Novel Hierarchically Ordered Porous Vanado-Silicate Nanocomposites for the Application in Industrial Catalysis

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ABSTRACT

Hierarchically ordered porous vanado-silicate (HOPVS) nanocomposties were prepared by multiple templating route such as polystyrene latex spheres, tri-block copolymer F_{127} ($EO_{107}PO_{70}EO_{107}$) in the presence of a co-solvent (n-butanol). Novel materials exhibited high surface area consisting of macropores of diameter ~330nm with interconnecting windows of ~80nm. The walls of the macropores were formed with disordered meso (~7 nm diameter) and microporosity (< 2 nm diameter). Vanadyl (VO^{4+}) species were homogeneously dispersed in the un-calcined nanocomposites (8 line hyperfine patterns in ^{51}V EPR signal) whereas calcined form exhibited no hyperfine pattern due to the aerial oxidation of paramagnetic (VO^{4+}) species to diamagnetic vanadium species. The calcined form exhibited good catalytic activity for the (i) oxidation of toluene to benzaldehyde, benzyl alcohol and cresols; (ii) oxidation of cis-cyclooctene to cyclooctene oxide; (iii) oxidation of phenanthrene to biphenyl 2,2'-dicarbaldehyde and 9,10 phenantrhaquinone in the presence of hydrogen peroxide.

Keywords: Nanoporous, Macroporous, Vanado-silicate, Oxidation, Catalysis

1 INTRODUCTION

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]. Various heterogenous catalytic systems containing vanadyl ions have been been developed using clays [2,3], microporous [4-8] and mesoporous silica supports [9] for oxidation of organic molecules. Diffusional restriction of bulkier molecules through the micro and mesopores or poor surface area of macroporous supports have lead to the development of high surface area materials containing pore sizes on three different length scales i.e. micropores (< 2nm), mesopores (2nm to 50nm) and macropores (> 50nm) with hieracrhal ordering [10,11]. Recently Sen et al [12] have reported that isolated vanadyl ions can be incorporated into the hierarchically ordered porous silica matrix for the oxidation of cis-cyclooctene to epoxide. Herein, we are reporting the synthesis of hierarchically ordered vanado-silicate nanocomposites for the oxidation of a series of organic molecules having different dimensions (toluene to bulky phenanthrene) of industrial importance.

2 EXPERIMENTAL

2.1 Synthesis of HOPVS nanocomposites

Polystyrene latex spheres (template) in aqueous suspension were synthesied by a reported protol [10] and packed by centrifugation at 5000 rpm for 1hr. A white solid was settled at the bottom of the centrifuge tube. Water was removed by decantation and the white precipitated solid was dried overnight at 60^0C. The interestices sites of polystyrene latex monolith of uniform diameter (420 nm) were filled with a silica gel containing vanadium ions, F_{127} and a co-solvent (butanol). The vanadium containing silica gel was prepared by mixing 20g of tetraethyl orthosilicate (TEOS), 20.5 mg of hydrated vanadyl sulphate, 0.541g of Pluronic F_{127}, 10g of deionised H_2O, 4.2mL of n-butanol, 5mL of 0.1M HCl. The final vanadium containingg silica gel filled polystyrene latex nanocomposites were calcined at 500^0C in air at a heating rate of 1^0C min^{-1} for the period of 10 hrs. The vanadium concentraion of the calcined materials was determined by X-ray fluorescnce (XRF) using a calibrted curve generatted previously using a series of known concentration of vanadium in the silica matrix.

2.2 Characterisation of HOPVS nanocomposites

The macro and mesopore diameters were determined by electron microscopes: scanning electron microscopy (SEM: Hitachi S4800, Japan) and transmission electron microscpy (TEM: JEOL 2000EX, Japan). The calcined materials were also characterised by mercury porosimetry (Micromeritics Autopore IV, USA) to obtain the sizes of macropores and interconnecting windows. The surface area and the presence of meso and microporsity were determined by nitrogen gas adsorption (Micromeritics ASAP 2010,

Autopore, USA). The presence of Si-O-V bonding was determined by Fourier transform Infra-red (FT-IR) spectroscopy (SHIMADZU 8300, Shimadzu Corp. JAPAN) with ATR attachment.

