$^{131}I^-$ sorption from aqueous solutions by nitrated hydrotalcites

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The sorption of radioactive iodide anion from aqueous solutions on hydrotalcite in the nitrate form has been investigated as a function of the Al/(Mg+Al) ratio. It was found that I⁻ can replace only a small fraction of the nitrates in hydrotalcites and that I⁻ sorption depends highly on Al/(Mg+Al) ratio. $^{131}I^-$ was sorbed by anion exchange in the interlayer of hydrotalcite with an Al/(Mg+Al) ratio of 0.20 and, for higher ratios, $^{131}I^-$ sorption increased more than 3 times. Hydrotalcites in the nitrate form were prepared using microwave irradiation in the hydrotreatment step. The radionuclide content was determined by γ-spectrometry. Solids were characterized by BET, X-ray diffraction and atomic absorption analyses.

Introduction

^{131}I, formed in nuclear reactors with a fission yield of about 0.7%, is a hazardous radionuclide ($T_{1/2}$ = 8.05 days and E_γ = 0.364 MeV). Anionic species as I⁻ in radioactive waste waters are of serious environmental concern. Still, of the radionuclides present in nuclear fuel waste, ^{129}I may reach the biosphere before decaying to insignificant levels, because of its long half-life (1.7·10⁷a), and the fact that it does not interact strongly with most geological materials such as clay, sand, and rock.[1] Organic resins have been applied to remove anionic species from radioactive waste waters. However, they are not recommended for practical application as sorbent because of their radiolytic decomposition. As an alternative inorganic anion exchange material, hydrotalcites have been proposed in Reference 2.

Hydrotalcites (HT) are laminar clays capable of anion-exchange reactions, they can be conceptualized as the anionic equivalent of cationic clays. They have positively charged brucite layers neutralised by anions and water molecules occupying the interlayer space. Magnesium atoms in hydrotalcites are octahedrally coordinated to the surrounding hydroxide ions and share adjacent edges to form sheets of layers. Some of the magnesium atoms are isomorphously replaced by aluminum, (Al^{3+}), which produces net positive charges on the metal hydroxide layers as aluminum (Al^{3+}) remains octahedrally coordinated to the hydroxyl groups. Values between 0.20 and 0.33 are usually reported for Al/(Mg+Al) atomic ratios in synthetic samples. They have a relatively large surface area (20–120 m²·g⁻¹) and an anion exchange capacity of 2–5 mmol g⁻¹.[3–8]

Different members of this family have already been synthesized with CO_3^{2-}, SO_4^{2-}, Cl⁻ or NO_3^- as interlayer anions.[9] MIYATA[7,8] determined the stability of nitrated hydrotalcite, also expressed in this work as HT-NO₃, in NaF and NaOH solutions by examining the molar ratio Al/(Mg+Al) in the HT-NO₃ before and after contact with these solutions. He found that the molar ratio Al/(Mg+Al) in HT-NO₃ did not change, and Al was virtually undetectable in the solution. He concluded that hydrotalcite aluminum did not react with F⁻ or OH⁻ anions. MIYATA[8] has found that the ion exchange equilibrium constant for HT's of monovalent anions are in the sequence OH⁻ > NO_3^- > I⁻. The ion exchange equilibrium constant tends to increase as the diameters of the anions decrease.

Considering that immobilization of I⁻ using hydrotalcite is a matter of controversy, the work exposed in the present paper studies further if hydrotalcite, prepared in presence of microwave irradiation,[10] permits the ion exchange of nitrate ion by I⁻ ions. The microwave irradiation produces, indeed, purer solids whose crystallite size is small. Iodine should, then, diffuse easily between the layers and reach the core of the hydrotalcite crystallites. We discuss the sorption of $^{131}I^-$ from aqueous solutions by nitrated hidrotalcites with a varying Al/(Mg+Al) ratio.

