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Incorporation of a dioxomolybdenum(VI) complex in a Zr^{IV}-based Metal–Organic Framework and its application in catalytic olefin epoxidation

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The complex $[MoO_2Cl_2(bpydc)]$ (**1**) (H_2bpydc = 2,2′-bipyridine-5,5′-dicarboxylic acid) has been incorporated into a Zr^{IV}-based Metal–Organic Framework (UiO-67) by partial replacement of 4,4′-biphenyldicarboxylic acid (H_2bpdc) in the solvothermal synthesis by the complex $[MoO_2Cl_2(H_2bpydc)]$. The resultant material, designated as UiO-67-MoO_2Cl_2(bpydc) (**3**), was isotypical with the parent UiO-67 framework as shown by powder X-ray diffraction (PXRD). MOF **3** was also characterised by elemental and thermogravimetric analyses, FT-IR spectroscopy and $^{13}C\{^1H\}$ MAS NMR, N_2 adsorption, and scanning electron microscopy. MOF **3** catalyses the epoxidation of *cis*-cyclooctene (Cy8) and limonene (Lim) with *tert*-butylhydroperoxide as oxidant. When using α,α,α-trifluorotoluene as cosolvent at 75 °C, very good epoxide selectivity was observed: 100% for Cy8 at 97% conversion, and 90% for Lim at 67% conversion. The catalyst was recovered, characterised, and used in consecutive batch runs. Drops in catalytic activity between runs were attributed to catalyst deactivation (caused by structural breakdown) rather than molybdenum leaching. Stability tests showed that protic media (due to the solvent and/or oxidant) and higher reaction temperatures (55–75 °C) prompted the loss of crystallinity and structural degradation. The related MOF UiO-67-bpdc (**2**) is more stable than **3**. The reduced stability of **3** may be related to the incorporation of the $bpydc^{2-}$ organic linker in the framework, as well the existence of a high number of missing-linker defects.

1. Introduction

For many years high-valent oxo-molybdenum [1–6] and oxo-rhenium complexes [6–9] have been used as catalysts for a wide variety of organic reactions. Dichlorodioxomolybdenum(VI), MoO_2Cl_2, is the simplest molybdenyl derivative and has proved to be active in various Lewis acid catalysed organic transformations, oxidation and reduction reactions [2,5,6]. The use of MoO_2Cl_2 as a catalyst for C–X bond formation has recently been reviewed [5,6]. For C–O bond formation, the most studied reaction catalysed by oxomolybdenum complexes is probably the epoxidation of olefins [10,11]. Although MoO_2Cl_2 is very effective for this reaction [12], its use is hampered to some extent by the fact that it is coordinatively unsaturated, hygroscopic and very moisture sensitive. The MoO_2X_2 moiety can be stabilised by adduct formation with Lewis base ligands such as 2,2′-bipyridine (bpy) and derivatives, giving complexes with the general formula $[MoO_2X_2(L)]$ [13–21]. With bpy and methyl-substituted derivatives, the resultant complexes display only moderate catalytic activities, which seems to be due at least in part to the low to moderate solubility of the complexes in the most common organic solvents. By appropriate choice of the substituents on the bpy ligand, much more soluble and catalytically active complexes are obtained. For example, a recent report showed that the complex with L = 5,5′-bis-methoxycarbonyl-2,2′-bipyridine gives turnover frequencies (TOFs) for the epoxidation of *cis*-cyclooctene (used as a benchmark substrate) at 55 °C of up to 2000 h^{-1} without additional solvent or ca. 8000 h^{-1} in ionic liquids [21].