2.3 Oxidation catalysis using HOPVS nano-composites and hydrogen peroxide (H_2O_2)

0.1g of calcined vanado-silcate nanocomposites were used for each catalytic experiments. The materials were transferred into a 100mL round bottom flask (reaction vessel) fitted with condenser. (i) toluene, (ii) cis-cyclooctene and (iii) phenanthrene of each 1g mixed with 10mL acetonitrile solvent and were transferred to three different reaction vessels. The mixtures were then heated to 70^0C (oil bath) under magnetic stirring. Hydrogen Peroxide (30%, 1mL) was then added to each reaction mixture. The reaction mixtures were stirred for 24hrs before the analysis of the reaction mixtures.

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

3 RESULTS AND DISCUSSION

Figure 1 (a to d) presents the electron microscpe images of un-calcined and calcined HOPVS nanocomposites. The uncalcined sample (Fig.1a) exhibited near spherical particles.
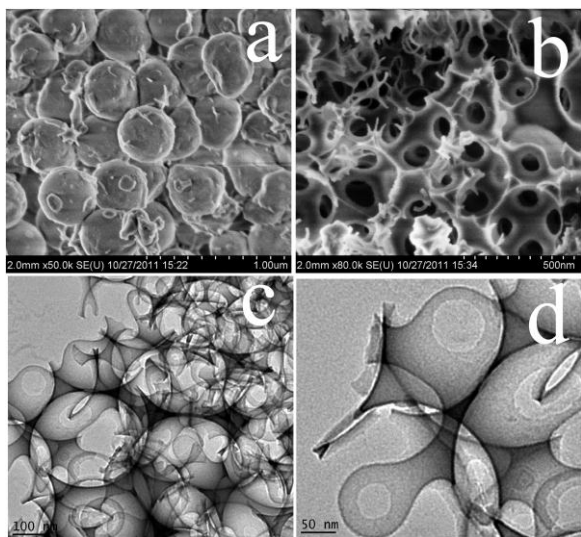

Figure 1: SEM images of uncalcined (a), calcined (b) and TEM images of calcined (c & d) forms of HOPVS nanocomposites

The polystryene latex particles were spherical in shape of diameter 420 nm with the roughness on the surface due to the presence of coated vanadium containing silica gel.

Upon calcination, the HOPVS nanocomposites were observed to be highly porous in nature (see Fig.1b) with macropores of ~330 nm with interconnecting windows of ~80 nm. The presence of macroporosity and thhe interconnecing windows were further confirmed by TEM (Figs. 1c and 1d). The walls of macroporous nanocomposites were observed to be formed wih small mesopores of disordered structure (Fig.1d). The mechanism of formation of hierarchically ordered structure of macro-meso-microporosity with interconnecting windows has been previously reported by Sen et al [10] in the context of pure silica.

Figre 2 presents the detailed investigation of macro-meso-microporosity of HOPVS nanocomposites. The materials exhibited a high value of porosity (86.4%) with total mercury intruusion of 4.8 mL g^{-1}. The macropore diameter was measured to be ~300 nm with interconnecting windows of ~80 nm in diameter.
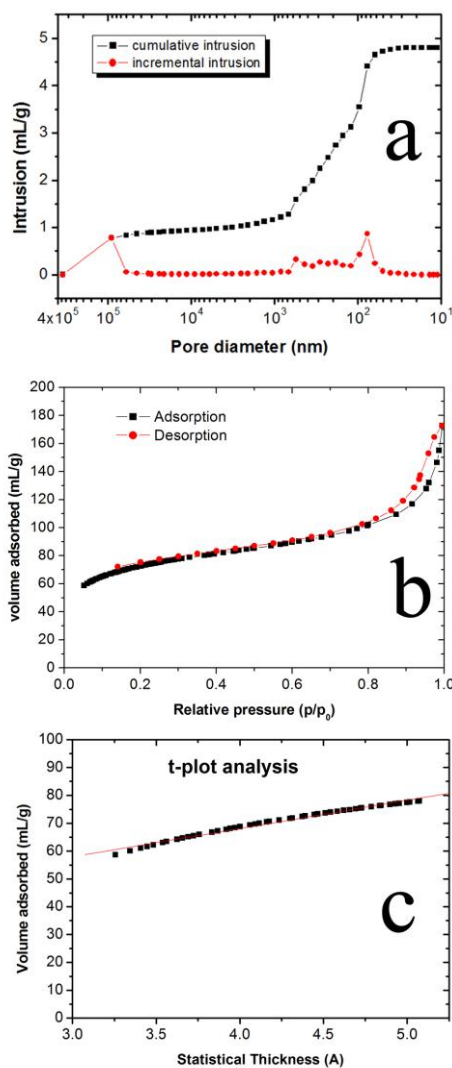

