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A hierarchically ordered porous novel vanado-silicate catalyst for highly efficient oxidation of bulky organic molecules[†]

Tapas Sen,*^{ab} Jacob Whittle^a and Matthew Howard^a

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A novel hierarchically ordered porous vanado-silicate nanocomposite with interconnecting macroporous windows and meso-microporous walls containing well dispersed vanadyl species has been fabricated and used as a heterogeneous catalyst for the oxidation of a bulky organic molecule, namely cyclooctene.

Oxidation catalysis plays a large role in industry whether it is used in the production of fine chemicals or in the removal of hazardous contaminants.¹⁻⁴ Vanadyl ions under homogeneous conditions serve as a powerful oxidation catalyst in the presence of hydrogen peroxide.⁴ However the vanadyl catalyst under homogeneous conditions suffers from (i) the difficulty in separation of catalyst from the reaction mixture and (ii) lack of product selectivity. Various heterogeneous catalytic systems containing vanadium ions have been developed using clays,^{5,6} microporous,⁷⁻¹⁰ mesoporous materials¹¹ and macroporous^{12,13} supports for oxidation of both organic and inorganic molecules. Diffusional restriction of bulkier molecules through the micro/ mesoporous solids and the poor surface area of macroporous materials has led to the development of high surface area materials containing pore sizes of three different length scales i.e. micropores (<2 nm), mesopores (2 nm to 50 nm) and macropores (>50 nm) with hierarchical ordering. Sen *et al.* have reported^{14,15} the fabrication of large surface area hierarchically ordered porous silicate materials with poreinterconnectivity in three length scales in a controlled fashion. Such materials have great potential as a support for industrial catalysis or for the separation of biomolecules as they have the ability to allow such bulky molecules to diffuse through the macroporous windows (~ 85 nm) while the incorporation of meso and micropores into the materials increases the surface area. Recently, we have reported^{16,17} a novel hierarchically ordered porous silicate with superparamagnetic property (i) for magnetic bioseparation and (ii) as a support for the immobilisation of lipase for bio-catalysis. However, such materials have never been used

for the incorporation of transition metal cations *i.e.* vanadium ions for the oxidation of bulky organic molecules. Herein, we report the fabrication of hierarchically ordered porous vanado-silicate catalyst with highly dispersed vanadyl species (supported by electron paramagnetic resonance spectroscopy) for potential application in oxidation of bulky organic molecules using hydrogen peroxide as an oxidising agent under heterogeneous conditions.

A novel vanado-silicate catalyst was synthesized (see ESI[†]) by filling the interstice sites of polystyrene latex monolith of uniform diameter 423 nm (see Fig. S1 in the ESI[†]) using silica gel in an acidic medium (aqueous hydrochloric acid) containing a tri-block copolymer (F_{127} : $EO_{107}PO_{70}EO_{107}$) as a surfactant, *n*-butanol as a co-solvent and hydrated vanadyl sulfate as the vanadium source. The vanadium containing silica gel filled polystyrene monolith composite was dried overnight at 60 °C (uncalcined form). The dried nanocomposite was calcined at 500 °C in air for a period of 12 h at a heating rate of 1 °C min⁻¹. The formation of macropores was monitored on a range of materials calcined at various temperatures (100 °C, 200 °C, 300 °C, 400 °C and 500 °C) under identical conditions.

The vanado-silicate catalyst (MH0.01) was observed to be ordered macroporous structure consisting of macropore voids of diameter 380 nm with interconnecting windows of diameter 84 nm (see Fig. 1a and b). TEM micrographs (see Fig. 1c and d) exhibited a mesoporous wall of disordered structure. The mesopore size was measured to be around 7 nm with a mesopore wall thickness of around 2 nm.

The formation of macropores and their interconnectivity was monitored via mercury intrusion through the materials under very high pressure (upto 60 000 psi). The total intrusion of mercury through a polystyrene template was measured to be 0.624 mL g^{-1} (see Fig. 2a) due to the presence of interstice sites with a total macropore area of 36 $m^2 g^{-1}$ and total porosity of 30% with a bimodal pore size distribution (see Fig. S2 in the ESI⁺) centred at 122 nm (octahedral interstice sites) and 67 nm (tetrahedral interstice sties). Upon calcination at different temperatures, the intrusion of mercury and total porosity initially reduced (see Fig. 2a) to 0.1 mL g^{-1} , 10% (at 100 and 200 °C), followed by a gradual increase to 0.2 mL g⁻¹, 59% (300 °C), 1.635 mL g⁻¹, 75.4% (400 °C), and 7.11 mL g⁻¹, 92.7% (500 °C). Calcination below 300 °C resulted in the melting of polystyrene nanoparticles and hence in the loss of porosity of the composites. The exceptionally high value of porosity (92.7%) with interconnecting windows

^a Centre for Materials Science, School of Forensic and Investigative Sciences, Preston, PR1 2HE, UK. Fax: +44(0) 1772894981; Tel: +44(0) 1772894371

^b Institute of Nanotechnology and Bioengineering,

University of Central Lancashire, Preston, PRI 2HE, UK. E-mail: tsen@uclan.ac.uk

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Fig. 1 Scanning electron micrographs (a and b) and transmission electron micrographs (c and d) of MH0.01 calcined at 500 °C.



