Applied Catalysis A: General 526 (2016) 147–154

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Electrospinning synthesis of $H_3PW_{12}O_{40}/TiO_2$ nanofiber catalytic materials and their application in ultra-deep desulfurization

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ARTICLE INFO

Article history:
Received 6 June 2016
Received in revised form 15 August 2016
Accepted 24 August 2016
Available online 24 August 2016

Keywords:
Electrospinning
Phosphotungstic acid
Titanium dioxide
Nanofiber
Desulfurization

ABSTRACT

$H_3PW_{12}O_{40}/TiO_2$ (abbreviated PW_{12}/TiO_2) nanofibers catalysts have been successfully prepared *via* calcinating off the respective electrospun PVP/[PW_{12} + $Ti(OC_4H_9)_4$] composite nanofibers for the first time and they show ultra-deep desulfurization catalytic performance in mild conditions. PW_{12}/TiO_2 nanofibers consist of anatase phase TiO_2 and Keggin structure PW_{12}, the diameter of which is approximately 100 nm. Compared with PW_{12}/TiO_2 nanoparticles, 40 wt.% PW_{12}/TiO_2 nanofibers (the weight percentage of PW_{12} loading on TiO_2 nanofibers was 40%) exhibited the higher catalytic activity under the same conditions. DBT could be removed completely within 30 min at 70 °C using 0.02 g 40 wt.% PW_{12}/TiO_2 nanofibers as catalysts, when ionic liquid (IL) [Bmim]PF_6 was as extraction agent. Additionally, sulfur removal of different substrates decreased in the following orders: DBT > BT > 4,6-DMDBT under the same conditions. Even after 5-times recycling, the catalytic activity of 40 wt.% PW_{12}/TiO_2 nanofibers was not significant decreased. As a total result, these novel PW_{12}/TiO_2 nanofibers can be used to deeply desulfurize in the industry.

1. Introduction

Recently, the problems of environmental and energy have become the two major issues for human society. Especially, the combustion of sulfur-containing fuels emits sulfur oxides (SO_X), which exert a detrimental impact on human health, environment and economy. In order to reduce the emissions of SO_X from fuels, deep desulfurization methods are urgently sought for the production of clean fuels. In present, the dominant desulfurization methods include hydride-sulfurization (HDS) [1], oxidative desulfurization (ODS) [2], extraction desulfurization (EDS) [3], bio-desulfurization [4], and adsorption desulfurization [5–7]. However, each of these methods still has respective disadvantages. For example, the severe operation conditions at high temperatures (300–400 °C) and pressures (20–100 atm of H_2) are required in HDS. In addition, many organic sulfides including the dibenzothiophene (DBT), benzothiophene (BT), 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) and their derivatives are difficult to remove by HDS [8–10]. Moreover, H_2S produced in HDS system can result in secondary pollution. This is also true for the EDS method using organic extraction agent [3]. As a simple, direct and economic deep desulfurization method, ODS is attracting increasing attentions. The ODS system commonly contains two steps including the oxidization sulfur compounds to sulfoxides or sulfones and their removal by appropriate extractions or adsorbents. A great efforts have recently been paid to simplify the ODS processes [2,11,12]. Fortunately, employment of ionic liquids (IL) as the extractions or adsorbents in the ODS system led to the development of extraction catalytic oxidation desulfurization system (ECODS), as a green and effective one-pot deep desulfurization method. With the employment of conventional IL as extractants and H_2O_2 as an oxidant, clean-oil (concentration of sulfur compounds <10 ppm) was obtained [13–15]. In addition, an IL emulsion catalytic oxidation process was proposed by Li group for ultra-deep desulfurization [16,17]. At the end of this section, it is worth noting that a deep sulfur removal was achieved with the optimized $H_2O_2/DBT/LnW_{10}$ molar ratio at room temperature using IL as extraction in the ECODS system according to Song and coworkers [18–22].

