



Editor's choice paper

Facile synthesis of amphiphilic polyoxometalate-based ionic liquid supported silica induced efficient performance in oxidative desulfurization



Meng Li^{a,b}, Ming Zhang^b, Aimin Wei^a, Wenshuai Zhu^{a,*}, Suhang Xun^a, Yanan Li^a, Hongping Li^a, Huaming Li^{a,b,*}

^a School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China

^b Institute for Energy Research, Jiangsu University, Zhenjiang 212013, PR China

ARTICLE INFO

Article history:

Received 3 February 2015

Received in revised form 5 May 2015

Accepted 7 May 2015

Available online 8 May 2015

Keywords:

Amphiphilic hybrid materials

Polyoxometalates

Ionic liquids

Desulfurization

ABSTRACT

As strict regulations of fuel specifications implemented, oxidative desulfurization process (ODS) is considered as one of the promising technologies to achieve deep desulfurization under mild conditions. Herein, amphiphilic polyoxometalate-based supported silica [C₄mim]₃PW₁₂O₄₀/SiO₂ was successfully synthesized by a facile hydrothermal process and employed in ODS process. The composition and structure of obtained hybrid samples were characterized by means of FT-IR, XPS, Raman, ³¹P MAS NMR, UV-vis, wide-angle XRD, N₂ adsorption-desorption and SEM. The experimental results indicated that the as-synthesized materials maintained the integrity of architecture of polyoxometalate-based ionic liquids (POM-based ILs), which were finely dispersed into the silica matrix. Besides, the sample [C₄mim]₃PW₁₂O₄₀/SiO₂ possessed moderate hydrophilic-hydrophobic balanced surface leading to higher sulfur removal. Moreover, the effects of the amount of catalyst, H₂O₂/DBT molar ratio, temperature, types of sulfur-containing substrate on the sulfur removal were also investigated in detail. Under optimal conditions, dibenzothiophene (DBT) could be completely removed in 30 min.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Stricter legislations on the sulfur content in fuels have been enacted in order to prevent the environmental pollution from the emission of SO_x. In US and Europe, the sulfur content in fuels should be less than 15 ppmw and 10 ppmw since 2006 and 2009, respectively. To date, hydrodesulfurization (HDS) has been widely used to remove the sulfur compounds, because thiols, sulfides, and disulfides can be effectively removed in this process. However, this approach is not efficient on removing aromatic sulfur-containing compounds such as thiophene and its derivatives due to steric hindrance [1–4]. To achieve deep desulfurization target, high temperature (300–400 °C), high hydrogen pressure (2–10 MPa), and noble catalysts are required. Under this situation, other alternative desulfurization strategies under relatively mild conditions, e.g. extraction [5,6], adsorption [7–11], oxidation [12–18], biodesulfurization [19,20], and photocatalytic desulfurization [21,22] have been extensively investigated. At present, oxidative desulfurization

(ODS) is one of the most promising approaches in which aromatic sulfur compounds are conveniently oxidized its corresponding sulfones, subsequently decomposed the formed sulfone and recover biphenyl [23] or extracted with proper solvents [24].

Ionic liquids (ILs) as an immense family of molten salts, have been attracted wide attention as solvents [25,26], extractants [27,28], templates [29,30] and precursors [31,32] due to their unique physicochemical properties. Bosmann firstly developed an extractive desulfurization process using conventional ILs with different cations and anions as extractants [33]. However, it is difficult to reach deep desulfurization with simple extraction process. Hence, Lo et al. reported a novel approach combining the oxidation with the extraction by ILs to achieve deep desulfurization. This process is much more efficient compared to a simple extraction by ILs [34]. In the past years, various ILs have been developed [35–37]. Our group has engaged in developing specific ILs and employing them in extractive catalytic oxidative desulfurization (ECODS) [38,39]. Though these catalysts displayed good activity, the dosage of ILs in this process was relatively large. Moreover, the recovery of ILs after reaction was difficult. To solve these problems, many endeavours have been directed to create “supported ionic liquid materials” using solid supports, such as SiO₂ [40,41], TiO₂ [42], mesoporous

* Corresponding authors. Tel.: +86 511 88791800; fax: +86 511 88791708.
E-mail addresses: zhuws@ujs.edu.cn (W. Zhu), lihm@ujs.edu.cn (H. Li).