Figure 2: Mercury porosimetry data of calcined HOPVS nanocomposites (a), nitrogen gas adsorption isotherm (b) and t-plot analysis (c)

The BET surface area of calcined HOPVS nanocomposites was measured to be 237.9 m^2 g^{-1} with a hysteresis in the adsorption isotherm (Fig. 2b) indcating the presence of mesoporosity. The BJH adsorption pore diameter was calculated to be 7.2 nm corresponding to the meospores. The presence of microporosity was confirmed by t-plot analysis (Fig.2c) with micropore surface area calculated based on Harkins and Jara equation to be 87 m^2 g^{-1}.

The Si/V mass ratio of the calcined HOPVS nanocomposites calculated to be 551 (or 1005 as a molar ratio) by XRF measurement. The vanadium species in the uncalcined nanocomposites were paramagnetic in nature with isolated vanadyl species (8 line hyperfine EPR spectrum) similar to the recently reported materials [12]. The V-species in HOPVS was diamagnetic in nature (absence of EPR peaks).

The incorporation of vanadium in the hierarchically ordered porous silica matrix was further confirmed by FT-IR spectroscopy. A broad FT-IR peak at 961cm^{-1} (Fig.3) indicating the presence of V-O-Si bonding [13].
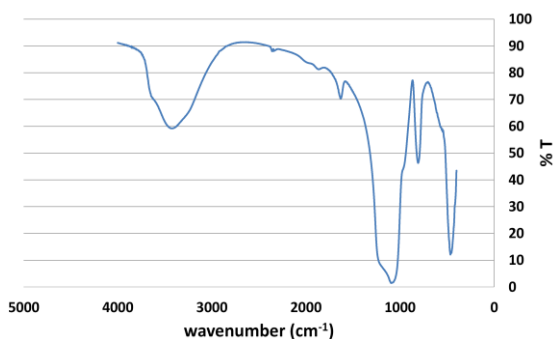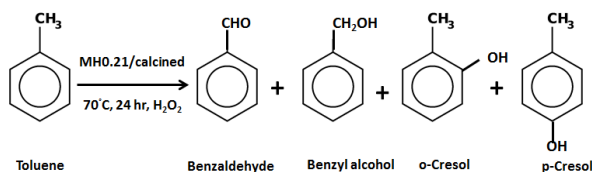

Figure 3. FT-IR spectrum of calcined HOPVS nanocomposites (T: transmission)

Schemes 1 to 3 presents the oxidation of three different organic compounds having different molecular dimension (toluene, cyclooctene and phenanthrene). The oxidation of the smallest organic compound (tolune) to corresponding product has been presented in reacttion scheme 1.

Reaction scheme 1: Oxidation of toluene

Oxidation of toluene has been previously reported using microporous vanado-silicate (VS-1 and VS-2) molecular seives [6,7]. Oxidation of toluene (see Fig.4) using HOPVS produced 45% conversion of toluene to the corresponding oxidised products (29.2% benzaldehyde, 18.9% benzyl alcohol, 24.7% o-cresol and 27.2% p-cresol).