Experimental

Synthesis of nitrated hydrotalcites

Nitrated HT materials with different Al/(Mg+Al) ratios ranging from 0.20 to 0.33 were synthesized as follows: for the first one 825 ml of a 1.86M NaOH (Baker) aqueous solution was added dropwise to a 2.5M aqueous solution containing 125.58 g of Mg(NO₃)₂·6H₂O (Baker) and 45.92 g of Al(NO₃)₃·9H₂O (Baker), with vigorous stirring at 298 K. The amount of reagents used corresponded to a Al/(Mg + Al) molar ratio of 0.20 (sample HT-0.20). The obtained gel was treated in a commercial microwave oven (Philco) operating at 2.45 GHz and power level of 80W for 5 minutes. The obtained solids were washed with water and the precipitate was recovered by decantation and dried under reduced pressure at 373 K. Deionized water was used throughout all the preparation as well as N₂ atmosphere.[10]

The samples HT-0.25, HT-0.30 and HT-0.33, corresponding to Al/(Mg+Al) molar ratios of 0.25, 0.30 and 0.33, respectively, were prepared following the procedure described above, differing only on the used amounts of Al $(NO_3)_3 \cdot 9H_2O$ which were 61.24, 78.73 and 90.49 g, respectively, and the volumes of the 1.86M NaOH aqueous solution: 830, 844 and 900 ml, correspondingly.

Characterization

X-ray diffraction: A Siemens D-500 diffractometer with a copper anode tube and a diffracted beam monochromator was used to identify the obtained compounds. A quartz standard was mixed with the solids to estimate the position of the (003) and (006) hydrotalcite peaks.

BET analysis: Samples were first dehydrated in vacuum at 333–393 K for 2 hours. The BET surface areas were determined by standard multipoint techniques adsorbing nitrogen. A Micromeritics Gemini 2360 instrument was used.

Chemical analyses: Mg and Al content in HT-NO_3 samples was analyzed by atomic absorption. Atomic absorption spectrophotometer Perkin Elmer 500 instrument was used.

^{131}I$^-$ Sorption

0.1M NaI-^{131}I solution, also referred as NaI-1, and Na ^{131}I$^-$ 10^{-14}M solution (carrier free), also referred as NaI-2 were utilized to study ^{131}I$^-$ sorption by hydrotalcites. The pH values of the NaI-1 and NaI-2 solutions were 6.1 and 7.4, respectively. The pH value of NaI solutions before and after the sorption process was measured in an Orion Research Microprocessor Ionaly Ser/90/potentiometer, with a combined glass electrode.

In the test for I$^-$ uptake from aqueous solution, 150 mg of HT-NO_3 samples were placed in the vessel to start the ^{131}I$^-$ uptake reaction. The samples were left in contact for 24 hours with 15 ml of NaI-1 or NaI-2 solutions and, then, they were stirred for 10 seconds. Finally each solution was separated from the solid by centrifugation and an aliquot was analysed by γ-spectrometry, using the characteristic^{131}I photopeak, 0.364 MeV, and half life, 8 days. The amount of ^{131}I$^-$ sorbed was estimated by determining the difference in activity between the original ^{131}I$^-$ solution and the corresponding aliquot. Measurement of the distribution coefficients (K_d) were made in the standard way[11,12] and calculated from:

$$K_d = \frac{\text{Amount of I}^- \text{ in HT}}{\text{Amount of I}^- \text{ in solution}} \cdot \frac{\text{Vol. of solution (cm}^3)}{\text{wt of HT (g)}}$$

Results and discussion

In Figure 1 the ^{131}I$^-$ uptake of the hydrotalcite samples is presented. Curve 1) corresponds to the I$^-$ uptake from a 0.1M NaI-^{131}I solution (NaI-1) and curve 2) shows the theoretical anion exchange estimation. Curve 1) shows in a first step, at low Al/(Mg+Al) ratio, a weak I$^-$ uptake (0.45 mmol I$^-$·g^{-1}), which increases linearly up to 1.45 mmol I$^-$·g^{-1} as Al/ (Mg+Al) increases to 0.33. For each molar ratios Al/(Mg+Al) the anion exchange capacity can be calculated (curve 2) assuming that all Al atoms are incorporated in the HT-NO_3 network and are anion exchange sites. By atomic absorption it was found that the experimental Al/(Mg+Al) ratio was in agreement with the stoichiometric Al/(Al+Mg) ratio. Only a fraction of the exchange sites were occupied by I$^-$ ions. In fact, experimental I$^-$ sorption is systematically around 2.2 mmol·g^{-1} lower than the theoretical estimation independently of the Al/(Mg+Al) ratio. Accordingly, I$^-$ is more efficiently sorbed in high Al/(Mg+Al) ratio nitrated hydrotalcites. Table 1 shows the I$^-$ sorption capacity of nitrated HT according to (a) Al/(Mg+Al) ratio, (b) ^{131}I$^-$ sorption (c) theoretical anion exchange estimation (AEE) and (d) AEE-^{131}I$^-$ sorption.

