The effect of immobilization on the catalytic activity of molybdenum η^3-allyldicarbonyl complexes with nitrogen donor ligands bearing N–H groups

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ABSTRACT

The two complexes [Mo(η^3-C$_3$H$_5$)Br(CO)$_2$(L)] (L = **L$_1$**, **C1**, and **L$_2$**, **C2**), where **L$_1$** and **L$_2$** are the ligands 2-(2′-pyridyl)imidazole (**L$_1$**, pym) and 2-(2′-pyridyl)benzimidazole (**L$_2$**, pyb) were immobilized in mesoporous MCM-41 and in Mg/Al hydrotalcite (HTC), in order to obtain new heterogeneous catalysts. Both the ligands and the complexes reacted with MCM-41 functionalized with a chloropropyl pendant arm; in the first approach, the immobilized ligands were then allowed to react with [Mo(η^3-C$_3$H$_5$)Br(CO)$_2$(NCMe)$_2$] to afford supported **C1** and **C2**. While spectroscopic data, DRX, and nitrogen isotherm adsorptions revealed the similarity of the two kinds of materials, and the preservation of the MCM characteristic structure, elemental analysis showed that the stepwise approach (ligand + complex precursor) allowed the introduction of a much larger amount of molybdenum. The attempts at immobilization of the complexes in HTC were less successful. Neither the deprotonated ligands or complexes were able to intercalate between the material layers, the experimental evidence suggesting the intercalation of OH$^-$ anions and the adsorption of the deprotonated ligands or complexes on the outside of the clay. Both materials exhibited higher activities in the epoxidation of cycloctene and styrene, in the presence of TBHP, than the free complexes in homogeneous conditions, with conversions close to 100% for both substrates, in the MCM based materials prepared through a stepwise route.

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1. Introduction

The development of new and efficient heterogeneous catalysts, combining the selectivity of homogeneous catalysts with the advantages of heterogeneous processes, namely easy recovery of products and recycling of the promoter, continues to be a priority in chemistry [1,2].

Active centers may be immobilized in several ways, depending on the binding between active center and support. The family of the silicon based porous MCM materials, developed by Mobil in 1992 [3,4], led to new paths for the reaction between suitable precursors with the SiOH groups in the internal walls of the large surface of the hexagonally ordered parallel channels. The applications of the resulting materials containing inorganic active centers in several fields, from catalysis to optoelectronics, followed [1,5–7]. Typical approaches for such reactions include direct grafting, where a functionalized complex reacts with the OH groups, or tethering where a step by step route is followed, starting by reaction between the walls and a functionalized organic molecule (ligand) which then

binds the metal center [8,9]. When no suitable function is available, a spacer can be used [6,10].

Other kinds of porous materials may be more suitable, depending on the nature of the metal complex and the reactions to perform. Some layered materials can be used with success to immobilize ionic species by means of electrostatic interactions. In particular, layered double hydroxides are clays with a structure based on hydroxides, such as Mg(OH)$_2$. Some Mg^{2+} cations in the edge-sharing Mg(OH)$_6$ octahedra layer may be replaced by M^{3+} cations, yielding a charge unbalance that requires anions. These and water molecules occupy the interlayer space. In hydrotalcite (HTC), the cationic layer contains Mg^{2+} and Al^{3+}, with compositions [M$_{1-x}^{2+}$M$_x^{3+}$(OH)$_2$](A^{m-})$_{x/m}$ · nH$_2$O (M^{2+} = Mg^{2+}, Zn^{2+}, Ni^{2+}, etc., M^{3+} = Al^{3+}, Cr^{3+}, Ga^{3+}, etc.) [11,12], and the ratio between cations (x) is associated with the interlayer distance in the structure. Anion exchange provides the easiest route for functionalization of the clay, and may also change this distance, depending on the size of the anion. A common procedure, more efficient than direct anion exchange, consists of calcination of the precursor clay, usually containing carbonate, followed by rehydration in the presence of another anion, leading to swelling of the structure [11a,12,13]. The intercalated anion may then react with inorganic species [14]. Substitution of the cations is another possibility for modifying and functionalizing clays. Some authors have prepared double hydrox-

