



Selective oxidation of olefins with aqueous hydrogen peroxide over phosphomolybdic acid functionalized knitting aryl network polymer



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ABSTRACT

A phosphomolybdic acid (PMA)-based heterogeneous catalyst, denoted as PMA/KAP, was prepared by immobilizing PMA onto a knitting aryl network polymer (KAP) based on triphenylphosphine (PPh₃). The catalytic property of PMA/KAP was investigated for the selective oxidation of olefins with aqueous hydrogen peroxide (H₂O₂) as oxidant. When using ethyl acetate (EAC) as reaction medium, PMA/KAP performs higher activity and selectivity to epoxide for a variety of olefins, and it can be reused for several times without obvious loss of activity. When the reaction was carried out in acetonitrile (AN) medium, deactivation of PMA/KAP catalyst can be observed immediately. A variety of characterization results suggest that the degradation of PMA unit to (PO₄[MoO(O₂)₂]₄)³⁻ occurs easily when the PMA/KAP catalyst is operated in H₂O₂/AN system, while such degradation behavior could be significantly inhibited when the catalyst is used in the system of H₂O₂/EAC. We proposed that the neighbouring P-containing ligands dispersed in the framework of KAP can produce a steric pocket with low electron density, which can promote the formation of multi-weak coordination interaction between PMA unit and several P ligands. Such multi-weak interaction can inhibit the degradation of PMA to (PO₄[MoO(O₂)₂]₄)³⁻, thus avoiding the leaching of active species from the KAP support, and resulting in the formation of relatively stable heterogeneous PMA supported catalyst for olefin epoxidation with H₂O₂ in the media of EAC.

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1. Introduction

Porous organic frameworks (POFs) have received increasing attention due to their unique properties like large surface, low skeletal density, and high chemical stability [1–10]. Compared with traditional inorganic materials, one particular advantage of POFs is its ability to introduce various organic chemical functionalities for constructing novel advanced materials. Recently, a variety of POFs containing functional units have been reported, which have shown potential applications in adsorption, ion exchange, nanotechnology, and catalysis [11–16].

Knitting aryl network polymers (KAPs) are a new family of POFs, which can be prepared through a simple one-step Friedel–Crafts reaction using aromatic compounds as the monomer and formaldehyde dimethyl acetal as the external cross-linker [17–19]. In the field of catalysis, a few recent works showed that a functionalized KAP material, obtained by knitting triphenylphosphine (PPh₃) and

benzene with an external cross-linker, could be used as suitable support to fabricate efficient heterogeneous catalysts. For instance, Pd nanoparticles supported PPh₃-functionalized KAP exhibited excellent activity and selectivity for the Suzuki–Miyaura crossing coupling reaction of aryl chlorides [18]. Rh supported PPh₃-based KAP showed higher activity and stability than Rh supported silica catalyst for the hydroformylation of higher olefins [20]. It was believed that the special coordinating ability of PPh₃ ligands as well as the porous characteristics of KAP play critical role in stabilizing the nanoparticles of noble metal.

Recently, numerous contributions have been made to develop highly active and stable polyoxometalates (POM)-based heterogeneous catalysts for the application in liquid-phase oxidation (or epoxidation) of olefins. By selecting different supports and preparation strategies, a variety of relatively active and stable POM-supported heterogeneous catalysts have been obtained [21–23]. For instance, Kholdeeva et al. immobilized [PW₁₁CoO₃₉]⁵⁻ and [PW₁₁TiO₄₀]⁵⁻ into MIL-101 through electrostatic interaction, and found that the resulting materials were active heterogeneous catalysts for the oxidation of olefins with H₂O₂ or O₂ as oxidant [21]. Bordoloi et al. reported that molybdovanadophosphoric acids sup-

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ported amine-modified mesoporous silicas, were highly active and stable catalysts for selective oxidation of anthracene with *t*-BuOOH as oxidant [22]. Kasai et al. immobilized [r-1,2-H₂SiV₂W₁₀O₄₀] on *N*-octyldihydroimidazolium cation-modified SiO₂, to obtain an efficient catalyst for the oxidation of olefins and sulfides with H₂O₂ as oxidant [23]. Our recent work showed that phosphomolybdic acid supported COF-300 (a covalent organic framework material) exhibits high activity and stability for the epoxidation of cyclooctene and 1-octene with *t*-BuOOH as oxidant [24]. In spite of these considerable progresses, most of the POM supported catalysts commonly suffer from active species leaching from the supports, which is particularly serious when H₂O₂ is used as oxidant [25]. This can be mainly attributed to the strong complexing and solvolytic properties of H₂O₂ and solvents, which can usually transfer PMA cluster into dissolvable compound, or turn it to smaller species by oxidative degradation [26,27]. Besides, it is quite hard to get truly heterogeneous supported POM catalysts, since the relatively large size of POM clusters brings serious difficulty to build stable linkages between supports and POM. Therefore, it is still a very significant subject to develop novel efficient POM-based heterogeneous catalysts for the oxidation of olefins with H₂O₂, and to reveal the key factors favoring the improvement of the stability of the POM supported catalysts.

