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Oxazine containing molybdenum(VI)–oxodiperoxo complex immobilized on SBA-15 as highly active and selective catalyst in the oxidation of alkenes to epoxides under solvent-free conditions

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ABSTRACT

Molybdenum(VI)–oxodiperoxo complex containing an oxazine ligand, ([$MoO(O_2)_2$(phox)], phox: 2-(2′-hydroxyphenyl)-5,6-dihydro-1,3-oxazine) was conveniently synthesized and immobilized onto chloro-functionalized mesoporous silica SBA-15 by covalent bonding between the chloropropyl group on the internal surface of the pores and the nitrogen atom of oxazine ligand yielding [$MoO(O_2)_2$(phox)]/SBA-15. The resulting material was characterized by FT-IR, TGA, XRD, SEM, TEM, EDX, ICP-AES, BET and UV–vis spectroscopy. The heterogeneous catalyst [$MoO(O_2)_2$(phox)]/SBA-15 was employed in the epoxidation of alkenes, exhibiting high catalytic performance and selectivity for epoxide similar to that of homogeneous catalyst, [$MoO(O_2)_2$(phox)] under solvent-free conditions. Finally, it was found that the heterogeneous catalyst had virtually no degree of leaching, which allowed its recyclability to nine cycles without loss of catalytic performance.

1. Introduction

Epoxides are important materials in the chemical industries which can be used for the synthesis of important products such as perfumes, plasticizers, epoxy resins, drugs, sweeteners, etc [1,2]. During the last decades, many homogeneous catalytic systems have been investigated in selective oxidation of olefins to epoxides [3–5]. Among them, molybdenum complexes were found to be efficient homogeneous catalysts for this reaction [6–8]. However, the utilization of homogeneous molybdenum catalysts have processing difficulties such as the separation and recycling of the catalysts, as well as leaching of the active metal into the solvent and the insufficient stability of the catalysts. Therefore, there is a continuous effort to develop more efficient and practical methods for immobilization of homogeneous catalysts. An efficient way for anchoring the soluble catalysts is to use mesoporous silicas as support [9–12].

Introduction of a wide variety of chemical groups into the pores of mesoporous silica can give rise to materials presenting various potential applications such as catalysis, separation, chemical sensing, molecular sieves, etc [13–16]. Among them, the material SBA-15 is of special interest owing to its highly ordered hexagonal arrays of cylindrical channels, very uniform pore size distribution, remarkable thermal stability, high surface area, thick silica walls and a large number of silanol groups at the surface of its channels [17,18]. According to a large amount of literature reports and also our own work on heterogeneous catalysts, we believe that the anchoring of the homogeneous catalysts via covalent bonding of a suitable functional linker or tether to the support is the most reliable method for immobilization of complex molecules. Herein, we report an efficient way to covalent anchoring of diperoxo molybdenum(VI) complex bearing oxazine ligand, previously synthesized by our research group [19], onto mesoporous SBA-15 under mild conditions. The catalytic material was prepared from the reaction of the molybdenum(VI) complex of oxazine with mesoporous silica

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containing 3-chloropropyl groups obtained by hydrolysis and co-condensation of tetraethylorthosilicate (TEOS) and 3-chloropropyltrimethoxysilane in the presence of the triblockcopolymer P123 as template under acidic conditions. In this study, the molybdenum complex was firstly synthesized and characterized and then incorporated into the pores of SBA-15. Therefore, we obtain convincing analytical and spectroscopic data firmly supporting the nature and purity of the complex in the step before the final preparation of the heterogeneous catalyst. Also, this method avoids the existence of adventitious, undefined (or ill defined) and catalytically inactive or unselective sites such as free, uncoordinated metal ions and metal oxide clusters. Moreover, This paper provides very efficient solvent-free method for epoxidation of various alkenes to epoxides using the heterogenized catalyst, which has catalytic performance comparable to that of the corresponding homogeneous one. In addition, the lifetime and reusability of the heterogenized catalyst were tested by conducting the reaction in repeated runs of epoxidation in the presence of the catalyst isolated from the previous run. The recycling experiments show that the complex provides high catalytic performance with almost complete conversion of cyclooctene to the epoxide without noticeable loss of the metal over several runs. Furthermore, comparison of the present catalytic system with other systems reported in the literature shows that the activity and selectivity of our new system is high in epoxidation under the solvent free conditions.

