Oleate Epoxidation in a Confined Matrix of Hydrotalcite

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Supporting Information

ABSTRACT: Oleate ion was intercalated into a hydrotalcite obtained using a conventional precipitation method and an alternative, novel method involving microwave-assisted ion exchange. The latter method gave a more crystalline hydrotalcite with better textural properties than the former. The spacing between layers in the hydrotalcites was used to epoxidize the double bond in oleate ion. X-ray diffraction patterns revealed that the layered structure of the hydrotalcites was not altered by the reaction. The epoxidation of oleate ion with m-chloroperbenzoic acid (mCPBA) was monitored using Raman spectroscopy. The results of this work testify to the high potential of hydrotalcites as molecular reactors for reactions in confined spaces.

INTRODUCTION

Hydrotalcite-like compounds (HTICs) are a family of naturally occurring substances also known as “anionic clays”, “layered double hydroxides” (LDH), or, simply, “hydrotalcites” (HTs), of general formula \([\text{M(II)}_x \cdot \text{M(III)}_{1-x} \cdot (\text{OH})_{1-y} \cdot [\text{A}_m \cdot \text{nH}_2\text{O}]] \), where \(\text{A}\) is an anion countering positive charge and \(x\) (usually 0.20–0.36) is the fraction of trivalent metal replacing the divalent metal in the layers.1–3 All HTs are assumed to be derived from the natural mineral called “hydrotalcite”, \(\text{Mg}_6\text{Al}_2\text{CO}_3\cdot (\text{OH})_{16} \cdot 4\text{H}_2\text{O}\), which is structurally similar to brucite \([\text{Mg(OH)}_2]\). In fact, brucite has a layered structure consisting of an infinite number of \(\text{Mg(OH)}_6\) octahedra, the layers being joined by hydrogen bonds to form stacks. In hydrotalcites, a number of \(\text{Mg}^{2+}\) ions are replaced by a trivalent metal, which causes a charge deficiency in the layers that is offset by anions occupying the interlayer spacing together with water molecules. However, \(\text{Mg}^{2+}\) can also be replaced with another divalent metal to form a variety of compounds (the HT family). The sole condition to be met by the divalent or trivalent metal is that its ionic radius should be similar to that of magnesium.4 Electrostatic interactions between interlayer anions and trivalent cations allow the three-dimensional structure of hydrotalcite to be preserved.5

The anion in HTs can range wide in nature and even be an organic one.4 Organic ions possessing a long enough hydrocarbon chain can result in considerable hydrophobic interactions.5–7 Also, the intercalated anion causes the formation of various supramolecular structures in hydrotalcites; in fact, intercalation of long-chain molecules can cause the interlayer region in HTs to self-assemble into mono- or bilayers.7 Hybrid (organic–inorganic) nanocomposites can be obtained using the typical methods for the direct synthesis of HTs, that is, coprecipitation of salts of divalent and trivalent metals in the presence of the organic anion to be intercalated.8–11 The are other equally effective methods based on ion exchange or rebuilding the hydrotalcite from mixed oxides prepared by calcining an HT precursor.

These hybrid materials have found interesting uses based on the ability of hydrophobized HTs to readily adsorb organic compounds12–15 and metals14,16 (especially, environmentally significant substances). Also, the special properties of these nanocomposites allow their use as polymer additives, magnetic materials, and catalysts (or catalyst precursors).17 The long-chain organic anions used as intercalates for HTs include oleate, an alkenylcarboxylate ion5,18,19 that has been used to obtain organic polymer nanocomposites for use as flame retardants20,21 and also in typical applications of organo-HTs such as rheology controlling reagents, environmental purification sorbents, pillared clay precursors, and catalysts or catalyst supports.

