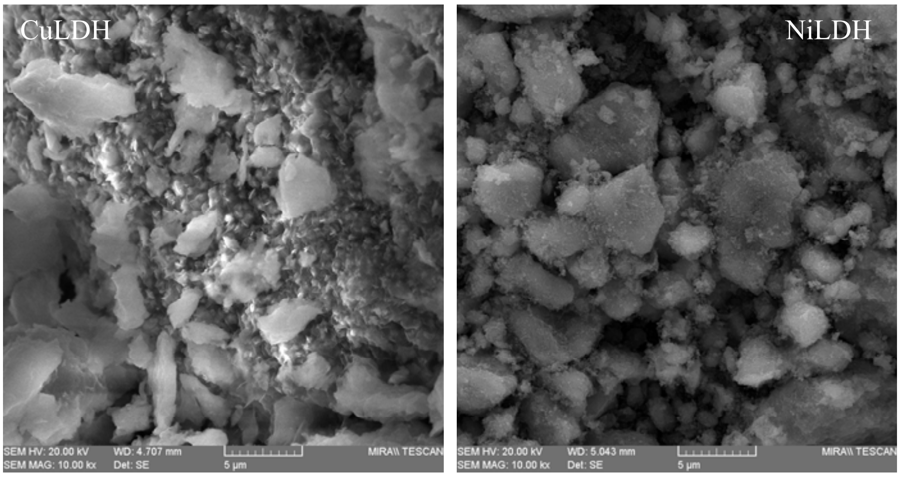

Figure 3. SEM micrographs for CuLDH and NiLDH.

The FE-SEM photographs of the samples are presented in Figure 3 and Figure 4. The SEM image of CuLDH shows that the large LDHs nanoparticles have a rough but clean surface. At lower magnification (10kx) both samples consist of irregular particles. The samples are agglomerated.

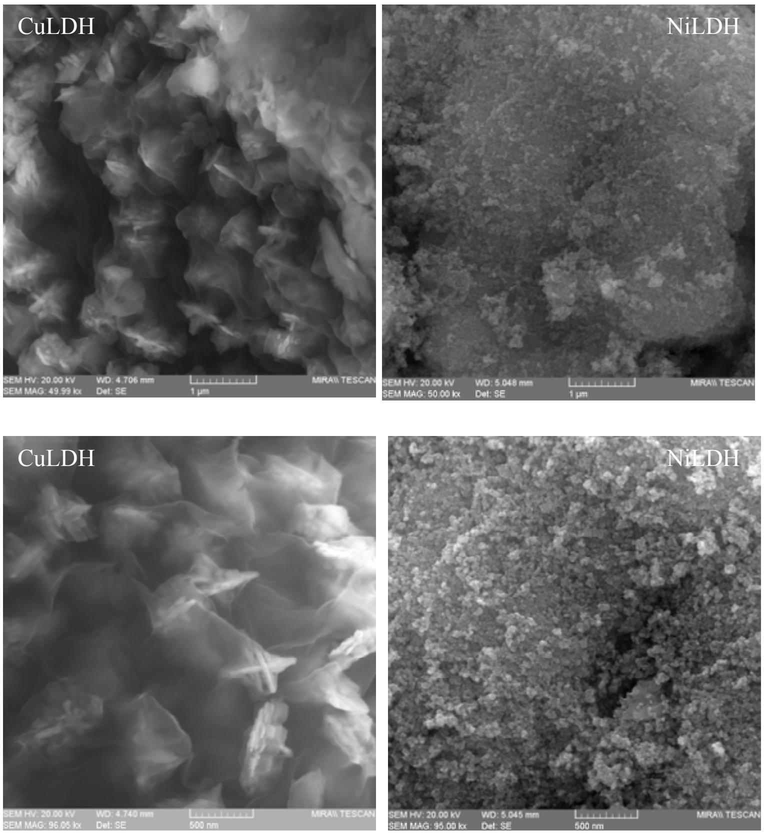

Figure 4. SEM micrographs for CuLDH and NiLDH.

The images obtained at higher magnification (50kx) show that sample CuLDH has a rougher and looser surface than sample NiLDH.

The analysis of SEM micrographs reveals that CuLDH samples are highly crystalline. Intersected, nearly hexagonal-shaped particles, interconnected with each other, enough uniform as sizes (average size equal to 100 nm) are formed in the case of the hydrotalcite-like clay CuLDH. This morphology is typical for the layered double hydroxides – non incorporated clays. Agglomerated, crumpled and irregular sheets, lying on top of one another and giving rise to a mille-feuille organization of the ensembles of the particles can be clearly observed. Not the same observation can be done for the NiLDH sample. From the SEM micrographs it can be observed that the shape of nanoparticles is not only hexagonal. The particles are much agglomerated.

Experimental

The coprecipitation method is the most widely used method to synthesize LDHs, in which the mixed alkali soda solution is added to a mixed salt solution and the resultant slurry is aged at a desired temperature.[6]

The copper-substituted hydrotalcite-like clay, denoted as CuLDH: copper containing hydrotalcite-like clay was obtained by the coprecipitation method following the procedure described by Carja et al.[7] The obtained samples was aged at ambient temperature, washed, centrifuged, and dried under vacuum. The same procedure was used for the preparation of nickel-substituted hydrotalcite-like clay denoted as NiLDH.

Structural characteristics, crystallinity, and purity information were recorded by X-ray diffraction (XRD) using a diffractometer with monochromatic Cu Kα radiation (λ= 0.1541 nm), operating at 40 kV and 30 mA over a 2h range from 4º to 70º.

The morphology of the samples were studied by a Mira II LMU Tescan Field Emission Scanning Electron Microscope (FE-SEM).

Conclusions

Copper or nickel-containing anionic clays, type LDHs, are synthesized using different metal salts as precursors in the anionic clay synthesis process. The nature of the salt precursors gives rise to the specific structural and textural characteristics of the obtained anionic clay matrices.

The nature of the metal salts, used as precursors during the synthesis process of layered double hydroxides, is used as a controlled variable synthesis parameter to obtain copper and/or nickel-containing anionic clay matrices with specific properties.

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