



Surfactant-assisted sol–gel synthesis of zirconia supported phosphotungstates or Ti-substituted phosphotungstates for catalytic oxidation of cyclohexene

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ABSTRACT

The Keggin-type polyoxometalates (POMs) including phosphotungstate and Ti-substituted phosphotungstates were supported on zirconia (ZrO₂) matrix by a surfactant-assisted sol–gel copolymerization technique. The resultant ZrO₂ supported POMs composite materials (ZrO₂–POMs) were characterized by X-ray power diffraction, transmission electron microscopy, Fourier transform infrared spectra, diffuse reflectance ultraviolet–visible spectra, thermogravimetry–differential scanning calorimetry analysis, and ³¹P magic angle spinning (MAS) nuclear magnetic resonance (NMR) analysis. The results showed that the ZrO₂–POMs materials have worm-like disordered mesoporous, and the primary structure of POMs is preserved after the formation of the composite materials. All the ZrO₂–POMs materials are catalytically active for the H₂O₂-mediated oxidation of cyclohexene with relatively high selectivity to allylic oxidation products. Moreover, these materials exhibit high stability against leaching of active species, and can be easily recycled without obvious loss of activity and selectivity. The existence of relatively strong interaction between the POM units and the ZrO₂ framework should play important role in fabricating the stable heterogeneous ZrO₂–POMs catalysts.

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1. Introduction

Catalytic oxidation of alkenes with environmentally benign and inexpensive oxidant, aqueous H₂O₂, is a highly desirable catalytic process for the synthesis of various important chemical intermediates, like epoxides, α,β -unsaturated ketones and alcohols [1,2]. Among various catalyst systems for alkene oxidation, polyoxometalates (POMs), including metal-substituted POMs, have received much attention for their hydrolytic and thermal stability, tunable acid and redox properties [3–5]. Recently, numerous attempts on developing supported POM heterogeneous catalysts have been made for the purpose to solve the separation and recycling problems of homogeneous POM catalysts [6–11]. However, most of the supported POM catalysts are not very stable during the liquid-phase oxidation course, and leaching of active POM species easily occurs since it is quite difficult to establish a stable linkage between the

solid support and the POM clusters with relatively large molecular size.

A few literature studies suggested that ZrO₂ is a suitable support for immobilizing POM clusters to obtain relatively active and stable heterogeneous ZrO₂ supported POMs (ZrO₂–POMs) catalysts for the application in some liquid-phase catalytic reactions and photocatalysis processes [12–16]. For examples, Patel et al. reported that ZrO₂ supported lacunary undecatungtophosphate, prepared by impregnating method, showed high activity and stability for the catalytic oxidation of styrene to benzaldehyde with H₂O₂ [15]. Hu and co-workers reported that zirconia-supported Ti-substituted Keggin-type POMs, prepared by hydrolysis of zirconium *n*-butoxide in the presence of Li₅PW₁₁TiO₄₀ or K₇PW₁₀Ti₂O₄₀ cluster, exhibited excellent catalytic activity and recyclability for the photo degradation of dye naphthol blue black [16]. It was believed that the relatively high stability of ZrO₂–POMs catalysts could be mainly assigned to the existence of a strong interaction between the POMs clusters and ZrO₂ support.

Recently, Armatas et al. developed a surfactant-assisted sol–gel copolymerization route to prepare ZrO₂-based 12-phosphomolybdic acid nanocomposite (ZrO₂–PMA) [17]. By using

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this method, ZrO₂–PMA materials with ordered mesopore structure and high loading of PMA could be obtained. It was found that the Keggin structure of PMA clusters is preserved intact into the mesoporous frameworks, forming a solid solution with the ZrO₂ species. More interesting, the ZrO₂–PMA materials show exceptional catalytic activity and stability (against leaching) in oxidation of alkenes using H₂O₂ as oxidant.

Here, we try to extend this surfactant-assisted sol–gel copolymerization strategy to prepare ZrO₂ supported phosphotungstate and Ti-substituted phosphotungstates, in which the POM ions include [PW₁₂O₄₀]³⁻, [PW₁₁TiO₄₀]⁵⁻, and [α,α-P₂W₂₀Ti₄O₇₈]¹⁰⁻. Previously, it was already known that these POMs are active homogeneous catalysts for some selective oxidation reactions [18–20]. In the present work, we found that mesoporous composites based on ZrO₂ and the POMs could be obtained by sol–gel copolymerization of the tetra-*n*-butyl-ammonium (TBA) salt of the POM, zirconium oxide dichloride and Pluronic P123 (triblock copolymer EO₂₀PO₇₀EO₂₀) surfactant. The resultant materials were characterized by a variety of means, and their catalytic performance were investigated for the liquid-phase oxidation of cyclohexene using H₂O₂ as oxidant.

2. Experimental

2.1. Materials

The following chemicals were purchased from commercial suppliers and were used without further purification: 12-phosphotungstic acid (H₃PW₁₂O₄₀), ZrOCl₂·8H₂O, Ti(SO₄)₂, Na₂WO₄·2H₂O, 85% H₃PO₄, glacial acetic acid, anhydrous ethyl alcohol, P123 surfactant, tetra-*n*-butyl-ammonium bromide (TBABr), cyclohexene, 30 wt% H₂O₂ aqueous solution, acetonitrile, and chlorobenzene.