Organo-HTs are typically obtained by coprecipitation. This method provides aggregates consisting of nanocrystals containing hundreds or thousands of HT-like layers.22,23 The last two decades have seen increasing efforts at preparing HTs consisting of particles of a small, uniform size in addition to a high specific surface area. One of the most successful methods for synthesizing HTs in the absence of organic ions uses microwave irradiation.24–29 Although Komarneni et al.30 reported the first synthesis of an organo-HT with this method

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more than two decades ago, relatively few organo-hybrid materials have been produced in this way since then.\textsuperscript{31–36}

The ability of hydrotalcites to host molecular reactions in the spacing between their layers is also underexploited. The restricted geometry of organic molecules can lead to specific stereochemical outcomes or alter reaction rates and product distributions. Epoxidation has been widely used to obtain products of industrial interest and synthesize pharmaceutical and fine chemistry intermediates and end-products. The epoxidation of fatty acids gives epoxides for use in the polymer industry.\textsuperscript{37} The process, based on the Prilezhava reaction, uses a peroxide for oxygen transfer to a double bond in the fatty acid. The reaction mechanism is well known and occurs in a concerted manner, which allows the stereochemistry of the starting reactant to be preserved.

This paper reports the first synthesis of an oleate/Mg,Al-HT prepared by microwave-assisted ion exchange in an LDH-containing nitrate as an interlayer anion. The hydrotalcite acts as a host and oleate ion as a guest (interlayer anion). An alternative method, the conventional method, in fact, was used to prepare an oleate/Mg,Al-HT by ion exchange with heating in a thermostatic poly(ethylene glycol) bath. The aim was to obtain two organo-HTs differing in crystallinity to study the epoxidation of the olefinic double bond in oleate ion with a view to assessing the potential use of the resulting organo-HTs and their efficiency as nanoreactors.

\textbf{RESULTS AND DISCUSSION}

\textbf{Metal Ratio.} All HTs were subjected to elemental analysis. As can be seen from Table 1, their Mg/Al metal ratio was close to that in the starting solution. The only, slight differences were those between solids obtained with or without microwave irradiation and those between HTs containing a different intercalated anion.\textsuperscript{34}

\textbf{X-ray Diffraction (XRD) Patterns.} Figure 1 shows the X-ray diffraction patterns (XRD) for the nitrate- (HT-NO\textsubscript{3}-COP) and oleate-containing HTs (HT-OLE-EXC and HT-OLE-MW-2). As can be seen from Figure 1a, the pattern for HT-NO\textsubscript{3}-COP was typical of a hydrotalcite, with narrow, sharp, strong peaks at low 2\theta values but weaker, less symmetric peaks at high 2\theta values. These patterns are consistent with those previously reported for HTs by other authors\textsuperscript{2} and our own group.\textsuperscript{38}

X-ray diffraction analysis allows one to distinguish between baseline reflections (00l), which are typically high, sharp bands at low 2\theta values, from other reflections. Baseline reflections correspond to successive orders in the baseline spacing \(c'\) (viz., the distance between two brucite-like layers as measured from the center of the layer, or, in other words, the interlayer spacing plus the thickness of one layer). The first of the two weak reflections observed above 60° was indexed as (110). This reflection is independent of the type of packing, so it can be used to calculate parameter \(a\) from \(a = 2d_{(110)}\). \(a\) is a measure of the distance between two neighboring cations in a brucite-like layer. Table 1 shows the calculated values of \(a\) and also of the lattice parameter \(c = 3/2(d_{(003)} + 2d_{(006)})\), which is three times \(c'\). Obviously, \(c\) depends on the particular intercalated anion and its orientation, and also on the strength of electrostatic interactions between the anion and brucite-like layers. The \(c\) value for nitrate-containing hydrotalcite is similar to those for solids with a similar metal ratio and nitrate as an interlayer anion.\textsuperscript{2,39}

Figure 1b,c shows the XRD patterns of the oleate-intercalated solids obtained by ion exchange in HT-NO\textsubscript{3}-COP. As can be seen, the patterns exhibited the same reflections but differed in strength. Thus, the peaks for the solid obtained with microwave irradiation for 2 h (HT-OLE-MW-2) were much stronger than those for the thermally prepared solid (HT-OLE-EXC). Also, the solids differed slightly in their 2\theta values, and hence in \(c\) and \(a\). The presence of oleate ion intercalated in the interlayer region of both HTs was confirmed by an expanded baseline spacing (3.379 and 3.368 nm for the oleate-containing solids vs only 0.877 nm for the nitrate-intercalated solid; Table 1). A spacing of ca. 3.4 nm is consistent with partial overlap of oleate chains (see Figure 2) as previously observed by Xu et al.\textsuperscript{5} The oleate-containing solids exhibited a broad halo at about 20° that was assigned to sodium oleate molecules possibly forming micelles in the composite samples. The halo was much more marked in the least-crystalline solid.