A major drawback in using homogeneous catalysts like $[MoO_2Cl_2(L)]$ is the difficulty in separating the product from the catalyst at the end of the reaction. With heterogeneous catalysts this can be achieved in a straightforward manner, such as by filtration, allowing facile recovery and reuse of the solid catalyst. The heterogenisation of molecular oxo-molybdenum catalysts

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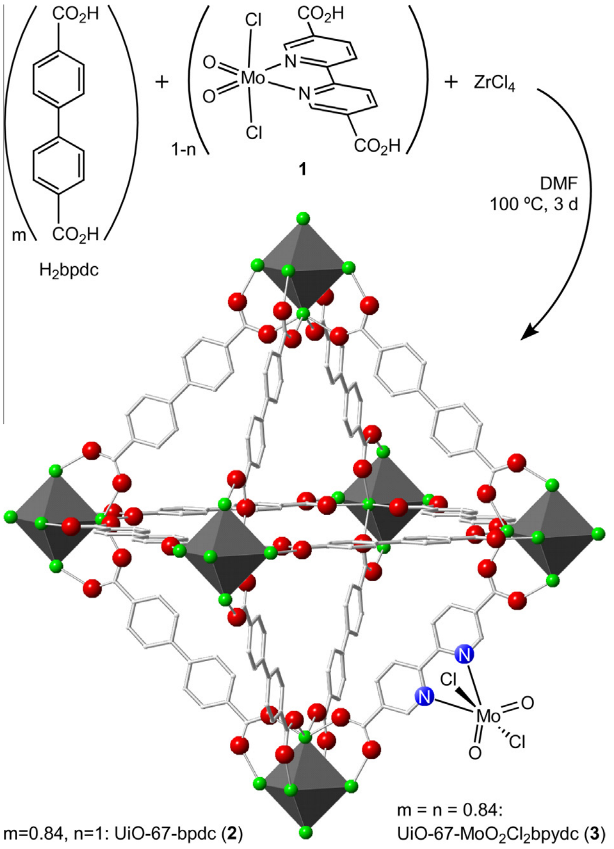
has therefore been a topic of ongoing interest and importance [22–24]. For complexes of the type [MoO$_2$Cl$_2$(L)], immobilisation strategies rely on functionalisation of the organic ligand. Two attempts to immobilise complexes of the type [MoO$_2$Cl$_2$(bpy)] involved the preparation of solid ligands by either functionalisation of the ordered mesoporous silica MCM-41 with bipyridyl groups via a covalently grafted alkoxysilane spacer group [25], or intercalation of 2,2′-bipyridine-5,5′-dicarboxylate (bpydc) anions in a layered double hydroxide [26]. Both materials were subsequently treated with the solvent adduct [MoO$_2$Cl$_2$(THF)$_2$] with the intention of forming supported [MoO$_2$Cl$_2$(L)] complexes by ligand exchange. However, spectroscopic data indicated the presence of unidentate-bridged entities of the type O$_2$Mo–O–MoO$_2$ rather than mononuclear [MoO$_2$Cl$_2$(L)] species. Although the resultant materials were active as catalysts for the epoxidation of olefins, the catalytic performance was compromised by poor accessibility of the active sites and/or leaching of catalytically active molybdenum species.

Molybdenum oxide/bipyridine hybrid materials are a potentially interesting alternative as solid-state bipyridine-based dioxomolybdenum(VI) complexes. For example, the polymeric crystalline materials [MoO$_3$(bpy)] [27,28], {[MoO$_3$(bpy)][MoO$_3$(H$_2$O)]}$_n$ [29] and ((CH$_3$)$_2$NH$_2$)[MoO$_3$(Hbpydc)]·H$_2$O [30] all contain the same type of one-dimensional polymer, $^{1}_{\infty}$[MoO$_3$(L)], composed of corner-sharing {MoO$_4$N$_2$} octahedra. These 1D chains can be considered as polymeric versions of monomeric [MoO$_2$(OR)$_2$(bpy)] complexes. Unfortunately, the nonporous, low surface area nature of these materials imposes severe limitations on their catalytic performance. When the materials are employed in catalytic olefin epoxidation, the reactions are usually at least partially homogeneous in nature, i.e., the materials act as a source of active soluble species.



