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# Metal oxide-triazole hybrids as heterogeneous or reaction-induced self-separating catalysts

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ABSTRACT

The hybrid metal oxide-triazole materials $[MoO_3(trz)_{0.5}]$ (**1**) and $[W_2O_6(trz)]$ (**2**) (trz = 1,2,4-triazole) have been hydrothermally synthesized and characterized by different techniques (TGA, SEM, $^1H$ and $^{13}C$ MAS NMR, FT-IR spectroscopy, and structure determination by Rietveld analysis of high resolution synchrotron powder XRD data). Materials **1** and **2** display distinct behaviors when applied as catalysts for oxidation reactions with alcohol, aldehyde, olefin and sulfide substrates, and are more effective with hydrogen peroxide as the oxidant than with *tert*-butylhydroperoxide. The $Mo^{VI}$ hybrid **1** transforms into soluble active species during *cis*-cyclooctene epoxidation with $H_2O_2$. When consumption of $H_2O_2$ reaches completion, spontaneous reassembly of the 2-dimensional molybdenum oxide network of **1** takes place and the hybrid precipitates as a microcrystalline solid that can be easily separated and recycled. Reaction-induced self-separation behavior occurs with **1**, $H_2O_2$ and other substrates such as methyl oleate and methylphenylsulfide. The $W^{VI}$ hybrid **2** behaves differently, preserving its structural features throughout the heterogeneous catalytic process.

## 1. Introduction

An important goal in transition metal catalysis science is the development of systems that combine the advantages of homogeneous catalysts (high activities and selectivities, absence of diffusion limitations, ability to fine-tune performance through ligand modification) with those of heterogeneous catalysts (ease of catalyst-product separation and catalyst recycling) [1,2]. The principal approach to solving this problem has been the immobilization of molecular catalysts onto organic, inorganic or hybrid organic–inorganic supports [3–6]. However, the resultant materials suffer from a number of drawbacks, which include catalyst "leaching", leading to deactivation, and poor accessibility of the active sites for the substrate. In the period 2001–2003 two papers reported on a new approach involving catalyst self-separation or self-precipitation. The first report, by Xi et al., described reaction-controlled phase-transfer catalysis for propylene oxidation to propylene oxide [7]. The insoluble W-based catalyst precursor formed a soluble active species by the action of $H_2O_2$. Exhaustion of the oxidant led to spontaneous precipitation of the catalyst which could be recovered and used again. Later, Dioumaev and Bullock developed an alternative solid–liquid–solid phase separation procedure (for the solvent-free hydrosilylation of carbonyl compounds) that relied on differences in solubility of the catalyst in the liquid substrate and product [8]. The tungsten carbonyl catalyst was initially soluble in the polar substrate but then precipitated upon complete conversion of the substrate and formation of the non-polar liquid product. Since the publication of these two landmark papers, progress on self-precipitating transition metal catalysts has been slow. With some exceptions, such as a redox-switchable phase-tagged ruthenium-based catalyst [9], the solid–liquid–solid phase separation procedures are either reaction-controlled [10–20] or thermoregulated [21–24], and involve polyoxometalate salts of large organic cations [25].

In the present work, we describe a new type of self-separating catalyst based on a molybdenum oxide hybrid material. The material $[MoO_3(trz)_{0.5}]$ (trz = 1,2,4-triazole), which was first reported by Zubieta and co-workers [26], was chosen for study as part of our ongoing investigations into the catalytic properties of molybdenum(VI) and tungsten(VI) oxide-organonitrogen hybrid materials [27–32]. Depending on the structure and composition of these hybrids, as well as the catalytic reaction conditions, the materials typically act either as sources of soluble active species or (more

