Deep desulphurization of gas oil and model compounds by an anatase nanocomposite sandwich-type polyoxometalate as a novel, reusable and green nano mercaptan scavenger

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Abstract: The oxidative desulphurization of gas oil and model compounds that exist in gas oil with hydrogen peroxide/acetic acid using nanoparticle $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2$ $((Bu_4N)_7H_3[P_2W_{18}Cd_4]$–$TiO_2)$ as a nano scavenger has been studied. This sandwich-type nanoparticle was shown to be able to scavenge hydrogen sulphide and mercaptans in high yields. The addition of acetic acid enhanced the conversion. This system provides an efficient, convenient and practical method for scavenging sulphur compounds. The $(Bu_4N)_7H_3[P_2W_{18}Cd_4]$–$TiO_2$ nanoparticle was a very active catalyst system for the oxidation of model compounds, while other polyoxometalate systems were much less active.

Keywords: polyoxometalates; desulphurization; anatase; scavenger; mercaptans.

INTRODUCTION

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.[1,2] Desulphurization techniques have been investigated widely, among which oxidetive desulphurization (ODS) is considered to be one of the promising new methods for super deep desulphurization of fuel oil.[3–5] In the ODS process, the refractory dibenzothiophene (DBT) and 4,6-dimethydibenzothiophene (4,6-DMDBT) are oxidized to their corresponding sulphones under mild conditions, which are subsequently removed by extraction, adsorption, distillation, or decomposition. Various oxidants have been used in ODS, such as NO_2,[1] O_3,[2] H_2O_2[3] and solid oxidizing agents.[4] Among these oxidants, H_2O_2 is mostly chosen as the oxidant as only water is

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produced as a by-product. Peracids produced *in situ* from organic acids, catalysts and H_2O_2 are reported to be very effective for the rapid oxidation of sulphur compounds in fuel oils under mild conditions. At present, several members of the sandwich-type heteropolyanion families, such $[P_2W_{18}M_4 (H_2O)_2O_{68}]^{10-}$ and $[P_4W_{30}M_4(H_2O)_2O_{112}]^{16-}$ (M = Co(II), Cu(II) or Zn(II)) have been synthesized.[6–8] Their chemistry was discussed and recently, they have attracted much attention in the oxidative desulphurization (ODS) of gas oil.[9] The first cadmium-containing heteropolyanions, related to the mono lacunary anions of Keggin and Dawson structures (PW_{11} and P_2W_{17}) were synthesized by R. Contant.[10] In 1995, Kirby and Baker[11] reported the first sandwich-type heteropolyanions including Cd^{2+} based on the $[P_2W_{15}O_{56}]^{12-}$ defect structure, and later Bi *et al.*[12] prepared a series of dimeric polytungstates by reacting $[As_2W_{15}O_{56}]^{12-}$ with different metal ions, *i.e.*, Cu(II), Mn(II), Co(II), Ni(II), Zn(II) and Cd(II). Herein, the synthesis of a new cadmium-containing heteropolyanion, in which two lacunary $PW_9O_{34}{}^{9-}$ units sandwich four cadmiums, is described.

Homogeneous catalysts cannot be separated from the reaction media and consequently, cannot be reused. Fixation of homogeneous catalysts onto a solid support may be a strategy to overcome this problem. Recently, supported heteropolyacids were synthesized and applied as effective catalysts in organic reactions.[13–16] Supporting heteropolyacids on solids with high surface areas improve their catalytic performance in various liquid–solid and solid surface heterogeneous reactions. Titanium dioxide is a wide-band-gap semiconducting material that has received intense scrutiny for a broad range of applications, thanks to its intriguing physicochemical properties and cheap, abundant, and reasonably non-toxic nature. TiO_2, also a widely used catalyst support as well as a catalyst itself, is known to enhance catalytic activity in many cases because of the strong interaction between the active phase and the support.[19] In continuation of research on the synthesis and application of polyoxometalates (POM) and anatase,[15–18] anatase TiO_2 crushed nano leaf coupled by a sandwich-type polyoxometalate was designed and synthesized at 100 °C *via* a sol–gel method under oil-bath conditions. The chemical characterization of this compound was accomplished by means of elemental analysis, infrared spectroscopy (IR), X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM) and [113]Cd nuclear magnetic resonance ([113]Cd-NMR) spectroscopy. The catalytic performances of these homogenous and heterogeneous catalysts were tested on the oxidative desulphurization of model sulphur compounds, such as benzothiophene (BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) and gas oil using hydrogen peroxide/acetic acid as the oxidizing reagent. The POM–TiO_2 nanocomposites presented much higher catalytic activity than those of the corresponding unsupported polyoxometalates. The catalyst could be easily separated and reused at the end of reaction without a

significant loss of their catalytic activity, which suggests that the catalysts are stable under different conditions.

