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Iodine sorption by microwave irradiated hydrotalcites

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Abstract

Mg–Al hydrotalcite-like compounds (HT) were prepared by the microwave method on the one hand with ethoxide–acetylacetonate and on the other with acetylacetonate as precursors. They presented a maximum sorption capacity of 2.179 and 1.517 meq of $^{131}I^-$/g of hydrotalcite respectively. When the hydrotalcites were calcined and rehydrated in a $^{131}I^-$ solution, iodine sorption decreased in both samples to 1.515 and 1.446, respectively. The corresponding value for nitrated hydrotalcite which was prepared by the conventional method for comparison purposes, was 0.570. The radionuclide content in hydrotalcites was determined by γ-spectrometry. $^{131}I^-$ sorption is dependent on two main parameters: one is the type of the interlayer organic material and the second the surface area. It was found that hydrotalcites prepared with ethoxide–acetylacetonate were better sorbents for $^{131}I^-$ than those with acetylacetonate. Still, if the specific surface area increased, $^{131}I^-$sorption increased as well; nitrated HT resulted in low specific surface area and a low sorption capacity. It is, therefore, concluded that organic residues present in the samples prepared by the microwave method favor the sorption of radioactive anions, in particular $^{131}I^-$ if compared with nitrated and/or carbonate interlayered hydrotalcites.

1. Introduction

Hydrotalcite-like compounds are laminar clays capable of anion-exchange reactions. They are the anionic equivalent of cationic clays. Magnesium atoms in hydrotalcites are octahedrally coordinated to the surrounding hydroxide ions and share adjacent edges to form sheets. Some of the magnesium cations may be replaced by aluminum cations, which produce net positive charges on the metal hydroxide layers as aluminum remains octahedrally coordinated to the hydroxyl groups. The positive charges are neutralized by anions and water molecules occupying the interlayer space [1], Fig. 1. If hydrotalcites undergo dehydroxylation and decarbonation, the layered structure is destroyed, for example when they are heated at about 450–600 °C [2,3].

$$\underset{\text{(hydrotalcite)}}{[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{m^-})_{x/m}\cdot nH_2O}$$

$$\rightarrow \underset{\text{(metal oxides)}}{MO + M_2O_3 + \text{anion(A)oxides} + H_2O}$$

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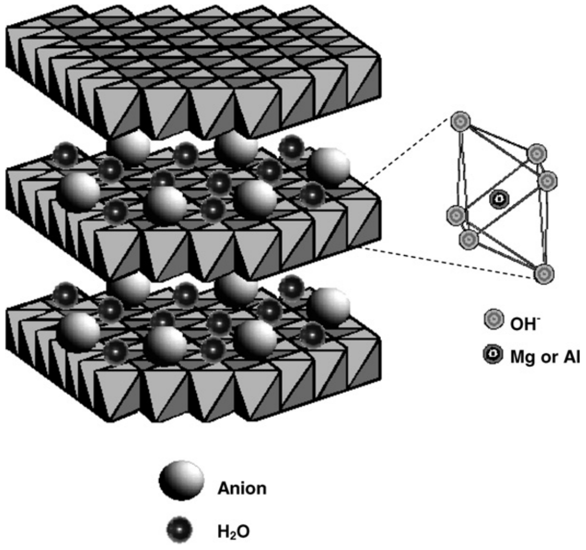

Fig. 1. Structure representation of the hydrotalcite-like compounds.

where in hydrotalcite x cations M^{2+} may be replaced by three-valent atoms, M^{3+}, which produce positively charged layers. This charge is neutralized by A, a compensating anion with charge m^- as CO_3^{2-}, SO_4^{2-}, Cl^- or NO_3^- among others. The calcined hydrotalcite which is composed by metal oxides as determined by X-ray diffraction, may be rehydrated again contacting the solid with an anionic aqueous solution; the hydrotalcite structure is, then, recovered incorporating the solution anions [4].