Among catalysts, polyoxometalates (POM) known as the transition metal (eg. W, Mo, V, Nb, Ta, and so on) oxygen clusters, present high catalysis property due to their tunable acidity and redox properties, inherent resistance to oxidative decomposition, high thermal stability, and impressive sensitivity to light and electricity [23,24]. Keggin structure POMs with their unique stability [25] has been most well studied. Yan et al. revealed that POMs as Lewis acidic sites are very important for removing sulfur oxidanrs [26].

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http://dx.doi.org/10.1016/j.apcata.2016.08.021

However, POMs in the homogeneous catalytic reaction systems are not easy to be separated from the reaction system for recycling since they are soluble in aqueous solution associated with their crystalline feature and high lattice energy [23]. For the purpose of solving these problems, heterogeneous catalysts are preferred because of the advantages of facile catalyst/product separation [24]. Many endeavors have been directed to create "supported POM materials" using solid supports, such as SiO_2 [22,27–29], activated carbon [30], MCM-41 [31], SBA-15 [32], TiO_2 [33,34] and metal-organic framework [35]. Among these solid supports, anatase TiO_2 has been proved to be an excellent catalyst in ODS [36]. Therefore, combination with POMs and anatase TiO_2 could not only solve the recycling problem of POMs but also improve the catalytic activity [33,37]. In present, the morphology of these catalysts is mainly focus on nanoparticles, while the study of nanofibers catalysts is few. In comparison with particles, nanofibers have obvious advantages owing to their anisotropy, large length-diameter ratio, unique optical, electrical and magnetic properties [38,39]. It is noteworthy that inorganic superfine nanofibers have been simply prepared by electrospinning technology using polymer/inorganic composite as the precursor [40,41], with the morphology easily tuned by adjusting experimental parameters, such as the precursor solution viscosity, the structure of spinneret, voltage and the distance between the spinneret and the collector [42–44].

Herein, PW_{12}/TiO_2 nanofibers were prepared by calcinating the electrospun PVP/[PW_{12} + $Ti(OC_4H_9)_4$] composite nanofibers for the first time. Their morphology and structure have been investigated using field emission scanning electron microscopy (FESEM), X-ray diffractometry (XRD), and energy dispersion spectroscopy (EDS). More importantly, the deep desulfurization performances of PW_{12}/TiO_2 nanofibers for fuel oil in ECODS were systematically investigated, indicating the significant effects of the amount of PW_{12}-loaded, the dosage of catalysts, the value of H_2O_2/DBT molar ratio (O/S), the substrates feature, and the morphology of catalyst and reaction temperature on the catalysis performance. In addition, the desulfurization mechanism of PW_{12}/TiO_2 nanofibers was also proposed.

2. Experimental

2.1. Chemicals and materials

Tetrabutyl titanate ($Ti(OC_4H_9)_4$, TBOT, 99%, Tianjin GuangFu Fine Chemical Research Institute), *N,N*-dimethylformamide (DMF, AR, Tianjin Tiantai Chemical Co. Ltd.), polyvinyl pyrrolidone (PVP, Mw = 90000, Aladdin), acetyl acetone (Xilong Chemical Co. Ltd.), acetic acid (Beijing Chemical Works), hexadecyl trimethyl ammonium Bromide (CTAB, Energy Chemical), dibenzothiophene (DBT, China Pingmei Shenma Energy & Chemical Group Co., Ltd.), benzothiophene (BT, China Pingmei Shenma Energy & Chemical Group Co., Ltd.), 4,6-dimethyl-dibenzothiophene (4,6-DMDBT, China Pingmei Shenma Energy & Chemical Group Co., Ltd.), hydrogen peroxide (H_2O_2, 30 wt.%, Beijing Chemical Works), *n*-octane (Tianjin GuangFu Fine Chemical Research Institute), and biphenyl (Sinopharm Chemical Reagent Co., Ltd) were directly used as received without further purification. 12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$, PW_{12}) was synthesised according to reported method [45].

