Poster Presentation

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New Oxomolybdenum(VI) Hybrid Materials

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The chemistry of Mo^{VI} oxides is dominated by complexes containing the cis-dioxomolybdenum(VI) structural units. Many of these complexes have been investigated as epoxidation catalysts and a number of papers have been published on the effect of nitrogen donor ligands. The motivation to study these discrete, homogeneous catalysts in the form of monomeric or dimeric species stemmed from the fact that they are well-defined, single site catalysts, which usually favour high reaction activities and product selectivities. Our research group has investigated the reaction of dichlorodioxomolybdenum(VI) complexes with excess water using three distinct heating methods: hydrothermal, reflux or microwave-assisted synthesis. The main challenge was to design and prepare novel heterogeneous Mo^{VI} catalysts with the same catalytic properties and kinetics usually attained from the homogeneous counterparts. The results led to the isolation of several higher nuclearity oxomolybdenum(VI) compounds, namely the octanuclear complex $[Mo_8O_{22}(OH)_4(di\text{-}t\text{-}Bu\text{-}bipy)_4]$ (di-tert-butyl-2,2'-bipyridine),[1] and the polymeric materials $\{[MoO_3(bipy)][MoO_3(H_2O)]\}n$ (2,2'-bipyridine)[2] and $\{[Mo_3O_9(pzpy)\}n$ (2-[3(5)-pyrazolyl]pyridine).[3] These compounds where characterized by using solid-state techniques, namely elemental analyses, thermogravimetry, FT-IR, solid-state NMR, electron microscopy and powder X-ray diffraction (both from laboratory and/or synchrotron sources). The catalytic behaviour of the discrete complexes and the polymeric compounds was tested in olefin epoxidation reactions. Fundação para a Ciência e a Tecnologia (FCT, Portugal; PTDC/EQUEQU/121677/2010; PTDC/QEQ-SUP/1906/2012; SFRH/BPD/97660/2013; EXPL/CTM-NAN/0013/2013 - FCOMP-01-0124-FEDER-041282), the European Union, QREN, FEDER, COMPETE, and Associate Laboratory CICECO (PEst-C/CTM/LA0011/2013) are gratefully acknowledged for funding.

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