



Bio-nanohybrid catalysts based on L-leucine immobilized in hydrotalcite and their activity in aldol reaction



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ABSTRACT

Nanohybrid materials based on L-leucine (L-Leu) and hydrotalcites (HT) were prepared by the ion-exchange and reconstruction method, under mild synthesis conditions. The location, amount and the form of the immobilized L-Leu are affected not only by the time of synthesis, but also by temperature and ultrasound treatment. The XRD results demonstrate that the immobilization occurs in either a vertical or oblique orientation with respect to the HT layers. The catalytic activity of these materials was tested in the aldol addition reaction of cyclohexanone with different aromatic aldehydes, affording mainly the syn-diastereomer. Furthermore, the present study demonstrates that both diastereo- and enantioselectivity can be easily modulated by the appropriate combination of nanohybrid catalyst, solvent and reaction time.

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1. Introduction

Nowadays, considerable attention is focused on the synthesis of nanohybrid materials, which exhibit new and better properties than the corresponding constituent materials. Research into and understanding the organic/inorganic interaction between bioactive molecules and the surface of inorganic materials have led to their use in many biochemical applications [1] or as catalysts [2] and drug delivery carriers [3], although these interactions remain only partially understood. Many bioactive molecules (e.g. peptides, amino acids, proteins, etc.) are anions under neutral and basic pH, so they can easily be immobilized in positively charged solids. Examples of such solids are the hydrotalcites (HTs), a family of naturally occurring layered clays with low or null toxicity, good biocompatibility and a high anion swelling capacity. These properties make

HTs interesting materials for applications in the pharmaceutical field [4], cosmetics [5], catalysis [6] or even medical field [7].

The anionic exchange properties of HTs transform these materials in excellent candidates for the immobilization of amino acids (AAs). Starting with 1997 when Whilton et al. studied the immobilization of aspartic and glutamic acid in the interlayer space of layered double hydroxides through coprecipitation method [8], a series of AAs have been immobilized into HT materials by means of three general methods: coprecipitation [9–12], anionic exchange [12–15] and reconstruction method [16,17]. Regarding the nature of the interaction, it is now clear that the immobilization of AAs in HTs structures is pH-dependent, although other factors should be taken into account: the kind of HT, the synthesis and the physical and chemical properties of the AAs.

AAs are organocatalysts which display several advantages such as non-toxicity, easy manipulation and stability and have been widely used in the asymmetric aldol reaction [18]. For example, Córdova et al. obtained *anti* diastereoselectivity in a direct asymmetric aldol reaction between cyclohexanone and *p*-NO₂-benzaldehyde using a series of AAs [19]. Wu et al. used a threonine derivative in the aldol addition reaction, producing the *anti*-diastereomer when cyclohexanone was the substrate and

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syn-isomer in the case of hydroxyacetone [20]. Similar results were obtained by Ramasastry et al. [21], Jiang et al. [22] and Xu et al. [23]. Itoh et al. observed that in the presence of *L*-*t*-Leu compounds with *syn* diastereoselectivity were obtained in the case of cyclopentanone, cycloheptanone and cyclooctanone and with *anti* diastereoselectivity when cyclohexanone was used [24]. Thus, obtaining the *syn*-product when cyclohexanone is used as substrate seems to be a challenge. Moreover, AAs used in their natural form can react with aromatic aldehydes to form the corresponding ammonium salts which, by decarboxylation, will form a stable side-product [24,25].

In this study, we present the synthesis of nanohybrid materials based on *L*-Leu immobilized in HTs. We studied different synthetic procedures and their effects on the nature of the inorganic/organic interaction in order to evaluate: (i) the role of the immobilization time on one hand, and the relationship between the immobilization speed and the strength and kind of basic centres in the HT on the other hand; (ii) the role of the HT precursor in the immobilization process and (iii) the nature of the AA structure in the immobilization process. To achieve this goal, the nanohybrid materials were synthesized using the anion-exchange and reconstruction method and the organic/inorganic interactions were investigated by EA, ICP, XRD, FT-IR, Raman, ^{13}C , ^{27}Al MAS NMR and thermal evolution using TG/DTA analyses.

The new nanohybrid materials were tested in the aldol addition reaction of cyclohexanone with different aromatic aldehydes. The synergistic effect between the bio-organic guest (*L*-Leu) and the inorganic host (HTs) proved to play an important role in modulating both the diastereoselectivity and enantioselectivity of the final product. Herein, we report that the *anti-syn* selectivity depends not only on the nature of the catalyst but also on the solvent used.

2. Experimental

2.1. General

All chemicals and solvents were commercially available (Aldrich Chemical, Fluka) and used without further purification/drying unless otherwise mentioned.

Molecular formulae were calculated from the results of elemental analyses (EA) and inductively coupled plasma analyses (ICP). EA were performed using an elemental analyser EA-1108C.E. instrument from Thermo Fisher Scientific with a Mettler Toledo MX5 microbalance. The analyses were carried out using atropine as a standard and Vanadium as an additive to facilitate combustion. ICP analyses were performed in an ICP-OES Spectro Arcos FHS16 Instrument.

