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A Mo^{VI} grafted Metal Organic Framework: Synthesis, characterization and catalytic investigations

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ABSTRACT

We present the post-modification of a gallium based Metal Organic Framework, COMOC-4, with a Mo-complex. The resulting Mo@COMOC-4 was characterized by means of N_2 sorption, XRPD, DRIFT, TGA, XRF, XPS and TEM analysis. The results demonstrate that even at high Mo-complex loadings on the framework, no aggregation or any Mo or Mo oxide species are formed. Moreover, the Mo@COMOC-4 was evaluated as a catalyst in the epoxidation of cyclohexene, cyclooctene and cyclododecene employing TBHP in decane as oxidant. The post-modified COMOC-4 exhibits a very high selectivity toward the epoxide (up to 100%). Regenerability and stability tests have been carried out demonstrating that the catalyst can be recycled without leaching of Mo or loss of crystallinity.

1. Introduction

It is well known that compounds containing certain transition metals, such as Mo, W, Ti and V, are able to catalyze the liquid-phase epoxidation of olefins using alkyl hydroperoxides as oxidants in homogeneous solution. The catalysis is most effective when these transition metals are in their highest oxidation state. During the last decade, several molybdenum (VI) complexes have shown to be successful catalysts for various reactions ranging from Lewis acid catalyzed transformations to oxidation and reduction reactions [1]. Treatment of $[MoO_2X_2]$ species (X = halide, OR, $OSiR_3$) with monodentate or bidentate Lewis bases (L or L_2), such as pyridine and 2,2′-bipyridine, in the presence of a donor solvent, form a series of dioxomolybdenum complexes with the composition of $[MoO_2X_2L]$. Such dioxomolybdenum(VI) complexes are well documented as efficient oxo-transfer catalyst for various organic transformations, such as acylation reaction, hydrosilylation of aldehydes and ketones, oxidation of alcohols and thiols [1]. In the epoxidation of olefins, many reports on such homogeneous molybdenum complexes have been described. Within this context, Kuhn et al. reported that $MoO_2Br_2L_2$ complexes with bidentate nitrogen donor ligands exhibit very high selectivities (~90%) in the epoxidation of cyclooctene applying TBHP in decane as oxidant [2,3]. Amaranta et al. examined Mo-complexes of the type MoO_2Cl_2L with L = bipyridine-based ligands as catalysts for the epoxidation of the biorenewable olefins DL-limonene and methyl oleate [4]. The Mo catalysts rendered the epoxide monomers in high selectivity and high conversions (89% selectivity for 96% limonene and 99% selectivity for 94% methyl oleate conversion). Whereas the previous studies employed TBHP as oxidant, others report on the use of H_2O_2 in combination with $NaHCO_3$ as cocatalyst to study the Mo-complexes as catalyst in the epoxidation of various olefins showing high conversions and selectivities at room temperature [5,6]. However, as these homogeneous Mo-complexes have some well known disadvantages (difficulties with separation and recyclability), many attempts to immobilize these Mo-complexes have been performed. In the paper of Kühn et al., the different supports and immobilization techniques ranging from direct grafting to tethering *via* a functionalized spacer ligand are described [7]. Different supports have been applied, for example, silica-based supports e.g. MCM-41 [8–10], polymers [11,12], hybrid materials [13] or ionic liquids [14,15]. However, it should be noted that several reports point out that octahedral coordinated Mo^{VI} sites cannot be easily incorporated into the tetrahedral positions of porous silicas (zeolites/mesoporous materials) [16,17].

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Alternatively, attempts have been made to synthesize active metal containing organic frameworks as well. This is another efficient way to heterogenize the homogeneous metal complexes. Metal Organic Frameworks (MOFs) are crystalline porous materials consisting of metal ions held in place by multidendate organic linkers to build up a framework. MOFs have been examined for many potential applications, for example in gas sorption and separation [18–20], sensing [21–23], luminescene [23–25], and catalysis [26,27]. In the latter field, for instance, MIL-47(V^{IV})-, MIL-125(Ti^{IV})-, and Mo^{III}-based MOFs have been reported and have shown promising catalytic activity in epoxidation reactions. However, synthesizing MOFs with active metal centers in their highest oxidation state is very difficult. This limits the application in oxidation catalysis. Up to now, no MOFs with Mo^{VI} centers have been reported.

In this study, we report on the immobilization of a homogeneous Mo^{VI} catalyst on a MOF support to obtain a well dispersed single-site catalyst. Yaghi's group synthesized an Al-based MOF, Al(OH)(bpydc) ($bpydc^{2-}$ = 2,2′-bipyridine-5,5′-dicarboxylate) denoted as MOF-253 [28]. This MOF has free 2,2′-bipyridine sites which form excellent anchoring points for the grafting of metal complexes. The successful post-modification of MOF-253 has been demonstrated by Zou and co-workers for the incorporation of $RuCl_3$ on MOF-253 [29] and by Li et al. [30], who anchored Cu^+ ions onto MOF-253 to catalyze the cross-coupling of phenols and alcohols with aryl halides. The post-modification, however, resulted in a significant reduction in surface area and pore volume, which is much higher than the volume taken by the complex, suggesting a partial collapse of the framework during the post-modification. In this work, we used a novel Ga-based MOF, denoted as COMOC-4, which is isostructural to MOF-253 and which is stable in air and water (50 °C for 24 h) [31].

