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New organic-inorganic LDH composites: synthesis, characterization and

catalytic behavior in the green epoxidation of α , β -unsaturated esters

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Abstract

New organic-inorganic based LDH composites have been prepared using different methodologies, *ie* the ion-exchange method (Org@LDH-*exch*), the reconstruction (Org@LDH-*mem*) and the direct intercalation (Org@LDH-*inter*) method, respectively. Irrespective of the procedure, the -C=O group of levulinate moiety was envisaged as a potential active organocatalyst in the epoxidation of *trans*-methylcinnamate to methyl-phenyl-glycidate. The characterisation of these materials through adsorption-desorption isotherms of nitrogen at -196 °C, XRD, TG-DTA and DRIFT confirmed a successful intercalation only for Org@LDH-*inter*. The reactions were carried out *via in situ* generated dioxiranes using levulinate as active organocatalyst and H₂O₂/acetonitrile mixture as oxidant. Intercalated levulinate in aminoterephthalate/LDH structure led to conversions up to 25% with a total selectivity to methyl-phenyl-glycidate. Besides this, the heterogeneous organocatalyst behave as a green system: the constitutive levulinic acid represents one of the most important renewable platform molecules, while replacing the Oxone reagent with the more benign hydrogen peroxide and the substitution of an inorganic soluble base with the basic function of the LDH-support afford a more benign system.

Keywords: LDH-based organic-inorganic composite; direct intercalation of levulinate species; physical-chemical characterization; epoxidation; green catalytic system.

1. Introduction

Grafting the organic molecules into a layered double hydroxide (LDH) may generate new interesting properties of these materials, such as changes in the hydrophobic nano-pockets within the galleries of the inorganic solid [1] or enhancements in the catalytic behavior [2]. Related to this second direction, the use of the organic-LDH composite materials is expected to increase merely the selectivity.

In this respect, one of the most important targets is the identification of more efficient and practical epoxidation methods of a wide variety of olefins. This is currently justified by the broad utility of epoxides especially as intermediates for pharmaceutical industry [3, 4]. Thus, the epoxidation of olefins in chlorinated solvents using peroxy acids [5] or, very often, mchloroperbenzoic acid (m-CPBA) as epoxidation agents [6, 7] has been intensively studied. However, while the epoxidation with m-CPBA occurs efficiently on electron-rich substrates such as simple alkenes or functionalised alkenes, for cinnamic esters the reaction is either extremely slow as cinnamates possess electron withdrawing groups [8], or it takes place with the formation of diol ester derivatives as the major product (the case of cinnamates having electron donating groups). By replacing the primary oxidant from *m*-CPBA in CH_2Cl_2 to Oxone[®] (a triple salt with the formula 2KHSO₅ x KHSO₄ x K₂SO₄) in acetone, Curci *et al.* [9] reported the epoxidation of the (*E*)cinnamic acid with yields of 95%. Later, Shi et al. [10] showed that Oxone® in conjunction with a D-fructose-derived ketone, also known as Shi's ketone organocatalyst, is highly active in the epoxidation of a wide variety of (E)-di- and tri-substituted alkenes. However, a disadvantage of using Oxone® arises from its low stability under the basic reaction conditions required for the epoxidation of this kind of substrates. A greener alternative to Oxone® might be the use of hydrogen peroxide (H_2O_2) as primary oxidant, in combination with acetonitrile [11], able to

generate peroxyimidic acid species, the active oxidant for the formation of the dioxirane. Moreover, making the organocatalysts insoluble and, consequently, easily recoverable and reusable, it may be the way for a sustainable development in this field.

