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Synthesis and catalytic properties of manganese(II) and oxovanadium(IV) complexes anchored to mesoporous MCM-41

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Abstract

Reaction of [$Mn^{III}(acac)_3$] and [$V^{IV}O(acac)_2$] with the 1,4-diazabutadiene (DAB) ligands Ph–DAB–$(CH_2)_3R$ [R = $Si(OEt)_3$(**1a**); H (**1b**)] (L) leads to complexes of the type [$Mn^{II}(acac)_2L$] and [$V^{IV}O(acac)L$]Cl in good yields. These complexes were characterised by spectroscopic techniques, and magnetic measurements showed that in the case of the manganese the metal was reduced during the reaction with the nitrogen ligand.

The oxovanadium and manganese complexes bearing the ligand with triethoxysilyl groups Ph–DAB–$(CH_2)_3Si(OEt)_3$(**1a**) were immobilised in ordered MCM-41 by carrying out a grafting reaction. Tethered complexes of the same type were prepared by treating MCM-41 first with a toluene solution of **1a** under reflux; manganese(III) and oxovanadium(IV) precursors were then introduced into the MCM-41-ligand by pore volume impregnation of complex solutions. The modified materials were characterised by powder X-ray diffraction, solid-state NMR (^{13}C, ^{29}Si), FTIR, thermogravimetric studies and low temperature nitrogen adsorption isotherms. The grafted materials contained 0.7 wt% Mn and 0.8 wt% V, while higher metal loadings were achieved when the materials were prepared by tethering (2.9 wt% Mn and 2.4 wt% V).

The modified materials are active catalysts for the oxidation of *cis*-cyclooctene using *tert*-butylhydroperoxide as oxygen donor, at 328 K, yielding 1,2-epoxycyclooctane as the main reaction product and 1,2-cyclooctanediol as a by-product. The vanadium-containing materials are more efficient epoxidation catalysts than the manganese ones. The catalytic behaviour of the heterogenised catalysts was also compared with that observed in homogeneous phase for the complexes [$Mn(acac)_2L$] and [VO(acac)L]Cl. The vanadium catalysts exhibited the highest catalytic activity, whereas the manganese catalysts were the least active and selective to epoxide formation.

Keywords: Mesoporous materials; MCM-41; Manganese; Oxovanadium; Nitrogen ligands; Epoxidation

1. Introduction

Amorphous silica, alumina and other inorganic oxides have their surface covered by hydroxyl groups, which can be easily functionalised by reaction with appropriate molecules, and have thus found widespread applications as supports for species active in a variety of processes [1,2]. Properties such as the high specific surface area, mechanical stability, and promotion of well-dispersed active sites, make these supports interesting [2]. The discovery of ordered mesoporous materials in 1992 led to a resurgence in the area of supported reagents [3,4], with the emergence

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of micelle-templated inorganic oxides as promising alternatives [5]. These materials present as additional advantages relative to amorphous silicas, the fact that the ordered mesopores and higher specific surface area may allow higher loadings of supported reagents, improve active site accessibility and allow catalytic reactions to occur in constrained environments (for example, those involving bulky substrate and/or product molecules, in liquid phase) [6]. These materials have been used as hosts for the immobilisation of coordination compounds to be applied in several fields, such as catalysis and photo- or electro-chemistry [7,8]. Several works concerning the derivatisation of hexagonally ordered mesoporous MCM-41 for catalysis purposes can be found in the literature [9,10], offering the advantages of easy recovery and reuse of the catalyst. The application of MCM-41-supported Mo(VI) complexes, prepared by grafting and tethering techniques, as catalysts for olefin epoxidation, has been well documented [11–14]. The use of these host materials to support magnetically active derivatives of first row transition metals has been less investigated.

Compounds of Mn(II/III) and V(IV) play vital and versatile roles in the redox biochemistry of many organisms [15,16]. Manganese is the metal centre in enzymes such as catalase, superoxidase and dismutase, while vanadium plays an important role in haloperoxidases, as well as in nitrogenases, and an increased knowledge of their catalytic activity in oxidation processes can only be advantageous. Porphyrin ligands coordinate several metals, such as Fe, Mn and Ni, providing environments close to the biological ones [15,16]. Simpler bidentate nitrogen donor ligands, as 1,4-diazabutadienes (DAB), are also versatile since their electronic and steric properties may be fine-tuned by changing the nature of the substituent groups.

