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Short Communication

Phosphotungstic acid containing ionic liquid immobilized on magnetic mesoporous silica rod catalyst for the oxidation of dibenzothiophene with H_2O_2

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ABSTRACT

We have synthesized phosphotungstic acid (PA) containing ionic liquid 1-methyl-3-[(triethoxysilyl) propyl] imidazolium chloride (IL) immobilized on magnetic mesoporous silica rod to catalyze dibenzothiophene (DBT) for producing dibenzothiophene monoxide (DBTO) and dibenzothiophene dioxide ($DBTO_2$). The effects of reaction time and reaction temperature on the conversion of DBT were studied. It was demonstrated that the catalyst was extremely effective for the reaction and the catalyst could be easily separated from the reaction solution by applying an external magnetic field and recycled several times.

1. Introduction

Ultra-deep desulfurization of fuel oil has become an environmentally urgent subject worldwide [1,2]. The oxidative desulfurization is considered to be one of the promising new methods for super deep desulfurization of fuel oil [3]. Compared with traditional hydrodesulfurization method, oxidative desulfurization is more efficient for the elimination of dibenzothiophene (DBT) [4]. Indeed, oxidative desulfurization can be carried out at room temperature and under atmospheric pressure, which allows sulfones removed by conventional separation operations (e.g. distillation, solvent extraction, adsorption and so on) as their properties are significantly different from those of the hydrocarbons that comprise most of the fuel oils. We can find a number of studies on oxidative desulfurization method [5–11]. However, the main obstacles to the industrial application of the oxidative desulfurization are 1) the low-oxidation activity and long reaction time of the DBT, and 2) the difficulties in separation and recovery of the catalyst after the reactions [12–14].

Recently, phosphotungstic acid ($H_3PW_{12}O_{40}$) is of increasing interest in the oxidation of DBT and good results were obtained [15,16]. The proposed mechanism of oxidation of DBT by phosphotungstic acid with hydrogen peroxide as oxygen source has been reported [17,18]. In previous studies, hydrogen peroxide was found to be effective in the oxidation of organic sulfur compounds contained in fuels and it appeared as a promising oxidizing agent for the industrial desulfurization of gasolines and diesel oils [19]. Separation and recycling of the catalysts are essential steps in catalytic technology and frequently affect the overall process economy. Although the homogeneous catalysts are remarkably efficient, they share a universal handicap: separation and reuse of the catalyst are extremely difficult. For these reasons, developing efficient heterogeneous catalysts is quite necessary and immobilization of heterogeneous catalysts has therefore attracted much attention. A possible method is immobilizing catalytically active species in the surface of magnetic particles which can be separated and recovered from the reaction system by applying an appropriate magnetic field [20–23]. In particular, magnetic particles in the nanometer range with superparamagnetic and have therefore exceptional properties, are suitable both for catalytic reactions in solution and for magnetic recovery [24].

In the present work, we synthesized phosphotungstic acid containing ionic liquid (IL) 1-methyl-3-[(triethoxysilyl)propyl] imidazolium chloride immobilized on magnetic mesoporous silica rod to catalyze DBT for producing DBTO and $DBTO_2$ with hydrogen peroxide under mild conditions. Meanwhile, it was found that the catalyst showed a high reaction activity for the DBT. The catalyst can be readily separated from the reaction solution by applying an external magnetic field and recycled several times.

2. Experimental section

2.1. Materials

1-Methylimidazol (99%), hydrogen peroxide (30 wt.%),ammonia solution (25 wt.%), tetraethoxysilane (TEOS), phosphotungstic acid

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(PA), and cetyltrimethylammoniun bromide (CTAB), were all analytical grade reagents purchased from the Tianjin Institute of Guangfu Fine Chemical. DBT was obtained from Adamas Reagent Co., Ltd.

2.2. Synthesis of magnetite nanoparticles (MN)

Magnetite (Fe_3O_4) particles were prepared in a co-precipitation method. $FeCl_3 \cdot H_2O$ (4.8 g, 17.7 mmol), $FeCl_2 \cdot 4H_2O$ (2.0 g, 10.2 mmol) and 10 mL oleic acid were dissolved in 30 mL distilled water under argon with vigorous stirring at 363 K. The pH value of the solution was adjusted to 9 by ammonia solution. After 2.5 h, the black precipitate was collected with a permanent magnet. The sediment was MN (10 nm) capped with oleic acid and was obtained by using a magnet.

2.3. Synthesis of γ-Fe_2O_3 embedded with magnetic mesoporous silica rod (MMSR)

The preparation route of γ-Fe_2O_3 embedded with magnetic mesoporous silica rod (MMSR) was according to reference [25]. Briefly, 100 mg of oleic acid stabilized monodisperse MN dispersed in 10.0 mL of chloroform was added to 50 mL of aqueous solution containing 2.0 g of CTAB (4.9 mmol). The resulting solution was stirred for several hours; a homogeneous oil-in-water microemulsion was obtained. Using a rotary evaporator induced evaporation of the chloroform of the solution, which generated 50 mL aqueous phase dispersed nanoparticles. Then 50 mL of the resulting aqueous solution was diluted with 500 mL of water. Then 20 mL of ethyl acetate (203.0 mmol), 12 mL of ammonia solution (93.4 mmol), and 2.0 mL of TEOS (8.92 mmol) were successively added to the diluted aqueous solution containing the MN. The resulting mixture was stirred for 5 h at room temperature, then the suspension was separated from the solution by an external magnet, washed with distilled water and ethanol for several times and dried at 50 °C. Finally, the γ-Fe_2O_3 nanoparticles embedded in the mesoporous silica rod (MMSR) obtained by the calcination at 550 °C for 6 h.

