THE ROLE OF THE ORGANIC SOLVENT IN OBTAINING HYDROTALCITE - LIKE ANIONIC CLAY NANOPOWDERS WITH SPECIFIC TEXTURAL AND POROUS PROPERTIES[♦]

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Abstract: Hydrotalcite - like anionic clays were synthesized by the sol-gel method while ethanol and phenol were used as organic solvents in the synthesis medium. The X-ray diffraction analysis points out that the obtained nanopowders possess a well crystallized hydrotalcite – like anionic clay structure. The N_2 adsorption analysis reveals that the features of the nanoparticles ensemble pattern and the textural properties of the mesoporous structure are dependent on the nature of the organic solvent. When ethanol is used in the synthesis medium the emerged nanoclay present a relatively uniform porous structure with a specific surface area of 140 m^2/g and the value of N_2 adsorption volume is equal to 270 mL/g. On the contrary when phenol is present as major organic solvent in the synthesis medium a lower specific surface area is obtained (77 m^2/g) while the value decreases to 170 mL/g. These results point out that the nature of the organic solvent is important for tailoring the textural and porous properties of hydrotalcite – like anionic clay nanostructures.

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INTRODUCTION

Layered double hydroxides (LDH), also known as anionic clays or hydrotalcites, consist of two types of metallic cations accommodated with the aid of a close packed configuration of OH - groups in a positively charged brucite-like layer. The charge typically results from the substitution of the lower valence metal in the brucite structure by a metal of higher valence. The interlayer space in the LDH is, typically, occupied by water and various anions for charge compensation [1]. The general LDH chemical structure can be represented by the general formula: $[M^{II}_{1-x} M^{III}_{x} (OH)_2]^{x+} [A^{m-}_{x/m} \cdot nH_2O]^x$ where MII is a divalent (e.g. Mg, Co, Mn,Ni, Cu, Fe, Zn) and MIII a trivalent metal cation (e.g. Al, V, Fe, Mn), A^{m-} is the intercalating anion, such as Cl^-, SO_4^{2-}, NO_3^- and n represents the water content [2]. An extensive development of these materials for various applications such as anion exchangers host structures for the synthesis of nano-composite materials and precursors of catalysts [3]. In this latter case the attractive interest comes from the control of the crystallinity and texture, as well as the intrinsic acid–base and redox properties, which can be fine tuned by the composition, the synthesis method and the activation process [4]. Co-precipitation of mineral salts in aqueous medium followed by hydrothermal treatments of the gels constitutes the conventional elaboration process of LDH materials [1]. However it has been demonstrated that LDHs can also be obtained by the sol–gel method. It is needed to note that the solids thus obtained exhibited specific surface areas generally larger than those obtained using a conventional co-precipitation procedure. The aim of our work was to study the role of organic solvent in obtaining specific textural properties for MgAl- type hydrotalcite. More precisely we want to report here new results about BET surface area (S_{BET}), pore volume, (V_p), and N_2 adsorption volume, (V_{N2}) when ethanol and phenol were used as organic solvents in the synthesis medium when MgAl layered double hydroxides (LDHs) were obtained by the sol – gel synthesis method.

EXPERIMENTAL

Synthesis of MgAlHT samples by the sol – gel method

Layered double hydroxides samples are synthesized by using a specific sol –gel method. Typically 0.15 mol of Mg acetylacetonate was solved in 200 mL of the used organic solvent (ethanol or phenol – ethanol molar ratio 2/1) by addition of the required amount of HCl (Carlo Erba, 35% RPE). The solution was refluxed for 4 h under continuous stirring. The solution was then added dropwise for about 1h to 200 ml solution of 0.125 mol of Al acetylacetonate in organic solvent containing ca. 0.5 cm^3 HCl. The pH of the mixture was adjusted to 11 with an aqueous ammonia solution 0.2 M and the obtained mixture was refluxed under continuous stirring until a gel was formed. The gel was aged in ethanol or phenol, isolated by centrifugation and dried at 323 K for 12 hours.

The samples were denoted as HT_1 when ethanol was used as organic solvent and HT_2 when phenol was the major organic solvent in the synthesis medium.

Characterisation of the LDHs studied samples

X-ray fluorescence spectroscopy (XRF), Shimadzu XRF - 1700 sequential XRF spectrometer, was used to determine the chemical composition of the samples. Powder X - ray diffraction (XRD) patterns were recorded using a Philips PW 1840 diffractometer under the following conditions: 40 kV, 30 mA, monochromatic CuKα radiation (λ = 0.15418 nm) over a 2θ range from 4 to 70º. The nitrogen adsorption – desorption isotherms were recorded at 77 K on a Coulter SA 3100 automated gas adsorption system on samples previously degassed at 383 K for 7 h under vacuum. Microcomputer processing controlled the analysis. Specific surface areas (S_{BET}) were determined with the Brunauer–Emmett Teller (BET) method on the basis of adsorption data. The pore volume (Vp) values were determined by using the t-plot method of De Boer.

