Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 256 (2006) 90–98
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Hepta-coordinate halocarbonyl molybdenum(II) and tungsten(II) complexes as heterogeneous polymerization catalysts

Jorge Gimenez [a], Carla D. Nunes [a], Pedro D. Vaz [a], Anabela A. Valente [b], Paula Ferreira [c], Maria José Calhorda [a,*]

[a] *Department of Chemistry and Biochemistry, CQB, Faculty of Science, University of Lisbon, C8 Campo Grande, 1749-016 Lisboa, Portugal*
[b] *Department of Chemistry, CICECO, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal*
[c] *Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal*

Received 27 February 2006; received in revised form 6 April 2006; accepted 8 April 2006
Available online 5 June 2006

Abstract

$[MX_2(CO)_3(DAB)]$ (M = Mo, W; X = I, Br) (**5**–**8**) complexes bearing the 1,4-diazobutadiene (DAB) ligand RN=C(Ph)–C(Ph)=NR $[R = (CH_2)_3Si(OEt)_3]$ were immobilized in MCM-41 mesoporous silica. The tethering, stepwise procedure started with treatment of the MCM-41 mesoporous material with a toluene solution of the 1,4-diazobutadiene ligand, under reflux. The molybdenum and tungsten organometallic cores were subsequently introduced into the ligand-silicas by pore volume impregnation of a solution of the complexes $[MX_2(CO)_3(NCMe)_2]$ (M = Mo, W; X = Br, I). The modified materials were extensively characterized by several techniques, such as FTIR, solid-state MAS and CP MAS NMR (^{13}C, ^{29}Si), powder XRD, and nitrogen adsorption–desorption measurements. These new materials (containing 2.6–2.9 wt.% Mo or 0.4–0.6 wt.% W) catalyze the ring-opening metathesis polymerization (ROMP) of norbornene (NBE) and norbornadiene at 328 K, in contrast with the very low activity exhibited by the precursor complexes and with their behavior at lower temperature. Addition of $AlCl_3$ as a co-catalyst enhanced the catalytic performance of the material MCM-DAB-$MoBr_2$ (**12**) in the ROMP of NBE.

Keywords: Molybdenum; Tungsten; MCM-41; Polymerization; DAB ligands; Hepta-coordination; Catalysis

1. Introduction

Organometallic complexes can efficiently and selectively catalyze many reactions and are widely applied in industrial processes. One drawback of such homogeneous catalysts is the difficulty of separating the products from the reaction solution and recovering and recycling the catalyst. Therefore, the possibility of incorporating complexes in materials to yield heterogeneous catalysts has opened new possibilities in recent years [1,2]. Seven-coordinate Mo(II) complexes $[MX_2(CO)_3L_2]$ (M = Mo, W; X = halogen) and their derivatives, obtained by replacing the labile nitrile ligands, have been extensively investigated [3–5]. Their synthesis [6–9], structures [10,11] and properties have been studied since they were reported for the first time by Nigam and Nyholm in 1957 [12], and they have been shown to exhibit catalytic activity [13,14]. Complexes $[M(CO)_3X_2(NCMe)_2]$ have been successfully used by Baker and co-workers in the ring-opening metathesis polymerization (ROMP) of norbornene (NBE) and norbornadiene (NBD) [15,16] with satisfactory results, though some of the complexes were only active upon the addition of a Lewis acid, such as $AlCl_3$ or $ZrCl_4$. Szymańska-Buzar et al. carried out the study of ROMP reactions with seven-coordinate Mo(II) and W(II) complexes [17–19].

The micelle templated silicas MCM-41 (hereafter denoted as MCM) belong to the M41S family developed by Mobil Corporation in 1992 [20,21], and display a set of properties, such as a stable and ordered mesoporous structure, large surface area (usually $>1000\,m^2\,g^{-1}$), and narrow pore size distribution, which make them ideal for hosting molecules of various sizes, shapes and functionalities. These features are suitable for the inclusion of organometallic complexes and have led to significant developments, among others, in the fields of catalysis, adsorption/sorption, separation, sensors, optically active materials [1,22]. The number of papers describing this type of chemistry has been growing each year [1,2,23].

* Corresponding author. Tel.: +351 217500196; fax: +351 217500088.
E-mail address: mjc@fc.ul.pt (M.J. Calhorda).