Fig. 2 Change of pore volume due to the formation of macropores on MH0.01 by mercury porosimetry (a); nitrogen adsorption isotherm of MH0.01/calcined (b) and *t*-plot analysis (c).

of sizes 87 nm and macropores of size 375 nm (see Fig. S2 in ESI⁺) support the electron microscopy data.



Fig. 3 X-band electron paramagnetic resonance spectra of uncalcined form of MH0.01 (a), and V-impregnated hierarchically ordered porous silica HOPS (b).

The BET surface area of the novel vanado-silica catalyst was measured to be $372.5 \text{ m}^2 \text{ g}^{-1}$ with the hysteresis loop (see Fig. 2b) indicating the presence of mesopores. The mesopore diameter using BJH pore size distribution (both adsorption and desorption) was measured to be 6.1 nm which is close to the value obtained from TEM data. *t*-plot analysis (see Fig. 2c) using the Harkins and Jara equation was measured to be 211.9 m² g⁻¹, indicating that the material has a large number of micropores due to the removal of the EO chain of the surfactant molecules similarly to our previous report.¹⁴ The disordered structure of micro and mesoporosity was further confirmed by small angle X-ray scattering (a broad peak, see Fig. S3 in ESI†) and powder diffraction pattern (no peaks) in the high angle region.

The eight-line hyperfine pattern with anisotropy in the electron paramagnetic resonance spectrum (see Fig. 3a) is an indication of the presence of well dispersed paramagnetic vanadium ions (V^{+4}) in the uncalcined form of MH0.01. Upon calcination, all paramagnetic V^{+4} species have been converted to diamagnetic V-species (see Fig. S4 in ESI[†]). The nature of V-species was further confirmed by comparing the EPR parameters with literature data. The g_{\parallel} and g_{\perp} values of the uncalcined MH0.01 were calculated to be 1.9342 and 1.974. Similarly A_{\parallel} and A_{\perp} values were calculated to be 195.2 G and 74.9 G. The g and A values corresponded to vanadyl (V=O) species connected to silica (V-O-Si) in a distorted square pyramidal environment.^{15,18} The V-impregnated sample exhibited a single line without any hyperfine splitting (Fig. 3b), indicating the paramagnetic vanadium species as the aggregated state. A characteristic peak at 960 cm⁻¹ in the FT-IR spectrum (see Fig. S5 in ESI[†]) is an indication of Si-O-V bonding in the materials.¹⁹

The silica to vanadium molar ratio of MH0.01/calcined was calculated to be 581 using X-ray fluorescence spectroscopy by comparing with a series of standard samples of known vanadium concentration.



Fig. 4 A comparative study of oxidation of cyclooctene to various products using novel vanado-silicate catalyst (MH0.01/calcined) and V-impregnated HOPS.

When MH0.01/calcined sample was used for the oxidation of cyclooctene (see the method and reaction scheme, Scheme S1, in ESI†), the novel hierarchically ordered porous vanado-silicate (MH0.01/cal) exhibited a high conversion (38.5%, see Fig. 4) with the product selectivity of cyclooctene epoxide (24.8%) and cyclooctanone 2-ol (12.7%). The Turn Over Number (TON) calculated based on the moles of cyclooctene converted (38.5%) per mole of vanadyl species present (1.16 × 10⁻⁶ moles in 0.1 g catalyst) in the calcined MH0.01 was 3019. The TON value for the present system is exceptionally high compared to the TON value reported^{7,20} for vanadyl species in MEL and MFI zeolite systems for oxidation of toluene. A poor conversion (<0.1%) of cyclooctene was observed when V-impregnated HOPS was used for similar reaction.

In conclusion, a template assisted hierarchically ordered porous vanado-silica nanocomposite has been fabricated and used for the oxidation of a bulky organic molecule (cyclooctene). The exceptionally high TON of the vanadium species in the hierarchically ordered porous vanado-silicate for the oxidation of cyclooctene makes this material a potential catalyst for many important oxidation catalyses in the near future under heterogeneous conditions. The authors thank National EPR facility, School of Chemistry, The University of Manchester, for providing the facility and Dr J. Hawkett for his time to run the samples. The authors also thank Dr C. Muryan, School of Chemistry, The University of Manchester, for helping them to run the samples in SASX. MH thanks the Centre for Research-informed Teaching, University of Central Lancashire, for providing the summer internship in 2009–2010. The authors also thank Dr Jenny Readman who helped MH to run XRF.

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