2.4. Synthesis of ionic liquids immobilized on magnetic (γ-Fe_2O_3) mesoporous silica rod (MMSR-IL)

A total of 0.5 g MMSR and (3-chloropropyl) triethoxysilane (4.5 mmol) was dissolved in toluene (100 mL), and the solution was refluxed at 383 K for 24 h under N_2 atmosphere, Then 1-methylimidazol (7.97 mmol) added into the above solution and the solution was refluxed at 383 K for 8 h under N_2 atmosphere [26]. The suspension was separated from the solution by an external magnet, washed several times with distilled water and ethanol respectively, then oven-dried at 50 °C.

2.5. Synthesis of phosphotungstic acid containing ionic liquid immobilized on magnetic mesoporous silica rod catalyst (MMSR-IL-PA)

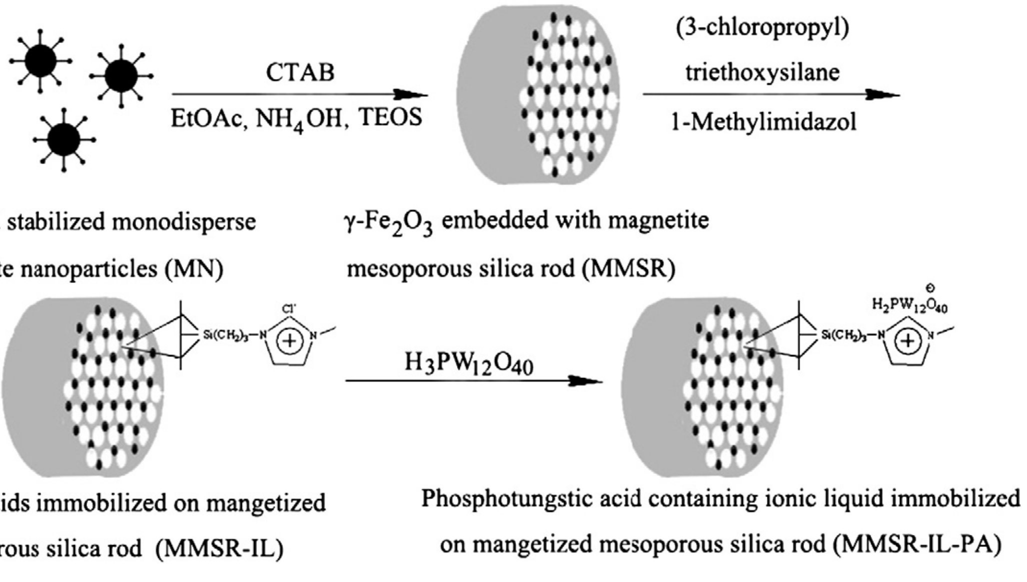
A total of 0.5 g MMSR-IL and 1.0 g PA were dissolved in THF (50 mL), and the solution was refluxed at 333 K for 10 h under N_2 atmosphere. The solid was then filtered and washed with water and acetone thoroughly and dried under vacuum at 60 °C overnight (Scheme 1). The resulting reddish brown powder was denoted as MMSR-IL-PA. The weight percentages of W and Fe in the catalyst measured by AAS analysis were 14.62 wt.% and 7.31 wt.%, respectively.

2.6. Characterization

The morphology and chemical composition of the catalyst were characterized by Tecnai G2 F30 transmission electron microscopy (TEM) equipped with an energy dispersive X-ray (EDX) detector. W and Fe contents of the catalyst were measured by atomic absorption spectroscopic (AAS). The low-temperature N_2 adsorption–desorption experiments were carried out using a Tristar II 3020. The pore diameter distributions were calculated from desorption branches using the BJH (Barrett–Joyner–Halenda) methods, and the surface areas were calculated using the BET (Brunauer–Emmett–Teller) method based on the desorption isotherms. FT-IR spectra were recorded on a Nicolet NEXUS 670. The magnetic measurements of samples were investigated with a vibrating sample magnetometer (Lake Shore 7304) at room temperature.

2.7. Catalytic reaction

The catalytic reactions were carried out in a 10 mL flask equipped with a reflux condenser. The oxidation of DBT was carried out as follows: catalyst (25 mg), acetonitrile (5 mL), DBT (0.5 mmol), and H_2O_2 (30% aq., 5 mmol) were charged in the reaction flask. The reaction was carried out at 303 K, 313 K, and 323 K. After the reaction was finished, the catalyst was separated by adding a magnet. The product was analyzed by GC-MS (TRACE DSQ) and HPLC (Waters 600).



Scheme 1. Synthesis of phosphotungstic acid containing ionic liquid immobilized on magnetic mesoporous silica rod (MMSR-IL-PA).