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Levulinate-intercalated LDH: A potential heterogeneous organocatalyst for the green epoxidation of α,β-unsaturated esters

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ABSTRACT

Green efficient organocatalytic heterogeneous epoxidation of *trans*-methylcinnamate was achieved on LDH-intercalated levulinate using H_2O_2/acetonitrile as oxidant. The layered double hydroxide (LDH) was prepared by co-precipitation starting from an aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$. The preparation of the LDH hybrid organocatalyst was carried out following four different routes: i) step-by-step ion exchange in air (LEV@LDH-air); ii) one charge ion-exchange in N_2 atmosphere (LEV@LDH-N_2); iii) direct synthesis by co-precipitation (LEV@LDH-pp); and the iv) reconstruction method (LEV@LDH-mem). The synthesized catalysts were characterized using different 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 (DRIFT) spectroscopy techniques. The levulinate was successfully intercalated by ion exchange and co-precipitation. In the investigated series the LEV@LDH-pp catalyst showed the highest performances at 40 °C and 24 h ($C_{cinnamate}$ = 21.4%, $S_{glycidate}$ = 100%).

1. Introduction

The broad utility of epoxides justifies the current interest of synthetic chemists for more efficient and practical methods for the epoxidation of a wide variety of olefins [1,2]. Recent reports on the oxidation with hydrogen peroxide in the presence of different catalysts like iron in combination with porphyrin [3] or pyridine-2,6-dicarboxylic acid and different amines [4], polyoxovanadometalate [5], and different other metal catalysts [6] already confirmed the advantages of this strategy. However, the leaching of the metals and their presence in the synthesis products are nowadays considered as major limitations for the industrial development of the epoxidation processes.

As another alternative, the epoxidation of olefins using dioxiranes as oxidants has also been studied. In this respect, both the traditional and the current methods proposed working in chlorinated solvents using peroxy acids [7] or, very often, *m*-chloroperbenzoic acid (*m*-CPBA) as epoxidation agents [8,9]. With *m*-CPBA the oxidation occurs via an attack by electron-rich substrates such simple alkenes or alkenes carrying a variety of functional groups (e.g., ethers, esters, ketones) to the weak O—O bond. Following this, the oxygen is transferred from the intermediate dioxirane to the substrate [10]. However, for cinnamic esters presenting electron withdrawing groups, epoxidation with *m*-CPBA is extremely slow [11], while in the case of cinnamates having electron donating groups, the epoxides react with the liberated *m*-chlorobenzoic acid to give diol ester derivatives as the major product [11]. On the other hand the epoxidation of the *(E)*-cinnamic acid, which had failed to react with *m*-CPBA in CH_2Cl_2, was achieved by Curci et al. [12] with high yields (95%) using as oxidant Oxone® (a triple salt with the formula $2KHSO_5 \times KHSO_4 \times K_2SO_4$) dispersed in acetone.

On this basis, organocatalysts (ie, acetone in the previous example [12]) able to generate dioxirane, have been suggested as possible alternative to the homogeneous metal catalysts for the epoxidation reactions [13,14]. Among these, Oxone® in conjunction with a D-fructose-derived ketone, also known as Shi's ketone organocatalyst, already proven to be highly active in the epoxidation of a wide variety of *(E)*-di- and trisubstituted alkenes [15]. However, as an inconvenient, Oxone® may gradually decompose under the basic reaction conditions required for this type of epoxidation (*ie*, epoxides are usually more stable under basic conditions). Therefore, a greener alternative to the epoxidation with Oxone®, also imposing substantially less solvent and salts, might be the use

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of hydrogen peroxide (H_2O_2), as primary oxidant, in combination with acetonitrile [16]. In this system, the peroxyimidic acid is likely to be the active oxidant for the formation of the dioxirane.

However, in spite of the recent improvements and irrespective to their advantages upon the metal-complexes (e.g., robust, inexpensive, readily available, non-toxic), the homogeneous organocatalysis still preserve the main "classical" homogeneous catalysis disadvantage, difficulties in the recovery and the re-use of the organocatalytic species. Although in many cases it has been claimed that the absence of the metal lowers the price of the catalyst, based on the green chemistry principles, the resulted wastes generate technological inconveniences. Therefore, making organocatalysts insoluble and consequently, easily recoverable and reusable may be the way for a sustainable development in this field.

In the nowadays chemistry organocatalysts also have an important place in asymmetric epoxidations providing an efficient way for the synthesis of important building blocks in the production of pharmaceuticals [17]. In the context of this work, not long ago, some of us reported the synthesis of an efficient magnetic and recyclable green SBILC (Supported Basic Ionic Liquid Catalyst)-based heterogeneous Shi-ketone organocatalysts for the asymmetric epoxidation of the *trans*-methylcinnamate to chiral (2R, 3S)-phenyl glycidate ($Y = 35\%$, $S_{glycidate} = 100\%$ and e.e. of 100%) [18]. This synthesis strategy combined a number of concepts leading to an efficient green catalyst for the asymmetric epoxidation of the *trans*-methylcinnamate, as: i) *di-acetate chiral ketone Shi as organocatalyst* – generates suitable conformations for the epoxidation of *trans*-methylcinnamate with enhanced stability towards the basic species present in the reaction mixture; ii) *hydrogen peroxide as oxidizing agent* – compared to Oxone significantly reduced the amount of the solvent and introduced salt, which is in line with the principles of the green chemistry; *iii) base ionic liquids* – ensure the benefits of using a base in the epoxidation reaction, but expel the large amounts of generated wastes, corrosion problems and issues related to the organocatalyst recovery; iv) *magnetic nanoparticles* – ensure an efficient and elegant solution for the issue of recycling and reuse of the catalyst; v) *MWCNT support* – ensures the chemical stabilization of the ultrafine magnetic nanoparticles and offers the advantage of the simple functionalization.

