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ABOUT MESOPOROSITY CHARACTERISTICS OF IRON CONTAINING HYDROTALCITE-LIKE MATERIAL STUDIED BY USING N_2 ADSORPTION METHOD

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SUMMARY. *Layered double hydroxides in which iron was introduced in the hydrotalcite layer were synthesized by a coprecipitation method. X-ray diffraction (XRD) and N_2 adsorption were used like physical-chemical techniques to characterize the emerged materials. The treatment of the adsorption isotherms by different computation models show that nonuniformity and the constrictions of the mesoporous structure accentuated, BET surface area increased while pore volume decreased when iron was introduced in the hydrotalcite network.*

Keywords: hydrotalcite, layered double hydroxides, mesoporosity characteristics, BET surface area

INTRODUCTION

Hydrotalcite is a naturally occurring anionic clay with the formula $Mg_6Al_2(OH)_{16}CO_34H_2O$. It presents a positively charged brucite-like layers ($Mg(OH)_2$) in which some of Mg^{2+} are replaced by Al^{3+} in octahedral sites of the hydroxide sheets. Interstitial layers formed by CO_3^{2-} anions and water molecules compensate the excess of positive charge resulting from this substitution. Both magnesium and aluminum can be isomorphously substituted by other divalent or trivalent cations so a wide range of compositions containing various combinations of M(II), M(III) and different anions A^{n-} can be synthesized. The resulting materials, known as layered double hydroxides (LDHs) or hydrotalcite-like anionic clays, are layered mesoporous materials which have received considerable interests in recent years owing to their applications as catalysts, catalyst precursors, adsorbents and ion exchangers [1].

In defining or tailoring the catalytic and the adsorption properties of a material its crystallinity and textural characteristics are of particular importance. For example, the shape and the size of pores, associated with the uniformity of porous structure, can promote shape selectivity; a higher surface area will facilitate guest-host interactions; even mass transfer process depends on the porosity type. Despite this, many of the published studies concerning LDHs deal only briefly or not at all with their textural characteristics and with the possibility to tailor them for a required application [2,3].

In order to get new information about the possibility to tailor the mesoporous properties of LDHs, the aim of this study is to investigate by different physical-chemical techniques how these properties could be altered through direct synthesis when iron was introduced in LDH network.

EXPERIMENTAL

Synthesis of LDHs

All the samples were synthesized by a coprecipitation method in low supersaturation conditions [1], at 313 K, under a bubbling constant flow of nitrogen in the reaction medium and vigorous stirring. After an aging step, the obtained precipitates were separated by centrifugation, washed extensively with warm deionized water until sodium free and dried under vacuum at 338 K.

- hydrotalcite sample (MgAlLDH): 100 ml of an aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.03 mol) / $Al(NO_3)_3 \cdot 9H_2O$ (0.01mol) and an aqueous solution of NaOH / Na_2CO_3 ($CO_3^{2-}/Al^{3+}+Mg^{2+}=0.67$, $HO^{-}/Al^{3+}+Mg^{2+}=2.25$), were added dropwise together, in such a way that the pH remained at a constant value of 9.5. The resulting precipitate was aged at 338 K for 24 h under stirring.
- iron containing layered double hydroxide (FeLDH): an aqueous solution (85 ml) of $Mg(NO_3)_2 \cdot 6H_2O$ (0.03mol) / $FeSO_4$ (0.01mol) and an aqueous solution of Na_2CO_3 (1M, 30 ml) were added dropwise together over a period of 2 h at a constant pH value of 8.2. The resulting precipitate was aged at 305 K for 24 h under stirring.

Characterization

X-ray powder diffraction patterns were recorded on a Philips PW 1840 diffractometer using monochromatic CuKα radiation (λ=0.154 nm), operating at 40 kV and 30 mA over a 2θ range from 4 to 70 degree.

N_2 adsorption isotherms were measured on a Coulter SA 3100 automated gas adsorption system. Prior to the measurements the samples were heated for 5 h under vacuum at 383 K in order to expel the interlayer water molecules. The BET specific surface area (S_{BET}) was calculated by using the standard Brunauer, Emmett and Teller method on the basis of the adsorption data. Pore volume was determined by using the t-plot method of De Boer [4]. Pore size distributions were calculated from the desorption branches of the isotherms using the Barret, Joyner and Halenda method and the corrected Kelvin equation [4,5]. All these models are considered to be fully applicable to mesoporous materials. The IUPAC classification of pores and isotherms were used in this study.

