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Short Communication

Synthesis and characterization of novel nanocomposite, anatase sandwich type polyoxometalate, as a reusable and green nano catalyst in oxidation desulfurization of simulated gas oil

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ABSTRACT

$(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2$ nanocomposite have been synthesized first by reaction of A-β-$Na_8HPW_9O_{34}$ with cadmium nitrate and next condensation with titanium tetraisopropoxide at 100 °C via sol–gel method under oil-bath condition. The materials characterized by ^{113}Cd NMR, ^{31}P NMR, XRD, TEM and UV–vis techniques. The crushed nano leaf of anatase phase is 20 nm in nature and fixing of $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$ decreases its size. As seen in TEM image, the nano particles of $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2$ are small with a size of about 10 nm. This anatase nanocomposite polyoxometalate was shown be able to oxidative desulfurization of simulated gas oil with high yield.

1. Introduction

Solid heteropolyacids have attracted much attention in organic synthesis owing to easy workup procedures, easy filtration, and minimization of cost and waste generation due to reuse and recycling of the catalysts [1,2]. Supporting the heteropolyacids on solids with high surface areas improves their catalytic performance in various heterogeneous reactions. Titanium dioxide is a wide-band-gap semiconductor material that has received intense scrutiny for a broad range of applications, thanks to its intriguing physical–chemical properties and cheap, abundant, and reasonably nontoxic nature. TiO_2, also a widely used catalyst support as well as a catalyst is known to enhance the catalytic activity in many cases because of the strong interaction between the active phase and the support [3]. Deep desulphurization 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 [4]. In order to produce ultralow sulfur diesel fuel with hydrodesulphurization (HDS) process, higher temperature, higher pressure, larger reactor volume, and more active catalysts are required [5]. 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 desulphurization techniques have been investigated widely, among which oxidative desulphurization (ODS) is considered to be one of the promising new methods for super deep desulphurization of fuel oil [6–9]. 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. Various oxidants have been used in ODS, such as t-BuOOH [6], O_3 [7], H_2O_2 [8] and solid oxidizing agents [9]. Among these oxidants, H_2O_2 is mostly chosen as an oxidant, only producing water as a byproduct. In continuation of our group research on the synthesis and application of polyoxometalates (POM) and anatase [10–14], we designed anatase TiO_2 crushed nano leaf coupled by sandwich type polyoxometalate at 100 °C via sol–gel method under oil-bath condition. The chemical characterization of this compound was accomplished by means of elemental analysis, IR, XRD, TEM, ^{31}P and ^{113}Cd NMR spectroscopy. The catalytic performance of heterogeneous catalysts tested on oxidation desulphurization of the model sulfur compounds such as BT, DBT, 4-MDBT and 4, 6-MDBT, Scheme 1, using hydrogen peroxide as an oxidizing reagent. POM-TiO_2 nanocomposite has presented much higher catalytic activity than that of the unsupported polyoxometalates. The catalyst easily separated and reused at the end of reaction.

2. Experimental

2.1. Materials

All reagents and solvents used in this work are available commercially and were used as received, unless otherwise indicated. Model compounds and chemicals, including BT, DBT, 4-MDBT and 4, 6-MDBT,

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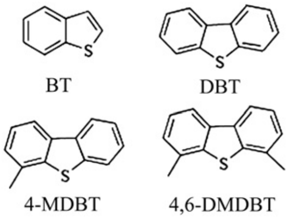

Scheme 1. Structures of sulfur model compound.

solvent (n-heptane) for experiments and analysis and hydrogen peroxide (30 vol.%) were obtained from Aldrich Chemical Company. The compound A-β-$Na_8HPW_9O_{34}\cdot 24H_2O$ (A-PW_9) and other catalysts were prepared as previously described [2,3,14]. Their chemical characterization was accomplished by means of elemental analysis, IR ^{31}P and ^{113}Cd NMR spectroscopy (Tables 1–6). Titanium (IV) tetraisopropoxide and glacial acetic acid were obtained from Merck Chemical Company.

2.2. Preparation of catalyst

$(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$ was prepared as following: To a stirred solution of (0.216 g, 0.7 mmol) $Cd(NO_3)_2\cdot H_2O$ in 8 ml H_2O (pH adjusted to 6 by acetic acid), 1.0 g (0.35 mmol) of A-PW_9 was added. The solution was put into reactor vessel. It is placed under microwave irradiation at 1000 W for 5 min. This work keeps on for 6 times. The solution cooled to room temperature. Potassium chloride (1.2 g) was added to the solution and the mixture was stirred for 15 min and filtered. This solid was recrystallized from 20 ml of hot water and dried under vacuum. Then, to a stirred solution of 2.0 g (0.37 mmol) of potassium salt of $[P_2W_{18}Cd_4(H_2O)_2O_{68}]^{10-}$ in 55 ml of warm distilled water was added a solution of 1.0 g (3.7 mmol) of tetrabutyl ammonium bromide in 5.0 ml of H_2O. The mixture was stirred at 60 °C for 3 h and then the precipitation was separated out by filtration. White precipitate filtered off, recrystallized with acetonitrile and ether, and air dried (Yield 0.65 g, 25%).