Recently, a new hydrotalcite synthesis method using microwave irradiation has been presented [5,6]. The crystallite size of the obtained solids is often found to be smaller than in the conventionally prepared hydrotalcites. If the particle size is smaller the diffusion is almost avoided. These solids can be utilized in the treatment of radioactive wastes. In the specialized literature, most work on radioisotope sorption deals with cation retention; studies on radioactive anion retention are less frequent. In this work, we have chosen iodine as a model anion as it is the most frequently found in hospital waste solutions. In previous papers [7,8], $^{131}I^-$ sorption by carbonated hydrotalcites was found to be very low, although the iodine sorption amount increased considerably when hydrotalcites were calcined [9]. The purpose of the present paper is to further study the I^- sorption on hydrotalcites prepared by the sol–gel and the microwave irradiation method.

2. Experimental

2.1. Synthesis of hydrotalcite-like compounds with organic compounds interlayered

Two types of hydrotalcite-like compounds, also referred as HT, were prepared, either utilizing magnesium ethoxide (Aldrich, 99%) and aluminum acetylacetonate (Aldrich, 99%) precursors (samples EA) or utilizing magnesium acetylacetonate (Aldrich, 99%) and aluminum acetylacetonate precursors (samples AA) as described elsewhere [10]. A solution was prepared with 150 mL of ethanol (Baker, 99%) and 4 mL of 35% chlorhydric acid (Baker). The solution was constantly stirred during 1 min in presence of nitrogen flow. Magnesium ethoxide (4.25 g) for the first type of HT (samples EA), and 10.43 g of magnesium acetylacetonate for the second type (samples AA), were mixed with 4.32 g of aluminum acetylacetonate and were, then, added to the ethanol and chlorhydric acid solution, which was constantly stirred during the whole process (100 rpm). The final pH value of the mixtures was found to be 5.65 and 6.25, respectively.

The obtained gels were irradiated in an autoclave heated by microwave irradiation (MIC-I from Sistemas y Equipos de Vidrio S. A. de C. V.) for 20 min (t_1) operating with a power level of 120 W at 120 °C and a pressure of 600 kPa. The final pH value of the mixtures was adjusted to 11.5 with ammonium hydroxide and then 4 mL of deionized water was added to the mixture. The resulting solutions were, once more, irradiated for a second period (t_2), in the microwave autoclave, for 10 and 30 min, controlling always pressure, temperature and maintaining the stirring. The solids were recovered by decantation and washed with ethanol several times. Ethanol was evaporated from the solution with a nitrogen flow. The solids were dried in an oven at 70 °C for 3 h. Samples with 10 and 30 min t_2 irradiation periods were referred to as EA10 and EA30 and AA10 and AA30, respectively. A schema of the synthesis process is presented in Fig. 2.

2.2. Synthesis of nitrated hydrotalcite-like compound

The nitrated hydrotalcite-like compound with an Al/(Mg + Al) molar ratio of 0.25 was synthesized as reported in a previous work [8]: 830 mL