RESULTS AND DISCUSSION

The XRD patterns of synthesized samples (not shown) exhibit sharp and symmetric reflections for the *(003)*, *(006)*, *(110)* and *(113)* planes and broad symmetric peaks for the *(102)*, *(105)* and *(108)* planes, which are characteristics of these materials [1]. The lattice parameters (see table I) are calculated by indexing the peaks under a hexagonal crystal system, using a least squared method.

The parameter ***a*** corresponds to the cation-cation distance within the brucite like layer while the parameter ***c*** is related to the total thickness of the brucite-like layer and the interlayer distance [1]. The decrease of the parameter ***a*** for the FeLDH sample clearly indicates the incorporation of iron into the brucite-like layer, as the ionic radius of Fe^{2+} hexacoordinate is 0.61 Å.(after Shanon [6]) which means smaller than the ionic radius of Mg^{2+} hexacoordinate (0.71 Å. after Shanon) The decrease of the parameter *c* and the d_{003} (basal spacing calculated from the 003 reflection position in the XRD pattern [1]) can be attributed to the modified electrostatic interactions between the layer and the interlayer network when another metal is introduced in the LDH layer.

Table I

The chemical composition and lattice parameters of MgAlLDH and FeLDH

Sample	Mg:Fe:Al	XRD phase	Lattice parameters (Å)		
			a	*c*	d_{003}
MgAl LDH	3: 0: 1	LDH	3.059	23.38	7.79
FeLDH	1: 2: 1	LDH	3.042	23.11	7.70

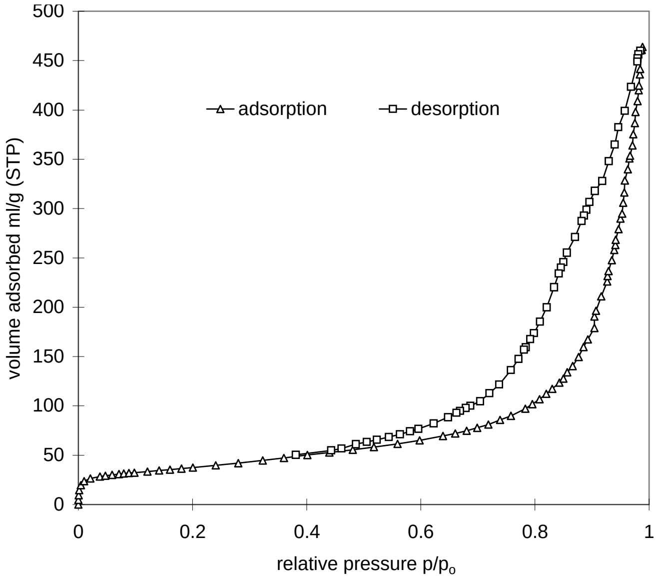

Figure 1. N_2 adsorption-desorption isotherms at 77 K of MgAlLDH

The nitrogen adsorption isotherms of MgAlLDH, and FeLDH are shown in figure 1 and figure 2, respectively. Their different appearances suggest the modifications of the porosity characteristics when iron substituted magnesium in the LDH network.

For MgAlLDH (figure 1) we observe a type IV isotherm with a broad type H_3 hysteresis loop, in the middle range of relative pressure. 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. Hysteresis loop type shows that aggregates of plate-like particles forming enough nonuniform slit shaped pores [5] are present in this sample. For FeLDH (figure 2) the adsorption isotherm changed its shape and the irregular form of type H_3 hysteresis loop indicates the presence of nonuniformity in pores size and/or shape. These characteristics allow us to conclude that for FeLDH the nonuniformity of the mesoporous structure accentuated.

