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Oxodiperoxomolybdenum complex immobilized onto ionic liquid modified SBA-15 as an effective catalysis for sulfide oxidation to sulfoxides using hydrogen peroxide

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ABSTRACT

A supported ionic-liquid-phase (SILP) was prepared by the reaction of 1-methyl-3-(3-(triethoxysilyl) propyl)-1H-imidazol-3-ium chloride with a mesoporous SBA-15 silica and then an oxodiperoxomolybdenum complex was immobilized onto the obtained SILP. The resulting material, identified as SBA-15 + ImCl + MoO5, was characterized by solid state NMR (^{1}H, ^{13}C and ^{29}Si), and their textural and thermogravimetric properties were determined. The SBA-15 + ImCl + MoO5 material was investigated as catalyst for the oxidation of methylphenylsulfide, as model reaction, with aqueous hydrogen peroxide as oxidant at room temperature. The presence of the molybdenum species was crucial for achieving good conversions and methanol was selected as the best solvent (conversion of 95% and selectivity toward sulfoxide 98%). The optimized reaction conditions were applied for the oxidation of several selected sulfides. In general, good catalytic activity and selectivity to sulfoxide were obtained and, remarkably, the selectivity toward sulfoxide is higher than those observed in the study of the same process carried out in [C_4min][PF_6] (C_4mim = 1–butyl-3-methylimidazolium) and catalyzed by a molecular molybdenum complex, under the same reaction conditions. The importance of the IL-functionalization in the SBA-15 material was evidenced by recycling experiments. The SBA-15 + ImCl + MoO5 catalyst was used for the sulfoxidation of the methylphenylsulfide substrate for ten reaction cycles without a significant change in conversion, selectivity to sulfoxide and molybdenum content.

1. Introduction

The use of environmentally-benign catalytic processes is a priority of modern chemistry [1–3]. For this reason, the search of *greener* processes in traditional organic transformations, which generally employed stoichiometric reagents and volatile solvents, is a challenge. One example of such a process is the oxidation of organic sulfides, which is one of the more important and useful strategies for the synthesis of added value sulfoxides [4–10]. There are several significant drawbacks of this reaction, as for example: (i) the catalyst nature, its complicated synthesis and/or its metal price often leads to expensive processes; (ii) the overoxidation to sulfones is frequently difficult to prevent; and (iii) the catalyst recycling in homogeneous catalysis is difficult. A possible solution for the latter negative aspect is the immobilization of the catalyst and several alternatives are now available. One of them is the substitution of common organic solvents by ionic liquids (ILs). The catalyst can be solubilized in the IL whilst being immiscible with the extraction solvent. This means that the products can be separated by extraction, allowing the catalyst to be recycled [11–16]. A further advanced option is the use of a “heterogenized” type of catalysis using ILs known as Supported Ionic Liquid Phase (SILP) catalysts [17–21]. In these systems, an IL is immobilized on a high-surface area porous solid (by covalent anchoring or by absorption) and a transition-metal complex is dissolved in the thin film of the ionic liquid. The resulting catalyst is a solid with the active species dissolved in the IL phase and behaving as a homogeneous catalyst, thus combining the attractive features of the latter with the benefits of heterogeneous catalysis. Furthermore, SILP-catalysts are good candidates for their application for bioreactors [22,23] and for continuous-flow processes using conventional solvents or supercritical fluids [24–26]. For these reasons, the use of SILPs in catalysis is an emergent area and, in particular, several examples of typical oxidation reactions like epoxidation [27], alcohol oxidation [28], and olefin oxidation

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[29] were recently reported. Sulfide oxidation was also investigated and SILP-catalyzed examples with titanium [30] and tungsten [31] metals are known.

Following our recent research on catalyzed oxidations in non–conventional media [32–35] and the acquired knowledge on oxodiperoxomolibdenum-catalyzed olefin epoxidation in ionic liquids [36–40] we decided to explore the oxodiperoxomolibdenum-catalyzed sulfide oxidation. In fact, we recently described a green approach to this process using hydrogen peroxide in ILs media [41]. Here, we present the next step in our research and report the preparation and characterization of a SILP based on mesoporous silica SBA-15, functionalized covalently with an imidazolium-based IL, and the use of this material in the oxidation of organic sulfides. The *green* advantages are (i) the use of easily available oxodiperoxomolybdenum complexes as catalysts, coming from economic and commercial MoO_3, and efficient in oxidation reactions carried out in ILs [36–40]; (ii) the use of cheap and environmentally-benign aqueous hydrogen peroxide as oxidant [42,43]; (iii) favored selectivity to sulfoxide by the heterogeneization [44]; and, (iv) efficient catalyst recycling.

2. Experimental

2.1. General

Synthetic reactions were performed under nitrogen by using Schlenk techniques where necessary. Solvents were purified and dried appropriately prior to use, by standard procedures. Chemicals were obtained from commercial sources and used as supplied. Infrared spectra were recorded on a Perkin-Elmer Model 883 spectrophotometer (Nujol emulsion in NaCl or KBr plates or in pressed KBr pellets). NMR spectra were recorded using a Bruker AMX-300 spectrometer with $^{13}C\{^1H\}$ and ^1H shifts referenced to the residual solvent signals. All data are reported in ppm downfield from $Si(CH_3)_4$. Solid state NMR spectra were recorded using a Bruker Avance III WB 600 MHz spectrometer. Gas chromatography experiments (GC) were recorded on a Varian CP-3800 Chromatograph with nitrogen as carrier gas, flame ionization detector (FID), and a Varian column, model CP-8741. Elemental analyses (C, H, N) were conducted by the Centro de Investigaciones, Tecnología e Innovación (CITIUS) of the University of Sevilla on an Elemental LECO CHNS 93 analyzer. Small Angle X-ray Scattering (SAXS) analysis of the mesoporous samples were carried out by using PanAnalytical X'Pert Pro® diffractometer in the 0.5–4 theta range. Thermo Gravimetric Analysis (TGA) were performed on SDTQ60 thermobalance from 30 to 900 °C at a constant heating ramp of 10 °C. min^{-1} in flow of air.

