



Wells-Dawson heteropoly acid immobilized inside the nanocages of SBA-16 with ship-in-a-bottle method: A new recoverable catalyst for the epoxidation of olefins

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ABSTRACT

Wells-Dawson structured heteropoly acid ($H_6P_2W_{18}O_{64}$) was immobilized into the SBA-16 mesoporous material by ship-in-a-bottle method. The obtained material was characterized by Fourier transform infrared (FT-IR) and inductively coupled plasma-atomic emission (ICP-AES) spectroscopies, X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption-desorption analysis, and thermogravimetric analyses (TGA-DTA). The results indicated that the surface area of SBA-16 support decreased after immobilization of the heteropoly acid and next modification with silylating agent. The prepared material exhibited excellent catalytic performance in the epoxidation of olefins and allylic alcohols in the presence of hydrogen peroxide as green oxidant. The catalyst showed all of the expected advantages of the heterogeneous systems and was shown to be recoverable and reusable several times without major loss of activity.

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1. Introduction

In recent years, environmental considerations and handling problems have raised great interest in the development of eco-friendly materials and processes to eliminate the use of harmful substances and the production of toxic waste materials. In this respect, heterogeneous catalysis could play a key role in the development of environmentally benign processes particularly in the petroleum and chemical industries. In terms of green chemistry, high activity of the catalyst is not the only concern, and good reusability and environmental friendliness are also important. Immobilizing soluble homogeneous catalysts on insoluble inorganic supports is a strategic way for preparing heterogeneous solid catalysts [1–3].

Heteropoly acids (HPAs) are well defined molecular clusters that are remarkable for their molecular and electronic structural diversity and their significance is quite diverse in many areas, e.g. catalysis, medicine, and materials science [4–11]. They have been chosen as catalysts because of their easy availability, efficient and cleaner processes compared to conventional mineral acids and

extreme stability in solution as well as in solid state. In view of green chemistry, the substitution of harmful liquid acids by HPAs which are also eco-friendly and green catalysts in organic synthesis have attracted great attentions [4,12–18]. HPAs were also found highly efficient for epoxidation of olefins by Venturello et al. [19–22], and Ishii et al. [23,24]. Various H_2O_2 -based epoxidation systems have been efficiently catalyzed by HPAs based systems [19–29].

The main disadvantages of pure HPAs as homogeneous catalysts are their very low surface area in solid state and high solubility in polar solvents, which results in separation problems. It becomes necessary to disperse HPAs on solid supports that possess large surface area [30–39]. Heterogenization of the HPAs on these supports significantly increases the specific surface area, which is very important for heterogeneous catalysis processes. The supports also influence the catalytic activity of HPAs. Conventionally HPAs have been immobilized on various organic polymers such as resins [30,31], inert porous solids such as activated carbon [32,33], magnetite nanoparticles [34,35], or encapsulated in the pores and cavities of microporous and mesoporous materials such as zeolites, MCM-41 and SBA-15 [36–39].

The ship-in-a-bottle synthesis has become an efficient method for immobilizing homogeneous catalysts within the solid porous materials [40–44]. The concept of ship-in-a-bottle synthesis, first used by Herron [40], is to introduce reactants in the cages of porous

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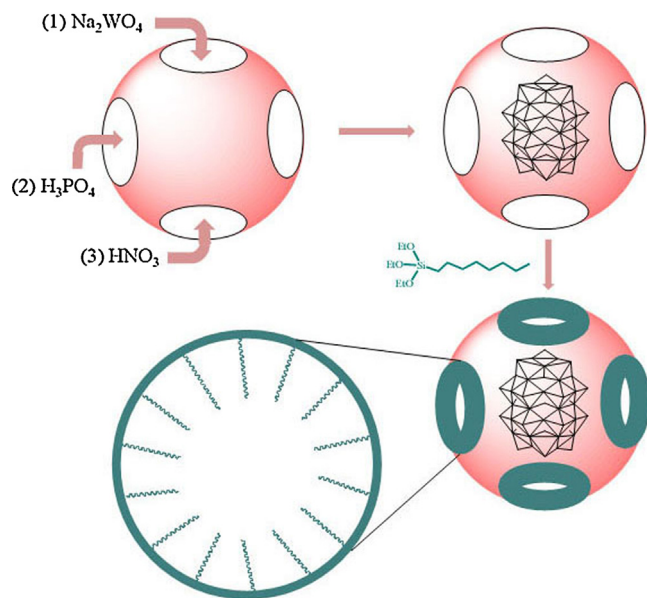


Fig 1. Schematic description of preparation of Wells-Dawson structured heteropoly acid ($H_6P_2W_{18}O_{62}$) inside the nanocages of SBA-16 through the “ship-in-a-bottle” method.

materials to react within the cages and the products are physically entrapped inside the rigid cages. This procedure is a method of immobilization for species that can act as catalyst without the need for developing specific interactions with the surface of support. The advantage is that there is no covalent bond between the entrapped species and the support, which make them very similar to their homogeneous counterparts in terms of structure, activity and selectivity.