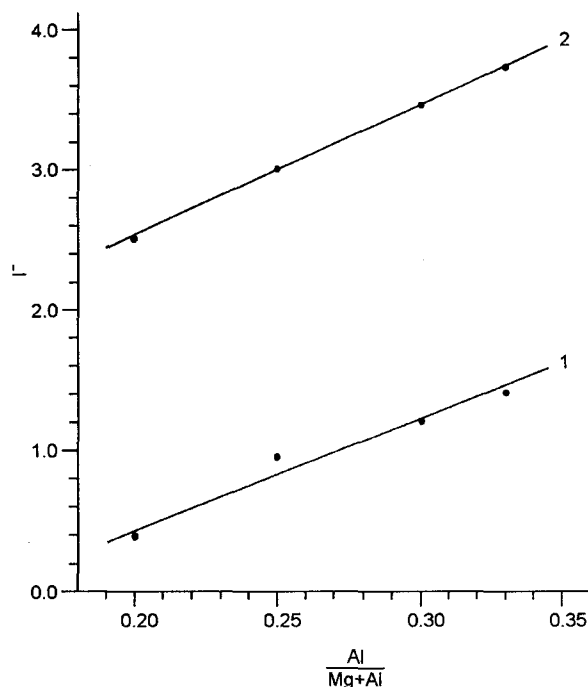*Fig. 1.* Sorption of ^{131}I on nitrated hydrotalcites (mmol·I$^-$·g^{-1}) vs. Al/(Mg+Al) ratio from (1) 0.1M NaI solution, (2) theoretical anion exchange estimation
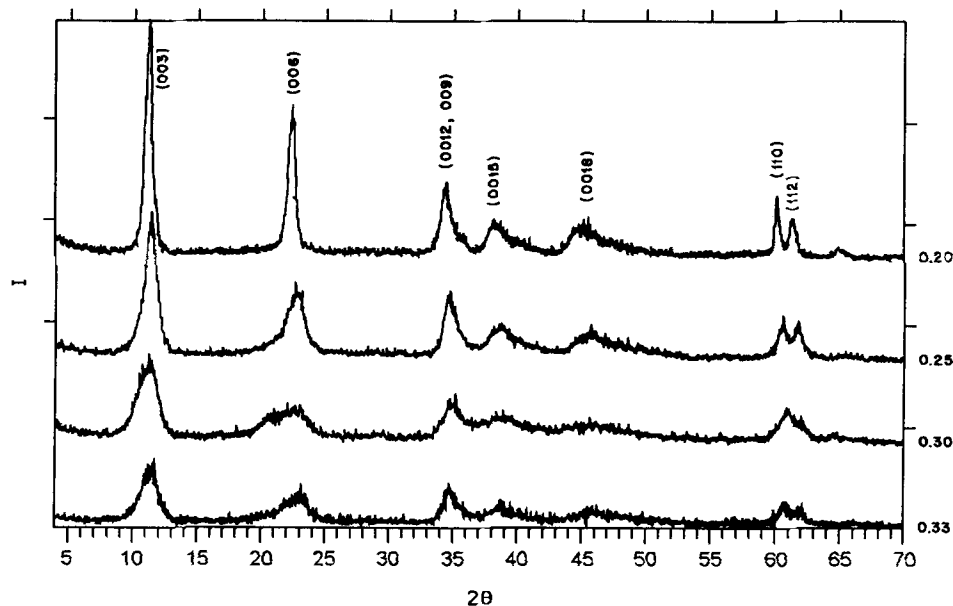
Fig. 2. X-ray diffraction patterns of different Al/(Mg+Al) ratio (0.20, 0.25, 0.30, 0.33) nitrated hydrotalcites

Table 1. Sorption capacity of nitrated samples according to (a) Al/(Mg+Al) ratio, (b) ^{131}I$^-$ sorption, (c) theoretical anion exchange capacity (AEC), (d) difference of AEC and ^{131}I$^-$ sorption

