Electronic Supplementary Material (ESI) for Chemical Communications

Electronic supplementary informationn

Hierarchically ordered porous novel vanado-silicate catalyst for highly efficient oxidation of bulky organic molecules

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Experimental

Synthesis

Polystyrene nanoparticles template

a) Styrene (105mL) was washed five times with NaOH (100mL, 0.1M) using a separating funnel followed by five times with deionised water (each 100mL).
b) A 5000mL round bottom flask was fitted with a thermometer, septum and pasture pipette connected to a nitrogen gas cylinder with rubber tubing, a stirring rod connected to electric motor (Heidolph RZR2020). The 3 necked round bottom flask was then filled with 875mL of deionised water and heated to 70^0C on a isopad isomantle with nitrogen bubbling through the system. The washed styrene (100ml) was then added to the 3 necked round bottom flask.
c) In a separate 100ml beaker, potassium persulfate (0.3315g) was dissolved in deionised water (25ml). This solution was then added to the 3 necked round bottom flask containing the deionised water and washed styrene.
d) The mixture was stirred at 300 rpm for 28hrs at 70^0C. The clear solution turned to a milky white suspension.
e) The particle size in the suspension was characterised by Scanning Electron Microscopy (SEM). Figure S1 present the polystyrene particles were uniform in sizes of around 420nm.