Once microwave irradiation was found to provide the most crystalline solid, the influence of the treatment on the structure of the resulting hydrotalcite was examined. Figure 3 shows the XRD patterns for the solids obtained by irradiation for 1, 2, and 3 h. The resulting HTs were quite crystalline. The strength of the (00l) reflections, and hence crystallinity, increased upon increasing the length of the treatment from 1 to 2 h; however,
such a strength decreased upon further expanding the treatment to 3 h. Parameter $c$ was smallest for the solid irradiated for 2 h, possibly as a result of the loss of interlayer water. Increasing the treatment time to 3 h increased the interlayer spacing, thereby decreasing the strength and increasing the width of baseline reflections. As previously suggested by Herrero et al. for other organo-HTs, the increased spacing was possibly due to the HT structure starting to collapse.

After epoxidation reaction, XRD patterns of hydrotalcites did not show any structural changes, just a slight decrease of crystallinity (Figure S1).

**Raman Spectroscopy.** Raman spectroscopy allows the interlayer anion in a hydrotalcite to be identified and the nature of its hydroxyl groups to be elucidated. In this work, we used this technique not only to confirm that, as previously revealed by the XRD patterns, the anion had been successfully intercalated but also to check that nitrate had been thoroughly removed from the interlayer region.

The bands for O–H bond stretching in a Raman spectrum typically appear in the region from 2800 to 3700 cm\(^{-1}\). In this region, a hydrotalcite should exhibit the bands for O–H bonds of water molecules in the interlayer spacing and brucite-like structural units. However, water is a very poor Raman scatterer, so Raman spectroscopy is of limited use here except for studying O–H groups bound to metals in brucite-like units. Figure 4 shows the Raman spectra in the 2500–3800 cm\(^{-1}\) region for the target hydrotalcites. The bands for HT-NO\(_3\)-COP (Figure 4a) were exclusively due to hydroxyl groups, the two strong bands at 3610 and 3502 cm\(^{-1}\) corresponding to O–H bond stretching in hydroxyl groups of brucite-like layers in Mg\(_3\)OH and Mg\(_2\)OH structural units, respectively. Deconvoluting the band at 3502 cm\(^{-1}\) (results not shown) revealed that it comprised two additional components at 3326 and 3115 cm\(^{-1}\). Similarly, to the IR spectra for hydrotalcites, the band at 3100 cm\(^{-1}\) can be assigned to O–H bond stretching in hydroxyl groups connected to the interlayer nitrate anions through hydrogen bonds. This signal has also been assigned to OH bonds in water molecules acting as both donors and acceptors of hydrogen bonds between MgOH and carbonate ions, or nitrate ions in our case. The band at ca. 3300 cm\(^{-1}\) can be assigned to OH groups of water molecules in the interlayer region.

As can be seen from Figure 4b,c, the Raman spectra for the hydrotalcites containing intercalated oleate were virtually identical; however, only that treated for 2 h among those obtained by microwave irradiation was studied. The first salient feature of the spectra was the virtually complete absence of bands for O–H bonds by effect of an increased hydrophobicity in the interlayer region considerably reducing the presence of water molecules. One other salient feature was the very strong bands for C–H bond stretching, which reduced the relative strength of those for O–H bond stretching. The presence of oleate in the solids was confirmed by bands at 3011 and below 3000 cm\(^{-1}\), characteristics to =C–H and C–H stretching vibration modes, respectively. It is further confirmed by the presence of typical Raman bands associated with the oleate molecules in the range 200–2000 cm\(^{-1}\) (Figure 5). The spectrum for HT-NO\(_3\)-COP exhibited a sharp, strong band at 1056 cm\(^{-1}\), which was assigned to stretching of N–O bonds in interlayer nitrate ions. This band was accompanied by other, smaller ones, the most salient of which fell at 555 and 717 cm\(^{-1}\). The former, together with a very small one at ca. 470 cm\(^{-1}\), was assigned to the symmetric stretching of Al–OH bonds (the A\(_{2g}\) and E\(_g\) vibration mode, respectively). On the other hand, the band at 717 cm\(^{-1}\) was assigned to vibrations of Mg–O bonds. In this spectral region, oleate-containing HT's
show bands for C−C, C=C, and C=O bond stretchings and also for deformation of these and C−H bonds. For comparison, Figure 5 also shows the Raman spectrum for pure sodium oleate, which exhibits all the bands seen in the spectra for the oleate-containing HTs except those at 555 and 717 cm$^{-1}$, due to M=O bonds in brucite-like layers. Also worth noting is the absence of the stretching band at 1056 cm$^{-1}$ present in the spectra for the two oleate-containing HTs, which clearly shows that ion exchange occurred to an optimum extent in both cases.