In this context, we recently explored the potential of the LDH-intercalated materials with renewable derived levulinate as efficient solid catalysts for the epoxidation of *trans*-methyl cinnamate to methyl-3-phenyl-glycidate by using H₂O₂/acetonitrile as oxidant [2]. The low toxicity of sodium levulinate and the middle oxidation conditions obey the green chemistry requirements. Besides this, its anchoring on the corners of the LDH layers through ion exchange method led to solid catalysts able to convert *trans*-methylcinnamate into corresponding epoxides in an efficient manner (C_{cinnamate} = 21.4%, S_{glycidate} = 100%). Encouraged by these results and with the aim to improve the former results, here we report novel procedures for the synthesis of organic-inorganic composites prepared from MgAl-LDH and structurally-modified levulinic acid as organocatalyst. The epoxidation of *trans*-methylcinnamate to methyl-3-phenyl-glycidate using H₂O₂/acetonitrile as oxidant has been considered as test reaction. The catalytic results are discussed by comparison with the previously reported LDH-intercalated levulinate materials [2].

2. Experimental

2.1. Organic-inorganic composites preparation

2.1.1. Layered double hydroxides (LDH) synthesis

The layered double hydroxides (LDH) were prepared by co-precipitation at pH = 10, using an aqueous solution of Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O. The quantities of the Mg and Al salts were calculated for a Mg /Al molar ratio of 3.0 in the final material. The preparation procedure follows the reported method in Ref. [2]. Briefly, two solutions of a) 44.8 g of Mg(NO₃)₂·6H₂O and

21.75 g of Al(NO₃)₃ · 9H₂O in 100 mL of deionized water and b) 8.3 wt% Na₂CO₃ · 10H₂O in 100 mL solution of NaOH 2M were simultaneously added drop wise to 200 mL of deionized water, at room temperature with controlled rate to maintain the pH \cong 10. After complete precipitation, the slurry was aged at 80°C overnight under vigorous stirring. After the suspension separation, the wet precipitate was washed and dried at 80°C for 12 h. The obtained LDH material was denoted MgAl-LDH.

2.1.2. Levulinate-based organic structure synthesis

The synthesis of the organic part of the composite is schematized in Scheme 1.



Scheme 1. The synthesis of levulinate-based organocatalyst

A. In a 100 mL round-bottom flask equipped with a condenser and a magnetic stirrer bar, 30 mL (49.14 g) of thionyl chloride (SOCl₂) was drop wise added to 3.48 g (0.03 moles) of levulinic acid, at such a rate (2 mL/min) that the temperature of the reaction mixture did not exceed 50°C. The reaction mixture was then held at about 50°C under a reduced pressure of about 30 mmHg to remove HCl, SO₂ and excess SOCl₂. Levulinoyl chloride was recovered with a yield of 95% (3.83g; 0.0285 moles). B. 6.5g (0.065 moles) of KHCO₃ and 2.63g (0.015 moles) of 2-amino terephthalic acid were dissolved in 100 ml water. The mixture was stirred for 1h, at 80°C and then the solvent was removed in an oven at 80°C. The crude potassium amino-terephthalate was recovered as a white solid, with a yield of 90% (3.45 g). C. To the levulinoyl chloride (3.83 g, 0.0285 moles), 50 mL of dimethyl-formamide (DMF) and the 3.45 g of potassium amino-terephthalate (0.0143 moles) were added and heated at 80 °C, for 72 h. At the end of the reaction the solvent was removed in vacuum at room temperature, then the crude product was dissolved in CH₂Cl₂ (50 mL), dried with anhydrous MgSO₄, and filtered. The final solid obtained after evaporating the CH₂Cl₂ was not further purified.