2.3. Preparation of nano catalyst

Titanium tetraisopropoxide was added into glacial acetic acid with stirring and a solution of $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$ in water was drop wised in it. The mixture was stirred to dissolve any solid. Then, the sol was heated to 100 °C under oil bath condition until a homogenous $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2$ hydrogel was formed. Finally, the gel was filtered, washed with deionized water–acetone and dried in oven at 50 °C overnight.

2.4. Oxidation desulphurization (ODS) of simulated gas oil (model sulfur compounds)

The model sulfur compound (BT, DBT, 4-MDBT or 4, 6-DMDBT was dissolved in n-heptane to make a stock solution with a sulfur content of 500 ppm. Then, 5 ml of the model sulfur compound, 1.45 ml hydrogen peroxide was added to 0.06 g of nano catalyst ($(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2$)) in a round bottom flask. The flask was immersed in the heating bath and stirred at 500 rpm for 2 h. After the oxidation was finished, the mixture was cooled down to room temperature and 10 ml acetonitrile (MeCN) was added to extract the oxidized sulfur compounds. Two phases of MeCN and n-heptane were separated. The sulfur content in simulated gas oil before and after reaction was determined using X-ray fluorescence (a TANAKA X-ray fluorescence spectrometer RX-360 SH ASTM D-4294 method).

Table 2
Elemental analyses of $(NH_4)_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 27H_2O$.

Element	$(NH_3 + H_2O)$	P	W	Cd	H_2O
Calc. (mass%)	13.30	1.10	58.97	8.01	8.67
Found (mass%)	13.22	1.15	58.89	7.91	8.53

Table 3
Elemental analyses of $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Cl)_2O_{68}]\cdot 27\ H_2O$.

Element	P	W	Cd
Calc. (mass%)	0.93	49.54	6.73
Found (mass%)	0.88	49.33	6.79

2.5. Characterization methods

X-ray diffraction (XRD) patterns were recorded by a D8 Bruker Advanced, X-ray diffractometer using Cu Kα radiation ($\alpha = 1.54$ A). The patterns were collected in the range 20–70° 2θ and continuous scan mode. Transmission electron microscope (TEM) images were obtained on a Philips CM10 transmission electron microscope with an accelerating voltage of 100 kV. The electronic spectra of the synthesized catalysts were taken on a RAYLEIGH (UV-1800) ultraviolet–visible (UV–vis) scanning spectrometer. Infrared spectra were recorded as KBr disks on a Buck 500 scientific spectrometer. All NMR spectra were recorded on a Bruker BRX 500 AVANCE spectrometer. The resonance frequency for the ^{31}P and ^{113}Cd nuclei is 202.46 and 110.92 MHz, respectively. Chemical shifts for ^{31}P and ^{113}Cd NMR spectra were externally referenced relative to 85% H_3PO_4 and 0.1 M cadmium perchlorate, respectively.

3. Results and discussion

3.1. Characterization of synthesized catalysts

XRD patterns of TiO_2, $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$ and $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2$ are shown in Fig. 1. XRD patterns (a) and (b) in Fig. 1 correspond to pristine TiO_2 and $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$, respectively. The XRD pattern corresponding to pure TiO_2 was found to match with that of fully anatase phase. No peaks from any else impurities or rutile phase were observed, which indicates the high purity of the obtained powders. The sharp diffraction peaks manifest that the obtained TiO_2 have high crystallinity. When $(Bu_4N)_7H_3[P_2W_{18}\ Cd_4(Br)_2O_{68}]$ is bound to the TiO_2 surface, $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2$, all of signals corresponding to $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$ is disappeared

Table 1
Elemental analyses of catalysts.

Entry	Catalyst	Data	H_2O	Cd	Zn	W	P	K
1	$K_{10}[P_2W_{18}Cd\ Zn_3(H_2O)_2O_{68}]\cdot 20H_2O$	Calc. (mass%)	6.48	2.02	3.53	59.57	1.11	7.03
		Exp. (mass%)	6.31	1.92	3.60	59.41	1.01	6.92
2	$K_{10}[P_2W_{18}Cd_2Zn_2(H_2O)_2O_{68}]\cdot 20H_2O$	Calc. (mass%)	6.43	4.01	2.33	59.07	1.11	6.98
		Exp. (mass%)	6.30	3.87	2.41	58.89	1.04	6.81