



Organic-inorganic hybrid polyionic liquid based polyoxometalate as nano porous material for selective oxidation of sulfides



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ABSTRACT

Organic-inorganic hybrid nano porous materials based on poly(ionic liquid)-polyoxometalate (PIL-POM) were reported. These hybrid materials were synthesized by the reaction of 4-vinyl pyridine with 1,3-propanesultone, followed by the polymerization and also sulfonate-functionalized cross-linked poly(4-vinylpyridine) and combining these polymers with $H_5PMo_{10}V_2O_{40}$ ($PMo_{10}V_2$). Activity of prepared PIL- $PMo_{10}V_2$ hybrids were investigated as catalysts for oxidation of sulfides with H_2O_2 as oxidant. For understanding catalytic activities of the PIL- $PMo_{10}V_2$ hybrids in oxidation of sulfides, effect of catalyst composition, substrate, and reaction conditions were studied. The results show that the PIL- $PMo_{10}V_2$ hybrids are active as selective heterogeneous catalysts for oxidation of sulfides and can be recovered and reused. The catalyst was characterized by FT-IR, TGA-DSC, XRD, SEM/EDX, BET, CV and zeta potential measurement. Also, average molecular weight of prepared catalysts were measured.

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1. Introduction

In 1914 Paul Walden synthesized ionic liquid (IL). ILs are generally defined as organic/inorganic salts that are composed of cations and anions which melt below 100 °C [1]. These compounds are liquid because there is weak interactions between oppositely charged ions in ionic structures. Also, there are light intermolecular interaction (only electrostatic interactions, hydrogen bonds, or vander Waals interactions are involved) and asymmetric chemical structures. Phosphonium, ammonium, pyrrolidinium, imidazolium, and pyridinium are common IL cations. IL properties related to the kind of anion part more than cations, and anions commonly used are mineral acid, halides, metal oxide clusters such as polyoxometalates (POM) and polyatomic inorganics (PF_6^- , BF_4^-) [2]. Their negligible volatility, remarkable solubility, and potential recyclability of such ILs make these compounds as good solvents and catalysts for chemical reactions [3–7].

Polymerization of ionic liquids produce poly(ionic liquid)s (PILs), in these materials IL species are repeating units. Thus, the cationic or anionic centers are compelled to the repeating units in the polymer chain. PILs unlike ILs are solid in most cases [8]. PILs

potentially have both of IL and polymer properties, such as high thermal stability, easily molding, corrosion resistance, and multiplicity of available structures [2,9]. PILs have different applications including energy and environmental applications. These compounds are used in analytical chemistry, materials science, biotechnology, and surface science also using as catalysts [10–16]. Polymer supported catalysts are used as heterogeneous and recyclable catalysts in organic transformation that make reaction methods more convenient, economic and environmentally benign [17].

POMs are family of anionic inorganic metal oxide clusters. Because of their acidic and redox properties, POMs have received specific attention in the field of acidic or oxidation catalyst [18]. Many nano porous carriers with high surface areas, such as silica, active carbon, zeolite, and so on are used as support to impregnate onto or encapsulate POMs. Produced heterogeneous catalysts show higher efficiency compare to homogeneous ones [19–22]. Much attention has been focused on modification of POMs with organic species to produced POM-based hybrid catalysts with improved catalytic activity and convenient catalyst recovery and reusability. Hybrid organic POM could be produced by exchanging of the protons of the POM by ILs [23–25]. Nevertheless, catalytic stability of these catalysts needs to be improved. For this purpose POM based polymeric hybrid nano porous catalysts by combining SO_3H -functionalized IL polymer with POMs were produced. Because of the

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involvement of a polymeric framework these catalyst should possess a more structural stability. Also its catalytic performance increase for selective oxidation of organic sulfur compounds in a short time and mild conditions. In addition, in this work, we compared catalytic activity of $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ ($\text{PMo}_{10}\text{V}_2$) based poly(4-vinylpyridine) (PVPy) in two form not cross-link polymer and cross linked polymer with 2% divinyl benzene (DVB).

