



Organometallic Mo complex anchored to magnetic iron oxide nanoparticles as highly recyclable epoxidation catalyst



Cristina I. Fernandes^a, Maria Deus Carvalho^b, Liliana P. Ferreira^{c,d}, Carla D. Nunes^a, Pedro D. Vaz^{a,*}

^a CQB, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, Ed. C8, 1749-016 Lisboa, Portugal

^b CCMM, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

^c CFMC, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

^d Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-516 Coimbra, Portugal

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ABSTRACT

The organometallic fragment $[\text{Mo}_2(\text{CO})_3]$ was coordinated to magnetic iron oxide nanoparticles of different sizes (average size of 11 and 30 nm) which have been previously coated with a silica shell and grafted with a pyridine derivative ligand. The Mo loading was found to be approximately 0.37 wt-% Mo and 0.57 wt-% Mo, corresponding to $0.150 \text{ mmol}_{\text{Mo}} \text{ g}^{-1}$ and $0.230 \text{ mmol}_{\text{Mo}} \text{ g}^{-1}$ for materials **MNP₃₀-Si-*inic*-Mo** and **MNP₁₁-Si-*inic*-Mo**, respectively. Preparation of these organometallic decorated magnetic nanoparticles was further confirmed by evidence obtained from extensive characterization by powder XRD, SEM/TEM analysis, as well as from data of ^{57}Fe Mössbauer and FTIR spectroscopy.

Olefin epoxidation of a variety of substrates promoted by these organometallic nano-hybrid materials using *tbhp* as oxidant, was performed with very good results. The catalytic studies show that the catalysts yield selectively the desired epoxides of a series of olefins. In addition, these catalysts are found to work under a wide temperature range and over several catalytic cycles without notorious performance loss in most cases.

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1. Introduction

Nowadays nanoparticles (NPs) research is a very dynamic field that ranges across many areas of science, from physics to chemistry and medicine, among many other fields, regarding its applications. In the particular case of catalysis many studies have been addressed showing that the investment in this kind of systems is beneficial, since the high surface/volume ratio presented by these systems yields, generally, high performance. The catalytic properties in many cases are combined with others (such as magnetism) which allow an important added value for the use of multi functionalized NPs in such processes.

Intrinsic properties of metal oxide NPs are determined mainly by their size, shape, composition, crystallinity and structure with either of these parameters being able to control those intrinsic properties [1,2].

Heterogeneous catalysis offers as the main advantage the easy recovery of the catalyst from the reaction products, making

it the preferred approach in most industrial applications. As a drawback, selectivity is usually lower than that of many homogeneous systems. Although in recent times this difference has become narrower, the design of more active and selective heterogeneous catalysts still remains a priority and a challenge. The quest for efficient heterogeneous catalysts strongly depends on the capability to assemble an active and selective homogeneous catalyst for a given reaction with an appropriate support that will prevent catalyst loss and facilitate its recovery, keeping the activity. Products can be also easily obtained, a fact that contributes to the preference for heterogeneous processes in chemical industry [3,4]. Environmental issues are also relevant, namely the search for product selectivity or the use of solventless conditions [5–7].

To this respect the development of catalysts that allow easy separation from reaction media through magnetic separation have been the aims of much research in recent times [2,8–15]. The *Catalysis* research topic is largely addressed covering a wide scope of catalytic reaction and systems. For instance, Bagherzadeh and coworkers reported the use of Mn(III) complexes supported in Fe_3O_4 magnetic nanoparticles (MNPs) in the selective oxidation of

* Corresponding author. Tel.: +351 217 500 877; fax: +351 217 500 088.
E-mail address: pmvaz@fc.ul.pt (P.D. Vaz).

thiols to disulfides [16]. CO₂ sequestration, through a hydration mechanism has also been studied by the development of a magnetically supported Zn(II) complex with histidine that mimics the bio-catalytic activity of Carbonic Anhydrase [17]. The catalyst was found to maintain activity after 10 cycles. Immobilized Pd(II) systems with catalytic activity in Suzuki–Miyaura and high recyclability were also reported by the group of Thiel [18].

Olefin epoxidation is a major field of research in the preparation of relevant building blocks for organic synthesis [19–21]. Among other metal systems, Mo-catalyzed olefin epoxidation has received interest from both academic and industrial research laboratories [22,23]. Since the first example of a molybdenum oxo complex catalyzing the epoxidation of alkenes with peroxides such as organic hydroperoxides and hydrogen peroxide [24], a variety of different complexes have been developed [25–28]. Inclusive, in recent times, many efficient epoxidation Mo-based catalysts are based on Mo^{II} organometallic complexes which work as pre-catalysts [29]. Such pre-catalysts are simply organometallic Mo^{II} carbonyl complexes which can be oxidized to the dioxo Mo^{VI} homologues which are the active species [5].

The use of complexes from the MoX₂(CO)₃L_n (X = Br, I; L_n = mono or bidentate Lewis base ligands) heptacoordinate halocarbonyl family were reported to possess catalytic activity in olefin epoxidation [30–33]. These complexes were developed in pioneering work by Baker for catalytic applications other than oxidation [34]. However, such systems were found to have quite high performances, although it was found very recently that such systems suffer from the ligand dependency which leads in some cases to deactivation. This is true when ligands hold NH moieties as already reported in the literature [31].