RESULTS AND DISCUSSIONS

Figure 1 illustrates the XRD patterns of hydrotalcite – like anionic clay synthesized samples; the diffraction peaks typical of layered double hydroxides structure [1] with sharp and symmetric reflections of the basal (003), (006) and (009) planes and broad, less intense and asymmetric reflections for the nonbasal (012), (015) and (018) planes can be clearly identified. The intensity and the sharpness of the peaks reveal also some differences in the crystallinity of the samples. The XRD reflections were indexed using a hexagonal cell with rhombohedral symmetry (R – 3m), commonly used as a description of the LDH structure. The parameter *a*, calculated as 2 × *d(110)*, is a function of the metal - metal distance within the layers pointing out the cations stacking in the 003 planes while the *c* parameter, calculated as 3 × *d(003)*, 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. The Mg / Fe atomic ratio obtained by XRF, the calculated lattice parameters and the interlayer free space are shown in Table 1. The values of the lattice parameter *a* are almost constant and agrees well to the previous reported values of iron substituted hydrotalcite – like materials [4]; this result reveals that the specific properties of the used aqueous – organic synthesis medium (e.g. dielectric constant, viscosity, swelling properties) doesn't alter the average inter - metallic space of the layered clay matrix. On the contrary the *c* parameter and interlayer free space (IFS) values (see Table 1) modify when the organic solvents are used in the synthesis process.

In fact, the solvents bring in the synthesis medium their own electrostatic properties that are able to develop new electrostatic features of the synthesis medium thus to establish new electrostatic interactions not only between the reactants but also between the clay layers; this can modify the distance between the clay layer and change the values of *c* parameter. Therefore the value of *c* parameter is equal to 23.37 Å for HT_1 but increases

to 23.54 Å when phenol is also present in the synthesis medium. The interlayer free spacing (IFS) values are calculated by subtracting the thickness of the LDH layer (4.8 Å, [1]) from the calculated d_{003} spacing. The values increase from 2.99 Å for HT_1 to 3.04 Å for HT_2, respectively. The decrease in IFS values point out that the nature of the solvent influences the space between the anionic clay layers.

Table 1. *The samples name, chemical compositions and XRD lattice parameters*

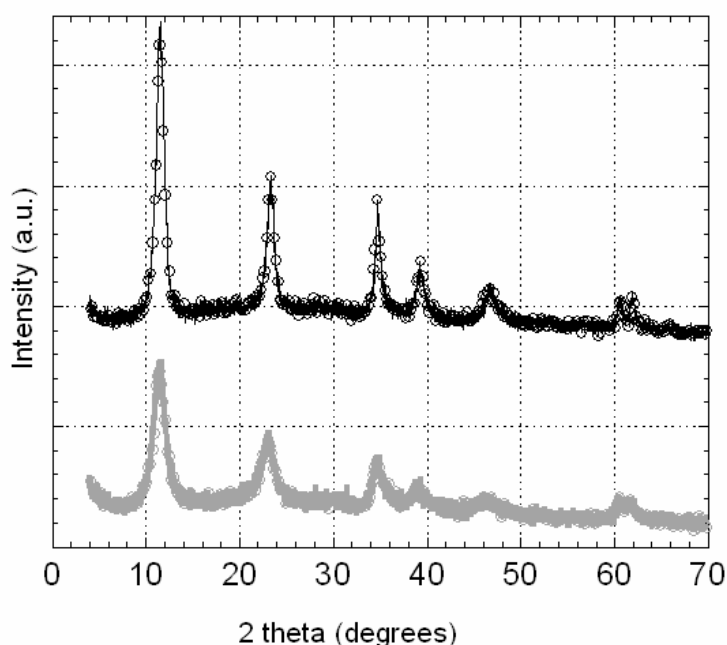| Sample	Mg : Al molar ratio (from XRF)	Solvent (molar ratio)	Lattice parameters (Å)	
			a	*c*
HT_1	1.9 : 0.97	ethanol	3.059	23. 37
HT_2	2.1 : 0.94	phenol / ethanol (2 / 1)	3.059	23. 54