Although catalytically highly efficient, the laborious preparation procedure of this system involving large quantities of raw materials and high number of steps (in some of which dangerous reagents to the environment were used) restrain its development on a broader scale. Therefore, we invested a considerable effort by applying the green chemistry rules for the development of a novel environmentally more acceptable synthesis of an efficient catalytic system for the epoxidation of cinnamates. For comparison, catalytic results were compared with those obtained in homogeneous conditions by using sodium levulinate (*ie*, [Na][LEV]) as organocatalyst, a readily biodegradable and low toxicity ionic liquid, as recently classified [19].

Here we explored novel potential renewable organocatalysts-intercalated layered double hydroxide (LDH) materials as efficient solid catalysts for the epoxidation of *trans*-methyl cinnamate to methyl-3-phenyl-glycidate. Layered double hydroxides (LDHs) or hydrotalcite-like compounds are anionic clays with the general formula of $M^{2+}_{1-x}M^{3+}_{x}(OH)_2A^{n-}_{x/n} \cdot mH_2O$ with $0.2 \leq x \leq 0.4$ [20]. M^{2+} and M^{3+} cations are hexa-coordinated to hydroxyl groups forming brucite-like sheets which stack to create a layered structure. A large variety of inorganic and organic A^{n-} anions can be intercalated in the interlayer space to compensate the positive charge introduced by the M^{3+} cations partially replacing M^{2+} ones in the layers. Up to now, a high number of nanohybrids obtained by intercalating catalytically active species in LDHs such as metal complexes, oxometalates and polyoxometalates were investigated as heterogeneous catalysts in liquid-phase oxidation [21]. However, to the best of our knowledge, levulinate species were never intercalated in LDHs to obtain solid catalysts for liquid-phase oxidation. Several advantages like the simple catalyst preparation methodology from cheap and renewable raw materials, the heterogeneous character of the organocatalyst, the use of H_2O_2 and the absence of any inorganic soluble base were envisaged. All these elements can successfully compensate any additional costs related to the separation of enantiomers from the racemic (±)-phenyl glycidate consisting in the kinetic resolution of racemic (±)-phenyl glycidate through a lipase-catalyzed asymmetric hydrolysis [22]. The catalytic results are discussed by comparison with those obtained with previously developed and reported SBILC (Supported Basic Ionic Liquid Catalyst)-based heterogeneous Shi-ketone organocatalysts [18].

2. Experimental section

2.1. Catalysts preparation

2.1.1. Preparation of the reference LDH (layered double hydroxide)

The layered double hydroxide (LDH) was prepared by co-precipitation at a constant pH of 10, starting from an aqueous solution of $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$. The quantities of the Mg and Al salts were calculated for a molar ratio of $Mg/Al = 3/1$ in the final material.

The preparation procedure was as follows: an aqueous solution containing 44.8 g of $Mg(NO_3)_2{\cdot}6H_2O$ and 21.75 g of $Al(NO_3)_3{\cdot}9H_2O$ in 100 mL of deionized water was first prepared. Then, a solution containing 8.294 g of $Na_2CO_3{\cdot}10H_2O$ in 100 mL of deionized water was mixed with 100 mL solution of NaOH 2 M to obtain the precipitating agent. The solution of salts and the precipitating agent were simultaneously added dropwise into a beaker containing 200 mL of deionized water at room temperature with controlled rate to maintain the pH close to 10. After complete precipitation, the slurry was aged at 80 °C overnight under vigorous stirring. The suspension was then separated by centrifugation, washed with deionized water and finally dried at 80 °C for 12 h. The obtained LDH material was denoted MgAl-LDH.

2.1.2. Preparation of the intercalated LDH hybrid organocatalyst

[Na][LEV] (density = 1.345 g mL^{-1}, dynamic viscosity = 36.21 mPa s) was prepared as follow: 17.54 g of $NaHCO_3$ were dissolved in 160 mL of distilled water and to this solution 9.44 mL levulinic acid (LA) were added ($NaHCO_3$/LA molar ratio of 2.7/1.2). The mixture was stirred for 1 h, at room temperature and then the solvent was removed at 80 °C, for 2 h.

The intercalation of [Na][LEV] in the LDH structure followed four different routes:

i) *Step-by-step ion exchange in air (LEV@LDH-air)*: 3 g of MgAl-LDH and 1 g (7.2 mmoles) of [Na][LEV] were suspended in 150 mL of deionized water. The mixture was heated to 80 °C for 9 h under stirring and then stirred at room temperature, overnight. The resulted product was centrifuged, washed twice with deionized water, four times with ethanol, once with acetone, and finally dried. The recovered product was then suspended with another 1 g (7.2 mmoles) of [Na][LEV] in 150 mL of deionized water, under the same conditions as in the first treatment and this procedure was repeated four times. The final [Na][LEV] loading was 21.7 mmoles. In the last treatment cycle the mixture was simply stirred without any [Na][LEV] addition. After the separation and washing, the final product was dried in oven at 80 °C, for 8 h.

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