The compounds of Na₇[PW₁₁O₃₉] and Na₉[A-PW₉O₃₄] were prepared following the literature procedures [21,22]. TBA₃[PW₁₂O₄₀], TBA₅[PW₁₁TiO₄₀] and TBA₁₀[α,α-P₂W₂₀Ti₄O₇₈] were prepared in the light of the method reported in literatures [18,23,24]. The FT-IR and ³¹P NMR spectra of these TBA salts of POMs (TBA-POMs) were in good agreement with the references [18–24].

2.2. Preparation of ZrO₂–POMs catalysts

ZrO₂ supported POMs composites were prepared by a surfactant-assisted sol–gel method similar to the literature procedure for preparing ZrO₂-based 12-phosphomolybdic acid nanocomposites [17]. Typically, 1.6 g (5.0 mmol) of zirconium oxide dichloride (ZrOCl₂·8H₂O) was added to the anhydrous ethanol solution (10 ml) of P123 (0.6 g). The mixture was stirred vigorously at room temperature for 2 h. After this, a clear solution of the TBA salts of phosphotungstate or Ti-substituted phosphotungstates in 3 ml of warm CH₃CN was added slowly into the above mixture solution under stirring. The obtained mixture was then heated to 70 °C, and homogeneous sol formed gradually under stirring. Transparent gel appeared when all the solvents were vaporized in open air at 70 °C for 24 h. White solid of the ZrO₂–POM precursor were obtained after drying the gel at 100 °C under vacuum for 10 h. The solid precursors were calcined at 250 °C for 4 h, and then at 350 °C for 6 h in air, to obtain three ZrO₂ supported POMs composites, designated as ZrO₂–PW₁₂O₄₀, ZrO₂–PW₁₁TiO₄₀ and ZrO₂–P₂W₂₀Ti₄O₇₈ respectively. The loading of POMs is around 0.05 mmol/g (based on P), which is determined by the feed ratio in the starting solutions. For comparative studies, mesoporous zirconia (*m*-ZrO₂) was also prepared by the same method, just without addition of the POM compound.

2.3. Characterization methods

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffraction (40 kV, 30 mA) using Ni-filtered Cu Kα radiation. N₂ adsorption/desorption isotherms were measured at –196 °C using a Micromeritics ASAP 2010N analyzer. The samples were evacuated at 150 °C for 24 h before measurements. Specific surface areas were calculated using the BET model. The pore size distributions were determined by the non-local density function theory (NLDFT) method based on the adsorption data. Transmission electron microscopy (TEM) images were taken with a H8100-IV electron microscope with an energy-dispersive X-ray spectroscopy (EDX) 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. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet Impact 410 spectrometer. The diffuse reflectance ultraviolet–visible spectra (UV–vis) were recorded on a Shimadzu 3600 instrument. The ³¹P MAS NMR spectra were recorded on a 400 MHz Bruker spectrometer. All ³¹P MAS NMR chemical shifts are referenced to the resonances of monoammonium phosphate (NH₄H₂PO₄) standard. A Netzsch Thermoanalyser STA 449F3 was used for simultaneous thermal analysis combining thermogravimetry and differential scanning calorimetry (TG–DSC) at a heating rate of 10 °C/min in air from 50 to 800 °C.

2.4. Reaction procedure for the catalytic oxidation of cyclohexene

The reaction was typically performed according to the following procedure: the catalysts (contained 0.01 mmol POMs), 30% H₂O₂ (5 mmol) aqueous solution, cyclohexene (2.5 mmol), chlorobenzene (2.5 mmol, as internal standard) and acetonitrile (3 ml, as solvent) were added in a round-bottomed flask with the oil bath equipment (catalyst:oxidant:cyclohexene = 1:500:250). The reaction mixture was vigorously stirred and refluxed at 60 °C. The products of the reaction were analyzed and quantified on a Shimadzu GC-8A gas chromatograph with HP-5 capillary column. Blank experiments showed that the oxidative reactions do not take place without catalyst.

The hot catalyst filtration tests were performed to verify the heterogeneous nature of catalytic systems. During the catalytic oxidation of cyclohexene, the solid catalyst was separated from the reaction mixture by filtration after 1.5 h of the reaction and the filtrate obtained was continuously stirred under the same reaction conditions. The recyclability of the catalyst was also investigated by consecutive reusing the catalyst. In each catalytic cycle, the catalyst was recovered by filtration, washed with fresh acetonitrile several times and dried at 100 °C under vacuum.

3. Results and discussion

3.1. Characterization of the materials

The low-angle XRD patterns of ZrO₂–PW₁₂O₄₀, ZrO₂–PW₁₁TiO₄₀, ZrO₂–P₂W₂₀Ti₄O₇₈ and *m*-ZrO₂ are shown in Fig. 1A. A weak and broad reflection in low-angle range could be observed for all tested materials, indicating that these materials contain disordered mesopores [25,26]. The wide-angle XRD patterns of the ZrO₂–POMs composites and *m*-ZrO₂ are presented in Fig. 1B. The two broad peaks at ca. 25 and 55° are attributed to the amorphous ZrO₂ frameworks. The absence of diffraction peaks associated with the crystalline phase of POMs suggests that the POMs clusters should be highly dispersed in the ZrO₂–POM composites.

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