Sample	(a) Al/(Mg+Al)	(b) ^{131}I$^-$ Sorption (mmol/g)	(c) AEC (mmol/g)	(d) Difference (c–b)
HT-0.20	0.20	0.39	2.50	2.11
HT-0.25	0.25	0.95	3.00	2.05
HT-0.30	0.30	1.20	3.45	2.26
HT-0.33	0.33	1.40	3.72	2.32

It is clear that a considerable fraction of the NO_3^- ions of HT did not exchange with I$^-$. In fact this was expected as the Gaines-Thomas equilibrium constant ($\log K_g$) for I$^-$ reported by MIYATA,[8] is much smaller (–0.60) than the one reported for NO_3^- (0.00). Last but not least, no diffusional behavior was observed as the experimental curve reproduces the shape of the theoretical curve. We attribute this feature to the small size of the hydrotalcite crystallites obtained with the microwave irradiation.

The X-ray diffraction patterns of the synthesized hydrotalcites are presented in Fig. 2. All patterns correspond to a hydrotalcite structure (JCPDS card: 22-0700). As Al/(Mg+Al) increased, the crystallinity of the samples decreased as shown by the definition and the size of the X-ray diffraction peaks. The corresponding interplanar distances (d_{006}) are presented in Table 2. The X-ray diffraction patterns of HT samples after I$^-$ sorption from Na-1 solution were crystalline and the peak position was slightly shifted for Al/(Mg+Al) ratios of 0.30 and 0.35. Iodide ions are, then, occupying the anionic sites of the hydrotalcites.

In order to obtain information on the sorption behavior, very different concentrations of I$^-$ were used. The experimental data of the sorption experiments are summarized in Fig. 3 which shows the distribution coefficients (K_d) of I$^-$ from Na-1 and Na-2 solutions in the different HT-NO$_3$ materials. The K_d distribution coefficients are from one to two orders of magnitude higher for Na-2 solution than for Na-1 solution. The influence of I$^-$ concentration is clear from these two sorption experiments.

K_d values were very low for the 0.1M NaI-^{131}I solution, however a small dependence on the Al/(Mg+Al) ratio was still observed. K_d values increased considerably when carrier free Na-^{131}I solutions were utilized. Dramatic differences were observed for samples with different Al/(Al+Mg) ratios, values increased from 28 for Al/(Al+Mg) ratio = 0.2 to 233 cm^3·g^{-1} for Al/(Mg+Al) ratio = 0.35. The differences in K_d values reflected the different Al/(Mg+Al) ratio samples.

Table 2. Interplanar distances (d) of the nitrated hydrotalcites with different Al/(Mg+Al) ratio

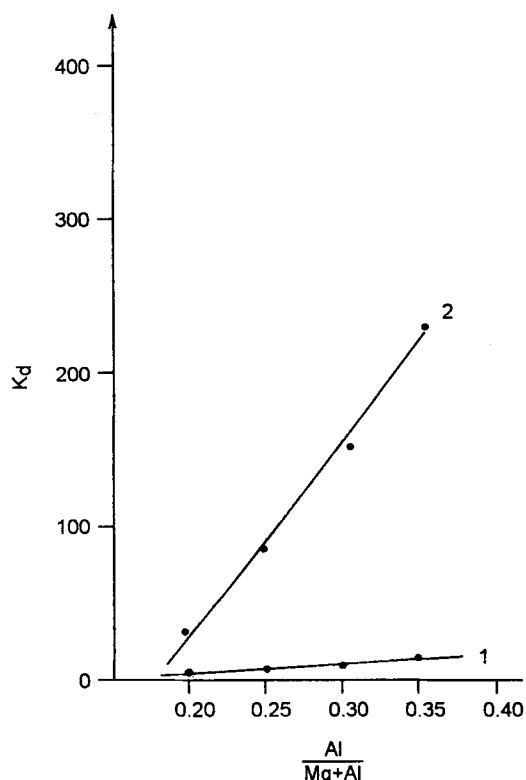| Sample	2θ degree	d(006), Å
HT-0.20	24.06	3.70
HT-0.25	23.86	3.73
HT-0.30	24.12	3.69
HT-0.33	23.58	3.77

Fig. 3. Distribution coefficients (K_d) of I$^-$ from (1) 10^{-1}M and (2) 10^{-14}M NaI solution in nitrated hydrotalcites vs the Al/(Mg+Al) ratio