The Turn Over Number (TON) based on the moles of toluene converted (45.24%) per moles of vanadyl species present (1.66×10^{-6} moles in 0.1g catalyst) in the calcined HOPVS nanocomposites and the value was calculated to be 2951.
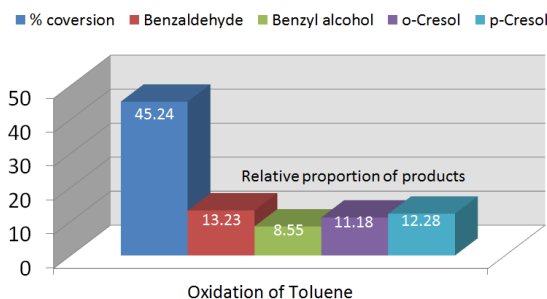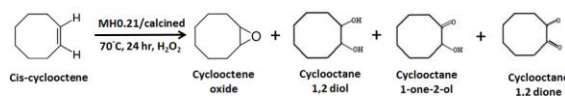

Figue 4: Oxidation of toluene to various products in the presence of calcined HOPVS nanocomposites

The oxidation of the bulky cis-cyclooctene to possible oxidised products has been presented in reacttion scheme 2.

Reaction scheme 2: Oxidation of cis-cyclooctene

Oxidation of cis-cyclooctene has recenly been reported [12] with TON value of 3019. Oxidation of cyclooctene (see Fig.5) using HOPVS produced 15.33% conversion of cis-cyclooctene to single product (cyclooctene oxide). The product selectivity to epoxide formation is an important step for industrial catalysis. The Turn Over Number (TON) based on the moles of cis-cyclooctene converted (15.33%) per moles of vanadyl species present (1.66×10^{-6} moles in 0.1g catalyst) in the calcined HOPVS nanocomposites was calculated to be 837.
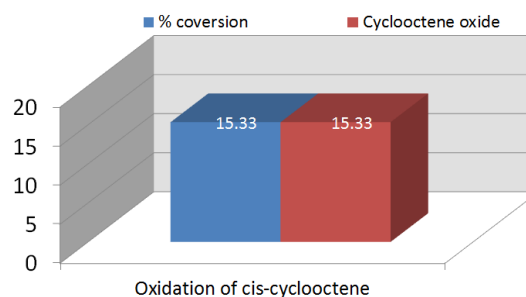

Figue 5: Oxidation of cis-cyclooctene to epoxide in the presence of calcined HOPVS nanocomposites

The oxidation of the bulky phenanthrene to corresponding oxidised products has been presented in reacttion scheme 3. Oxidation of phenanthrene (see Fig.6) using HOPVS produced 12.52% conversion with two different products (83.4% biphenyl-2,2'-dicarbaldehyde and

16.6% 9,10-phenanthraquinone). The Turn Over Number (TON) based on the moles of phenanthrene converted (12.52%) per moles of vanadyl species present (1.66×10^{-6} moles in 0.1g catalyst) in the calcined HOPVS nanocomposites and the value was calculated to be 423.
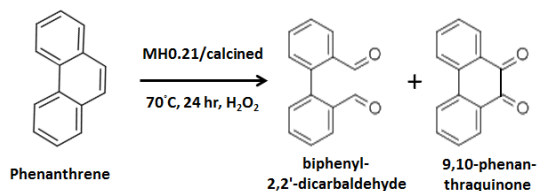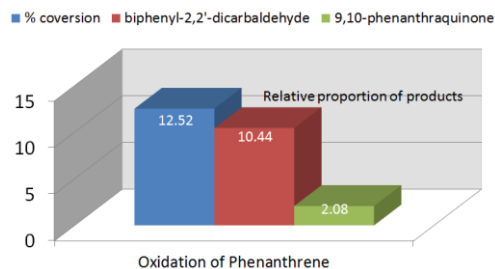

Reaction scheme 3: Oxidation of phenanthrene

Figue 6: Oxidation of phenanthrene to various products in the presence of calcined HOPVS nanocomposites

4 CONCLUSIONS

Hierarchically ordered porous vanado-silicate nanocomposites (HOPVS) were successufully synthesised and characterised by multple techniques. The novel nanocomposites were highly porous in nature (86.4%). The surface area of the materials was determined to be high due to the presence of macro, meso and microporosity with interconnecting windows. The dispersed vanadium species were used as the catalytic centres and observed to be highly efficient in the oxidation of various organic molecules of different molecular dimensions. The catalytic conversion was observed to be highest for smallest organic molecule (toluene) and lowest in the bulkiest molecule (phenanthrene).

ACKNOWLEDGEMENT

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