Previously, Sulikowski and coworkers have separately succeeded in immobilizing HPAs in Y-type zeolite by directly synthesizing their molecules in the micropores of the zeolite [43,44]. Although this catalyst showed fairly high activities in liquid phase reactions which involve water, their usage is thought to be limited due to the fairly low stability of the support [44]. This drawback can be overcome by using alternative stable materials as the support, for example, SBA-type mesoporous materials. In recent years, due to its large cage, ordered pore structure, high surface area and high thermal stability, SBA-16 mesoporous material has been appeared to be one of the best candidates for catalytic support and packing materials for separation [45–48]. SBA-16 is a porous silica with large cage-like mesopores arranged in a three dimensional cubic body-centered $Im\bar{3}m$ symmetry. Due to its high thermal stability, high surface area, and large pore volume, SBA-16 can be regarded as a good support for the accommodation of catalytic active species such as HPAs. But, there is only one report on the immobilization of HPAs on SBA-16 material without investigation of its catalytic properties [48].

To the best of our knowledge, no attempt has been made to immobilize Wells-Dawson structured phosphotungstic acid ($H_6P_2W_{18}O_{62}$) onto the nanocages of SBA-16. In the present study, Wells-Dawson structured phosphotungstic acid was immobilized on mesoporous SBA-16 by ship-in-a-bottle method. The catalytic activity of the prepared material as heterogeneous catalyst was examined in the presence of H_2O_2 as green oxidant. The advantages of this system are the easy recovery of the solid catalyst at the end of reaction as well as good activity, selectivity and high stability in the epoxidation of olefins. Moreover, as it releases only water as by-product, the process is environmentally friendly.

2. Experimental

2.1. Materials and instrumentation

Pluronic copolymer F-127 ($EO_{106}PO_{70}EO_{106}$) was purchased from Sigma Company. All other chemicals were purchased from Merck chemical company. All of the solvents were used after distillation.

Fourier transform infrared (FT-IR) spectra were recorded on Perkin-Elmer Spectrum RXI FT-IR spectrometer using pellets of the materials diluted with KBr. Elemental analyses were performed by a VARIAN VISTA-MPX ICP-AES spectrometer. X-ray powder diffraction (XRD) measurements were performed on a SIEFERT XRD 3003 PTS diffractometer using $Cu\ K\alpha$ radiation (wavelength, $\lambda = 0.154\text{ nm}$). Thermogravimetric measurements were made on a Perkin Elmer Diamond Thermogravimeter. The temperature was increased to $700\text{ }^\circ\text{C}$ using a rate of $10\text{ }^\circ\text{C}/\text{min}$ in static air. Transmission electron microscopy (TEM) analysis was performed using a Philips EM 208S instrument with an accelerating voltage of 100 kV. Samples were prepared for TEM analysis by placing droplets of a suspension of the sample in acetone on a polymer microgrid supported on a Cu grid. Nitrogen sorption studies were performed at liquid nitrogen temperature ($-196\text{ }^\circ\text{C}$) using Quantachrome Nova 2200e, Version 7.11 Analyzer. Before the adsorption experiments the samples were outgassed under high vacuum at $120\text{ }^\circ\text{C}$. All calculations were performed using the program of Quantachrome Nova 2200e surface area analyzer.

2.2. Preparation of the catalyst

The mesoporous material, SBA-16, was prepared according to the literature method [49] and calcined at $550\text{ }^\circ\text{C}$ for 6 h to remove the surfactant from the mesopores. The neat $H_6P_2W_{18}O_{62}$ heteropoly acid was also synthesized in the homogeneous phase according to literature method [4].

Preparation of $H_6P_2W_{18}O_{62}$ heteropoly acid within the pores of SBA-16 was performed according to the following method: SBA-16 (1 g, evacuated at $120\text{ }^\circ\text{C}$ for 8 h) was suspended in a solution of Na_2WO_4 (0.82 g) in distilled water (25 ml) and stirred for 24 h at room temperature. After addition of 1 ml H_3PO_4 and HNO_3 , the suspension was refluxed for 24 h. The solvent was evaporated and the resulting solid dried in vacuum oven for 24 h.

The surface modification of the obtained material with triethoxyoctylsilane was performed according to the literature method [50]. The obtained solid was added to a mixture containing dry toluene (5 ml) and anhydrous pyridine (5 ml). After addition of triethoxyoctylsilane (5 mmol), the resulting suspension was refluxed for 24 h under N_2 atmosphere. The resulting solid was isolated by filtration and thoroughly washed with dichloromethane to remove any unreacted silylating reagent from the surface of the solid. Finally, the obtained solid was Soxhlet extracted with distilled water and then dried in vacuum oven for 24 h.

2.3. Catalytic epoxidation of olefins in the presence of the prepared catalyst

Epoxidation of olefins was carried out in a 25 ml round bottomed flask equipped with a condenser and a magnetic stirrer. In a typical procedure, 100 mg of catalyst was added to a solution of olefin or allylic alcohol (8 mmol) in acetonitrile (10 ml), and 1.6 ml 30% H_2O_2 (12.8 mmol) as oxidant was added to the mixture. The reaction mixture was refluxed for appropriate time under nitrogen atmosphere. Samples were withdrawn periodically and were analyzed using a gas chromatograph (HP, Agilent 6890N) equipped with a capillary column (HP-5) and a FID detector. Products were quantified using isooctane (8.75 mmol) as internal standard. GC-MS of the products

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