**Thermogravimetric Analysis (TGA) Results.** TGA analyses were performed to determine the amount of oleate and epoxidized products in the hydrotalcites. TGA curves were similar to those reported in literature for other HTs with oleate anions in their interlamellar region. They showed three main weight losses (Figure 6). The first, below 220 °C, was related to the loss of water adsorbed into interparticle pores. The second in the range 220−550 °C would correspond to the decomposition of HT into mixed-oxide MgAlO$_x$ along with the loss of all organic matter. Finally, a third loss above 500 °C might be assigned to the transformation of the previous oxides into a spinel (MgAl$_2$O$_4$). Table 2 collects the results obtained from thermogravimetric analysis for HT-OLE-EXC and HT-OLE-MW-2 and the epoxidized product of this latter, HT-OLE-MW-2-EPO. HT-OLE-MW-2 showed a slight increase of oleate amount (around of 4−5%) in comparison to that synthesized by the ion-exchange method.

**Epoxidation of Intercalated Oleate.** The epoxidation of oleate intercalated in the hydrotalcites produced 9,10-epoxyhexadecanoate ion. As noted in the Introduction section, the reaction with m-chloroperbenzoic acid (mCPBA) occurs in a concerted manner and the resulting epoxide retains the starting stereochemistry. mCPBA enables rapid reaction under mild temperature conditions and produces no olefin derivatives. Also, it is a readily handled reagent whose only disadvantage is that it leads to the formation of a byproduct (m-chlorobenzoic acid), which must be removed after the reaction has completed.

The epoxidation reaction was monitored by recording periodic Raman spectra. As can be seen in Figure 7, which shows the spectral region from 2800 to 3200 cm$^{-1}$, intercalated oleate ion exhibited a band at 3011 cm$^{-1}$ due to stretching of olefin =C−H bonds that was absent from the spectrum for mCPBA, whose aromatic =C−H stretching band appeared at 3079 cm$^{-1}$. Since epoxidation caused the olefinic double bond in oleate ion to break, the associated band was used to monitor the reaction. By way of example, Figure 8a illustrates the results for the epoxidation of HT-OLE-MW-2, and Figure 8b shows the temporal variation of the conversion of interlayer oleate ion into the corresponding epoxide. As can be seen, conversion

![Figure 5. Raman spectra in the 2500−3800 cm$^{-1}$ region for the hydrotalcites HT-NO$_3$-COP (a), HT-OLE-EXC (b), and HT-OLE-MW-2 (c) and for sodium oleate (d).](image-url)

![Figure 6. TGA of different synthesized materials.](image-url)

![Figure 7. Raman spectra for HT-EXC-OLE (red line) and m-chloroperbenzoic acid (black line).](image-url)

![Figure 8.](image-url)

Table 2. Results Obtained from TG Analyses Performed to Hydrotalcites in Percentage

| entry | LDH | 30−220 °C | 220−500 °C | 500−800 °C | 30−800 °C |
|-------|-----|-----------|-----------|-----------|-----------|
| 1     | HT-OLE-EXC | 12 | 54 | 2 | 68 |
| 2     | HT-OLE-MW-2 | 11 | 50 | 3 | 64 |
| 3     | HT-OLE-MW-2-EPO | 10 | 48 | 5 | 63 |
was somewhat faster in HT-OLE-EXC than that in HT-OLE-MW-2; in any case, both reactions completed within 10 min. Based on these results, the marked differences in crystallinity between the two hydrotalcites scarcely influenced the epoxidation of the interlayer anion.

Hydrotalcites therefore provide an effective method for epoxidizing alkenes in confined spaces. This, together with the high reactivity of the oxirane ring, opens up highly promising avenues for synthesizing compounds of great interest through hydrotalcite intercalates that would otherwise be very difficult to prepare.

