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Heterogeneous oxidative desulfurization for model fuels using novel PW-coupled polyionic liquids with carbon chains of different lengths

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ABSTRACT

Novel PW-coupled polyionic liquids with different alkyl chain lengths, poly(1-*n*-ethyl-3-vinylimidazolium bromide) (PEVImPW), poly(1-*n*-butyl-3-vinylimidazolium phosphotungstate) (PBVImPW), poly (1-*n*-octyl-3-vinylimidazolium phosphotungstate) (POVImPW), and poly(1-*n*-dodecyl-3-vinylimidazolium phosphotungstate) (PDVImPW), have been successfully synthesized and characterized by FTIR, XRD, TG, ^{13}C NMR, ^{31}P NMR, ICP and CHN elemental analysis. The obtained catalysts have been applied in heterogeneous oxidative desulfurization (ODS) processes. Their ODS performances have been studied. The results indicated PBVImPW was revealed to be a highly efficient catalyst and the benzothiophene removal of 99% was achieved in 2.5 h, 50 °C. The catalyst could be recycled four times.

1. Introduction

Sulfur compounds in transportation fuels are a major source of air pollution from automobiles. In order to obtain ultralow-sulfur fuels, deep desulfurization of fuels has become an environmentally urgent subject worldwide. Compared with traditional hydrodesulfurization, oxidative desulfurization (ODS) is more efficient elimination heterocyclic sulfur compounds. Hence, ODS is considered to be a promising new method for the deep desulfurization of fuel oil [1].

ODS processes catalyzed by polyoxometalates (POMs) have been extensively studied [2]. A signal POM catalyst can show good activity coupled with extraction. However, as semi-homogeneous catalyst, recovery of the POMs after ODS is very difficult, which limits the application of this method [3].

Recently, the hybrid materials POM-ILs consisting of inorganic POMs and organic ionic liquids (ILs), have gradually come to prominence. POMs' polarity, redox property and modulated solubility could be modified through counter anions for ILs [4]. The POM-ILs, such as $[(C_4H_9)_4N]_4NiMo_{6-x}W_xO_{24}H_6$ ($x = 0$, 2, 4, 6) [5], $[(CH_3)N(n\text{-}C_8H_{17})_3]_2W_2O_{11}$, $[(CH_3)N(n\text{-}C_8H_{17})_3]_2Mo_2O_{11}$ [6], $[Bmim]_3[PMo_{12}O_{40}]$ [7], and MMSR-IL-PA [8], have been studied as catalysts for ODS processes. However, POM-ILs still exist some drawbacks. For instance, the POM-ILs usually encounter severe the leaching problems in strong polar reaction media, especially with protic solvents [9]. In addition, when the POM-ILs used for ODS, the solvent such as ILs or organic compounds, was often added to improving mass transfer efficiency. The use of these organic solvents would cause an unavoidable environmental problem. It is worthwhile to note that polyionic liquids (PILs) expand the properties of ILs, mostly its stability and heterogeneous property. Zhao et al. [10] reported that a heteropolyanion-based porous copolymer of polydivinylbenzene and poly(1-*n*-butyl-3-vinylimidazolium bromide), with high activity and good reusability, can be used as highly efficient heterogeneous catalyst for the hydroxylation of benzene with H_2O_2 to phenol. Sahiner and Yasar [11] synthesized PIL microgels from 1, *n*-dialkyl-3,3 0-bis-1-vinyl imidazolium bromide ILMs. These PIL microgels, $P[C_4VIM][Br]$, $P[C_6VIM][Br]$ and $P[C_{10}VIM][Br]$, were employed as catalysts for H_2 generation through the methanolysis and hydrolysis of $NaBH_4$. Liang [12] found that PIL showed high activities and stability for one-pot biodiesel and ion clusters of PIL can enhance the efficiency of mass transfer. Up to date, no studies have been reported with POM-PILs as catalysts for ODS reaction. Hence, it is of interest to investigate the influence of different PILs cations on the performance of POM-coupled polyionic liquids for ODS.

In this study, PW-coupled polyionic liquids (PILsPW) catalysts with different alkyl chain lengths ($n = 2$, 4, 8 and 12) have been synthesized and characterized. A highly efficient ODS is accom-

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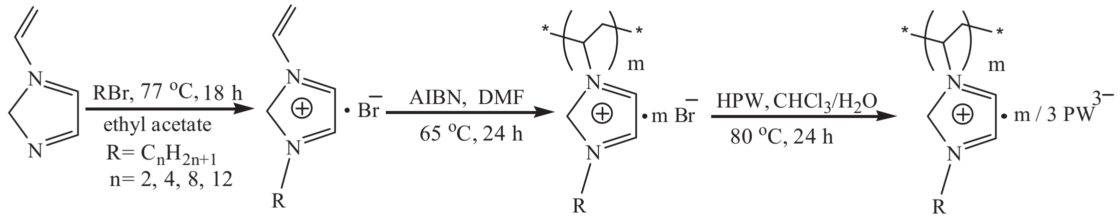

Scheme 1. Synthesis of PW-coupled polyionic liquids and their structures.

plished over PILsPW catalysts using H_2O_2 in the absence of any organic solvent for the first time.

