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Immobilisation of methyltrioxorhenium on functionalised MCM-41

Sandra Gago [a], José A. Fernandes [a], Marta Abrantes [b], Fritz E. Kühn [b,*], Paulo Ribeiro-Claro [a], Martyn Pillinger [a], Teresa M. Santos [a], Isabel S. Gonçalves [a,*]

[a] Department of Chemistry, CICECO, Campus de Santiago, University of Aveiro, 3810-193 Aveiro, Portugal
[b] Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching bei München, Germany

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Abstract

Methyltrioxorhenium (MTO) was immobilised in the mesoporous silica MCM-41 functionalised with a pyrazolylpyridine ligand. Elemental analysis indicated that the rhenium loading in the final material (3.6 wt.%, 0.19 mmol g^{-1}) was about 35% of the ligand content. Powder X-ray diffraction confirmed that the regular hexagonal symmetry of the host was preserved during the grafting experiments. The functionalised material was also characterised by ^{13}C and ^{29}Si magic-angle spinning NMR, FTIR and Raman spectroscopy. Analysis of the vibrational spectra was supported by preparing a model complex containing the ligand ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate and by carrying out ab initio calculations. The results indicate that bidentate and monodentate coordination of the N-base ligand to the rhenium centre coexist for the model complex in the solid state. In solution, ^{17}O-NMR spectroscopy for the model complex indicates a dynamic behaviour without a solely bidentate coordination even at low temperature. The coordination seems to be relatively weak, even for a monodentate adduct. For MTO immobilised in MCM-41 functionalised with the pyrazolylpyridine ligand, monodentate coordination of the pyridyl nitrogen atom to the metal centre was also found to be the major form present.

Keywords: Mesoporous materials; Chelating ligands; Methyltrioxorhenium; Ab initio calculations; Supported catalysts

1. Introduction

Methyltrioxorhenium(VII), CH_3ReO_3, is an extremely versatile catalyst for oxy functionalisations, aldehyde olefination and olefin metathesis [1]. Pertinent oxidation reactions include the epoxidation of olefins and the oxidation of conjugated dienes, alkynes, alcohols, ethers, allylic alcohols and aromatic compounds. The MTO-catalysed epoxidation of olefins was the first reaction to be studied and is particularly important since H_2O_2 can be used as the oxidant, rather than an alkyl hydroperoxide [2]. Due to the Lewis acidity of the rhenium centre, a major limitation of this system is the opening of the epoxide ring, leading to the formation of diols in the presence of water [3]. However, with the addition of pyridine as Lewis base, epoxidations can be performed in biphasic water–organic solvent systems using 30% aqueous hydrogen peroxide as oxidant, selectively giving epoxides in high yields [4,5]. It was subsequently shown that 3-cyanopyridine and especially pyrazole as Lewis bases are even more effective and less problematic than pyridine [6,7]. The additives promote an increase in the reaction rate by taking part in the transfer of the active peroxospecies of MTO into the organic solvent. Moreover, the ligands coordinate to the metal centre, thereby reducing the Lewis acidity of the catalyst [8]. This chemistry has been quite well explored and it is known that MTO forms trigonal–bipyramidal adducts with pyridines and related bases [9], and distorted octahedral adducts with bidentate Lewis bases, e.g. 4,4′-dimethyl-2,2′-bipyridine, 1,10-phenanthroline and 2,2′-bipyrimidine [10].

As an alternative approach to improve MTO-catalysed reactions, host–guest chemistry has been used. The urea/hydrogen peroxide complex is a very effective oxidant in non-aqueous heterogeneous olefin epoxidations and silane

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* Corresponding authors. Tel.: +351 234 378190; fax: +351 234 370084.
E-mail addresses: fritz.kuehn@ch.tum.de (F.E. Kühn), igoncalves@dq.ua.pt (I.S. Gonçalves).

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oxidations catalysed by MTO [11]. Using NaY zeolite as host for these reactions also resulted in high yields and excellent product selectivities [12]. MTO has also been supported on polyvinylpyridines [13], inorganic oxides [14], and silica tethered with polyethers or with 2,2′-dipyridylamino groups [15,16]. In a further example, MTO was heterogenised inside the porous system of a hybrid silica matrix via the sol–gel method using 4-((3-triethoxysilyl)propylamino)pyridine hydrochloride as a hydrolysable ligand [17]. A supported catalyst of this type may combine the advantages of a Lewis base adduct of MTO with the well-known benefits of a heterogeneous catalyst system, i.e. easy catalyst separation and recycling. Other studies along these lines include the immobilisation of previously synthesised Lewis base adducts of MTO on polystyrene by use of the microencapsulation technique [18], and the immobilisation of MTO in the ordered mesoporous silica MCM-41 functionalised with bipyridyl groups [19]. In the present work, we describe the successful encapsulation and characterisation of MTO in MCM-41 functionalised with a pyrazolylpyridine ligand. The mesostructured ligand–silica was previously shown to be an effective solid-state complexation material for oxodiperoxo molybdenum and manganese acetonitrile complexes [20].