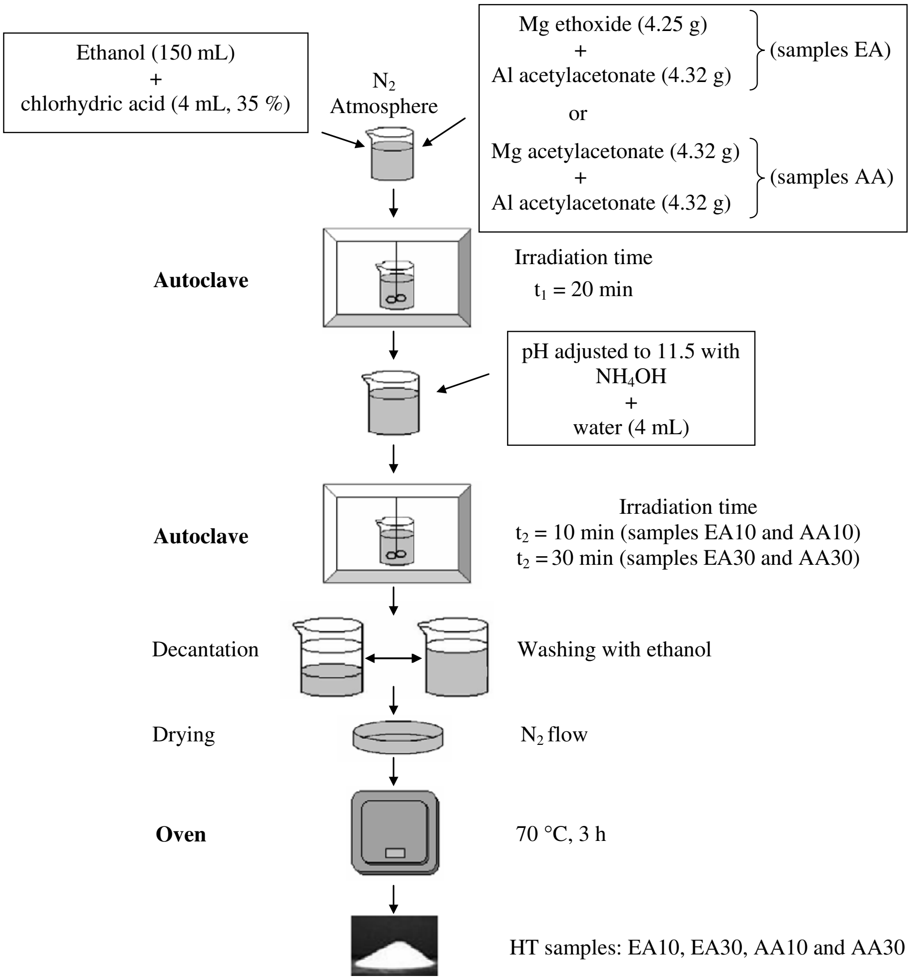

Fig. 2. Schema of the synthesis process of hydrotalcite-like compounds.

of a 1.86 M NaOH (Baker) aqueous solution was added dropwise for 10 min to 118.4 mL of a total 2.5 M aqueous solution containing 125.58 g of $Mg(NO_3)_2 \cdot 6H_2O$ (Baker) and 61.24 g of $Al(NO_3)_3 \cdot 9H_2O$ (Baker), with vigorous stirring at 25 °C for 3 min. The pH varied up to a final value of 13. The obtained gel was treated in a commercial microwave oven (Philco) operating at 2.45 GHz for 5 min. This sample will be referred as HT–NO_3. The use of microwave irradiation is recommended as it drastically shortens the hydrotreatment time [5]. The obtained solids were washed with water and the precipitate was recovered by decantation and dried in an oven at 70 °C. Deionized water was used throughout all the preparation. As all samples were synthesized in N_2 atmosphere, the amount of carbonates is expected to be very low [11].

2.3. *Calcined hydrotalcites*

Calcined hydrotalcites, also referred to in this paper as CHT, were obtained by heating hydrotalcite-like compounds in air at 500 °C for 18 h.

2.4. *$^{131}I^{-}$ Sorption*

The solution was prepared dissolving 7.49 g of NaI in 500 mL of water. A drop of radioactive iodine solution was added with an activity of 1 mCi per 100 mL. The final iodine concentration was 0.1 N. Batch experiments were carried out by shaking 10 mL of the previously prepared radioactive $^{131}I^{-}$ solution and 0.100 g of the hydrotalcite sample for 24 h. Previous kinetics experiments [9] have shown that this shaking time is enough to reach equilibrium. Finally, each solution was separated from the solid by centrifugation and an aliquot of 5 mL was analyzed by γ-spectrometry, using the characteristic ^{131}I photopeak, 0.364 MeV. The amount of $^{131}I^-$ sorbed was estimated determining the difference in activity between the original $^{131}I^-$ solution and the corresponding aliquot after shaking it with the HT sample.

2.5. Characterization

The BET surface areas were determined by standard multipoint techniques. A Micromeritics Gemini 2360 instrument was utilized. To determine if the hydrotalcite network was destroyed with temperature or if the hydrotalcite structure was recovered when the HT samples were in contact with iodine solution, X-ray diffraction patterns were obtained. A Siemens D-500 diffractometer coupled to a copper anode X-ray tube was used. A diffracted beam monochromator selected the Kα radiation. Compounds were identified in the conventional way using the JCPDS cards.

