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Synthesis and characterization of mesoporous phosphotungstic acid/TiO_2 nanocomposite as a novel oxidative desulfurization catalyst

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ABSTRACT

A series of mesoporous phosphotungstic acid/TiO_2 (HPW/TiO_2) nanocomposites with various HPW contents have been synthesized by evaporation-induced self-assembly method. These nanocomposites were used as catalysts for oxidative desulfurization of model fuel, which was composed of dibenzothiophene (DBT) and hydrocarbon, and used H_2O_2 as oxidant. These catalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption–desorption isotherm, transmission electron microscopy (TEM), FTIR and UV–vis. Characterization results suggest that these mesoporous HPW/TiO_2 possessed relatively uniform channel-like pores with Barrett–Joyner–Halenda (BJH) pore size of about 4 nm. The Brunauer–Emmett–Teller (BET) surface of the mesoporous HPW/TiO_2 slightly increases with the increase of HPW content and reach to a peak value of 176 m^2/g and 0.25 cm^3/g when the HPW content is 30 wt%. Keggin-type heteropolyacids (HPAs) has been encapsulated into anatase TiO_2 framework and the average size of TiO_2 nanoparticles is 8 nm. Catalytic oxidation results show that the catalysts are very active in refractory bulky molecule organosulfur compounds in fuel oil. The oxidative removal of DBT increases as the HPW content increases. The mesoporous HPW/TiO_2 also shows high selectivity for DBT oxidation in the DBT–petroleum ether–benzene system. The selective desulfurization ratio reach to 95.2% with mesoporous HPW/TiO_2 (20 wt%) catalyst under the reaction condition of 333 K, 2 h. In addition, the mesoporous HPW/TiO_2 catalyst shows excellent reusing ability, which makes it a promising catalyst in oxidative desulfurization process.

1. Introduction

Deep desulfurization of transportation fuels has become an important research subject due to the increasingly stringent regulations and fuel specifications in many countries for environmental protection purpose [1]. Conventional hydrodesulfurization (HDS) process is difficult to remove alkylsubstituted dibenzothiophenes like 4,6-dimethyldibenzothiophene, which are refractive to HDS due to steric hindrance. In order to produce ultralow sulfur diesel fuel with HDS process, higher temperature, higher pressure, larger reactor volume, and more active catalysts are required [2]. In addition, the severe conditions lead to negative effects, such as the decrease of catalyst life, higher hydrogen consumption, and higher yield losses resulting in higher costs. Therefore, alternative desulfurization techniques have been investigated widely, among which oxidative desulfurization (ODS) is considered to be one of the promising new methods for super deep desulfurization of fuel oil [3]. In the ODS process, the refractory dibenzothiophene (DBT) and 4,6-dimethydibenzothiophene (4,6-DMDBT) are oxidized to their corresponding sulfones under mild conditions, which are subsequently removed by extraction, adsorption, distillation, or decomposition [4–8].

Various oxidants have been used in ODS, such as NO_2 [9], O_3 [10], H_2O_2 [2], *tert*-butyl hydroperoxide [11], molecular oxygen [12], K_2FeO_4 [13] and solid oxidizing agents [14]. Among these oxidants, H_2O_2 is mostly chosen as an oxidant, only producing water as a byproduct. Peracids produced in situ from organic acids catalysts and H_2O_2 are reported to be very effective for rapid oxidation of sulfur compounds in fuel oils under mild conditions. Heteropolyacid catalysts in H_2O_2 oxidation system have also exhibited high catalytic activity for the oxidation of BTs and DBTs [2,15,16]. However, the main obstacles for these catalysts to the industrial application of the process at present are the difficulties in separation and recovery. Therefore, the use of solid catalysts in ODS processes has been developed in recent years. Many types of solid catalysts have been attempted, such as Ti molecular sieves [17,18], WOx/ZrO_2 [19] and vanadium oxide [20]. However, the selectivity of these catalysts for sulfides in fuels is not high, and some components of the fuel are also oxidized. Therefore, the solid catalysts with high selectivity is highly desirable in heterogeneous ODS system.

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In the current research, an efficient heterogeneous ODS catalyst mesoporous HPW/TiO_2 nanocomposite was obtained by incorporating tungstophosphoric acid into mesoporous titania with evaporation-induced self-assembly method. The nanocomposites were characterized by various analytical and spectroscopic techniques such as X-ray diffraction (XRD), nitrogen adsorption–desorption isotherm, transmission electron microscopy (TEM), FTIR and UV–vis. The catalytic activity and selectivity of the catalysts were systematically evaluated in the desulfurization of model fuel.

2. Experimental

2.1. Synthesis of mesoporous HPW/TiO_2

The mesoporous HPW/TiO_2 was prepared by using $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Sigma) as a structure-directing agent, and using tetrabutyl titanate ($Ti(C_4H_9O)_4$, Sigma–Aldrich) as the titania precursor. In a typical synthesis, 3.40 g $Ti(C_4H_9O)_4$ and 2.40 g acetic acid were dissolved in 20 mL ethanol with stirring, and then an amount of 12-phosphotungstic acid was added slowly. The mixture was adjusted to pH 1–2 by adding hydrochloric acid (HCl, 36%) to form sol A. 1.20 g P123 was dissolved in 15 mL ethanol to prepare solution B. After the sol A was magnetically stirred for about 2 h at room temperature, the solution B was filled slowly and magnetically stirred for another 2 h. The resulting sol solution with molar composition 1 $Ti(C_4H_9O)_4$:0.02 P123:4HOAc:60 C_2H_5OH:xHPW was poured into Petri dish and maintained for 2 days at 313 K and then was transferred into a 333 K oven and aged for another 2 days. As-synthesized mesostructured composites were calcined at 673 K in air for 10 h (ramp rate 1 °C/min) to obtain mesoporous HPW/TiO_2 with 10–40 wt% HPW concentration.