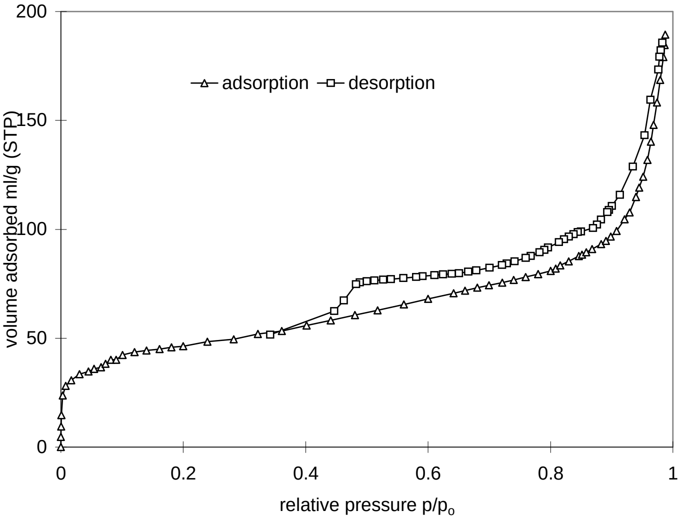

Figure 2. N_2 adsorption-desorption isotherms at 77 K of FeLDH

Pore size distribution (PSD), obtained from BJH method, is further used to check and to complete the previous results. The PSD curves, figure 3, points out important modifications in the pore size range of the samples. The PSD curve of MgAlLDH has two maximums at 9.5 and 12.6 nm. Pores with sizes belonging to the entire range characteristic for mesoporosity appear in this case. The PSD curve of FeLDH with two maximums at 27 and 37 nm shows clearly the enlargement of the pore size. All the pores are larger than 5 nm and we observe no mesopores with sizes larger than 45 nm. Moreover the PSD curve of FeLDH is broader showing also that nonuniformity of the porous structure accentuates when iron is introduced in the hydrotalcite network.

The values of BET surface area and pore volume (V_p) of synthesized samples are given in table II. It can be seen that the FeLDH develops lower BET surface area in comparison to MgAlLDH whereas the value of pore volume increases.

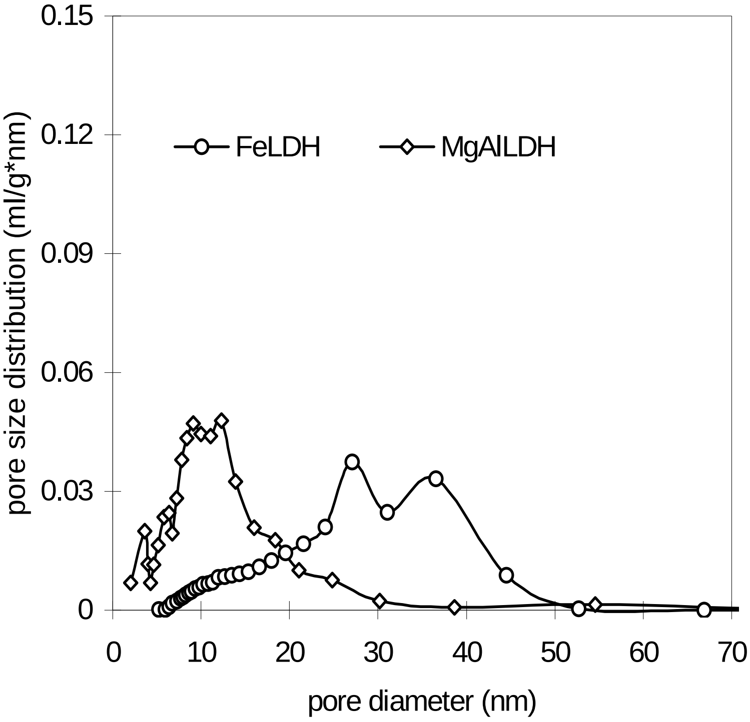

Figure 3. Pore size distribution calculated using BJH method from adsorption data

Table II.

The values of BET area and pore volume of synthesized samples

Sample	BET area (m^2/g)	V_p (ml/g)
MgAlLDH	132	0.640
FeLDH	107	0.680

CONCLUSIONS

The current study demonstrated that N_2 adsorption method proved to be a useful technique for studying the features of the porous structure of layered double hydroxides when vanadium is introduced in the LDH layer. As a general trend the iron containing layered double hydroxide presents a mesoporous structure with larger mesopores, lower BET surface area value and a higher nonuniformity of the porous structure than MgAlLDH. The possibility of altering the textural properties of LDHs when a new metal is introduced in the layer may offer new perspectives in tailoring the textural characteristics of these materials for potential applications.

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