3. Results and discussion

3.1. $^{131}I^-$ Sorption in non thermally treated samples (organic species effect)

Hydrotalcite-like compounds with organic interlayered species (acetylacetonate and/or ethoxide) were found to be efficient I^- sorbents (Figs. 3 and 4). Fig. 3 shows the sorption of $^{131}I^-$ on hydrotalcite samples EA10 and EA30 and, for comparison purposes, on nitrated hydrotalcite, for different contact periods between the solid samples and the $^{131}I^-$ solution. The maximum I^- sorption was achieved by EA10 sample, 2.179 meq I^-/g. EA30 sample I^- sorption capacity was found to be lower, 1.214 meq I^-/g. On the other hand, these values are quite high if compared with nitrated hydrotalcite, 0.570 meq I^-/g.

Fig. 4 shows I^-sorption on hydrotalcite samples AA10 and AA30, which are compared, as for the previous case, with the I^- sorption capacity of the nitrated hydrotalcite. The maximum I^- sorption capacity (1.517 meq I^-/g) was found, once more, to correspond to AA10 sample irradiated for a t_2 period of 10 min. In sample AA30, I^- sorption capacity was found to be 1.058 meq I^-/g. Although these values are lower than the values obtained for samples EA, they are, indeed, higher than the I^- sorption capacity of nitrated hydrotalcite.

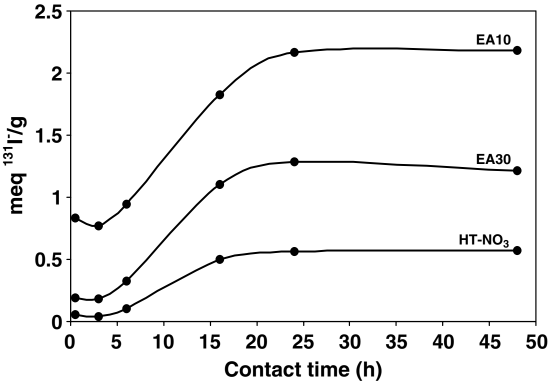

Fig. 3. Amount of $^{131}I^-$ sorbed as a function of the contact time for samples EA10, EA30 and HT–NO_3.

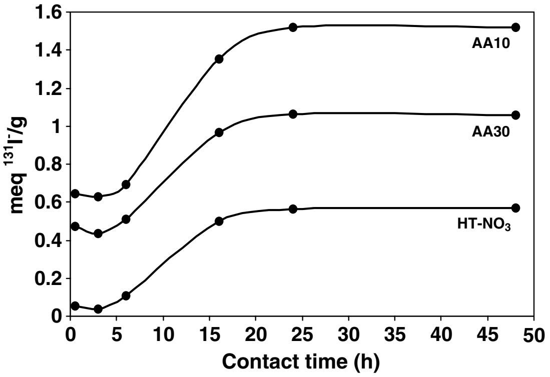

Fig. 4. Amount of $^{131}I^-$ sorbed as a function of the contact time for samples AA10, AA30 and HT–NO_3.

In our previous work [10] it was shown that different organic species were included between the layers of the resulting hydrotalcite depending on the sol–gel precursors. If ethylenediamine (EDA) is added during cobalt sorption in clays or zeolites the final amount of cobalt retained is much higher [12,13]. In hydrotalcite, most probably, iodine forms complexes with the organic species as cobalt does in clays and zeolites. In this way, the amount of retained iodine turns out to be much higher than the values reported for nitrated hydrotalcites.

3.2. $^{131}I^-$ Sorption in non thermally treated samples (surface area effect)

Fig. 5 compares iodine sorbed in the samples EA, AA and HT–NO_3, showing that sorption is higher in samples that present a high surface area. Samples irradiated for a t_2 period of 10 min had a higher

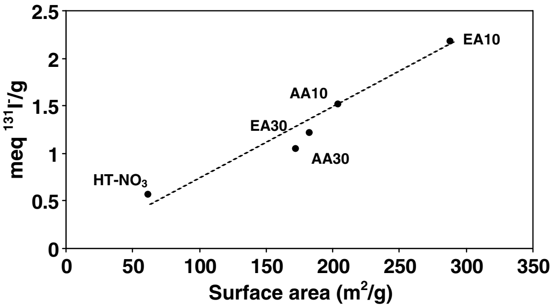

Fig. 5. Comparison between the amount of $^{131}I^-$ sorbed and the surface areas of the series EA, AA and HT–NO_3.

sorption capacity. Samples irradiated for longer t_2 periods, 30 min, showed a much lower surface area as they were constituted by bigger particles.