2. Experimental

2.1. Materials and methods

Starting reagents (Pluronic P123, 3-chloropropyltriethoxysilane, and tetraethylorthosilicate) were purchased from Merck or Aldrich. All solvents were reagent grade and dried and distilled before use according to standard procedures. $MoO(O_2)_2$(phox) was prepared following the procedure described elsewhere [19]. Powder X-ray diffraction (XRD) data were collected with a Philips X'Pert MPD diffractometer (Cu-Kα X-radiation, $\lambda = 1.54056$ Å). Samples were step-scanned in 0.02°(2θ) steps with a counting time of 1 s per step. Nitrogen adsorption isotherms at −196 °C were measured by using Belsorp mini II Instrument. The mesostructured materials were degassed at 100 °C for 15 h prior to each adsorption measurement. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and pore sizes were calculated by the Barrett–Joyner–Halenda (BJH) method. The metal loading of the host materials and leaching of molybdenum into the solution were determined by inductively coupled plasma atomic emission spectroscopy (ICP–AES) on Perkin-ElmerAA-300 spectrophotometer. FT-IR spectra of samples in the form of KBr pellets were recorded using an ABB Bomem MB-100 FT-IR spectrophotometer. The UV–Vis absorption spectra of the complexes were recorded by a CARY 100 Bio VARIAN UV–Vis spectrophotometer in quartz cells having a 1.0 cm path in length. Transmission electron microscopy (TEM) analysis was carried out using a JEOL-2010 microscope operating at 200 kV. The scanning electron microscopy (SEM) images were taken on a KYKY-EM3200 scanning electron microscope. The TGA and DTA analysis were carried out by using Thermogravimetric System Mettler Toledo TGA/DSC1 at a heating rate of 5 °C min^{-1} under air. The elemental analysis was recorded with an energy dispersive X-ray (EDX) analyzer (KEVEX Delta series) mounted on the Hitachi S-800. Gas chromatography (GC) analyses were performed on Agilent Technologies 6890N, 19019 J-413 HP-5, 5% phenyl methyl siloxane, capillary column 60.0 m × 250 μm × 1.00 μm.

3. Preparation

3.1. Synthesis of chloropropyl functionalized mesoporous SBA-15(Cl/SBA-15)

The ordered mesoporous silica containing chloropropyl groups was synthesized according to the previously published procedure [10,20,21] using the tri block copolymer [poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)], $EO_{20}PO_{70}EO_{20}$, as a template in acidic conditions. In a typical preparation, a solution of Pluronic P123 (4 g) in H_2O (30 mL) was added to the solution of 2 M HCl (120 mL) while stirring at room temperature. Then, tetraethylorthosilicate (8.28 g) was added and the resulting mixture was stirred for 3 h at 40 °C. Afterward, 0.244 g 3-chloropropyltriethoxysilane precursor (CPTES) was added. The resultant solution was stirred for 24 h at 40 °C, and then autoclaved at 100 °C for 24 h in Teflon-lined stainless steel reaction vessels. The resultant solid was filtered off and then, washed with hot water and dried at 60 °C for 24 h. Removal of the copolymer surfactant P123 was performed by Soxhlet extraction with ethanol for 3 days. The obtained material was dried at 60 °C for 24 h to yield the as-synthesized Cl/SBA-15 and characterized by a combination of analytical methods including BET, XRD, SEM and TEM.

3.2. Immobilization of [$MoO(O_2)_2$(phox)] into the pores of Cl/SBA-15 ([$MoO(O_2)_2$(phox)]/SBA-15)

To a solution of [$MoO(O_2)_2$(phox)] in methanol (100 mL), 1 g of Cl/SBA-15 was added and the mixture was vigorously stirred at 50 °C for 72 h. The resulting yellow solid material was filtered, washed with methanol, and then dried at 50 °C for 24 h.

4. Catalytic reactions

The liquid-phase olefin epoxidation reactions were carried out in air and under autogenous pressure in a 5 mL batch microreactor equipped with a stir bar and a sampling valve, and immersed in a thermostated oil bath. To a solution of alkene (1 mmol), [$MoO(O_2)_2$(phox)]/SBA-15 or [$MoO(O_2)_2$(phox)] (0.0005 mmol Mo complex) and chlorobenzene (1 mmol) as internal standard, 1 mmol of t-BuOOH was added as oxidant. The system was stirred for 20–60 min at 95 °C. The reactions were followed by GC monitoring of the reactant and products. All the reactions were performed at least two times and the products were compared with standard samples.

5. Result and discussion

Mesoporous silica containing 3-chloropropyl groups was synthesized by a direct synthetic approach involving hydrolysis and co-condensation of tetraethylorthosilicate and 3-chloropropyltrimethoxysilane in the presence of the triblock copolymer P123 as template and under acidic conditions following the procedure described [10,20,21]. Then the SBA-15-supported molybdenum oxazine complex, [$MoO(O_2)_2$(phox)]/SBA-15 was conveniently produced via immobilization into the SBA-15 containing chloropropyl groups, through covalent bonding between the chloropropyl group on the internal surface of the pores and the nitrogen atom of the oxazine ligand (Scheme 1) [22–24].

The powder XRD patterns of Cl/SBA-15 and [$MoO(O_2)_2$(phox)]/SBA-15 samples are shown in Fig. 1. As seen in Fig. 1, Cl/SBA-15 shows three characteristic peaks at the 2θ values of 0.84, 1.59 and 1.68, which could be attributed for the 100 (strong), 110 (weak) and