2.1.3. LDH-based organic-inorganic composite synthesis

For the synthesis of the LDH-based organic-inorganic composites different methodologies such as ion-exchange, reconstruction and co-precipitation were applied as detailed below:

i) Ion-exchange method (Org@LDH-exch): 2.5g of reference MgAl-LDH was mixed with 0.1 g (0.3 mmoles) of organocatalyst (6) (Scheme 1) in 150 mL of deionized water. The slurry was stirred at room temperature, for 18h, in nitrogen atmosphere. The product was then filtered, washed with distilled water until a pH of 7 and finally dried in an oven at 80 °C, for 12 h.

ii) Reconstruction method (Org@LDH-mem): 2 g of the reference MgAl-LDH was calcined at 450°C to the corresponding layered mixed oxide. The product (1 g) was mixed with 0.1 g

compound (6) dissolved in 20 mL deionized water, under vigorous stirring at room temperature, for 10h. The precipitate was then filtered, washed until pH of 7 and dried at 80°C, for 12 h.

iii) Direct intercalation method (Org@LDH-inter): intercalated LDH structures were prepared by Mg^{2+} and Al^{3+} ions hydrolysis in the presence of 2-aminoterephthalic acid. The mixed solution of $1M Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ was drop-wise added to a 50mM aminoterephthalic acid solution ($Mg^{2+}/Al^{3+}/aminoterephthalic$ acid molar ratio = 2/1/1) under stirring and N_2 atmosphere. The pH of the reaction mixture was adjusted by drop-wise addition of 1M NaOH solution, and temperature was kept at $40^{\circ}C$. The resulted precipitate was aged overnight, filtered, washed with distilled deionized (DD) water and finally dried under vacuum, at $60^{\circ}C$ [12]. The obtained solid product was modified with levulinyl chloride following a similar procedure as described in the step C, Scheme 1. However, in this step adapted amounts of levulinyl chloride to keep a 2/1 molar ratio of levulinyl chloride/intercalated aminoterephthalic acid were used.

2.2. Catalysts characterization

The synthesized organic-inorganic composites were characterized using various techniques such as adsorption-desorption isotherms of nitrogen at -196°C, powder X-ray diffraction (XRD), differential thermal analysis and thermogravimetric analysis (TG-DTA), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). Textural characteristics (surface area, pore volume and pore diameter) were determined from the adsorption-desorption isotherms of nitrogen at -196 °C using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. The XRD patterns were recorded on a Shimadzu XRD-7000 diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å, 40 kV, 40 mA) at a step of 0.02° and a scanning speed of 2 degrees min⁻¹ in the 5 – 90 degrees 2 Θ range. The TG-DTA analyses were carried out using a Shimadzu DTG-60 Simultaneous DTA-TG Apparatus, under air atmosphere, with a flow rate of 10 mL min⁻¹ at a heating rate of 10°C min⁻

¹, from RT to 700°C and using alpha-alumina as reference. The DRIFT spectra were collected with a Thermo 4700 spectrometer (200 scans with a resolution of 4 cm⁻¹) in the range of 600–4000 cm⁻¹.

2.3. Catalytic tests

The LDH-based organic-inorganic composites were tested in the epoxidation of *trans*methylcinnamate (TMC) to methyl-3-phenyl glycidate (MPG). In brief, to a mixture of 0.162 g TMC in 3.0 mL acetonitrile, 0.8-1.5 mL H_2O_2 and 0.05-0.10 g of catalyst were added. The reaction mixture was stirred at 24-40°C for 18-24 h. After completion, the solid catalyst was separated by filtration, the filtrate was concentrated under vacuum and the resulted reaction products were analyzed by GC-FID chromatography (Shimadzu GC-2014 apparatus).

The retention times were 13.9 min and 14.5-14.9 min for *trans*-methyl cinnamate (TMC) and methyl-3phenyl glycidate (MPG), respectively. The identification of the products was made using a GC-MS apparatus (GC Trace 2000 DSQ system coupled with an MS detector, from Thermo Electron Corporation) equipped with a Factor Four VF-5HT column with the following characteristics: $0.32 \text{ mm x } 0.1 \text{ } \text{\mu m x } 15 \text{ m working with a temperature program at a pressure of } 0.38 \text{ Torr with He as carrier gas.}$

3. Results and discussion

The XRD patterns of the reference MgAl-LDH and Org@LDH-*exch* and Org@LDH-*mem* samples display sharp and symmetric diffraction lines at 20 11.4, 22.8 and 34.6° [13] indicating a well-formed crystalline layered structure. No intercalation of the levulinate-based organocatalyst occurred using these methods (Figure 1). In these cases only grafting onto the external surface of the LDH was possible. In all cases the basal spacing distance d_{003} corresponds to carbonate as

compensating anion (7.77 Å). Since the thickness of the brucite-like layer is 4.8 Å, the height of the gallery was calculated as being 2.97 Å [14].