2. Experimental section

2.1. Characterization

Fourier transform infrared (FTIR) data were acquired using a Tensor 27 infrared spectrometer. X-ray diffraction (XRD) analysis of the samples was carried out on a D/max–2000PC–X-ray diffractometer. Thermogravimery (TG) data were obtained using Dupont 2100 themogravimetry analysis. Determination of P and W was by 7500C ICP-MS. The CHN elemental analysis was performed on an elemental analyzer Vario EL cube. Solid-state ^{13}C NMR and ^{31}P NMR spectra were recorded on Varian InfinityPlus 300. The sulfur-containing compounds present in model fuels were analyzed by a gas chromatograph coupled to a flame photometric detector (GC-FPD). Gas chromatography: Clarus 680 GC (Perkin Elmer) equipped with a capillary column (PONA, 30 m ¥ 0.2 mm, id ¥ 0.5 mm). The analysis conditions were as follows: injection port temperature: 280 °C, detector temperature: 250 °C, oven temperature program: 100 °C, hold for 1 min, 100–150 °C at a 10 °C/min gradient, hold for 1 min, 150–280 °C at a 5 °C/min gradient, hold for 12 min, split ratio: 1/100, carrier gas: nitrogen, column flow: 0.9 mL/min, reagent gases air flow: 100 mL/min, hydrogen flow: 75 mL/min, the injection volume of the sample was 1 µL.

2.2. Synthesis of EVImBr, BVImBr, OVImBr, and DVImBr

1-*n*-Ethyl-3-vinylimidazolium bromide with an alkyl chain length of 4 (EVImBr, $n = 2$) was synthesized by following a procedure described in the literature [13]. EVImBr/DMF was prepared at 1.0 M by adding the as-obtained EVImBr to dimethylformamide (DMF). 1-*n*-Bthyl-3-vinylimidazolium bromide with an alkyl chain length of 4 (BVImBr, $n = 4$) was prepared from 1-bromobutane, 1-*n*-octyl-3-vinylimidazolium bromide with an alkyl chain length of 8 (OVImBr, $n = 8$) was prepared from 1-bromooctane, and 1-*n*-dodecyl-3-vinylimidazolium bromide with an alkyl chain length of 12 (DVImBr, $n = 12$) were prepared from 1-bromododecane by following the same procedure as described above. BVImBr/DMF (1.0 M), OVImBr/DMF (1.0 M) and DVImBr/DMF (1.0 M) were also prepared as above.

2.3. Synthesis of PEVImBr, PBVImBr, POVImBr, and PDVImBr

EVImBr/DMF (0.015 mol), 2,2-Azobis (2-methylpropionitrile) (AIBN) (0.46 mmol), and DMF (7 mL) were added to a 50 mL round-bottomed flask equipped with a magnetic stir bar. The mixture was stirred at 65 °C in an oil bath for 24 h under an N_2 atmosphere. The solid was isolated through precipitation from acetone and then dried under vacuum at 80 °C overnight. The resulting solid was poly(1-*n*-ethyl-3-vinylimidazolium bromide), which is denoted as PEVImBr, poly(1-*n*-butyl-3-vinylimidazolium bromide), denoted as PBVImBr, poly(1-*n*-octyl-3-vinylimidazolium bromide), denoted as POVImBr, and poly(1-*n*-dodecyl-3-vinylimidazolium bromide), denoted as PDVImBr, were prepared by following the same procedure as used for PBVImBr.

2.4. Synthesis of PW-coupled polyionic liquids with alkyl chains of different lengths

A typical synthesis of PEVImPW was as follows. As-prepared PEVImBr (0.0263 mol repeat unit), phosphotungstic acid (HPW) (8.76 mmol), and $H_2O/CHCl_3$ (1:1, v/v; 120 mL) were added to a 250 mL round-bottomed flask. The mixture was stirred at 80 °C in an oil bath for 24 h. The precipitate obtained was washed with ethanol and distilled water until the washings were bromide-free (testing with aqueous $AgNO_3$) and dried overnight at 80 °C. The resulting white solid is designated as PEVImPW. PBVImPW, POVImPW and PDVImPW were obtained similarly (Scheme 1).

The elemental and ICP analysis for PEVImPW, PBVImPW, POVImPW and PDVImPW showed that C, H, N, P, W weight percentage are in well agreement with the calculated values from stoichiometry of catalysts (Table 1).

2.5. Oxidative desulfurization

The solution of benzothiophene (BT) in *n*-octane was used as model fuels, with a corresponding S-content of 500 mg/L. The catalytic reactions of oxidative desulfurization were carried out in a 50 mL flask equipped with stirrer and condenser. The typical oxidation of BT was carried out as follows, model fuels (5 mL), catalyst (PW^{3-} unit 3×10^{-5} mol) and H_2O_2 (30% aq., 0.048 mL) were added to the reaction flask and the mixture was stirred at 50 °C for 2.5 h. The reaction processes need not adding any organic solvent. The resulting mixture was washed by water and the sulfur content was determined by Clarus 680 GC (Perkin Elmer) equipped with FPD.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. XRD

The XRD patterns of HPW, PEVImPW, PBVImPW, POVImPW, and PDVImPW are shown in Fig. 1. HPW displays a set of sharp diffraction peaks typical of the crystal structure of a Keggin-type POM located at diffraction angles within the ranges 16–22°, 25–30°, and 33–39°. The similarity of the main peaks in the XRD patterns of PEVImPW, PBVImPW, POVImPW, and PDVImPW to those of HPW indicates that the typical crystal structure of a Keggin-type POM was essentially retained. However, these characteristic peaks were slightly shifted compared to those of HPW due to the introduction of the polyionic liquid cation into the structure.

3.1.2. FTIR

The FTIR spectra of the respective samples are shown in Fig. 2. For 1-VIm, a band at $\nu = 1650\ cm^{-1}$ could be clearly observed,

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