2.2. Characterization of the catalysts

The obtained mesoporous HPW/TiO_2 samples were first ground into fine powder for characterization. XRD patterns were recorded on a Rigaku D/MAX-RB diffractometer with a Cu Kα radiation operating at 40 kV, 50 mA. TEM images were taken with a FEI TECNAI G2 20 electron microscope operating at 200 kV. The TEM samples were prepared by dispersing the particles in alcohol, which then were deposited onto a Cu grid and left drying in air. Nitrogen adsorption–desorption data were measured with a Quantachrome Autosorb-1 analyzer at 77 K. The samples were outgassed at 473 K for 6 h prior to the measurements. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The pore size distribution was derived from the adsorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method. FTIR spectra (1400–600 cm^{-1}) were recorded on a Digilab-FTS60 spectrometer. The samples were pressed with KBr in the ratio 1:150. Diffuse reflectance UV–vis spectra were measured with a spectrometer of PE Lambda 35 equipped with the integrating sphere using $BaSO_4$ as the reference. The HPW content in solid samples was determined by the results of inductively coupled plasma analysis (ICP, Perkin-Elmer 3300DV).

2.3. Desulfurization of model fuel

The experiments of oxidative desulfurization were performed in a 150 mL flask equipped with stirrer and condenser. Two kinds of model fuels with sulfur content of 500 μg/g were obtained by dissolving DBT in petroleum ether, and petroleum ether + benzene (with volume ratio of 3:1), respectively. In the typical run, the water bath was first heated and stabilized to a certain temperature. 0.2 g of catalyst was added to a mixture of 20 mL of model fuels and 20 mL of acetonitrile. Then a certain amount of 30% aqueous H_2O_2 was added to start the reaction. The amount of oxidant was expressed as O/S mole ratio. The resulting mixture was stirred for 2 h at the reaction temperature and analyzed periodically. The catalyst was centrifuged off, the oil phase and solvent phase were respectively analyzed by WK-2C total sulfur analyzer and a gas chromatograph equipped with a pulsed flame photometric detector (PFPD, agilent-6890, capillary column HP-5). The catalyst was washed with toluene for several times, heated at 573 K for 4 h and reused in the next run.

3. Results and discussion

3.1. XRD patterns

Fig. 1 shows small-angle and wide-angle powder XRD patterns of mesoporous HPW/TiO_2 samples with different HPW contents. As is observed in Fig. 1A, the samples with HPW content of 10–30 wt% present well-resolved diffraction peak at $2\theta = 1–3°$ typical for mesostructured materials [21]. Only one XRD peak in the low angle range indicates that no long-range order pore arrangement exists in our samples. When HPW content in the HPW/TiO_2 composite increased to 40 wt%, significant shrinkage of the diffraction peak of above 50% is observed. At the same time, the diffractions slightly shift to the high angles, suggesting the destruction of the ordered mesostructure. The wide-angle XRD patterns of the

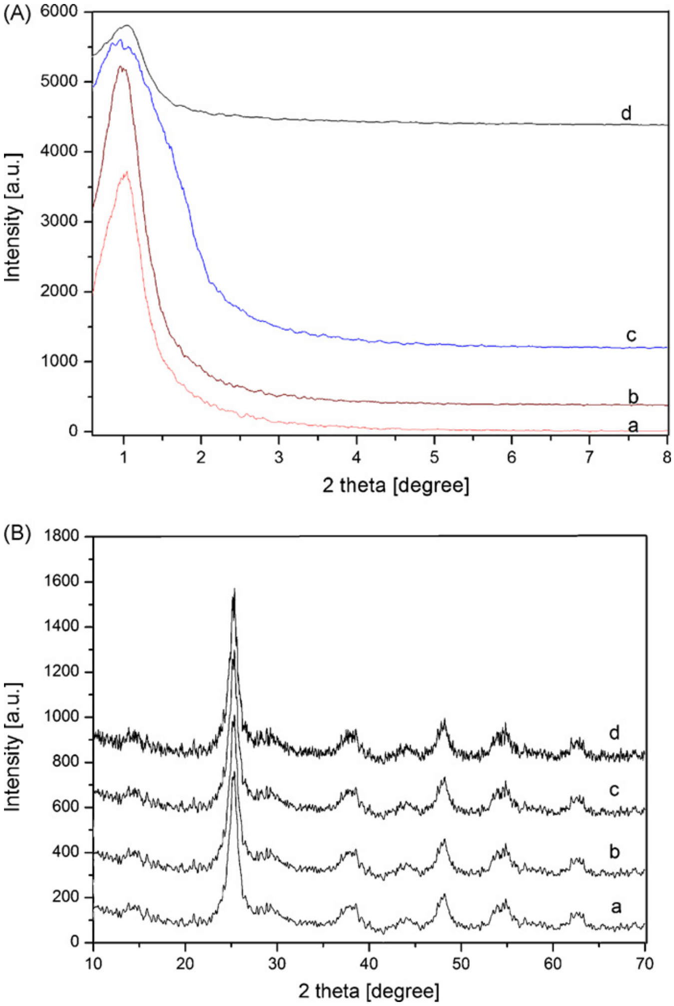

Fig. 1. Small-angle (A) and wide-angle (B) XRD patterns of mesoporous HPW/TiO_2 samples: (a) 10 wt%, (b) 20 wt%, (c) 30 wt% and (d) 40 wt%.