Figure 1. The XRD diffraction patterns of the reference MgAl-LDH sample and Org@LDH-*exch* and Org@LDH-*mem* intercalated samples

The IR spectrum and TG-DTA profile confirm the intercalation failure evidenced by the XRD diffraction patterns for the Org@LDH-*exch* and Org@LDH-mem samples. The DRIFT spectra of both Org@LDH-*exch* and Org@LDH-*mem* samples show only the presence of the CO_3^{2-} (1430 cm⁻¹) anions in the LDH gallery together with the OH⁻ (1647 cm⁻¹) ones (Figure 2). The broad shoulder present at ca. 3000 cm⁻¹ is attributed to carbonate hydrogen-bonded to the LDH hydroxides [15] while the broad band at 3588 cm⁻¹ is assigned to the (-OH) hydroxyl stretching vibration of the isolated and hydrogen bonded to the octahedral layer and water molecules [16].



Figure 2. The IR spectra of the Org@LDH-exch (A) and Org@LDH-mem (B) samples

Moreover, the TG and DTA profiles show three main steps characteristic to LDH materials, matching the literature reports: i) the loss of physically adsorbed and interlayer water molecules at temperatures lower than 200°C; ii) the dehydroxylation of the double hydroxide layers, at 200-400°C, and iii) the complete dehydroxylation together with the decomposition of the interlayer carbonate anions with the formation of mixed oxides, at temperatures higher than 400°C [17, 18] in good concordance to the XRD and IR results.

However, the co-precipitation route (direct intercalation) led to materials in which the carbonate ions were replaced by 2-amino-terephthalate ones. The XRD pattern (Figure 3) clearly confirmed the intercalation of 2-aminoterephthalate. It indicates the existence of two different anions, with different sizes, well intercalated into the gallery of the LDH support. The two different basal distances corresponding to the (003) and (006) diffraction planes account for this process. Indeed, the intercalation of the 2-amino-terephthalate species into the LDH host structure agrees with the shift towards lower 2 θ angles of the (00*l*) reflections ([#]). However, the diffraction lines corresponding to the interlayer (*) hydroxyl anions (d₀₀₃ = 7.4 Å) can still be observed, revealing an

incomplete intercalation of 2-amino-terephthalate species into the LDH host structure. Assuming a 3R stacking for the hexagonal structure of the LDH, the position of the (003) reflection allowed to calculate lattice c ($c = 3 \times d_{003}$) parameter of 33.5 Å in the intercalated LDH ($d_{003} = 11.15$ Å). Accordingly, the thickness of the LDH layer was of 4.8 Å, while the interlayer space for the intercalated LDH of 6.4 Å.



Figure 3. The XRD pattern of the intercalated 2-aminoterephthalate anion in the LDH structure

This sample was then subjected to the condensation of –COCl of the levulinyl chloride with –NH₂ groups from 2-aminoterephthalate, in accordance with the step C from Scheme 1.

Finally the XRD pattern of the Org@LDH-*inter* sample displays similar diffraction lines with those of the intercalated 2-aminoterephthalate anion showing the presence of levulinate into the LDH gallery without any further modification of the LDH structural characteristics.