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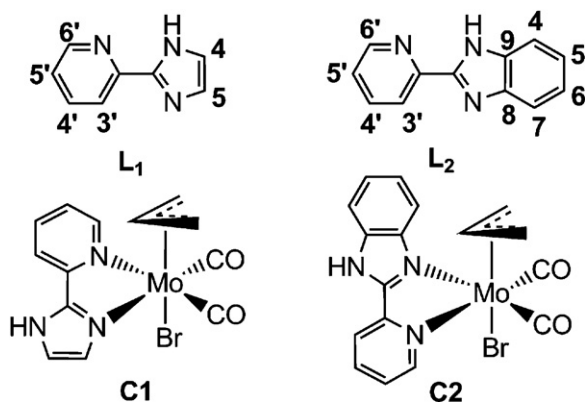
Scheme 1. Schematic representation of ligands **L₁** and **L₂**, and complexes **C1** and **C2**.

ides directly in presence of the anions designed to belong to the final structure [15]. Both the HTC material by itself and functionalized with metal active centers have shown catalytic activity in several reactions, namely aziridination of oxiranes [16] and olefin polymerization [14].

In this work, the two molecules 2-(2′-pyridyl)imidazole (**L₁**, pym) and 2-(2′-pyridyl)benzimidazole (**L₂**, pyb) were chosen as ligands (see Scheme 1) to functionalize MCM-41 and a Mg/Al HTC and to react with the Mo(II) complex $[Mo(\eta^3\text{-}C_3H_5)X(CO)_2(NCMe)_2]$ [17]. Organometallic complexes in general are very versatile as homogeneous catalysts in a wide variety of reactions, as well as in many other applications [18]. The $Mo(II)(\eta^3\text{-}C_3H_5)(CO)_2$ derivatives and their W(II) analogues have displayed activity in catalysis [19], namely imine aziridation [20], phosphine oxidation [21], allylic alkylations [22], and, more recently as precursors in olefin oxidation. $[Mo(\eta^3\text{-}C_3H_5)X(CO)_2(NCMe)_2]$ (X = Cl, Br) and some of their derivatives containing 1,4-diaza-1,3-butadienes or other bidentate nitrogen donor ligands promoted the selective olefin epoxidation in the presence of *t*-butyl hydroperoxide (TBHP) [23]. Active species usually contain Mo(VI), as in the industrial ARCO-Halcon process for homogeneous olefin epoxidation with TBHP as source of oxygen [24]. These catalysts have been shown to be as active as other well described Mo(II) precursors [25], with high conversions and turnover frequencies, and maintaining a high activity in the second run.

Since the two complexes $[Mo(\eta^3\text{-}C_3H_5)Br(CO)_2(L)]$ (L = **L₁**, **C1**, and **L₂**, **C2**, Scheme 1) have been previously described and their activity as precursors in the epoxidation of cyclooctene and styrene determined [26], we studied their immobilization in MCM-41 and a Mg/Al HTC and their catalytic activity in the same reaction, in order to evaluate the effect of the support on the catalytic activity and to compare it with related systems.

2. Experimental

2.1. General

All reagents and ligand 2-(2′-pyridyl)benzimidazole **L₂** were obtained from Aldrich and used as received. Commercial grade solvents were dried and deoxygenated by standard procedures (Et₂O, THF, and toluene over Na/benzophenone ketyl; CH₂Cl₂ over CaH₂), distilled under nitrogen, and kept over 4 Å molecular sieves. The ligand 2-(2′-pyridyl)imidazole (**L₁**) [27] and the complexes $[Mo(\eta^3\text{-}C_3H_5)Br(CO)_2(NCCH_3)_2]$ [17b] and $[Mo(\eta^3\text{-}C_3H_5)Br(CO)_2(L)]$ (L = **L₁**, **C1**, and **L₂**, **C2**) [26] were prepared according to literature methods. MCM-41 and derivatized materials were synthesized by adopting a methodology previously described, using $[(C_{14}H_{33})N(CH_3)_3]Br$ as templating agent [10]. Prior to the

grafting experiment, physisorbed water was removed from calcined (540 °C for 6 h under air) **MCM** (**1**) by heating at 180 °C in vacuum (10^{-2} Pa) for 2 h.