Both a pure silica and an aluminosilicate MCM-41 were the supports taken by Luan et al. [17] to immobilise 2,2′-bipyridine manganese(II) complexes [MnL_2] using an impregnation technique. The heterogeneous complexes were effective active sites for oxidation–reduction reactions at low temperature. A Mn(III) complex was also reported as having been immobilised onto the surface of MCM-41 [18] by a tethering approach. First, a functionalised ligand was covalently bound to the surface and then the metal species was directly added to this ligand, forming the complex directly inside the mesoporous material. Several complexes of Mo bearing DAB ligands have been successfully immobilised on the surface of ordered mesoporous silicas by grafting or tethering techniques, for application as catalysts for polymerisation reactions [19] and epoxidation of olefins [14].

In the present work, the immobilisation of manganese and vanadium complexes bearing 1,4-diazabutadiene ligands on MCM-41 host materials by grafting and tethering techniques, is described. A comparative study of the final hybrid mesostructured materials obtained by the two techniques was carried out, by means of solid-state techniques and determination of magnetic properties. The unsupported complexes were also synthesised and characterised. The catalytic performance of all prepared materials was investigated in the oxidation of *cis*-cyclooctene with *tert*-butylhydroperoxide (*t*-BuOOH).

2. Experimental section

2.1. Materials and methods

Starting materials were obtained from commercial sources and used as received. All preparations and manipulations were carried out using standard Schlenk techniques under nitrogen. Solvents were dried by standard procedures (toluene, methanol, and diethyl ether with Na/benzophenone ketyl; CH_2Cl_2 with CaH_2), distilled under nitrogen and kept over 4 Å molecular sieves. Elemental analysis was performed at the University of Vigo. Powder X-ray diffraction (PXRD) data was collected on a Phillips PW 1710 diffractometer using Cu–Kα radiation. The thermal studies were performed using a TG–DSC 111 from Setaram at a heating rate of 10 K min^{-1} under nitrogen. ^{29}Si solid-state NMR spectra were recorded at 79.49 MHz, on a (9.4 T) Bruker Avance 400P spectrometer. ^{29}Si MAS NMR spectra were recorded with 40° pulses, a spinning rate of 5.0 kHz, and 60 s recycle delays. ^{29}Si CP MAS NMR spectra were recorded with 4 μs ^1H 90° pulses, 8 ms contact time, a spinning rate of 5 kHz, and 4 s recycle delays. ^{13}C CP MAS NMR spectra were recorded with a 4.5 μs ^1H 90° pulse, 2 ms contact time, a spinning rate of 7 kHz, and 4 s recycle delays. Chemical shifts are quoted in ppm from TMS. ^{13}C CP MAS NMR spectra were also recorded in the solid state at 125.76 MHz on a Bruker Avance 500 spectrometer.

TGA studies were performed using a Perkin–Elmer TGA7 thermobalance system at a heating rate of 10 K min^{-1} under nitrogen. FTIR spectra were measured with a Nicolet 6700 FTIR spectrometer using KBr pellets (for complexes) in transmission mode and also using Diffuse Reflectance (for mesoporous materials). All FTIR spectra were measured using 2 cm^{-1} resolution.

The precursor complexes $Mn(acac)_3$ [20] and $VO(acac)_2$ [21] were prepared as described previously.

Purely siliceous MCM-41 was synthesised as reported using $[(C_{14}H_{29})N(CH_3)_3]Br$ ($C_{14}TMABr$) as the templating agent [6]. Before the grafting experiments with MCM-41, physisorbed water was removed from the calcined material by heating at 453 K in vacuum (10^{-2} Pa) for 2 h. Ph–DAB–$(CH_2)_3R$ [R = $Si(OEt)_3$(**1a**); H (**1b**)] ligands were synthesised by a described procedure [14].

2.2. Preparation of the complexes of the type [$Mn(acac)_2${Ph–DAB–$(CH_2)_3R$}] (**2a**, **2b**) and [$VO(acac)${Ph–DAB–$(CH_2)_3R$}]Cl (**3a**, **3b**) (R = $Si(OEt)_3$, H)

A solution of the precursor complexes [$Mn(acac)_3$] (0.70 g, 2 mmol) or [$VO(acac)_2$] (0.53 g, 2 mmol) in methanol (10 mL) was treated with 1 equivalent of either ligand