Continuing our research on olefin epoxidation [5,7,23,30–33], we describe in the present work the preparation and subsequent evaluation of the catalytic potential of a Mo complex anchored on the surface of silica-coated magnetic iron oxide nanoparticles with two different sizes. After preparation of the magnetic iron oxide cores, these nanoparticles were subsequently coated with silica for stabilization and to allow derivatization by grafting an organic pyridine derivative. The latter allowed coordination of a Mo organometallic complex. The resulting materials were used in olefin epoxidation reactions. The advantage of these nanocatalysts is that they are quite active in that transformation and can be easily separated from the reaction medium by a magnet. This is a crucial step in order to promote catalyst separation and recycling without compromising product recovery which is usually an elaborate task in homogeneous systems.

2. Materials and methods

2.1. General

All reagents were obtained from Aldrich and used as received. Commercial grade solvents were dried and deoxygenated by standard procedures distilled under nitrogen, and kept over 4 Å molecular sieves. The complex [Mo₂(CO)₃(CH₃CN)₂] was prepared according to a literature procedure [34].

FTIR spectra were obtained as KBr pellets on a Nicolet 6700 in the 400–4000 cm⁻¹ range using 2 cm⁻¹ resolution. Powder XRD measurements were taken on a Philips Analytical PW 3050/60 X'Pert PRO (theta/2 theta) equipped with an X'Celerator detector and with automatic data acquisition (X'Pert Data Collector (v2.0b) software), using a monochromatized CuK α radiation as incident beam. ¹H and ¹³C solution NMR spectra were obtained with a Bruker Avance 400 spectrometer.

Microanalyses (C, N, H, Mo) were performed at the University of Vigo.

The SEM images and EDX analyses were obtained on a FEG-SEM (Field Emission Gun Scanning Electron Microscope) from JEOL, model JSM-7001F. The TEM images were obtained on a microscope Hitachi, model H-1800 with a LaB₆ filament and an acceleration tension of 200 kV.

The ⁵⁷Fe Mössbauer spectra were recorded in transmission mode at room temperature using a conventional constant-acceleration spectrometer and a 50 mCi ⁵⁷Co source in a Rh matrix. The velocity scale was calibrated using an α -Fe foil. The spectra were fitted to Lorentzian lines using the *WinNormos* software program, and the isomer shifts reported are relative to metallic α -Fe at room temperature.

2.2. Methods

2.2.1. Synthesis of ligand isonicotinoyl chloride (**inicCl**)

SOCl₂ (5 mL) was added to isonicotinic acid (0.261 g, 2.12 mmol) and the solution was refluxed under vigorous stirring during 3 h. After that the solution was evaporated under vacuum [35,36].

IR (KBr ν /cm⁻¹): 3421 (s); 3112 (s); 1734 (vs); 1639 (s); 1507 (s); 1395 (vs); 1242 (s); 753 (m); 677 (m).

¹H NMR(400.13 MHz, CDCl₃, r.t., δ ppm): 9.17 (d, H₂), 8.55 (d, H₁).

2.2.2. Synthesis of magnetic iron oxide nanoparticles (**MNP**)

The iron oxide magnetic nanoparticles were prepared according to two different published procedures, allowing to obtain particles with mean sizes of 30 nm (MNP₃₀) [37] and 11 nm (MNP₁₁) respectively [38]. Both materials were coated with oleic acid acting as stabilizer.

In order to obtain the MNP₃₀-Si and MNP₁₁-Si materials, these nanoparticles were coated with silica following a published procedure [37].

MNP₃₀-Si: IR (KBr ν /cm⁻¹): 1400 (vs); 1066 (s); 572 (vs).

MNP₁₁-Si: IR (KBr ν /cm⁻¹): 1400 (vs); 1088 (s); 588 (vs).

2.2.3. Preparation of **MNP₃₀-Si-*inic*** and **MNP₁₁-Si-*inic*** materials

0.150 g of **inicCl** ligand were dissolved in 5 mL of dry CH₂Cl₂ and added to 0.300 g of **MNP₃₀-Si** or **MNP₁₁-Si** in 30 mL of dry toluene. The mixture was then stirred at 363 K under nitrogen atmosphere for 3 h. The solid material obtained was magnetically separated, washed repeatedly with toluene and CH₂Cl₂ to remove unanchored species and then dried under vacuum.

2.2.3.1. **MNP₃₀-Si-*inic***. IR (KBr ν /cm⁻¹): 3377 (m), 3415 (m), 3115 (m); 1728 (w); 1638 (m); 1602 (m); 1408 (w); 1054 (m); 756 (w); 563 (m).

Elemental analysis (%): found C 12.29; H 1.38; N 1.69.

2.2.3.2. **MNP₁₁-Si-*inic***. IR (KBr ν /cm⁻¹): 3407 (m), 3116 (m); 1732 (w); 1639 (w); 1402 (w); 1090 (m); 756 (vw); 668 (m).

Elemental analysis (%): found C 11.12; H 1.26; N 2.28.

2.2.4. Preparation of **MNP₃₀-Si-*inic*-Mo** and **MNP₁₁-Si-*inic*-Mo** materials

0.100 g of [Mo₂(CO)₃(NCMe)₂] dissolved in 5 mL of dry CH₂Cl₂ were added to a suspension of 0.600 g of **MNP₃₀-Si-*inic*** or **MNP₁₁-Si-*inic*** in 30 mL of dry toluene. The mixture was then stirred at 363 K under nitrogen atmosphere for 3 h. The solid material obtained was magnetically separated, washed repeatedly with toluene and CH₂Cl₂ to remove the unanchored species and then dried under vacuum.

2.2.4.1. **MNP₃₀-Si-*inic*-Mo**. IR (KBr ν /cm⁻¹): 3392 (m), 3152 (m); 1734 (m); 1653 (m); 1636 (m); 1617 (m); 1399 (w); 1091 (m); 724 (w); 668 (m).

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