The textural characterisation of the Org@LDH-*inter* sample also confirms the presence of the amino-terephthalate-based entity in between the LDH sheets. The intercalated Org@LDH-*inter* sample displays a higher BET surface than the corresponding MgAl-LDH (Table 1). Moreover, the narrow mesopores of the bimodal MgAl-LDH sample disappear while the novel formed mezopores

of the mono-modal Org@LDH-*inter* sample are larger than those of the corresponding MgAl-LDH (Figures 4 and 5). On this basis, the intercalation of the amino-terephthalate molecules in between the LDH layers or/and inside the narrow mesopores of the LDH is well justified [2]. In both cases, the hysteresis loops suggest mesopores with a regular geometry and uniform sizes, while no microporosity has been detected.



Table 1. Textural properties of the MgAl-LDH and Org@LDH-inter samples



sample [2]



Figure 5. Nitrogen adsorption-desorption isotherms and pore size distribution for the Org@LDH-

inter sample

The intercalation of the aminoterephthalate-based species is also confirmed by the TG analysis, carried out in nitrogen atmosphere. The TG profile (Figure 6) of the Org@LDH-*inter* sample shows an increased mass loss for the aminoterephthalate-intercalated sample (85.7% versus 46.7% [2]), accompanied by a maximum mass loss centered at 569°C (Figure 6). This peak is associated to the vaporization of the aminoterephthalate-intercalated species and their degradation product.



Figure 6. The TG-DTA profile of Org@LDH-*inter* sample

The IR spectra confirm through the presence of the secondary amide (bands at 3382 and 3488 cm⁻¹, corresponding to the N-H stretching, and 1690 and 1510 cm⁻¹, corresponding to N-H bending trans to the carbonyl oxygen) and ketone (band at 1700 cm⁻¹) groups the successful covalent binding of the levulinic species on the amino-terephthalate moiety already present in the LDH gallery (Figure 7).



Figure 7. The IR spectra of the 2-amino-terephthalic acid (A), reference MgAl-LDH (B) and Org@LDH-*inter* sample (C).

The kinetic diameter of the organic molecules used for the Org@LDH-*inter* sample preparation (*ie*, 2-amino-terephthalate and the coresponding levulinate-based terephtalate compound (structure (6), Scheme 1) and of the reactant and reaction product of the epoxidation reaction (*ie*, *trans*-methylcinammate and methyl-phenyl-glycidate, Scheme 2) has been estimated from the molecular weight correlation (Table 2), using the equation:

$$\sigma = 1.234 (M_w)^{1/3}$$

for aromatic hydrocarbons (M_w = molecular weight in g mol⁻¹) [19], in accordance with the approximation method for the kinetic diameters of oxygenated molecules reported by Huber et al. [20].



Scheme 2. Trans-methylcinnamate epoxidation to methyl-phenyl-glycidate





Obviously, the presence of levulinate connected to $-NH_2$ left unaffected the aminoterephthalate intercalated LDH layers, these species being orientated in a parallel direction to the LDH layers.



Scheme 3. Graphical illustration of the intercalated Org@LDH-inter sample

Due to its basic properties, the surfaces of the LDH-type materials efficiently afford the transformation of hydrogen peroxide into a perhydroxyl anion [21]. Therefore, such surfaces can be directly involved into the epoxidation of olefins and even of electron deficient olefins like 2-cyclohexen-1-one. However, for the case of the *trans*-methylcinnamate, the MgAl-LDH does not show any catalytic activity, as we recently reported [2]. Instead, the basicity of the LDH can obviate the need for the presence of an inorganic soluble base (e.g., K_2CO_3) in the catalytic system whiles the -C=O groups of the intercalated levulinate species may act as catalytic results with this catalyst and a comparison with those previously obtained using LEV@LDH- N_2 , and LEV@LDH-pp, prepared by the intercalation of levulinate species *via* ionic exchange and precipitation routes [2].