The N_2 -physisorption analysis of BET surface areas and average pore diameters were performed in a QuadStar Quantachrome surface analyser at 77 K. Before analysis all the samples were degassed in vacuum at 393 K for 12 h.

Powder X-ray diffraction (XRD) patterns of the samples were performed on a Bruker-AXS D8-Discover diffractometer with a 2θ angle ranging from 3° to 70° . The samples were dispersed onto a low background Si (510) sampler holder. The data were collected with an angular step of 0.03° at 5s per step and sample rotation. $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) was obtained from a copper X-ray tube operated at 40 kV and 40 mA. The crystalline phases were identified using JCPDS files. The interlayered spaces were analysed with the reflection bands of the (003) and (006) and calculated using the Bragg law.

Fourier transform infrared spectra (FT-IR) were recorded with Nicolet Nexus Fourier Transform instrument equipped with a DTGS KBr detector. Each analysis was performed using 100 scans in the range $4000\text{--}400 \text{ cm}^{-1}$. Pure powders diluted in KBr pressed

disks (about 1% w/w) were used for the analysis of skeletal vibrations. OMNIC software provided by ThermoElectron Corporation was used for spectra analysis.

Raman spectra were obtained using a Renishaw Raman via reflex instrument. The polarized radiation ($\lambda = 785 \text{ nm}$) of a Renishaw diode laser of 500 mW was used. A Laica DM2500 optical microscope was used to determine the part of the sample analysed. The RamaScope was calibrated using a silicon wafer. The focus (maximum opening 100%) and power (50%) were carefully optimized in order not to alter the sample during measurement. The spectral resolution was 2 cm^{-1} with an exposure time of 10 s and 5 accumulations for each run.

^{13}C and ^{27}Al Magic Angle Spinning-Nuclear Magnetic Resonance (MAS-NMR) spectra were obtained on a Varian Mercury VXR-400S spectrometer operating at 104.2 MHz with a pulse width of 1 ms. A total of 4000 scans were collected with a sweep width of 100 kHz and an acquisition time of 0.2 s. An acquisition delay of 1 s between successive accumulations was selected to avoid saturation effects. ^{13}C MAS NMR spectra were recollected using tetramethylsilane (TMS) as reference.

High-resolution transmission electron microscopy (HRTEM) was performed with a JEOL 2010F instrument equipped with a field emission source, working at an acceleration voltage of 200 kV. The point-to-point resolution of the microscope was 0.19 nm, and the resolution between lines was 0.14 nm.

Thermogravimetric Analyses and Differential Thermal Analyses (TGA/DTA) were measured on a TGA7 instrument from Perkin Elmer. The analyses were carried out using a sample amount of 10 mg in an N_2 atmosphere. The heating rate was $10^\circ\text{C min}^{-1}$ within the range $30\text{--}900^\circ\text{C}$.

The products were characterized by ^1H NMR using a Varian NMR System 400 MHz and HPLC-DAD (Diode Array Detector G1315D) Agilent Technologies and HPLC-RID 10A (Refractive Index Detector) Shimadzu using CHIRALPACK IA column ($250 \times 4.6 \text{ mm ID}$).

2.2. Synthesis of hydrotalcite materials (HTs)

Mg-Al HTs (Mg/Al molar ratio 2) containing nitrates and chloride anions were synthesized by the coprecipitation method at room temperature and $\text{pH} = 10$. The materials obtained were named HT_{NO_3} and HT_{Cl} respectively. After the drying process, HT_{Cl} was sonicated for 1 h, while HT_{NO_3} was decomposed by calcination at 450°C overnight in air. The calcined HT (HT_{CC}) was rehydrated in an inert atmosphere using decarbonated water and ultrasound treatment for 1 h. The materials obtained were named HT_{Clus} and HT_{rus} respectively.

2.3. Synthesis of LL/HT materials

2.3.1. Anionic-exchange method (method A)

Two procedures were used to synthesize LL/ $\text{HT}_x\text{-Ay}$ materials, where x is the type of HT used (HT_{rus} or HT_{Clus}) and y indicates the procedure followed. In the first case, 500 mg of HT was added to a solution containing 320 or 160 mg (2.4 or 1.2 mmol, respectively) of *L*-Leu. The mixture was stirred for 30 min at room temperature (method A1). In the second case, 500 mg of HT was added to a solution containing 840.4 mg (6.4 mmol) of *L*-Leu. The mixture was stirred for 3 h at 80°C (method A2). An Ar atmosphere and deionized-decarbonated water were used in all cases. Materials synthesized by the anionic exchange method were named LL/ $\text{HT}_{\text{rus}}\text{-A1}$, LL/ $\text{HT}_{\text{Clus}}\text{-A1}$, LL/ $\text{HT}_{\text{rus}}\text{-A2}$ and LL/ $\text{HT}_{\text{Clus}}\text{-A2}$.

2.3.2. Reconstruction method (method R)

Two procedures were used to synthesize LL/ $\text{HT}_x\text{-Ry}$ materials (where x is the type of HT and y indicates the procedure followed), in both cases using 250 mg of HT_{CC} added to a solution

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