1381-1169/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.04.023

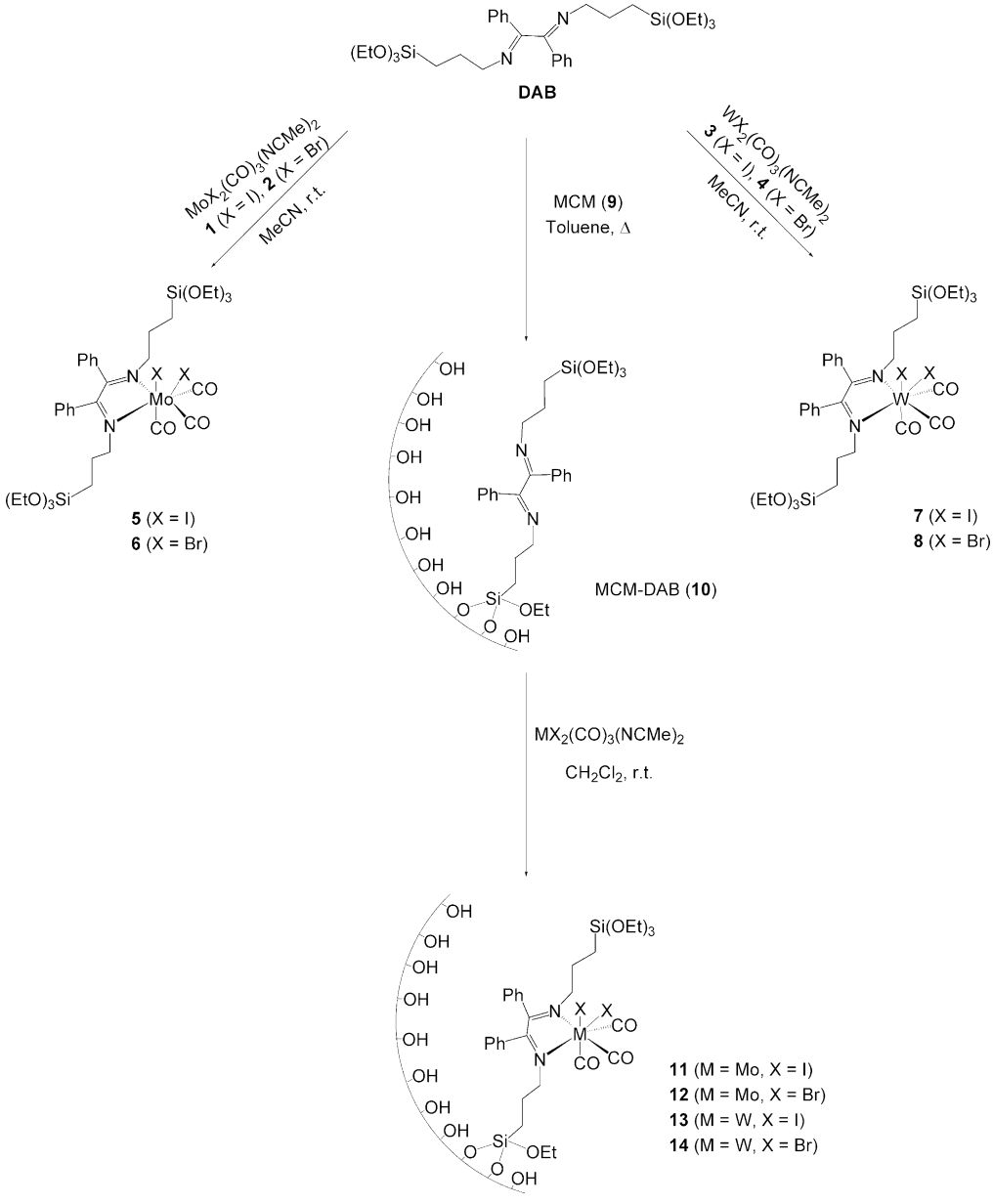
In the present work, bis(acetonitrile) Mo(II) and W(II) complexes were used as precursors for the immobilization of organometallic species in MCM, by a tethering approach. In the first step, the triethoxysilyl-*N*-substituted 1,4-diazobutadiene (DAB) ligand was grafted on the host material MCM-41, and was subsequently allowed to react with the organometallic complexes $[MX_2(CO)_3(NCMe)_2]$ (M = Mo, W; X = Br, I). The derivatized materials were fully characterized and tested as catalysts for the ring-opening metathesis polymerization (ROMP) of norbornadiene (NBD) and norbornene (NBE).

2. Results and discussion

2.1. The organometallic complexes

The functionalized triethoxysilyl ligand RN=C(Ph)–C(Ph)=NR (DAB) [R=$(CH_2)_3Si(OEt)_3$] was prepared by the reaction of benzil $[C_6H_5(CO)(CO)C_6H_5]$ with two equivalents of (3-aminopropyl)triethoxysilane, according to a well-known procedure [24]. The precursor complexes $[MX_2(CO)_3(NCMe)_2]$ (M = Mo, W; X = I or Br) (**1**–**4**) [25] were allowed to react with one equivalent of the DAB ligand, affording the complexes $[MX_2(CO)_3\{Ph\text{-}DAB\text{-}CH_2Si(OEt)_3\}_2]$ (M = Mo, W; X = I or Br) (**5**–**8**) by displacement of both labile acetonitrile ligands and in good yield. These complexes were subsequently immobilized on the MCM-41 host material, as outlined in Scheme 1 [24,26].

Both the ligand DAB [24] and the precursor complexes **1**–**4** [25] have been characterized elsewhere and therefore will not be discussed here. The ^{1}H NMR spectrum of $[MoI_2(CO)_3\{Ph\text{-}DAB\text{-}CH_2Si(OEt)_3\}_2]$ (**5**) shows a multiplet in the range $7.36 < \delta < 7.95$ ppm assigned to the phenyl groups, as well as multiplet signals at $\delta = 3.47$–3.52 ppm (NCH_2), 1.93–1.98 ppm ($CH_2CH_2CH_2$) and a broad singlet at 0.71 ppm ($SiCH_2$) for the propyl chains. The presence of ethoxy groups



Scheme 1.