2. Experimental

2.1. Materials and methods

Microanalyses were performed at the Mikroanalytische Laboratory of the Technical University of Munich (by M. Barth and co-workers). Powder X-ray diffraction (XRD) data were collected on a Philips X'pert diffractometer with a curved graphite monochromator (Cu-Kα radiation), in a Bragg–Brentano para-focusing optics configuration. Samples were step-scanned in 0.02° 2θ steps with a counting time of 2 s per step. IR spectra were obtained using KBr pellets and a FTIR Mattson-7000 infrared spectrophotometer. Raman spectra were recorded on a Bruker RFS100/S FT instrument equipped with a InGaAs detector and using the 1064 nm excitation of the Nd:YAG laser. ^{17}O NMR spectra were measured at 54.41 MHz on a Bruker GX-400 spectrometer. ^{17}O NMR enrichment of the oxo group in the studied complexes was carried out by treatment of a solution of the unlabelled complexes in CH_2Cl_2, in a manner analogous to that previously reported [21]. Solid-state magic-angle-spinning (MAS) NMR spectra were recorded at 79.49 MHz for ^{29}Si and 125.76 MHz for ^{13}C on Bruker Avance 400/500 spectrometers. ^{29}Si MAS NMR spectra were recorded with 40° pulses, spinning rates of 5.0–5.5 kHz and 60 s recycle delays. ^{29}Si CP MAS NMR spectra were recorded with 5.5 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 acquired with a 3.5 μs ^1H 90° pulse and 2 ms contact time with spinning rates of 7–9 kHz and 4 s recycle delays.

Where appropriate, the preparations and manipulations were carried out using standard Schlenk techniques under nitrogen. Solvents were dried by standard procedures, distilled under nitrogen and kept over 4 Å molecular sieves. Literature procedures were used to prepare the ligands 2-(3-pyrazolyl)pyridine (**1**) [22], ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate [23] (**2**) and (3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide (**3**) [20a,20b,20c]. Purely siliceous MCM-41 was synthesised as described previously using $[(C_{14}H_{29})NMe_3]Br$ as the templating agent [24]. After calcination at 540 °C for 6 h, the material was characterised by powder XRD and IR spectroscopy. Prior to grafting with **3** to give MCM-41-PP [20], physisorbed water was removed from calcined MCM-41 by heating at 180 °C in vacuo for 2 h. FTIR, Raman and MAS NMR (^{13}C, ^{29}Si) data for MCM-41-PP were in agreement with published results [20a,20b,20c]. Elemental analysis indicated: C, 11.67%; H, 1.92%; N, 3.14%.

2.2. Preparation of methyl(ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate)trioxorhenium (4)

One equivalent of ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate (**2**) was added to a solution of MTO (0.323 g, 1.3 mmol) in CH_2Cl_2 (15 ml) and the resultant yellow solution stirred for 1 h at room temperature. The solvent was evaporated and the solid product washed with hexane and dried in vacuo. Anal. Calcd for $C_{13}H_{16}N_3O_5Re$ (480.5): C, 32.50; H, 3.36; N, 8.75. Found: C, 32.66%; H, 3.38%; N, 8.51%. IR (KBr, cm^{-1}): 3446 (br), 3116 (m, C–H st py), 2982 (w), 2931 (w), 2905 (sh), 1748 (vs, C=O st), 1613 (m), 1593 (w), 1568 (w), 1533 (w), 1507 (w), 1491 (w), 1459 (m), 1438 (s), 1374 (s), 1343 (w), 1249 (m), 1213 (s), 1161 (sh), 1144 (sh), 1099 (m), 1081 (w), 1055 (w), 1024 (s), 942 (m, Re=O), 916 (m, Re=O), 852 (m), 766 (s), 713 (w), 693 (w), 643 (w), 619 (w), 576 (w), 507 (w), 479 (w), 445 (w), 419 (w), 393 (w). Raman (cm^{-1}): 3140 (w), 3087 (w), 3072 (w), 2984 (w), 2940 (w), 2905 (w), 1613 (s), 1595 (w), 1570 (s), 1533 (vs), 1510 (w), 1494 (w), 1424 (m), 1401 (w), 1378 (m), 1347 (w), 1293 (w), 1253 (w), 1187 (w), 1161 (w), 1081 (w), 1026 (s), 994 (w), 961 (w), 944 (m), 918 (w), 857 (w), 712 (w), 693 (w), 623 (w), 563 (w), 488 (s), 347 (w), 316 (w), 258 (w). ^{13}C CP MAS NMR: $\delta = 167.3$ (C=O), 147.1, 137.2, 124.1, 105.7 (py-C), 62.1 (CH_3CH_2O), 52.0 ($COCH_2N$), 29.2 ($ReCH_3$), 14.0 (CH_3CH_2O).

2.3. Preparation of MCM-41-PP/MTO

A solution of MTO (0.234 g, 0.94 mmol) in CH_2Cl_2 (10 ml) was added to a suspension of MCM-41-PP (1.6 g) in CH_2Cl_2 (30 ml) and the mixture stirred at room temperature for 24 h. The solution was filtered off and the pale yellow solid washed several times with CH_2Cl_2 and dried in vacuo at room temperature. Anal. Found: C, 11.98%; H, 1.91%; N, 3.01%; Re, 3.6%. IR (KBr, cm^{-1}): 3448 (br), 2982 (w), 2951 (sh), 1993 (w), 1868 (w), 1603 (w),