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rarely) as heterogeneous catalysts. For example, when the materials $[Mo_2O_6(2\text{-}(1\text{-pentyl-3-pyrazolyl})pyridine)]$ [30], $[Mo_3O_9(2\text{-}[3(5)\text{-pyrazolyl}]pyridine)]$ [31] and $[MO_3(2,2'\text{-bipy})]$ (M = Mo, W; 2,2′-bipy = 2,2′-bipyridine) [32] are used in catalytic olefin epoxidation with either *tert*-butylhydroperoxide (TBHP) or hydrogen peroxide as oxidant, they are irreversibly converted into soluble oxodiperoxo complexes of the type $[MO(O_2)_2(L)]$, which are responsible for the homogeneous catalytic reaction of the olefin. The efficient recovery and reuse of these complexes is not trivial, typically requiring precipitation with organic solvents. Herein, we describe an unprecedented behavior for the hybrid material $[MoO_3(trz)_{0.5}]$ when used in catalytic olefin epoxidation with $H_2O_2$ as oxidant. In a manner similar to that reported with polyoxometalate salts [7,10–20] a solid–liquid–solid phase transfer takes place, with spontaneous reassembly and self-precipitation of the original molybdenum oxide-triazole solid upon completion of the reaction. Results with the molybdenum(VI) hybrid are compared with those for the corresponding tungsten (VI) compound, and the catalytic performances of both materials have been further examined for the oxidation of benzyl alcohol and benzaldehyde. The crystal structures of both hybrids have been determined through Rietveld analysis of high-resolution synchrotron X-ray diffraction data.

## 2. Experimental

### 2.1. Materials and methods

For synthesis, $MoO_3$ (Analar, BDH Chemicals, 99.5%), $H_2WO_4$ (puriss p.a., Fluka), 1,2,4-triazole (98%, Sigma–Aldrich), and diethyl ether (puriss p.a., Sigma–Aldrich) were acquired from commercial sources and used as received. For the catalytic experiments, the substrates *cis*-cyclooctene (95%), anhydrous benzyl alcohol (99.8%), benzaldehyde ($\geqslant$99%), cyclohexene (99%), *trans*-2-octene (97%), DL-limonene ($\geqslant$95%), methyl oleate (99%), methylphenylsulfide (99%) and benzothiophene (95%) were obtained from Sigma–Aldrich and used as received. Acetonitrile (99.9%, Panreac), ethanol (99.9%, Carlo Erba), ethyl acetate (99.9%, Sigma–Aldrich), 5.5 M *tert*-butylhydroperoxide in decane (Sigma–Aldrich), 70 wt.% aq. *tert*-butylhydroperoxide (Sigma–Aldrich), and 30% aq. $H_2O_2$ (Sigma–Aldrich) were acquired from commercial sources and used as received.

Elemental analysis for C, H, and N was performed at the University of Aveiro with a Leco TruSpec 630–200–200 analyzer. Routine powder X-ray diffraction (PXRD) data were collected at ambient temperature on a Philips Analytical Empyrean ($\theta/2\theta$) diffractometer equipped with a PIXcel1D detector, with automatic data acquisition (X'Pert Data Collector software v4.2) using monochromatized Cu K$\alpha$ radiation ($\lambda$ = 1.5406 Å). Intensity data were collected by the step-counting method (step 0.01°), in continuous mode, in the *ca.* $5 \leqslant 2\theta \leqslant 50°$ range. Scanning electron microscopy (SEM) images were collected using a Hitachi S4100 microscope operating at 25 kV. Samples were prepared by deposition on aluminum sample holders followed by carbon coating using an Emitech K 950 carbon evaporator. Thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA-50 instrument, from ambient temperature to *ca.* 800 °C, under a continuous stream of air at a flow rate of 20 mL min$^{-1}$, and a heating rate of 5 °C min$^{-1}$.

FT-IR spectra were collected using KBr (Sigma–Aldrich, 99%, FT-IR grade) pellets and a Mattson-7000 infrared spectrophotometer. Attenuated total reflectance (ATR) FT-IR spectra were measured using a Specac Golden Gate Mk II ATR accessory having a diamond top plate and KRS-5 focusing lenses. Solid state $^{13}$C cross-polarization (CP) magic-angle-spinning (MAS) NMR spectra were recorded using a Bruker Avance 400 spectrometer (9.4 T) at 100.62 MHz with 3.25 μs $^{1}$H 90° pulses, 2 ms contact time, spinning rates of 10–12 kHz, and 3–4 s recycle delays. Chemical shifts are quoted in parts per million (ppm) from tetramethylsilane.

