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Exploring bulk and colloidal Mg/Al hydrotalcite–Au nanoparticles hybrid materials in aerobic olefin epoxidation

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ABSTRACT

Au nanoparticles (AuNPs) were immobilized on S-containing amino acids (cysteine and methionine) Mg/Al hydrotalcite clay in both bulk and exfoliated (colloidal) forms. The Au nanoparticles were prepared by a biomimetic method using an anti-oxidant tea extract to reduce the Au salt solution. The performance of bulk and exfoliated clays with Au nanoparticles in aerobic olefin epoxidation was assessed with very interesting results. Both catalysts were very active towards the epoxide products; selectivity was found to be dependent on the catalyst form. The exfoliated catalysts yielded higher product stereoselectivity in the case of limonene epoxidation. These results can be explained by the existence of a confined environment around the AuNPs structures provided by the clay nanosheets wrapping the nanoparticles, modulating how substrates interact with the catalytic active centres. Based on experimental data mechanistic proposals were also rationalized for these catalysts showing how they assist the catalytic process.

1. Introduction

The design of more active and selective heterogeneous catalysts leading to more environmental friendly processes is still a priority and a challenge [1].

In this context the use of clays has been receiving much attention in recent years in either bulk and, to a lesser extent, delaminated [2]. The use of bulk clays in oxidation catalysis has been mostly employed for alcohol oxidation or styrene epoxidation under aerobic conditions, which shows the environmentally relevance of such materials. These systems involve the use of metal nanoparticles or metal complexes [3–7].

Delaminated clay-based catalysts have been also developed. Delamination (or exfoliation) of Layered Double Hydroxides (LDH) yielding charged metal oxide nanosheets (single layers), has received increased attention in recent years [8]. According to some authors this procedure seems to be the most effective approach to access the interlayer spacing of these materials. Another advantage is the fact that the exfoliated layers (nanosheets), which are positively charged, show an extraordinary high 2D structure with molecular thickness, providing an ideal model system at nanometric level for several applications [9–11].

The use of nanoparticles spreads across many fields including catalysis, which is one of the most active in research terms [12,13]. The synthesis of nanoparticles is also a subject of much research and the development of biomimetic processes for synthesis of nanoparticles is seen as a green and sustainable approach. In the case of gold nanoparticles (AuNPs) these have attracted considerable attention in this field due to their biological applications [14].

Such catalysts work at the fringe between homo- and heterogeneous catalysts due to their colloidal nature. Applications have been reported on the reduction of nitro-compounds [15] and oxidation of olefins [16,17]. An interesting work by J. He and coworkers on asymmetric epoxidation of olefins by delaminated clays has reported the high performance of the achieved *ee*'s due to confinement effects arising from the nano-sheets surrounding the catalytic active sites [18].

The choice of the oxidant in the catalytic system is of utmost importance, as reactants will yield certainly by-products, a situation that must be minimized when developing efficient and selective catalytic applications. Although H_2O_2 is environmentally

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friendly (yields water upon decomposition), the perfect oxidant is molecular oxygen as it is abundant in the atmosphere and is therefore freely available. Catalytic systems where O_2 is used as oxidant can be considered as the ideal "green" processes and usually are based on silver or gold-based catalysts [19–23]. Given that the mechanism of such reactions is radical-based, there is the need to use an initiator, which can be seen as a drawback. The choice of oxidants is typically restricted to the use of H_2O_2 or *tert*-butylhydroperoxide (tbhp), although others are possible [19,24].

Within our quest to develop more selective and environmentally friendly processes [25,26] in this work we describe the preparation of clays intercalated with S-containing amino acids (cysteine and methionine), and with immobilized AuNPs. The AuNPs were synthesized through a bio-reduction method [27,28]. The clay-based catalysts were prepared in both bulk and delaminated forms and their performance in olefin epoxidation catalysis assessed using molecular oxygen as oxidant and tbhp as radical initiator. To the best of our knowledge this is the first report dealing with such performance evaluation on this type of catalysts and provides valuable insight on benchmarking the catalyst's performance for a green process as will be discussed throughout, especially in what concerns product selectivity.

2. Experimental

2.1. General

All reagents were obtained from Aldrich and used as received (except solvents). All preparations and manipulations were performed using standard Schlenk techniques under N_2 atmosphere. Commercial grade solvents were dried and deoxygenated by standard procedures, distilled under nitrogen and kept over 4 Å molecular sieves. Cysteine (*cys*) and methionine (*met*), Mg/Al-hydrotalcite (HT), *tert*-butylhydroperoxide (tbhp), *cis*-cyclooctene, styrene, 1-octene, *trans*-2-hexen-1-ol and *R*-(+)-limonene, were purchased from Aldrich and used as received.

2.2. Preparation of the tea leaf extract

The tea extract was carried out by modification of the protocol described in the literature [27,28]. In the present case, instead of using green tea extract of *Lippia citriodora* or *Geranium robertianum* herbs, Gorreana black tea leaves from Azores Islands was used, known to have a high content of antioxidants. The tea leaf aqueous extract solution was prepared by weighting 1.5 g of tea leaves in 100 mL of distilled water and then boiling the mixture for 5 min followed by filtration under vacuum and stored away from light and refrigerated until use. The extracts were produced freshly every time Au nanoparticles synthesis was required.