2. Experimental

2.1. General

All used reagents and solvents were purchased from Fluka, Aldrich or Merck Company and used without further purification. Poly(4-vinyl pyridine) cross-linked with 2% DVB (100–200 mesh, MW: 60000) was obtained from Fluka. $\text{PMo}_{10}\text{V}_2$ from Aldrich was used. FT-IR spectra were recorded as KBr pellets using a Shimadzu 470 spectrophotometer. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were used to know the morphology and composition of the catalyst on a model XL30 Philips. X-ray diffraction (XRD) patterns were collected on the STOE powder diffraction system. Differential scanning calorimetry (DSC) measurements were done on a METTLER with a scanning rate of $10\text{ }^\circ\text{C}/\text{min}$ in air. Thermogravimetric analysis was carried out using a Shimadzu TGA-50H spectrometer at heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under flowing rate nitrogen $30\text{ mL}/\text{min}$. Brunauer Emmett-Teller (BET) surface areas and pore volumes were evaluated on a sorptometer kelvin 1042 using nitrogen adsorption at 77 K . The electrochemical reduction of catalyst was studied in phosphate buffer (0.1 M), $\text{pH} = 2$. A glassy carbon electrode was used as the electrode and Ag/AgCl as the reference electrode. Cyclic voltammograms (v , 0.1 V s^{-1}) were obtained at ambient temperature ($20 \pm 5\text{ }^\circ\text{C}$). Measurements of charge distribution (Zeta potential measurements) and average molecular weight of the polymer synthesized were carried out using HPPS5001, Malvern, UK. The products of sulfoxidation were characterized by ^1H NMR and melting point using a Bruker Avance 200 MHz NMR spectrometer and Barnstead electro thermal 9200 respectively.

2.2. Preparation of the catalysts

2.2.1. Preparation of 4-vinylpyridine propane sulfone

To a solution of 1, 3-propane-sultone (0.1 mol , 12.2 g) in dry toluene (50 mL), 4-vinyl pyridine (0.1 mol , 10.5 g) was slowly added at room temperature and the mixture was stirred overnight until the solid formed. It was washed with ether and dried in vacuum at room temperature. The solid was used in next step without further purification.

2.2.2. Preparation of poly 4-vinylpyridine propane sulfone

The obtained 4-vinylpyridine propane sultone (VPyPS) (2.5 g) was dissolved in methanol (20 mL), and azobisisobutyronitrile (AIBN) (0.05 g) was added under nitrogen atmosphere, and the mixture was refluxed at $60\text{ }^\circ\text{C}$ for 24 h with stirring. Then the solvent was removed by distillation, and the residue was washed with ethanol to give a white solid hereafter named poly(VPyPS).

2.2.3. Preparation of poly(VPyPS)- $\text{PMo}_{10}\text{V}_2$

The solution of $\text{PMo}_{10}\text{V}_2$ (1 or 4 mmol) was added dropwise into the obtained poly(VPyPS) (monomer molar quantity 5 mmol) in methanol, followed by the refluxing for 24 h. On completion, methanol was removed in vacuum to give final products poly(-VPyPS)- $\text{PMo}_{10}\text{V}_2$ (PVPyPSPMo₁₀V₂) (1 mmol $\text{PMo}_{10}\text{V}_2$) and poly(-VPyPS)-4 $\text{PMo}_{10}\text{V}_2$ (PVPyPS4 $\text{PMo}_{10}\text{V}_2$) (4 mmol $\text{PMo}_{10}\text{V}_2$) as green solids.