■ CONCLUSIONS

In this work, oleate ion was intercalated in the interlayer region of hydrotalcite using two different synthetic methods. Microwave-assisted ion exchange provided a more crystalline solid than conventional coprecipitation. The former method shortened the synthesis time from 24 to only 2 h. Once intercalated, oleate ion was epoxidized in the confined space of the interlayer region of the hydrotalcites. Raman spectra provided very useful information about the reaction development. Irrespective of synthetic method, intercalated oleate was thoroughly epoxidized within minutes. The results of this work confirm not only the ability of hydrotalcites as nanoreactors but also that of using epoxidized oleate as a reactant to obtain more complex compounds that are difficult to prepare with the classical method (viz., direct intercalation of anions into a hydrotalcite).

■ EXPERIMENTAL SECTION

Hydrotalcite containing nitrate as an interlayer anion was prepared by coprecipitation as described elsewhere." Two solutions containing 0.25 mol of Mg(NO_3)_2·6H_2O and 0.1 mol of Al(NO_3)_3·9H_2O [Mg/Al = 2.5] in 25 mL of deionized water were used for this purpose. The mixture was slowly dropped over 75 mL of a carbonate solution at pH 10 at 60 °C under vigorous stirring, the pH being kept constant by adding appropriate volumes of 1 M NaOH during precipitation. The suspension thus obtained was allowed to stand at 80 °C for 24 h, after which the solid was filtered off and washed with 2 L of deionized water. The product thus obtained was named HT-NO_3-COP.

The ion-exchange method used to obtain hydrotalcite with oleate as an intercalated anion was similar to that previously developed by our group to obtain organo-HTs. An amount of 1 g of solid HT-NO_3-COP was suspended in 50 mL of a solution containing 0.45 g of sodium oleate in bidistilled, decarbonated water in a nitrogen atmosphere at 100 °C under continuous stirring for 24 h. Then, the solid was isolated by centrifugation and called HT-OLE-EXC.

Finally, the oleate-containing HT was prepared by microwave-assisted ion exchange. For this purpose, appropriate amounts of sodium oleate (0.20 g) and HT-NO_3-COP (0.50 g) were added to 20 mL of deionized water, the suspension being transferred to a 100 mL Teflon autoclave vessel and heated at 90 °C in an MA186-001 flexiWAVE microwave oven from Milestone Srl (Sorisole, Italy), using a power of 300 W for 1, 2, or 3 h. The resulting solids were recovered by decantation, washed with deionized water, and named HT-OLE-MW-X, where X is the irradiation time in hours (1, 2, or 3).

All LDHs were analyzed by X-ray diffraction to check that they possessed an HT structure, and also by Raman spectroscopy. The Mg/Al ratio of the solids was determined by inductively coupled plasma mass spectrometry (ICP-MS) on an ELAN DRC-E Perkin Elmer ICP-MS instrument operated under standard conditions. X-ray diffraction patterns were obtained on a Siemens D-5000 diffractometer using Cu Kα radiation. Patterns were recorded over the 2θ range from 1 to 70°. The Raman spectra for the solids were acquired with a Renishaw Raman instrument (InVia Raman Microscope) equipped with a Leica microscope furnished with various lenses, monochromators, and filters, in addition to a CCD. Spectra were obtained by excitation with a red laser light (750 nm) over the wavenumber range 2500−4000 cm⁻¹ and green laser light (532 nm) from 100 to 2000 cm⁻¹. These two lasers provided spectra of increased quality in all windows examined. A total of 32 scans per spectrum were done to improve the signal-to-noise ratio. All spectral treatments (baseline correction, smoothing, normalization, and deconvolution) were done with software Peakfit v. 4.11.

The epoxidation reaction was conducted by suspending 0.25 g of HT in 5 mL of chloroform. The suspension, under continuous stirring, was supplied with a solution of 82.86 mmol/L of m-chloroperbenzoic acid (mCPBA) in chloroform dropwise for 30 min with periodic sampling of the medium. The HT suspension was then isolated by filtration and washed several times with methanol to remove any residual mCPBA. The rate of the epoxidation reaction was examined by monitoring the Raman signals for C=O−H bonds in oleate ion. To this end, samples taken at regular intervals from the reaction medium were evaporated to a solid residue containing a hydrotalcite and residual mCPBA.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03212.
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