Series EA surface areas were, generally, higher than those of series AA, probably due to the presence of ethoxide ions (or its residues) in the interlamellar space, which, being smaller in size than acetylacetonate ions, left a larger internal space available. In fact, the highest surface area found was for sample EA30 (288 m^2/g), which was higher than the surface area of other hydrotalcites with carbonates in the interlayer space reported in the literature, 14–90 m^2/g [14]. The surface area values, then, condition the iodine diffusion: if the surface was high, large iodine anions (diameter of 0.432 nm) reached easily all the organic interlayered species.

Table 1 compares the specific areas of samples EA10 and AA10 before and after I^- sorption. In both cases, the specific surface area decreased to a very small value which shows that I^- occupies almost all the available space. Therefore, after sorption, I^- ions occupied the inner part of the structure. A second possibility could be the adsorption of iodine on the pore mouths not entering in the interlamellar space. However this hypothesis has to be rejected as the X-ray diffraction patterns present a shift in the 001 peak, showing that the anionic sites are occupied.

Table 1
Surface area values for the samples EA10 and AA10 before and after $^{131}I^-$ sorption

Sample	Before $^{131}I^-$ sorption (m^2/g)	After $^{131}I^-$ sorption (m^2/g)
EA10	288	25
AA10	204	10

3.3. $^{131}I^-$ Sorption in calcined samples

In a previous work, Olguín et al. [9] found that, when HT was calcined at 500 °C for 18 h before iodine sorption, $^{131}I^-$ sorption capacity increased from 0.24 to 2.08 meq/g for a 0.1 M NaI solution. In order to determine if the same effect was observed in the present HT's, we chose those samples that retained the maximum amount of $^{131}I^-$, samples EA10 and AA10, and we calcined them at 500 °C for 18 h. Fig. 4 compares the X-ray diffraction patterns of the resulting materials. They are constituted by metal oxides and the hydrotalcite structure has collapsed. These calcined samples are referred to as samples EA10C and AA10C, respectively. Note that the MgO peaks are sharper in the AA10C sample, hence the MgO crystals are much larger than in the EA10C (Fig. 6).

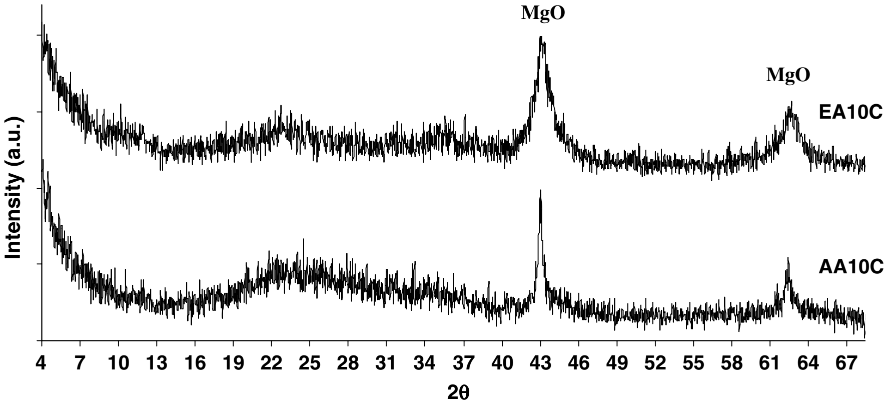

Fig. 6. X-ray diffractograms of the calcined samples EA10C and AA10C.

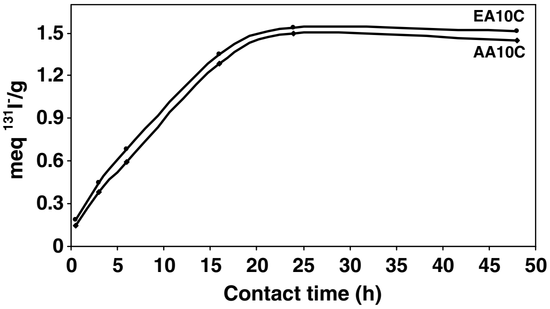

Fig. 7. Amount of $^{131}I^-$ sorbed as a function of the contact time for the calcined samples EA10C and AA10C.