Scheme 1. Schematic representation of the preparation and structures of MOFs **2** and **3**. For simplicity the organic linkers are drawn as capped sticks, hydrogen atoms have been omitted, and the [Zr$_6$O$_4$(OH)$_4$]$^{12+}$ clusters are represented as grey octahedra with zirconium atoms (green spheres) at the vertices. Red spheres represent oxygen atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

One can envisage that the ideal solid-state bipyridine-based dioxomolybdenum(VI) catalyst would comprise a porous crystalline material in which the bipyridine ligands are an integral part of the framework structure. Metal Organic Frameworks (MOFs), formed by the self-assembly of metallic centres and bridging organic linkers, appear to provide the perfect platform for designing such functional materials based on metal-bearing ligands [31–35]. Several MOFs containing 4,4′-biphenyldicarboxylate (bpdc) are known. By partially or completely replacing bpdc^{2-} with bpydc^{2-}, materials with open bpy coordination sites have been prepared. The first of these was [Al(OH)(bpydc)] (MOF-253), which was shown to readily complex metals [36]. More recently, bpydc^{2-} has been incorporated into the highly robust UiO-67 platform by either direct solvothermal synthesis or postsynthetic exchange [37–40]. The UiO series of MOFs is defined by the octahedral [Zr$_6$O$_4$(OH)$_4$]$^{12+}$ secondary building unit, which is 12-coordinated to 1,4-benzene dicarboxylate ligands in UiO-66, and bpdc^{2-} ligands in UiO-67 [41,42]. Metalation of UiO-67-bpydc produced immobilised Pd(bpy)Cl$_2$ species on the MOF strut that exhibited heterogeneous and recyclable catalytic features for the Suzuki–Miyaura cross-coupling reaction [39]. In other work, UiO-67 was doped with Ir, Re, and Ru complexes of bpydc^{2-} by using a mix-and-match synthetic strategy [43]. Complexes such as [Re^{I}(CO)$_3$(bpydc)Cl]$^{2-}$ and [Ru^{II}(bpy)$_2$(bpydc)] were successfully incorporated to give active catalysts for various photocatalytic transformations.

In the present work the neutral complex [MoO$_2$Cl$_2$(H$_2$bpydc)] (**1**) has been prepared and incorporated into the UiO-67 framework by direct solvothermal synthesis (Scheme 1). Both complex **1** and the derivatised MOF have been examined as catalysts for the epoxidation of olefins, with special attention paid to the stability of the MOF under the catalytic reaction conditions used.

2. Experimental section

2.1. Materials

The chemicals MoO$_2$Cl$_2$ (Sigma–Aldrich), ZrCl$_4$ (Riedel-de-Häen), 2,2′-bipyridine-5,5′-dicarboxylic acid (H$_2$bpydc, 97%, Sigma–Aldrich), 4,4′-biphenyldicarboxylic acid (H$_2$bpdc, 97%, Aldrich), *N,N*′-dimethylformamide (DMF, puriss p.a., Sigma–Aldrich), anhydrous tetrahydrofuran (THF, 99%, Sigma–Aldrich), hexane (99%, Sigma–Aldrich), pentane (>99%, Sigma–Aldrich), diethyl ether (99.9%, Sigma–Aldrich), ethanol (anhydrous, >99.9%, Carlo Erba), acetonitrile (CH$_3$CN, 99.5%, Sigma–Aldrich), anhydrous α,α,α-trifluorotoluene (TFT, 99%, Sigma–Aldrich) and *cis*-cyclooctene (Cy8, 95%, Sigma–Aldrich) were purchased from commercial sources and used as received without any further purification. 5.5 M *tert*-butylhydroperoxide in decane (TBHP, Sigma–Aldrich) and DL-limonene (Lim, ⩾95%, Merck) were dried prior to use by using activated 3 Å and 4 Å molecular sieves, respectively.

2.2. Characterisation methods

Elemental analysis for C, H and N was performed using a Truspec instrument. The Zr and Mo contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) at C.A.C.T.I., University of Vigo, Spain. Laboratory powder synchrotron X-ray diffraction data suitable for *ab initio* structure solution and refinement were collected at ambient temperature using a PANalytical Empyrean instrument equipped with a PIXcel 1D detector set at 240 mm from the sample. Cu-K$_{\alpha1,2}$ X-radiation