Figure 1. *The XRD pattern of HT_1 and HT_2 samples*

The nitrogen adsorption isotherms of the samples, shown in Figure 2, are similar to one another and correspond to a type IV in the IUPAC classification with a type H_3 hysteresis loop and no limiting adsorption at p/p_0 values close to unity; at low relative pressure the prevailing process is the formation of a monolayer while a multilayer adsorption takes place at a high relative pressure. For the values of relative pressure higher than 0.8 condensation takes place giving a sharp adsorption volume increase. This behavior indicates that this sample has a mesoporous character. This data suggest that these materials consist of aggregates of plates or edged particles forming slit shaped pores that are characteristics for LDH-like materials. The hysteresis loop is broader when ethanol is the only organic solvent in the synthesis medium revealing [21] an emphasized nonuniformity in pores size and/or shape. The BET surface area S_{BET}, pore

volume V_p, and the volume of nitrogen adsorbed at p / p_0 values close to unity, V_{N2}, are presented in Table 2.
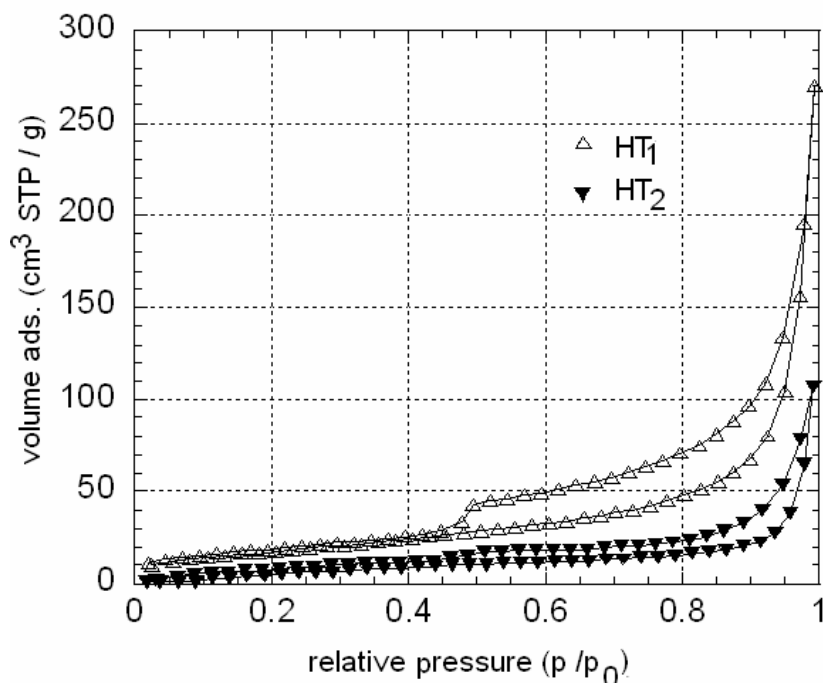

Figure 2. *N_2 adsorption-desorption isotherms of HT_1 and HT_2 samples*

When ethanol is used in the synthesis medium the emerged nanoclay present a relatively uniform porous structure with a specific surface area of 140 m^2/g and the value of N_2 adsorption volume is equal to 270 mL/g. On the contrary when phenol is present as major organic solvent in the synthesis medium a lower specific surface area is obtained (77 m^2/g) while the value decreases to 170 mL/g. Pore volume value also increases when ethanol is present as organic solvent in the synthesis medium.

Table 2. *Characteristics N_2 adsorption / desorption data for the studied samples*

Sample	BET area (m^2/g)	V_p (mL/g)	V_{N2} (mL/g)
HT_1	140	0.431	270
HT_2	77	0.354	170

CONCLUSIONS

The current study demonstrated that the microstructures of ternary layered double hydroxides, obtained by sol – gel method are significantly transformed when etanol and phenol are used as the organic solvents in the synthesis medium. Higher values of the BET surface area and pore volume are obtained when the sol - gel synthesis is done in ethanol though the corresponded values decreases when a mixture of ethanol and phenol

is used as the synthesis medium. These results can have important consequences in obtaining hydrotalcites – like materials with tailored porous properties.

ACKNOWLEDGEMENT

REFERENCES

1.   Cavani, F., Trifiro, F., Vaccari, A.: Layered double hydroxides, *Catal. Today* **1991**, __11,__ 173-*209, and references therein.*
2.   Jones, W., Chibwe, M.: *Pillared Layer Structures Current Trends and Applications*, Elsevier, London, **1991**, pp. 67-81.
3.   Carja, G., Nakamura, R., Aida, T., Niiyama, H.: Textural properties of layered double hydroxides:effect of magnesium substitution by copper or iron, *Microp. Mesopor. Mater.* **2001**, __47__, 275-284.
4.   Carja, G., Nakamura, R., Aida, T., Niiyama H.: MgVAl mixed oxides with mesoporous properties using LDHs as precursors, *J. Catal.* **2003**, __218,__ 104-111.
5.   Carja, G., Nakamura, R., Aida, T., Niiyama, H.: Tailoring the porous properties of iron containing mixed oxides for As (V) removal from aqueous solutions, *Microp. Mesopor. Mater.* **2005,** __94__, 94-100.