Entry	Catalyst	Reaction time, h	C_{TMC} , %	S_{MPG} , %	Reference
5	5	,	me	ini G	
1	Malidu	10	0		2
1	MgAI-LDH	18	0	-	Z
2	$LEV@LDH-N_2$	18	3.1	86.7	2

Table 3. Catalytic performances of the LEV-intercalated LDH materials

3 ^a	LEV@LDH-pp	24	0.7	100	2
4		24	1.5	100	2
5 ^b		24	21.4	100	2
6 ^a	Ora@IDU inter	24	10.2	100	This work
0	Olg@LDH-Inter	24	10.2	100	THIS WORK
7		24	16.5	100	This work
8 ^b		24	25.6	100	This work

Reaction conditions: 0.05 g catalyst, 0.162g TMC, 3mL AcCN, 0.8mL H_2O_2 , 40°C; ^a - room temperature; ^b - 0.1 g catalyst and 1.5 mL H_2O_2

As Table 3 shows, the catalytic results in the presence of the Org@LDH-*inter* are slightly superior to those obtained in the presence of the previously reported LEV@LDH samples [2]. While the selectivity to methyl-phenyl-glycidate has been preserved at 100%, irrespective of the catalyst structure, the conversion of the *trans*-methylcinnamate is improved with several percentages by changing the catalyst from LEV@LDH to Org@LDH-*inter* (from 21.4% to 25.6, entries 5 and 8, Table 3). Obviously, this enhancement is attributed both to the different location and to the different structural orientations of the catalytic active species (*ie*, -C=O group of the levulinate moiety). As we already shown, when the environment is not large enough to allow the diffusion of the reactant molecules (*ie*, *trans*-methylcinnamate) and the formation of the *spiro* transition state, in which the plane of the oxirane is perpendicular to the plane of the C=C π -system [22, 23] the oxygen transfer takes place in a restrictive way. However, the increased activity of Org@LDH-*inter* catalysts can not be explained strictly only on the basis of the steric hindrance effect. Different electronic effects induced by replacing carboxylic (levulinic acid) with amide

(levulinate-terephthalate compound) groups in the γ -position of the organocatalyst should also be taken into consideration.

It is also important to notice another achievement from the standpoint of the environmental concern. It arises from the fact that the basicity of the LDH can obviate the need for the presence of an inorganic soluble base (e.g., K_2CO_3) in the catalytic system. Moreover, the total selectivity in methyl-phenyl-glycidate and the use of hydrogen peroxide/acetonitrile as a benign oxidation agent bring high advantages from the green chemistry point of view, avoiding the generation of wastes.

Conclusions

Different methodologies for the synthesis of organic-inorganic based LDH composites were investigated. Irrespective of the procedure, the -C=O group of levulinate moiety was envisaged as potential active organocatalyst in the epoxidation of *trans*-methylcinnamate to methyl-phenylglycidate. The characterisation methods showed that the direct intercalation through the coprecipitation of the amino-terephthalate with Al and Mg salts constituted the only procedure able to intercalate the organic aggregate. This was followed by the levulinyl chloride covalent binding on the $-NH_2$ bond of the intercalated aminoterephthalate. The reactions were carried out *via in situ* generated dioxiranes using levulinate as active organocatalyst and H₂O₂/acetonitrile mixture as oxidant. Intercalated levulinate in aminoterephthalate/LDH structure led to conversions up to 25% with total selectivity to methyl-phenyl-glycidate. These results are slightly superior to the previously levulinate-intercalated MgAl-LDH (C =21%, S = 100%) catalysts, this enhancement being likely induced by both steric and electronic effects.

The use of the "heterogeneous organocatalyst" based on levulinic acid, one of the most important renewable platform molecules, the replacing the Oxone reagent with more benign hydrogen peroxide as primary oxidant and the homogeneous inorganic base substitution by the

basic function of the catalytic LDH-support may recommend this catalytic system as a valuable green candidate for the selective epoxidation of α , β -unsaturated esters.

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Highlights

- Levulinic acid is used for the synthesis of novel organic-inorganic LDH composites. •
- Levulinate was successfully grafted in aminoterephthalate/LDH through covalent bonds. •
- ai The heterogeneous organocatalyst exhibits catalytic potential in epoxidation reactions. •

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