COMOC-4 was applied as host matrix for the preparation of a MOF supported Mo^{VI} catalyst. To the best of our knowledge, this is the first post-modified MOF possessing Mo^{VI} active centers. So far, there is only one Mo^{II}-based MOF, denoted as TUDMOF-1 which is isotopic to $Cu_3(BTC)_2$ [32]. However, this MOF is very air sensitive which limits its practical use. In another report, $[Ni_2(dhtp)]$, a member of the isostructural CPO-27 or MOF-74 series, was post-modified with Mo via $Mo(CO)_6$ sublimation however, during the process, the Mo^{VI} was reduced to Mo^{IV} [33]. In this paper, we employed $MoO_2Cl_2(THF)_2$ as a Mo precursor to anchor different Mo^{VI} loadings on the COMOC-4 framework. The important feature of this MOF support is that the chelating bipyridine ligand binds strongly to the metal ion, and therefore, leaching of the metal ion is expected to be reduced. The resulting Mo@COMOC-4 materials were evaluated in the epoxidation of cyclohexene, cyclooctene and cyclododecene. We also investigated the recyclability and stability of the heterogeneous catalyst. Furthermore, (scanning) transmission electron microscopy ((S)TEM) provided additional valuable structural information on this supported catalyst. The (S)TEM images demonstrate that even at high Mo-complex loadings on the COMOC-4 framework, no aggregation or any Mo or Mo oxide species are formed.

2. Materials and methods

2.1. General procedures

All chemicals were purchased from Sigma-Aldrich or TCI Europe and used without further purification. Nitrogen adsorption experiments were carried out at −196 °C using a Belsorp-mini II gas analyzer. Prior to analysis, the samples were dried under vacuum at 120 °C to remove adsorbed water. X-ray powder diffraction (XRPD) patterns were collected on a ARL X'TRA X-ray diffractometer with Cu Ka radiation of 0.15418 nm wavelength and a solid-state detector. X-ray fluorescence (XRF) measurements were taken on a NEX CG from Rigaku using a Mo-X-ray source. All XPS measurements were recorded on an X-ray photoelectron spectroscopy S-Probe XPS spectrometer with monochromated Al (1486 eV) exciting radiation from Surface Science Instruments (VG). The catalyst powder was positioned on conducting carbon tape. In order to compensate for charging of the sample, a nickel grid was used, placed 2 mm above the sample. A low-energy electron flood gun 3 eV was used as a neutralizer. All measurements were calibrated toward a value for the C 1s peak of adventitious carbon at 284.6 eV. Calculation of the atomic concentrations and peak fittings was performed using a linear background subtraction. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were recorded on a Thermo Nicolet 6700 FT-IR spectrometer equipped with a N_2 cooled MCT-A (mercury–cadmium–tellurium) detector and a KBr beam splitter. An ultra-fast GC equipped with a flame ionization detector (FID) and a 5% diphenyl/95% polydimethylsiloxane column, with 10 m length and 0.10 mm internal diameter was used to follow the conversions of the products during the catalytic tests. Helium was used as carrier gas and the flow rate was programmed as 0.8 mL/min. The reaction products were identified with a TRACE GC × GC (Thermo, Interscience), coupled to a TEMPUS TOF-MS detector (Thermo, Interscience). The first column consists of a dimethyl polysiloxane package and has a length of 50 m, with an internal diameter of 0.25 mm, whereas the second column has a length of 2 m with an internal diameter of 0.15 mm. The package of the latter is a 50% phenyl polysilphenylene-siloxane. Helium was used as carrier gas with a constant flow (1.8 mL/min).

2.2. Synthesis of COMOC-4

COMOC-4 was synthesized according to our optimized procedure published elsewhere [31]. In general, 4.4 mmol $Ga(NO_3)_3{\cdot}H_2O$ and 5 mmol H_2bpydc were added to 120 mL DMF and stirred at 150 °C for 48 h. Hereafter, the precipitate was filtered and washed, respectively, with DMF, methanol, and acetone. To remove the unreacted linker from the pores, an extraction in DMF was performed at 80 °C for 2 h. In addition, a soxhlet extraction in methanol was carried out during 48 h to obtain a complete exclusion of the organic species. The resulting COMOC-4 material was activated prior to use.

2.3. Synthesis of Mo@COMOC-4

In a first step, the $MoO_2Cl_2(THF)_2$ complex was prepared according to the procedure reported by Kühn et al. [3]. It should be noted that this complex must be used immediately after synthesis as this complex is very unstable. All the manipulations to obtain Mo@COMOC-4 were carried out under an oxygen and water-free atmosphere with standard Schlenk techniques. Typically, 0.18 g MoO_2Cl_2 was added to 7.5 mL THF and stirred for 10 min at room temperature. The yellow solution was removed from the non-dissolved residue by employing a combined nylon membrane filter and evaporated to dryness to obtain the $MoO_2Cl_2(THF)_2$ complex. In a second step, the obtained $MoO_2Cl_2(THF)_2$ complex was redissolved in THF and COMOC-4 was added. Typically, 3 mL of the $MoO_2Cl_2(THF)_2$ solution was added to 0.25 g COMOC-4 material suspended in 37 mL of THF to obtain a high Mo loading material (25 mol% Mo, equals to 25% occupation of the bipyridine sites), namely $Mo_{0.25}$@COMOC-4. As for low Mo loading material, 1.5 mL of the $MoO_2Cl_2(THF)_2$ solution was added to 0.25 g COMOC-4 material suspended in 38.5 mL of THF to obtain a low Mo loading (14 mol% Mo, equals to 14% occupation of bipyridine sites), namely $Mo_{0.14}$@COMOC-4. The Mo loading was determined by means of XRF measurements, indicating a loading efficiency of 63% for high Mo loading and 59% for low Mo loading. After stirring