2.2.4. Preparation of cross-linked poly(4-VPyPS)- $\text{PMo}_{10}\text{V}_2$

1,3-propane-sultone (20 mmol) was slowly added to a dispersion of poly(4-vinylpyridine) cross-linked with 2% DVB (2.1 g) in toluene at ambient temperature, and the resulting mixture was stirred for 2 h. The temperature was then raised to $60\text{ }^\circ\text{C}$ and the mixture was stirred for 24 h. The mixture was cooled to ambient temperature and the resulting solid was filtered then washed sequentially with dichloromethane and methanol before being dried under vacuum at $55\text{ }^\circ\text{C}$. The solution of $\text{PMo}_{10}\text{V}_2$ (0.528 mmol) was added dropwise into the obtained cross-link poly (VPyPS) (0.3 g) in methanol, followed by refluxing for 24 h. On completion, methanol was removed in vacuum to give the final product cross-link poly(VPyPS)- $\text{PMo}_{10}\text{V}_2$ (CPVPyPSPMo₁₀V₂) as a dark green solid.

2.3. Oxidation of liquid sulfides

To a stirred mixture of the sulfide (5 mmol), and catalyst (0.036 g) in EtOH (10 mL), 30% aq. H_2O_2 (1.68 mL , 15 mmol) was added in one portion. The slurry was stirred at room temperature. After completion of the reaction followed by TLC, the catalyst was separated by filtration. Corresponding sulfoxide was extracted with Et_2O from the reaction mixture. Evaporation of the solvent afforded the crude product. The crude product was purified by column chromatography on silica gel using EtOAc/hexane as eluent.

3. Results and discussion

3.1. Catalyst characterization

The precursor poly(VPyPS) was prepared by reaction of 4-vinylpyridine with 1,3-propane sultone, followed by the polymerization with AIBN. The average molecular weight of the synthesized polymer has been characterized by light scattering technique that was 32300 g (Fig. S1a). Ultimately, methanol solution of the obtained poly(VPyPS) with an aqueous solution of $\text{PMo}_{10}\text{V}_2$ was refluxed, which afforded $[\text{poly}(\text{VPyPS})]_5\text{PMo}_{10}\text{V}_2$ catalyst, (PVPyPSPMo₁₀V₂) (Scheme 1).

The CPVPyPSPMo₁₀V₂ catalyst was readily prepared in two steps via the reaction of cross-link poly(4-VPy) with 1,3-propane sultone to render a positive charge, followed by acidification of the resulting product with $\text{PMo}_{10}\text{V}_2$ (Scheme 2).

For the synthesis of hybrid materials, two different molar ratios of PVPyPS and $\text{PMo}_{10}\text{V}_2$ were used: PVPyPS to $\text{PMo}_{10}\text{V}_2$ molar ratio is 5/1 to produce PVPyPSPMo₁₀V₂ and 5/4 for PVPyPS4 $\text{PMo}_{10}\text{V}_2$. Elemental analysis carried out using EDX (Fig. 1a) revealed the presence of several elements including C, Mo, V, and S which confirmed the formula of PILs- $\text{PMo}_{10}\text{V}_2$ compounds (Table 1). Based on the data, it seems that there is an active species of $\text{PMo}_{10}\text{V}_2$ in PVPyPSPMo₁₀V₂ and PVPyPS4 $\text{PMo}_{10}\text{V}_2$ per 10 and almost 7 monomer units respectively.

Morphology of the catalysts was investigated by SEM. It could be seen from Fig. 1b that the surface of the polymers is distinctly altered in each hybrid organic-inorganic catalysts. Particles of PVPyPS4 $\text{PMo}_{10}\text{V}_2$ as compared to other samples have more uniform distribution and less agglomeration.

Measurement of average molecular weights of PVPyPSPMo₁₀V₂ and PVPyPS4 $\text{PMo}_{10}\text{V}_2$ (1740000 , 1730000 g respectively) showed that with increasing of the amount of polar species $\text{PMo}_{10}\text{V}_2$, the average molecular weight of organic-inorganic hybrid polymer has been decreased (Figs. S1b and c). The reason of this reduction of molecular weight may be because of this fact that PIL is full of charges along the polymer chains and can be easily self-stabilized by Coulomb repulsion once nanoparticles are formed. So if ionic strength change this would induce PIL chains to aggregate, the PIL

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