### 2.2. $[MoO_3(trz)_{0.5}]$ (**1**)

A mixture of $MoO_3$ (0.14 g, 0.97 mmol), 1,2,4-triazole (0.05 g, 0.72 mmol) and water (15 mL) was heated in a rotating (15 rpm) Teflon-lined stainless steel digestion bomb at 180 °C for 1 h. After cooling down to ambient temperature, the resultant bluish white microcrystalline solid was separated from the aqueous liquor by filtration, washed with an excess of water and diethyl ether (4 × 10 mL), and finally dried at ambient temperature. Yield: 0.14 g, 83% (based on Mo). Anal. Calcd for $CH_{1.5}N_{1.5}O_3Mo$: C, 6.73; H, 0.85; N, 11.77. Found: C, 6.65; H, 1.13; N, 11.73. FT-IR (KBr, cm$^{-1}$): $\nu$ = 329 (m), 374 (s), 437 (m), 595 (vs, br), 626 (sh), 842 (vs, br), 937 (s), 964 (m), 1000 (m), 1058 (m), 1141 (m), 1176 (w), 1222 (w), 1253 (w), 1307 (m), 1425 (m), 1519 (m), 1779 (m), 2300–3000 (several weak bands due to trz), 3116 (s). $^{13}$C{$^{1}$H} CP MAS NMR: $\delta$ = 145.8 ppm.

### 2.3. $[W_2O_6(trz)]$ (**2**)

A mixture of $H_2WO_4$ (0.49 g, 1.96 mmol), 1,2,4-triazole (0.20 g, 2.90 mmol) and water (25 mL) was heated in a rotating (15 rpm) Teflon-lined stainless steel digestion bomb at 180 °C for 93 h. After cooling down to ambient temperature, the resultant yellowish white microcrystalline solid was separated from the aqueous liquor by filtration, washed with an excess of water and diethyl ether (4 × 10 mL), and finally dried at ambient temperature. Yield: 0.46 g, 89% (based on W). Anal. Calcd for $C_2H_3N_3O_6W_2$: C, 4.51; H, 0.57; N, 7.89. Found: C, 4.45; H, 0.55; N, 7.97. FT-IR (KBr, cm$^{-1}$): $\nu$ = 306 (vs), 372 (m), 406 (w), 426 (w), 447 (w), 622 (s), 684 (sh, br), 732 (vs, br), 906 (s, br), 950 (m), 975 (m), 1002 (w), 1062 (m), 1145 (w), 1226 (w), 1247 (w), 1263 (w), 1311 (m), 1427 (m), 1513 (m), 1521 (m), 1533 (w), 1789 (w), 2500–3000 (several weak bands due to trz), 3106 (s), 3436 (m, br). $^{13}$C{$^{1}$H} CP MAS NMR: $\delta$ = 145.1 ppm.

### 2.4. Synchrotron powder X-ray diffraction studies

High-resolution synchrotron PXRD data for **1** and **2** were collected at low temperature (100 K; cooling device from Oxford Instruments) on the powder diffractometer assembled at ID22 [33] at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The beam line receives X-rays from the synchrotron source, operating with an average energy of 6 GeV and a beam current of typically 200 mA, from an undulator device. The high signal-to-noise ratio of the data is due to the high brilliance of the synchrotron beam in combination with a Si(111) crystal multi-analyzer.

The monochromatic wavelength was fixed at 0.495958(7) Å and calibrated against the Si standard NIST 640c [certified cell parameter *a* = 5.4311946(92) Å]. Hard X-rays were selected for data collection in order to significantly reduce radiation damage, an occurrence observed in previous investigations using related materials but under different experimental conditions [27,29,31]. Even at low temperature the high brilliance of the synchrotron source led to visible damage of the samples. To minimize such effects consecutive data collections were performed on fresh portions of the samples by translating the capillaries by *ca.* 1.3 mm.

Finely powdered samples of compounds **1** and **2** were placed inside a Hilgenberg borosilicate glass capillary (*ca.* 0.9 mm in diameter) which was spun during data collection to improve powder averaging over the individual crystallites, ultimately removing