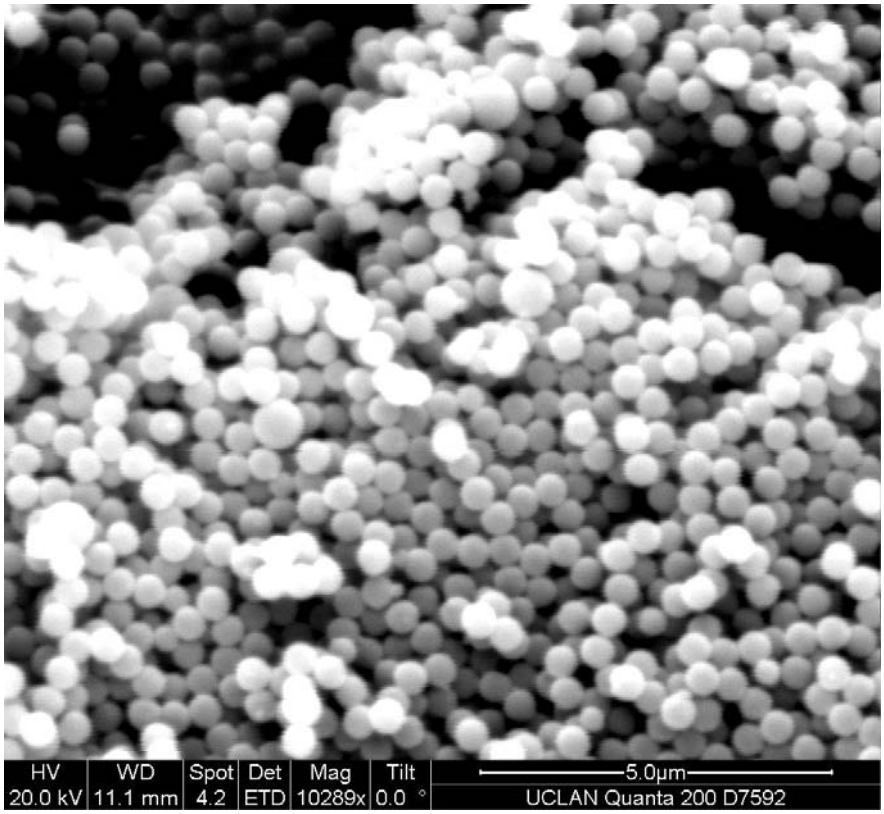


Fig S1. Scanning Electron Micrograph polystyrene nanoparticles as template

Synthesis of hierarchically ordered porous vanado-silicate catalyst

a) Polystyrene latex template: Polystyrene particles were packed by centrifugation at 5000rpm for 1hrs. A white solid was settled at the bottom of the centrifuge tube. Water was removed and then the white solid was dried overnight at 60^0C.
b) Preparation of silica gel: 20g of Tetraethyl orthosilicate was added to a solution containing 21.7 mg of hydrated vanadyl sulphate, 0.542g of Pluronic F_{127}, 10g of deionised H_2O, 4.2mL of n-butanol, 5mL of 0.1M HCl (5ml, 0.1M). The mixture was stirred for 25 mins. The approximate value of Si/V molar ratio in the gel calculated to be 1121 based on the hydration number of 5 in $VOSO_4$, xH_2O.
c) The silica gel from step b was passed through polystyrene monolith from step a. Then dried overnight at 60^0C.
d) The dried material was then calcined in air at 500^0C at a heating rate of 1^0C min^{-1} and labelled as MH0.01/calcined.
e) The concentration of vanadium in the calcined material was determined by X-ray fluorescence (XRF) using a calibrated curve generated previously using a series of known concentration of vanadium in the solid matrix. The Si/V molar ratio of MH0.01/calcined was calculated to be 581.

V-impregnated hierarchically ordered porous silica (HOPS)

21.7mg of hydrated vanadyl sulphate was dissolved in 10g of water. 5.76 g of HOPS was soacked in the solution of vanadium and dried at 60^0C for overnight. The material was also calcined at 500^0C and used for catalysis.

Physical Characterisation

The uncalcined and calcined materials at various temperatures (100, 200, 300, 400 and 500^0C) were characterised by mercury porosimetry (Micromeritics Autopore IV, USA) in order to understand the formation of macropores and interconnecting windows. The nature of vanadium ions and their aggregation behaviour of uncalcined and final calcined (500^0C) materials MH0.01 were determined by electron paramagnetic resonance (EPR) spectrometer (Bruker EMX, Germany) with X band frequency (9.439679GHz) under continuous field-sweep mode. The EPR parameters (g and A values) were calculated using Bruker WinEPR SymFonia software with an approximation of solution mode. More work on the simulation of such spectra is undergoing using powder pattern on various materials containing a range of vanadium ions concentrations in the materials. The calcined MH0.01 material was also characterised by SEM (FEI Quanta 200, USA), TEM (JEOL 2000EX, JAPAN), Nitrogen gas adsorption (Micromeritics ASAP 2010, Autopore, USA) and Fourier transform Infra-red (FT-IR) spectroscopy (SHIMADZU 8300, Shimadzu Corp. JAPAN) with ATR attachment. The presence of mesoporosity and their ordering tested by small angle X-ray scattering (SAXS) using HECUS S3 Micro, GMBH GRAZ instrument using Geni Xenocs software.

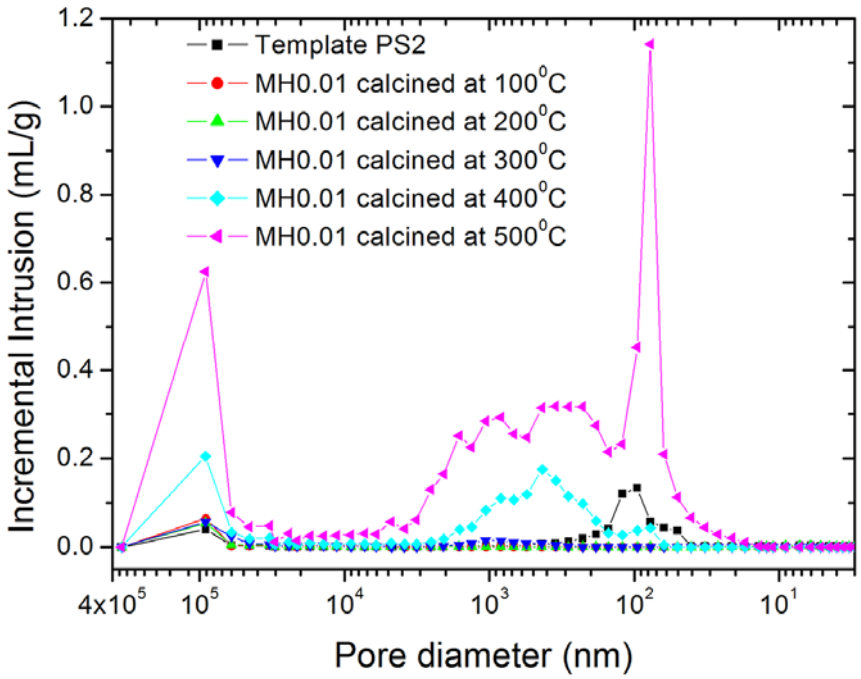


Fig.S2 Pore size distribution of polystyrene latex template along with MH0.01 calcined at various temperatures