2.3. Synthesis of the Au nanoparticles

The synthesis of Au nanoparticles (AuNPs) was carried out in a biomimetic way using the extract prepared above, by modification of the protocol described in the literature [27,28]. The filtered tea extract (100 mL) was added to 50 mL of a 1 mM aqueous solution of $HAuCl_4$ and the final volume was adjusted to 250 mL by the addition of Milli-Q type II water. The solution was heated to 363 K and kept for 1 h. AuNPs synthesis was visually detected by colour change from yellow (typical from $HAuCl_4$) to purple (characteristic of AuNP) [27,28]. After the reaction, the solution was cooled down, and the AuNPs were collected by centrifugation (10,000 rpm, 2 h, 280 K). The pellet was decanted and washed twice with Milli-Q water to remove any rests of the reducing solution. After this procedure, the AuNPs pellet was protected from light and stored in a refrigerator until use.

2.4. Preparation of the materials and catalysts

Prior to the intercalation experiments commercial Mg/Al hydrotalcite (hereafter denominated HT) was ion exchanged (298 K for 12 h) in order to replace all the carbonate by chloride anions, yielding the chloride-exchanged clay, denominated HT-Cl [9]. This was done by suspending 1 g of HT in 1 L of a 1 M NaCl/3.3 mM HCl aqueous solution. After purging with N_2 the sealed reactor was stirred for 12 h at room temperature. During this process, the structure of the lamellar material is maintained. The resulting material was then filtered off, washed with deionized water (3 × 20 mL), and dried in a vacuum oven (313 K) for 48 h.

The Cl^- anions were subsequently substituted by the deprotonated amino acids *cys* or *met* and were intercalated inside the interlayer space of HT-Cl [29,30]. Preparation of HT–AA (AA = *cys* or *met*) materials was done by taking a suspension of HT-Cl (1.00 g) in freshly distilled dimethylformamide (DMF, 25 mL) and adding an aqueous solution of deprotonated *cys* or *met* at 343 K for 48 h. Deprotonation of the amino acids was carried out by mixing the amino acids *cys* (7.30 mmol) or *met* (7.30 mmol) with KOH (1 equiv) in deionized water (20 mL) until a clear solution was obtained.

The resulting materials were then filtered off, washed with deionized water (3 × 20 mL). The resulting materials were then filtered off, washed with deionized water (3 × 20 mL), and dried in a vacuum oven (313 K) for 48 h.

Synthesis of the HT-AA-Au (AA = *cys* or *met*) catalysts was performed by adding AuNPs (17 mg) to a suspension of HT-AA (AA = *cys* or *met*, 700 mg) in deionized water. The resulting slurry was stirred under a N_2 atmosphere, at 298 K, for 12 h. The resulting materials were then filtered off, washed with deionized water (3 × 20 mL), and dried in a vacuum oven (313 K) for 48 h.

Exfoliation of the HT-AA LDH materials was achieved by shaking HT-AA sample (250 mg) in 250 mL of formamide under N_2 flow to avoid carbonate contamination. The mixture was stirred (160 rpm) at room temperature for 48 h. In order to remove unexfoliated particles the resulting colloidal suspension was centrifuged at 2000 rpm for 10 min. This procedure yielded colourless colloids of the clays denoted as ^{Ex}HT-AA (AA = *cys* or *met*). After that the exfoliated catalysts were prepared by adding AuNPs (4 mg) to 15 mL of ^{Ex}HT-AA colloid. Then the mixture was ultra-sonicated (37 kHz under normal mode, 303 K), for 1 min; after that the resulting colloidal mixture was stirred at room temperature for further 12 h, and potential catalysts were obtained, denominated *^{Ex}HT-AA-Au (AA = cys or met)*.

This procedure is simple and yielded systematically reproducible materials across 5 batches with a variation of Au content within 5%.

2.5. Catalysts characterization

FTIR spectra were measured with a Nicolet Nexus 6700 FTIR spectrometer using Diffuse Reflectance accessory for clay materials. All FTIR spectra were measured in the 400–4000 cm^{-1} range and using 4 cm^{-1} resolution. Powder XRD measurements were taken on a Philips Analytical PW 3050/60 X'Pert PRO (theta/2 theta) equipped with X'Celerator detector and with automatic data acquisition (X'Pert Data Collector (v2.0b) software), using monochromatized Cu-Kα radiation as incident beam, 40 kV–30 mA. UV/Vis spectra were measured on a Shimadzu UV2450 in the 400–700 nm range. Diffuse reflectance UV/Vis (DRUV) measurements were accomplished using the same spectrophotometer equipped with an integrating sphere in the 400–700 nm range, using $BaSO_4$ as reference material.

TGA studies were performed using a Perkin-Elmer TGA7 thermobalance system at a heating rate of 10 $K{\cdot}min^{-1}$ under N_2.