FTIR spectra were obtained as KBr pellets (complexes) and Diffuse Reflectance (DRIFT) measurements (materials) on a Nicolet 6700 in the 400–4000 cm⁻¹ range using 1 cm⁻¹ resolution. Powder XRD measurements were taken on a Philips PW1710 using Cu Kα radiation filtered by graphite. ¹H and ¹³C solution NMR spectra were obtained with a Bruker Avance 400 spectrometer.

Solid state NMR measurements were performed at room temperature on a Bruker MSL 300P spectrometer operating at 59.60 and 75.47 MHz for the observation of ²⁹Si and ¹³C resonances, respectively. The standard magic angle spinning (MAS) cross-polarization–dipolar decoupling RF pulse sequence (CP-DD) was used under about 4 kHz spinning rate. For the acquisition of ²⁹Si spectra, 5 ms contact time, 6 s recycling delay, and a number of scans always higher than 3000 were selected; the Hartmann–Hahn condition was optimized using tetrakis-trimethylsilylsilane and tetramethylsilane (TMS) was the external reference to set the chemical shift scale ($\delta = 0$). ¹³C spectra were recorded with 2 ms contact time, 4 s recycling delay and a number of scans higher than 900. The Hartmann–Hahn condition was optimized using glycine, also the external reference to set the chemical shift scale (¹³CO at 176.1 ppm).

The N₂ adsorption/desorption measurements were obtained in an automatic apparatus (ASAP 2010; Micromeritics). BET specific surface areas (S_{BET}, p/p^0 from 0.03 to 0.13) and specific total pore volume, V_p were estimated from N₂ adsorption isotherms measured at 77 K. The pore size distributions (PSD) were calculated by the BJH method using the modified Kelvin equation with correction for the statistical film thickness on the pore walls [28,29]. The statistical film thickness was calculated using Harkins–Jura equation in the p/p^0 range from 0.1 to 0.95. Microanalyses (C, N, H, and Mo) were performed at the University of Vigo, Spain.

2.2. Catalytic studies

The complexes and materials were tested in the epoxidation of *cis*-cyclooctene (cy8) and styrene (sty), using *t*-butylhydroperoxide (TBHP) as oxidant. The catalytic oxidation tests were carried out at 328 K under normal atmosphere in a reaction vessel equipped with a magnetic stirrer and a condenser. In a typical experiment the vessel was loaded with olefin (100%), internal standard (DBE), catalyst (1%), oxidant (200%), and 3 mL of solvent. Addition of the oxidant determines the initial time of the reaction. The course of the reactions was monitored by quantitative GC-analysis by collecting samples at 10, 30 min, 1 h and 1 h 30 min, then at 2, 4, 6, 8, and 24 h of reaction. These samples were treated as described previously prior to injection in the GC column [26].

2.2.1. Epoxidation of cis-cyclooctene

Cis-cyclooctene (800 mg, 7.3 mmol), 800 mg dibutyl ether (internal standard), 1 mol% of catalyst, 2.65 mL of TBHP (5.5 M in *n*-decane) and 3 mL of CH₂Cl₂.

2.2.2. Epoxidation of styrene

Styrene (800 mg, 7.7 mmol), 800 mg dibutyl ether (internal standard), 1 mol% of catalyst, 2.65 mL of TBHP (5.5 M in *n*-decane) and 3 mL of CH₂Cl₂.

MCM-Pr-Cl

2.0 mL of 3-(chloropropyl)-trimethoxysilane was added to a suspension of 1 g of MCM-41 (**1**) in 30 mL of toluene, and allowed to reflux for 24 h. The yellow suspension was filtered, washed with 4× 20 mL dichloromethane, and dried under vacuum. Different samples are indicated by *.

MCM-Pr-Cl (**2**)