



## Engineering of oxoclusters-reinforced polymeric materials with application as heterogeneous oxydesulfurization catalysts



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Dedicated to the memory of our friend and colleague Prof. Alessandro Bagno, Full Professor of Organic Chemistry at the University of Padova, unexpectedly and prematurely passed away on 23.3.2015.

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### ABSTRACT

In this paper we report the first example of hybrid materials based on poly(methylmethacrylate) (PMMA) matrices covalently reinforced by  $M_yO_x(OH)_w(O(O)CR)_z$  oxoclusters ( $M = Zr$  or  $Hf$ ), used as heterogeneous catalytic systems for hydrogen peroxide activation. The resulting hybrids were used to catalyze the oxidation of dibenzothiophene (DBT) to the corresponding sulfoxide (DBTO) and sulfone (DBTO<sub>2</sub>), in order to demonstrate their potential application for the oxydesulfurization (ODS) of a fuel. Thanks to catalyst confinement and to the higher affinity of the polymeric matrix towards polar substrates, the heterogeneous set-up displays improved performances with respect to the corresponding homogeneous systems. At 65 °C, a DBT conversion higher than 84% was obtained in 24 h, with a >94% selectivity for DBTO<sub>2</sub>. The stability of the hybrid materials under catalytic conditions was successfully assessed by a combined spectroscopic approach, based on FT-IR, resonance Raman, Solid State Nuclear Magnetic Resonance, X-ray Absorption and Small Angle X-ray scattering measurements.

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## 1. Introduction

Oxoclusters of early transition metals are a versatile class of polynuclear compounds built up of a limited number of 3–5 groups metal atoms, such as  $Ti^{IV}$ ,  $Zr^{IV}$ ,  $Hf^{IV}$  or  $Nb^{V}$ , linked by oxygen bridges and coordinated by organic ligands [1,2]. These compounds are globally neutral and discrete species with general formula  $M_yO_x(OH)_w(O(O)CR)_z$ , where typically organic carboxylates act as

bidentate ligands. They can display different nuclearities (i.e. number of constituent metal atoms,  $y = 2–12$ ), coordination number of the metal atoms (varying between 6 and 9) and connectivity modes (corner, edge or face sharing of polyhedral units). In some cases they also involve an alkaline earth (e.g. Ba, Mg) metal [3].

Since these oxoclusters are characterized by the presence of early transition metals in their highest oxidation state, they are appealing candidates as catalysts for peroxide activation [4,5]. Moreover, Zr and Hf-based multimetallic complexes have been reported to activate hydrogen peroxide, promoting the oxidation of different substrates (sulfides and sulfoxides, alcohols) both in water and in organic solvents [6–11]. As far as zirconium-based oxoclusters are concerned, we have recently evidenced the possibility to use two different complexes to activate hydrogen peroxide

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and oxidize organic substrates [12]. In such preliminary study, the oxidation of methyl *p*-tolylsulfide to the corresponding sulfoxide and sulfone was chosen as model reaction, showing an interesting reactivity towards sulfoxide oxidation [13]. However, despite the encouraging results, the hydrolytic stability of such oxoclusters is too low to allow a practical application in homogeneous catalysis, since they easily rearrange and precipitate from the reaction mixture.

Owing to the possibility to use oxoclusters as building blocks for the synthesis of different typologies of hybrid materials [14] with enhanced functional (e.g. dielectric, magnetic etc.) and structural (thermal, mechanical) properties [15], we have devised novel heterogeneous systems based on the covalent immobilization of Zr and Hf oxoclusters into a polymeric matrix.

The protection of a catalytically active system by embedding/anchoring it within a matrix is an underlying and widely used strategy in heterogeneous catalysis [16]. Within this scenario, the preparation of hybrid materials through the integration of the multimetallic catalytic active species into a polymeric matrix is a fertile field of research [17–20]. Indeed, this strategy offers interesting perspectives for devising continuous flow processes, where the polymer may contribute to improve the reaction selectivity and/or enable process intensification, by coupling catalysis and separation technologies [20,21]. Nevertheless, to the best of our knowledge, the hybrid materials here described are the first example of heterogeneous catalysts based on the covalent immobilization of oxoclusters. Not only the covalent bonds endow the final material with enhanced stability, but also prevent phases separation inside the polymer matrix and leaching.

In this framework, different acrylate copolymers were prepared by changing the nature of the oxocluster as well as the oxocluster/monomer molar ratio, which in turn, *inter alia*, affect the cross-linking degree of the resulting hybrid. The effectiveness of the hybrid materials as heterogeneous catalysts was evaluated in the oxidation of an aromatic sulfide by H<sub>2</sub>O<sub>2</sub>, in a biphasic *n*-octane/acetonitrile system, as an example of sustainable fuel desulfurization process [22,23]. In particular, we exploited the oxocluster reactivity to perform the oxidation of dibenzothiophene (DBT), dissolved in *n*-octane, to the corresponding sulfoxide (DBTO) and sulfone (DBTO<sub>2</sub>), whereby the oxidized products can be easily extracted by the polar solvent [20]. Thanks to the enhanced affinity of the polymeric matrix toward polar substrates and solvents, the heterogeneous set-up shows better performances than the corresponding homogeneous systems. Furthermore, the heterogeneous catalysts can be recovered and reused. FT-IR, resonance Raman, Solid State Nuclear Magnetic Resonance (SS-NMR), X-ray Absorption (XAS), and Small Angle X-ray Scattering measurements (SAXS) highlighted, indeed, that the hybrids are endowed with appreciable stability even after catalytic turnover.