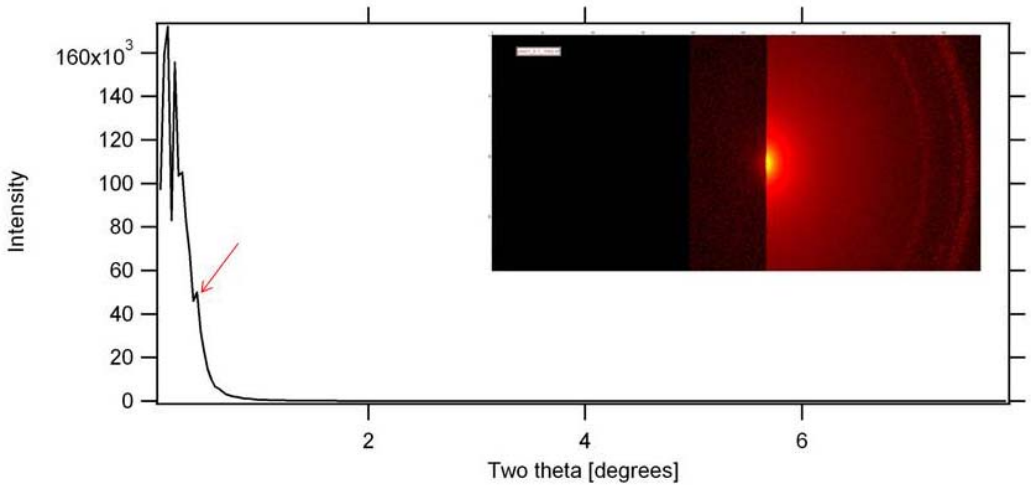


Fig.S3 Small Angle X-ray scattering data of MH0.01/calcined at 500°C

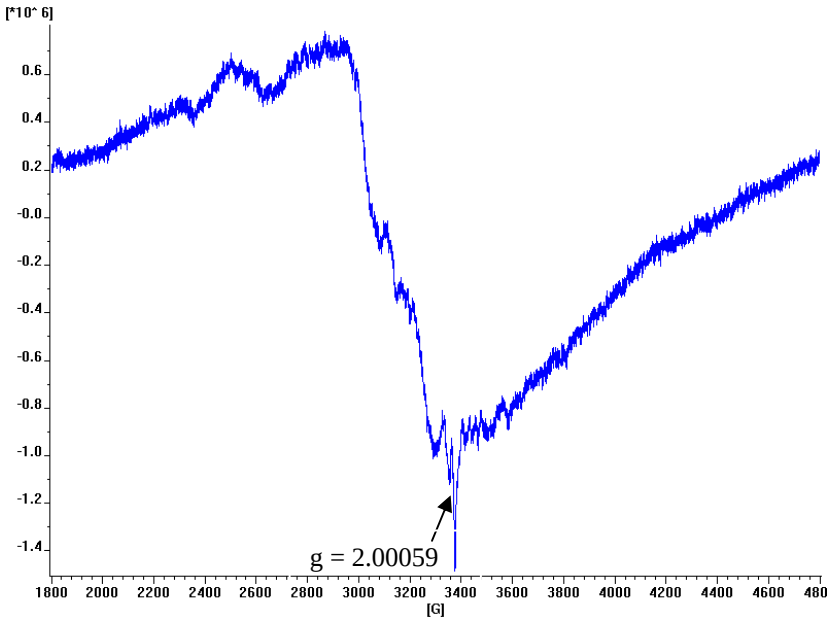


Fig.S4 X-band EPR spectrum of MH0.01 calcined at 500°C

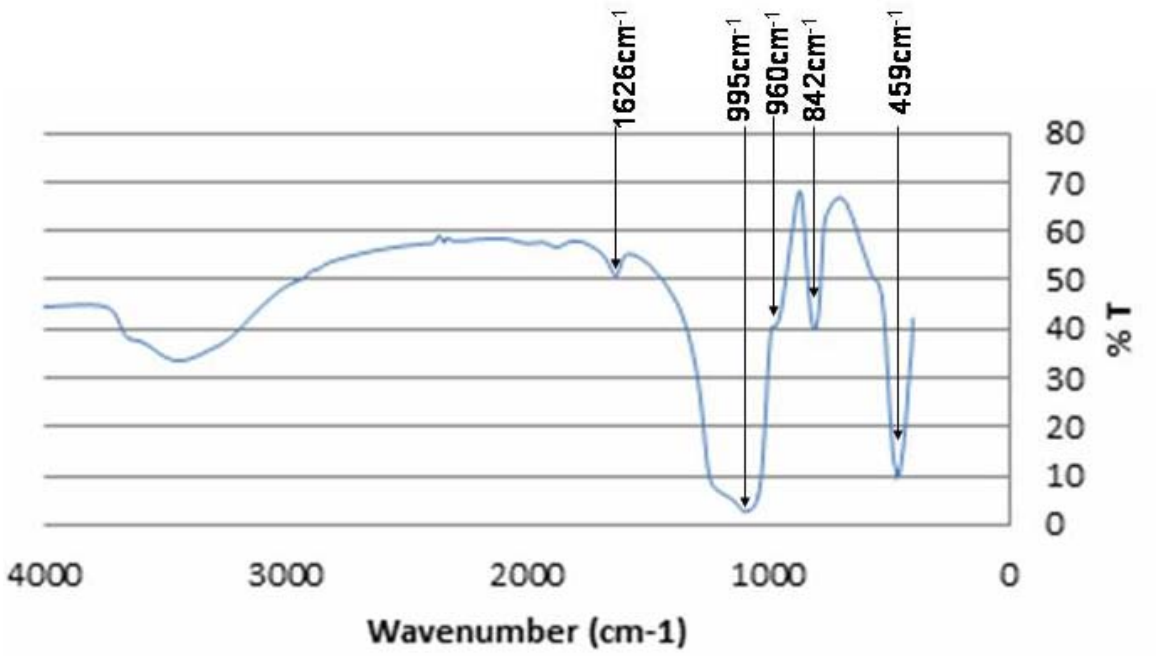


Fig.S5 FT-IR spectrum of MH0.01/calcined

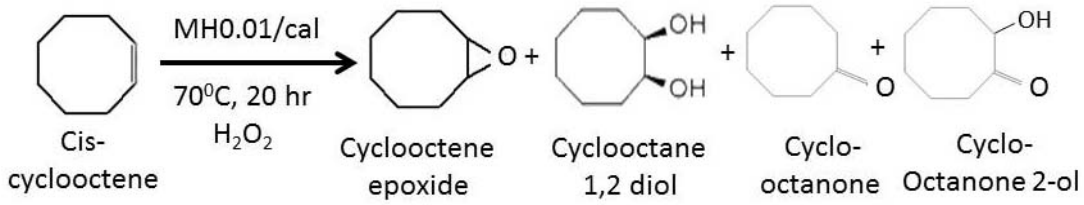
Catalysis

Oxidation of bulkier organic molecule (cis-cyclooctene)

0.1g of calcined MH0.01 and V-impregnated HOPS materials were used for catalysis. The materials were transferred into a 100ml round bottom flask (reaction vessel) fitted with condenser. Cis-cyclooctene (95% purity, 1g) was mixed with 10mL acetonitrile solvent and was transferred to the reaction vessel. The mixture was then heated to 70^0C placed in an oil bath under stirring using magnetic bar. Hydrogen Peroxide (30%, 1ml) was then added to the reaction mixture. The reaction mixture was stirred for 20hrs at 70^0C.

1ml of the reaction mixture was analysed by Thermo scientific trace GC ultra-fitted with Thermoscientific DSQII mass spectrometer with Perkin Elmer column (Length 30m, 5% Diphenyl, 95% dimethyl polysiloxane).

GC method: Start 50^0C for 2mins, 20^0C/min to 250^0C. Oxidation products were identified by the library software of the instrument.



Reaction Scheme S1. Oxidation of cis-cyclooctene to various products