2.2. Preparation of TiO_2/PW_{12} nanofibers

In the spinning solution, DMF, acetic acid and acetylacetone were used as solvent. In the typical procedure of preparation of spinning solution for 40 wt.% PW_{12}/TiO_2, TBOT (1.83 g) were dissolved in DMF (10.00 mL), acetic acid (1.00 mL) and acetylacetone (0.20 mL), which was marked solution A. Solution B was prepared by dissolving $H_3PW_{12}O_{40}$ (0.17 g, marked as PW_{12}) and CTAB (0.10 g) in DMF (5.00 mL), and then solution B was poured into solution A. After stirring 10 min, PVP (2.00 g) were added into the above solution. In this spinning solution, the mass ratios of salt (TBOT, PW_{12} and CTAB), PVP and solvent (DMF, acetic acid and acetylacetone) were equal to 10:10:80. The solution was magnetically stirred to form a homogeneous spinning solution.

PVP/[PW_{12} + $Ti(OC_4H_9)_4$] composite nanofibers were synthesised via electrospinning technology at room temperature. During the process of electrospinning, the above spinning solution was loaded into a plastic syringe with a spinneret, and the angle between spinneret and horizon was fixed to 10° for preparing nanofibers. A flat iron net was used as collector putting about 18 cm away from the spinneret. The voltage of direct current (DC) adjusted to 16 kV was applied between the spinneret and the collector to generate a stable continuous PVP-based composite nanofibers (PVP/[PW_{12} + $Ti(OC_4H_9)_4$] composite nanofibers). The as-prepared PVP/[PW_{12} + $Ti(OC_4H_9)_4$] composite nanofibers were calcined at 500 °C for 4 h with a heating rate of 1 °C/min in air. The temperature was then decreased to 100 °C at a rate of 1 °C/min. Finally, the sample was cooled down to room temperature naturally, and 40 wt.% PW_{12}/TiO_2 nanofibers were obtained. A series of x wt.% PW_{12}/TiO_2 (x = 20, 60, 80) nanofibers were prepared by the same procedure except for different mass rates between PW_{12} and TiO_2. The actual amount of TBOT, PW_{12}, CTAB, PVP, DMF, acetic acid and acetylacetone for x wt.% PW_{12}/TiO_2 nanofibers were shown in Table S1. The preparation process of pure TiO_2 nanofibers and 40 wt.% PW_{12}/TiO_2 nanoparticles was shown in Supporting information.

2.3. Catalytic experiments

In a typical run, 5 mL of oil sample with 500 ppm DBT (BT or 4,6-DMDBT), *n*-octane as solvent and biphenyl as the internal standard substance was put into two-necked round bottom flask, which immersed in a water bath with a temperature-controlling system and stirred vigorously at 70 °C. After 15 min, O/S of 8:1, 0.02 g catalysts and 1 mL IL [Bmim]PF_6 were added in above solution. The upper layer of oil was periodically withdrawn and analysed by gas chromatography (GC). The other catalytic experiments was operated by the same process besides different tempretuers, O/S and amount of catalyst. The temperature was fixed at 50, 60 and 80 °C, respectively. The molar ratio values of H_2O_2 and sulfur (O/S) was 2:1, 4:1 and 10:1, and amount of catalyst was 0.01 g and 0.03 g, respectively.

2.4. Techniques

The infrared (FT-IR) absorption spectra were measured on a Mattson Alpha-Centauri Fourier transform infrared spectrometer in the range of 4000–400 cm^{-1} using KBr pelles with the number of scan 64 and the resolution 4 cm^{-1}. XRD analysis was performed using a Rigaku D/max-RA XRD diffractometer in the 2θ range from 10° to 80° with Cu Kα radiation ($\lambda = 0.15418$ nm). The morphology of the catalyst was investigated by Hitachi SU8010 field emission scanning electron microscope (FE-SEM). The purities of the products were examined by OXFORD ISIS-300 energy dispersive spectrometer and elemental mapping. Transmission electron microscope (TEM) analysis was carried out using a JEM-2010 transmission electron microscope under a working voltage of 200 kV and images were acquired digitally on Gatan multiople CCD camera. The specific surface areas of the nanostructures were measured by specific surface area and pore size analyzer (V-Sorb 2800P) after the samples were outgassed under vacuum at 120 °C for 10 h. GC analysis was measured on Agilent 7820A-GC System using DB-5 chromatographic column with 30 m × 0.32 mm × 0.25 μm. The