The surface area of common hydrotalcites varies in a range of 20–120 m^2·g^{-1}. However, in the present work only sample HT-0.20 presented a typical surface area (61 m^2·g^{-1}). The other hydrotalcite samples presented surface areas less than 5 m^2·g^{-1}. Figure 4 compares the position of the (006) peak referred to an internal standard. The location of the peak of the HT-0.20 sample can be attributed to NO$_3^-$ anion exchanged sample. The other samples are, therefore, partially carbonated as the 2θ is close to 22.77°. Hence, during area measurements in our conditions the HT network does not sorb nitrogen. The measurement of the stability of nitrated hydrotalcite made by MIYATA[8] was based on its behavior in presence of NaOH and HF solutions. They did not find aluminium in the solution and concluded that the HT was stable. Hence, the standard BET estimations seem to depend on the Al/(Mg+Al) ratio for samples pretreated in vacuum at 333–393 K for 2 hours.

Conclusions

As expected from the Gaines-Thomas equilibrium constant only a small fraction of the exchange sites were occupied by I$^-$ ions. A very low sorption of I$^-$ in HT as anion exchange on external surface was found. The I$^-$ sorption behavior of hydrotalcites prepared in presence of microwave irradiation was found to be strongly influenced by the Al/(Mg+Al) ratio. In a first step at low Al/(Mg+Al) ratio a very weak uptake was observed,
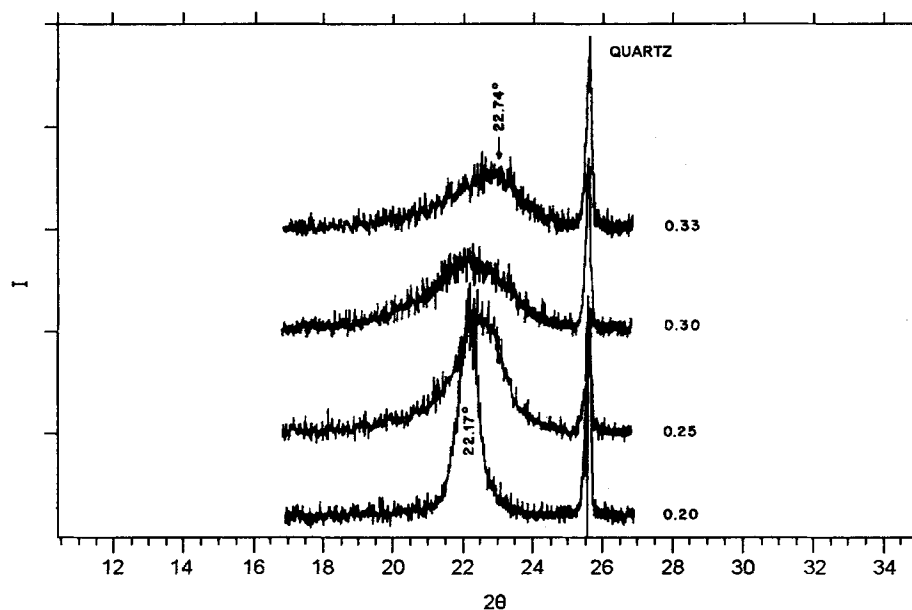

Fig. 4. X-ray diffraction peak position (006) of hydrotalcites referred to the quartz peak (internal standard). Samples HT-0.33, HT-0.30 and HT-0.25 present 2θ = 22.74° (close to 2θ = 22.77° reported in the 22-700 JCPDS card corresponding to a carbonated sample). Sample HT-0.20 has a 2θ = 22.17° corresponding to a nitrated sample

then it increased rapidly to reach an exchange capacity of almost 1.4 meq·g^{-1} of nitrated hydrotalcite. The form of the sorption curves were somewhat similar for very different NaI concentrations. Accordingly, I$^-$ was found to be more efficiently sorbed in high Al/(Mg+Al) ratio hydrotalcites. The K_d distribution coefficient of I$^-$ in the nitrated hydrotalcites from the NaI$^-$ solutions was much higher (of about 1 order of magnitude) for the very low concentration solution (10^{-14}M NaI$^-$ solution) than in the concentrated 0.1M NaI solution.

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