2.2. Syntheses

1-Methyl-3-(3-(triethoxysilyl)propyl)-1H-imidazol-3-ium chloride, ImCl. This compound was prepared by a slight modification of published procedures [20,45–47]. (3-chloropropyl)triethoxysilane (30 ml, 0.125 mmol) and 1-methyl-1H-imidazole (10 ml, 0.125 mmol) were mixed and heated at 95 °C with stirring for three days, under nitrogen. The resulting oily mixture was extracted with dry ethyl acetate. The solution was evaporated to dryness affording a yellow viscous oil (36.6 g, 95% yield). This oil was characterized spectroscopically (IR, ^1H and $^{13}C\{^1H\}$ NMR) and the obtained data were similar to those reported in bibliography.

Preparation of mesoporous SBA-15. 9.60 g of Pluronic 123 were dissolved in a mixture of water (225 ml) and 4 M HCl (150 ml) at room temperature. Over this solution 21.4 ml of TEOS was added under vigorous stirring. After aging at 40 °C for 24 h, the final product was obtained after hydrothermal treating at 80 °C for 24 h. The solid product was recovered by filtration, washed with water and ethanol and dried at 110 °C. Finally, the material was calcined at 500 °C for 10 h (1 °C/min).

SBA-15 functionalization, SBA-15 + ImCl. The mesoporous SBA-15 material (1 g) was heated at 300 °C for 2 h and, after that, a solution of 1-methyl-3-(3-(triethoxysilyl)propyl)-1 H-imidazol-3-ium chloride (1.5 g) in dry toluene (5 ml) was added, under nitrogen. The mixture was stirred at 90 °C for 16 h. The resulting solid was isolated by filtration and washed with CH_2Cl_2. Then, the solid was introduced in a Soxhlet system and extracted with CH_2Cl_2 at reflux for 24 h. A white powder was obtained and air-dried. Experimental elemental analyses: C, 15.52; H, 2.79; N, 5.33%.

Molybdenum impregnation on SBA-15, SBA–15 + MoO5. Over a sample of SBA-15 (100 mg) was added dropwise 100 μL of a 0.250 M aqueous solution of $[MoO(O_2)_2(H_2O)_n]$. During the addition, the mixture was manually stirred with a spatula until getting a yellow homogeneous solid.

Molybdenum immobilization onto the functionalized SBA-15 material, SBA–15 + ImCl + MoO5. Over a sample of the functionalized SBA-15 material (100 mg), SBA-15 + ImCl, was added dropwise 100 μL of a 0.250 M aqueous solution of $[MoO(O_2)_2(H_2O)_n]$. During the addition, the mixture was manually stirred with a spatula until to get a yellow homogeneous solid. Experimental elemental analyses: Mo, 1.74; C, 14.79; H, 3.27; N, 5.12%.

2.3. General procedure for catalytic oxidation of sulfide to sulfoxide

The reactor (a 5 ml vial equipped with a Young valve, containing a stirrer flea, and with the appropriated design for a direct centrifugation) was charged with the solid catalyst (100 mg of SBA-15 + ImCl with 100 μL added of 0.25 M [Mo] solution), the solvent (2 ml, usually methanol), the oxidant (1 mmol, in general 30% aqueous H_2O_2) and the substrate (1 mmol), in the aforementioned order. The reactor was sealed and the suspension reacted with constant stirring (600 rpm) in a thermostated oil bath (usually at 25 °C) for the desired time (usually 1 h). Upon completion the reactor was immediately cooled to 0 °C and then centrifuged (20 min). The liquid phase was decanted and the solid washed with vigorous stirring with the solvent reaction (2 × 4 ml) and Et_2O (4 ml). These washings were separated by centrifugation and combined with the liquid phase. The solution was evaporated to dryness by using a rotavap. The resulting residue was analyzed by GC (by adding 10 ml of Et_2O and 50 μl of dodecane as internal standard).

2.4. Catalyst recycling

The experimental procedure for the first cycle was conducted as detailed above. After the liquid phase separation and washings, the solid catalyst material was dried under vacuum. The reactor was charged again with the solvent (2 ml), the oxidant (1 mmol) and the substrate (1 mmol) and sealed. The reaction was carried out in the manner described above and analyzed similarly. Experimental elemental analyses (after ten catalytic cycles): Mo, 1.54%.

3. Results and discussion

3.1. Synthesis and characterization of molybdenum-immobilized SBA-15 materials

The SILP was prepared by reacting 1-methyl-3-(3-(triethoxysilyl)propyl)-1H-imidazol-3-ium chloride with the modified silica according to Scheme 1. Then, the material was treated with an aqueous solution of $[Mo(O)(O_2)_2(H_2O)_n]$, prepared as described elsewhere [38], and the catalyst material SBA-15 + ImCl + MoO5 was obtained (Scheme 1).