## 2. Experimental

### 2.1. Materials and chemicals

Zirconium butoxide (Zr(OnBu)<sub>4</sub>, 80% wt in *n*-butanol), zirconium propoxide (Zr(OnPr)<sub>4</sub>, 70% wt in *n*-propanol), vinylacetic acid, dibenzothiophene (DBT), dibenzothiophene sulfone (DBTO<sub>2</sub>), hydrogen peroxide (30% wt in water) were all purchased from Sigma–Aldrich and used as received. Hafnium butoxide (Hf(OnBu)<sub>4</sub>, 95% wt in *n*-butanol) was supplied by ABCR. Methacrylic acid 99%, and methylmethacrylate, purchased from Sigma–Aldrich, were filtered on neutral alumina to remove the inhibitor. All the chemicals were stored under argon, while the solvents were additionally stored on molecular sieves. Dibenzothiophene sulfoxide (DBTO) was synthesized following a literature procedure [24]. Oxoclus-

ters M<sub>4</sub>O<sub>2</sub>(O(O)CC(CH<sub>3</sub>)=CH<sub>2</sub>)<sub>12</sub> (Hf<sub>4</sub>, with M=Hf) [25] or (Zr<sub>4</sub>, with M=Zr) [26], Zr<sub>6</sub>(OH)<sub>4</sub>O<sub>4</sub>(O(O)CC(CH<sub>3</sub>)=CH<sub>2</sub>)<sub>12</sub> (Zr<sub>6</sub>) [27], [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(O(O)CCH<sub>2</sub>CH=CH<sub>2</sub>)<sub>12</sub> 6CH<sub>2</sub>=CHCH<sub>2</sub>C(O)OH (Zr<sub>12</sub>) [28], were synthesized under argon, using standard Schlenk techniques, according to literature procedures. The structure of all oxoclusters was confirmed by measuring the unit cell dimensions on a number of different single crystals by diffraction technique. Moreover, the nature of the bulk precipitate formed by a mixture of single crystals and an apparently amorphous solid has been investigated by X-ray powder diffraction techniques, by comparison with the spectra simulated from the single crystal data that has confirmed the purity of the products.

### 2.2. Hybrid materials syntheses

The hybrid materials were prepared by implementing a known procedure [29]. In a typical polymerization, a weighed amount (0.7 g, moles amount depending on the oxocluster) of oxocluster was dissolved in methyl methacrylate (3–12 g), so to achieve oxocluster: MMA molar ratios of 1:50, 1:100, and 1:200. The thermoinitiator benzoylperoxide (BPO) (3% wt. with respect to the monomer) was finally added to the suspension and the reaction mixture was heated at 80 °C for 1 h. Glassy monolithic materials were thus obtained. Samples were labeled as M<sub>x</sub>MMAnT with M=Zr and *x*=4, 6 or 12, or M=Hf and *x*=4, *n* (molar ratio)=50, 100 or 200, while *T* stands for thermal polymerization. Reference PMMA (poly(methylmethacrylate)) was prepared by using the same procedure, without adding the oxocluster. Porogenic solvents (1,4-butanediol and 2-propanol, 1:2 v/v) were added to the reaction mixture to produce porous polymers. In this latter case, samples were labeled as M<sub>x</sub>MMAnP.

### 2.3. Solid State NMR measurements

<sup>13</sup>C SS-NMR spectra were recorded on a Varian InfinityPlus 400 spectrometer, working at a Larmor frequency of 400.02 MHz and 100.59 MHz for hydrogen-1 and carbon-13 nuclei, respectively, using a 7.5 mm probehead with a 90° <sup>1</sup>H pulse duration of 5 μs. <sup>13</sup>C Cross Polarization-Magic Angle Spinning (CP-MAS) spectra were recorded with high-power decoupling from <sup>1</sup>H nuclei, spinning the samples at a MAS frequency between 5 and 6 kHz (depending on the sample), using a contact time of 1 ms, a recycle delay of 5 s and accumulating 10,000 transients. The <sup>13</sup>C chemical shift scale was calibrated using hexamethylbenzene and TMS as secondary and primary references, respectively. All the spectra were recorded at 25 °C, using air as spinning gas.

### 2.4. XAS measurements

The XAS measurements were performed at the XAFS beamline at Elettra Synchrotron (Trieste, Italy). A Si(311) double crystal monochromator was used for measurements at the Zr K-edge (17.998 keV). The second monochromator crystal was tilted for optimal harmonic rejection. The spectra were recorded in transmission mode using ionization chambers as detectors. Energy calibration was performed with a Zr metal foil. The solid samples were pressed into self-supporting pellets using cellulose as a binder.

Data evaluation started with background absorption removal from the experimental absorption spectrum by using the automated removal routine found in the Athena software [30]. The threshold energy E<sub>0</sub> was determined as the maximum in the first derivative spectrum. To determine the smooth part of the spectrum, corrected for pre-edge absorption, a piecewise polynomial was used. It was adjusted in such a way that the low-*R* components of the resulting Fourier transform were minimal. After division

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