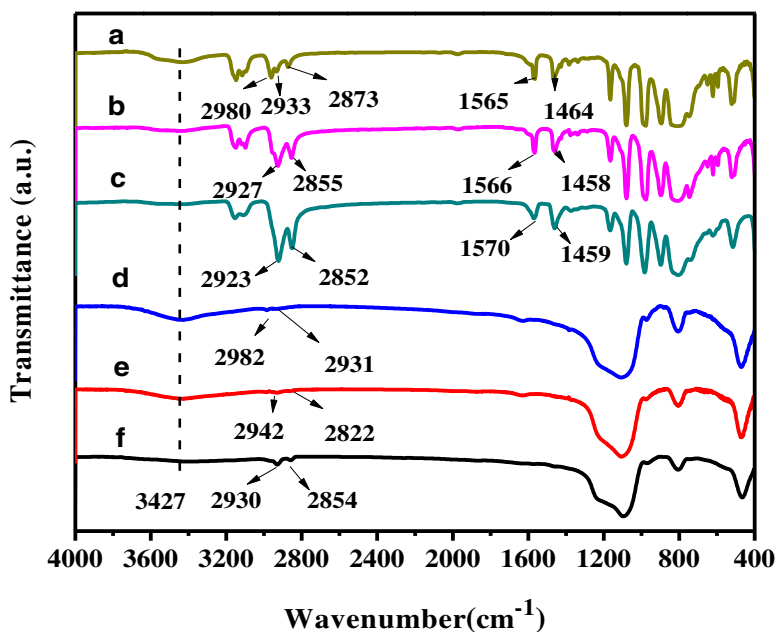


Fig. 1. FT-IR spectra of various samples (a) $[\text{C}_4\text{mim}]_3\text{PW}_{12}\text{O}_{40}$; (b) $[\text{C}_8\text{mim}]_3\text{PW}_{12}\text{O}_{40}$; (c) $[\text{C}_{16}\text{mim}]_3\text{PW}_{12}\text{O}_{40}$; (d) $[\text{C}_4\text{mim}]_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$; (e) $[\text{C}_8\text{mim}]_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$; (f) $[\text{C}_{16}\text{mim}]_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$.

materials [43], CNT [44] and MOF [31]. Noteworthy, these hybrid catalysts have been applied in various reactions with an ample prospect.

Polyoxometalates (POMs) are a family of transition metal-oxide clusters with unique structure diversity, specific physical properties, controllable redox and acidic properties. For these advantages, POMs have attracted wide interests in a variety of organic transformations, such as epoxidation of alkenes [45], selective oxidation of alcohols [46], esterification of acid with alcohol [47] and oxidation of sulfides [48]. However, POM clusters were hardly dispersed in the common organic solvents due to the crystalline feature and high lattice energy [49]. To confront this limitation, a series of POM-anions tethered with inorganic/organic functional groups have been developed, which obtained good catalytic performance in many types of organic reaction [50–54]. Recently, a series of W/IL emulsion systems with POM-based ILs were formed [55,56]. These systems were also proven to be more active compared to the previous works. However, these catalytic systems often suffered from slow reaction rate between organic substrates and catalyst. To overcome the obstacle, other attention has been paid to immobilization of POMs onto suitable support [57], which can not only provide large surface area to enhance the mass transfer rate but also benefit for the recovery of catalysts.

In the present work, to integrate the advantages of POMs-based ILs and heterogeneous materials, amphiphilic hybrid material $[\text{C}_4\text{mim}]_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ was synthesized over a facile hydrothermal process and evaluated in ODS system, where no other solvent was added. These hybrid materials characterized in detail were highly efficient on the removal of DBT and easily separated for recycling under mild conditions, which could be potentially applied in industry. Besides, the oxidation products in the reaction were also investigated by GC–MS analysis.

2. Experimental section

2.1. Materials

$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 14\text{H}_2\text{O}$ (AR grade), $\text{NH}_3\cdot\text{H}_2\text{O}$ (aqueous solution, 25%), acetonitrile (CH_3CN , AR grade), Tetraethylorthosilicate (TEOS,

AR grade), hydrogen peroxide (H_2O_2 , 30 wt%), benzothiophene (BT, 99%), dibenzothiophene (DBT, 98%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, 99%) were obtained from Sigma–Aldrich. *n*-octane (CP grade) and tetradecane (AR grade) were purchased from Sinopharm Chemical Reagent Co, Ltd. $[\text{C}_4\text{mim}]\text{Cl}$ (99%), $[\text{C}_8\text{mim}]\text{Cl}$ (99%) and $[\text{C}_{16}\text{mim}]\text{Cl}$ (99%) were gained from Shanghai Chenjie Chemical Co, Ltd. All the reagents were used directly without further purification.

2.2. Catalyst preparation

$[\text{C}_n\text{mim}]_3\text{PW}_{12}\text{O}_{40}$ ($n=4, 8, 16$) was synthesized according to the previous literature [58]. The hybrid materials $[\text{C}_n\text{mim}]_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ were synthesized by a facile hydrothermal method. The synthesis of $[\text{C}_4\text{mim}]_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ was taken as an example. In detail, a 0.25 g (0.076 mmol) portion of $[\text{C}_4\text{mim}]_3\text{PW}_{12}\text{O}_{40}$ was dissolved in 4 mL of acetonitrile at 50°C to form solution A. Afterward, solution A was added to 26 mL of deionized water drop by drop. After then, 2 mL of Tetraethylorthosilicate (TEOS) was transferred to the above solution, followed by addition of 0.5 mL of 25% aqueous ammonia. After stirring for 3 h at room temperature, the mixture was transferred into a Teflon-lined stainless-steel autoclave and maintained at 120°C for 24 h. Then resultant was filtered and washed several times with deionized water and dried in electric oven at 80°C overnight. The solid materials were collected and handled at 200°C for 3 h at a heating rate of $2^\circ\text{C}/\text{min}$. Finally, the white catalyst was obtained. In this reaction, the molar ratio of TEOS: $[\text{C}_4\text{mim}]_3\text{PW}_{12}\text{O}_{40}$: H_2O : $\text{NH}_3\cdot\text{H}_2\text{O}$ = 1.0:0.008:160:1.5. Other hybrid materials with different alkyl chain were synthesized with the equal molar ratio through the above method.

2.3. Characterization

FT-IR spectra of various samples were collected on a Nicolet Model Nexus 470 FT-IR apparatus using KBr pellets. SEM analysis was measured on JEOL JSM-7001F field-emission microscope. XPS of sample was performed on PHI530 with a monochromatic Mg K α source. Raman spectroscopy was carried out on a DXR Raman microscope using a 532 nm excitation laser power. UV–vis

Download English Version:

<https://daneshyari.com/en/article/64946>

Download Persian Version:

<https://daneshyari.com/article/64946>

[Daneshyari.com](https://daneshyari.com)