Fig. 7 shows that EA10C was able to sorb 1.51 meq I^-/g and AA10C 1.44 meq I^-/g. These amounts are much lower than those sorbed by EA10 and AA10, respectively. Hence, calcined EA10 and AA10 HT's retain less I^- than the non calcined samples.

In both calcined samples, a similar mixture of oxides is obtained. These oxides present a similar memory effect and reconstruct as comparable hydrotalcites retaining comparable iodine amounts, Fig. 8. In this sense, HT samples are independent of the sol–gel precursor or the initial surface area. However, the amount of iodine retained by the calcined samples is less than the value (2.08 meq I^-/g) obtained with other hydrotalcites by Olguín et al. [9]. Iodine ions are only retained in the exchange sites when hydrotalcites are reconstructed, hence in the present hydrotalcites some exchange sites are poisoned by the burnt organic residues, *i.e.*, with temperature although the oxides are formed they contain carbon or coke which occupy exchange positions in the reconstructed hydrotalcite reducing iodine sorption.

4. Conclusions

Our results may be summarized as follows:

(1) Sorbed amount of $^{131}I^-$ in calcined samples was much less when microwave irradiation time t_2 was increased.
(2) When magnesium ethoxide and aluminum acetylacetonate precursors (samples EA) or magnesium acetylacetonate and aluminum acetylacetonate precursors (samples AA) and nitrated hydrotalcites were compared, it was found that $^{131}I^-$ sorption was related to the increase of specific surface area.
(3) $^{131}I^-$ sorption capacity decreased if the samples were previously calcined.

Hence, the sorption velocities were similar for samples EA and AA and were higher than in sample HT–NO_3, showing that $^{131}I^-$ diffusion was promoted by the presence of the compensation anions ethoxide and acetylacetonate. Therefore, sorption capacity depended on the nature of the compensation anions and also on the available space in the interlamellar region.

The effect of calcinations on the sorption capacity may be attributed, in the first place, to the

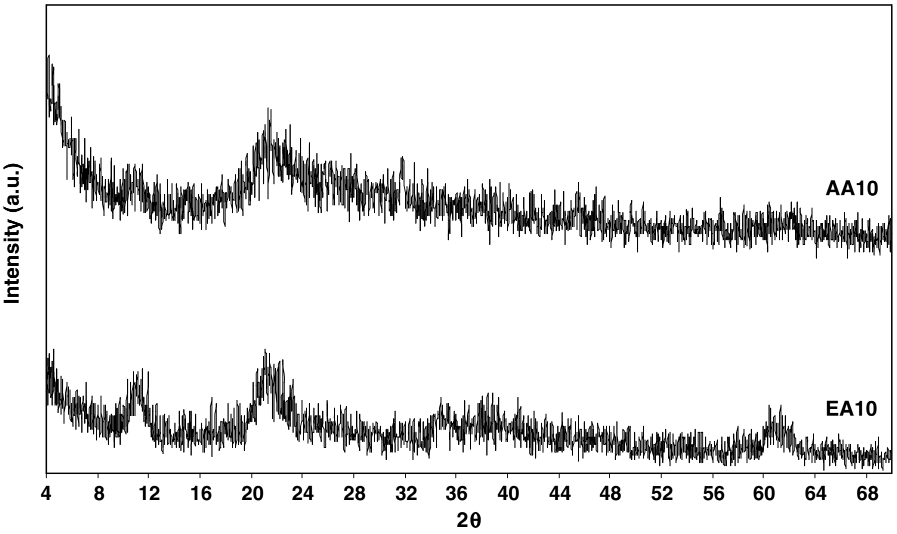

Fig. 8. X-ray diffractograms of the calcined samples AA10 and EA10 after iodine sorption.

decrease of the specific surface area after calcination and in the second to the reconstruction of the structure by the memory effect, as the only compensation anion was the iodine. Therefore, in non calcined samples $^{131}I^{-}$ was not adsorbed exclusively in the exchange sites and most probably interacted with the organic residues forming complexes.

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