In this work, we tried to use PPh₃-based KAP as support to prepare phosphomolybdic acid (PMA) supported heterogeneous catalyst, and the catalytic performance of the resulting material (PMA/KAP) was studied for the oxidation of olefins with H₂O₂ as oxidant in different reaction media. Besides, a homogeneous catalyst named PMA-(PPh₃)₃ was also prepared by coordinating PMA with free PPh₃ ligands for the purpose of comparison. By combining a variety of characterization results, it can be revealed that multi-interactions are present between one PMA unit and several P-containing ligands dispersed in the framework of KAP support, which can result in the formation of relatively active and stable PMA supported KAP catalyst for the epoxidation of olefins with H₂O₂ in the presence of EAC.

2. Experimental section

2.1. Materials

Benzene (PhH), triphenylphosphine (PPh₃), FeCl₃ (anhydrous), methanol, 1,2-dichloroethane (DCE), dimethylformamide (DMF), acetonitrile (AN), ethylacetate (EAC) and 30 wt% H₂O₂ aqueous solution were purchased from China National Medicines Corporation Ltd., all of which were of analytical grade and were used as received. Cyclooctene, cyclohexene, styrene, 1-hexene, 1-octene, *a*-piene and formaldehyde dimethylacetal (FDA) were purchased from Aldrich.

2.2. The preparation of catalysts

KAP was synthesized according to literature procedure [18]. Typically, 1.56 g PhH, 5.25 g PPh₃ and 4.56 g FDA were dissolved in 20 ml DCE containing 9.75 g FeCl₃ (anhydrous). The resulting mixture was stirred at 45 °C for 5 h to form original network, and then heated at 80 °C for 67 h to complete the reaction. The as-synthesized KAP was washed with methanol in a Soxhlet to remove residual FeCl₃. Catalyst PMA/KAP was prepared by adding 0.30 g KAP support into a methanol solution containing 0.053 g PMA, the mixture was then stirred for 24 h at room temperature. The resulting solid was washed three times with methanol, and then washed with methanol in a Soxhlet's extractor at 80 °C for 24 h, then dry in vacuum at 60 °C for 8 h. The PMA loading determined by atomic adsorption spectroscopy (AAS) was 0.05 mmol/g. The processes for

preparation of KAP and PMA/KAP are shown in Scheme 1. Element analysis (%): KAP, C 83.8, H 6.2, Fe 5.2. PMA/KAP: C 76.9, H 5.6, Fe 2.4.

For comparison, PMA-(PPh₃)₃ complex was synthesized through adding some PMA into a methanol solution containing PPh₃ ligands (the ratio of PPh₃/PMA is about 3.5). The mixed solution presents yellow at first, and the solid complex with light green color can be obtained finally after filtering and washing by CH₃OH. The resultant complex is denoted as PMA-(PPh₃)₃, in which the mole ratio of PMA/PPh₃ is determined by elemental analysis. The process for preparation of PMA-(PPh₃)₃ is shown in Scheme 2.

2.3. Catalytic reaction

The catalytic properties of PMA/KAP and PMA-(PPh₃)₃ were tested by the oxidation of olefins. The reactions were initiated by adding oxidant H₂O₂ into a 10 ml flask containing catalyst, solvent and corresponding reactants under beforehand designed temperature. The course of the reactions were monitored and quantified by Shimadzu GC-8A gas chromatograph with HP-5 capillary column.

2.4. Characterization techniques

FT-IR spectra were recorded on a Nicolet AVATAR 370 DTGS spectrometer in the range 4000–500 cm⁻¹. Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA), using Ni-filtered CuK α radiation. Thermogravimetry (TG) were carried out using A Netzsch Thermoanalyser STA 449F3 with a N₂ flow and heating rate of 10 °/min, from room temperature to 800 °C. Transmission electron microscopy (TEM) images were taken with a H8100-IV electron microscope operating at 200 kV. The samples were suspended in ethanol by sonication and then picked up on a Cu grid covered with a carbon film. Element analyzes of C and H were implemented with a PerkinElmer 2400CHN elemental analyzer. For determining the Fe amount remained in KAP support or PMA/KAP catalyst, the sample was firstly treated by 3 M HNO₃ aqueous solution, and then the Fe concentration in the filtration was detected by inductively coupled plasma-optical emission spectroscopy (ICP-AES). N₂ adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP 2010N analyzer. Samples were degassed at 110 °C for 8 h before measurements. Specific surface areas were calculated using BET model. XPS measurements were made on a VGESCA LAB MK-II X-ray electron spectrometer using Al K α radiation. Solid ³¹P MAS NMR spectra were recorded on a 400 MHz Bruker spectrometer. The ³¹P MAS NMR chemical shifts are referenced to the resonances of monoammonium phosphate (NH₄H₂PO₄) standard. Liquid ³¹P NMR spectra were recorded on a 500 MHz AVANCEIII500. ³¹P chemical shifts are referenced to 85% H₃PO₄ as an external standard.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the FT-IR spectra of KAP, PMA, PMA-(PPh₃)₃ and PMA/KAP. The characteristic bands of KAP are in agreement with the related literature results [18]. The benzene skeleton vibration peaks appear in the range of 1600–1450 cm⁻¹, while the peaks at around 1250–950 and 900–650 cm⁻¹ result from C–H bending vibrations of benzene ring. 1435 cm⁻¹ could be attributed to the P–CH₂ which shows that the phosphine ligands are embedded into the skeleton of KAP [28]. For PMA-(PPh₃)₃ and PMA/KAP, the characteristic bands of PMA appear in the range of 1100–700 cm⁻¹, confirming the presence of PMA units in the resulting catalysts.

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