EXPERIMENTAL

All reagents and solvents used in this work are available commercially and were used as received, unless otherwise indicated. The model compounds and chemicals, including benzothiophene (BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT), solvent (*n*-heptane) for the experiments and analysis and hydrogen peroxide (30 vol. %) were obtained from Aldrich. The compound A-*β*-$Na_8HPW_9O_{34}\cdot24H_2O$ (abbreviated as A-PW_9) and other catalysts $(NH_4)_{10}[P_2W_{18}Cd_4]$, $K_{10}[P_2W_{18}Cd_3Zn]$, $K_{10}[P_2W_{18}Cd_2Zn_2]$, $K_{10}[P_2W_{18}CdZn_3]$, $K_{10}[P_2W_{18}Zn_4]$, $K_6[P_2W_{21}O_{71}]$, $K_{10}[P_2W_{20}O_{70}]$ and $K_{14}[P_2W_{19}O_{69}]$, used for comparison, were prepared as previously described.[8,11] Their chemical characterization was accomplished by means of elemental analysis, IR, ^{31}P- and [113]Cd-NMR spectroscopy, which confirmed their structures. Titanium(IV) tetraisopropoxide and glacial acetic acid were obtained from Merck. Gas oil (density 0.8361 g mL^{-1} at 15 °C, total sulphur content 0.98 wt. %) was supplied from the terminal of the South Iranian Oil Company. Further properties of the gas oil are listed in Table I.

TABLE I. Properties of the south Iran (Kharg Island) gas oil; API GR. –API gravity (API – American Petroleum Institute); API = (141.5/Specific gravity) – 131.5; viscosity KIN – kinematic viscosity

Entry	Properties of gas oil	Method	Result
1	Specific gravity at 60/60 °F	ASTM D1298	0.8365
2	Density at 15 °C	ASTM D1298	0.8361
3	API GR. at 60/60 °F	Calculated	37.66
4	Flash point, °F	ASTM D93	142
5	Water content, vol. %	ASTM D4006	0.025
6	Total sulphur content, wt. %	ASTM D4294	0.98
7	Cloud point, °C	ASTM D2500	–4
8	Colour test	ASTM D156	1.5
9	Viscosity KIN at 50 °C. CST.	ASTM D445	2.8
10	Pour point, °C	ASTM D97	–9
11	Mercaptans, ppm	ASTM D3227	286
12	Distillation, °C	ASTM D86	
13	Initial Boiling Point, °C	ASTM D86	157.8
14	10 % Distillation, °C	ASTM D86	194.6
15	20 % Distillation, °C	ASTM D86	213.4
16	50 % Distillation, °C	ASTM D86	268.6
17	90 % Distillation, °C	ASTM D86	353.9
18	Final boiling point, °C	ASTM D86	384.9
19	Residue, vol. %	ASTM D86	1.5
20	Loss, vol. %	ASTM D86	1
21	Recovery, vol. %	ASTM D86	97.5

Preparation of the mercaptan scavenger

$(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$ was prepared as follows. 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 with acetic acid), 1.0 g (0.35 mmol)

of A-PW$_9$ was added. The solution was carefully transferred into a microwave reactor vessel and irradiated at 1000 W for 5 min. This step was repeated 6 times. After cooling 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 the potassium salt of $[P_2W_{18}Cd_4(H_2O)_2O_{68}]^{10-}$ in 55 mL of warm distilled water, a solution of 1.0 g (3.7 mmol) of tetrabutyl ammonium bromide in 5.0 ml of H$_2$O was added. The mixture was stirred at 60 °C for 3 h and then the white precipitate was separated by filtration, recrystallized from acetonitrile and ether, and air dried (yield 0.65 g, 25 %). The results of the elemental analysis are presented in Table II.

Preparation of the nanomercaptan scavenger

The (Bu$_4$N)$_7$H$_3$[P$_2$W$_{18}$Cd$_4$(Br)$_2$O$_{68}$]–TiO$_2$ nanocomposite was prepared as follows. Titanium tetraisopropoxide was added to glacial acetic acid under stirring and a solution of (Bu$_4$N)$_7$H$_3$[P$_2$W$_{18}$Cd$_4$(Br)$_2$O$_{68}$] in water was added dropwise. The mixture was stirred to dissolve any solid. Then, the sol was heated to 100 °C under oil bath conditions until a homogenous (Bu$_4$N)$_7$H$_3$[P$_2$W$_{18}$Cd$_4$(Br)$_2$O$_{68}$]–TiO$_2$ hydrogel was formed. Finally, the gel was filtered, washed with deionised water–acetone and dried in an oven at 50 °C overnight.

TABLE II. Elemental analysis of (Bu$_4$N)$_7$H$_3$[P$_2$W$_{18}$Cd$_4$(Br)$_2$O$_{68}$]·27H$_2$O

Element	P	W	Cd
Calcd., %	0.93	49.54	6.73
Found, %	0.88	49.33	6.79

Oxidative desulphurization (ODS) of model sulphur compounds

Some typical benzothiophenes and dibenzothiophenes, which represent easy, hard and very hard sulphur species to remove from gas oil, were selected to evaluate the catalysts and the reactivity of benzothiophenes and dibenzothiophenes in an oxidation reaction. A water bath was first heated up and stabilized at the desired reaction temperature (25–60 °C). The model sulphur compound (BT, DBT, 4-MDBT or 4,6-DMDBT was dissolved in *n*-heptane to make a stock solution with a sulphur content of 500 ppm. Then, 5 mL of the model sulphur compound and 0.06 mmol of the nano scavenger ((Bu$_4$N)$_7$H$_3$[P$_2$W$_{18}$Cd$_4$(Br)$_2$O$_{68}$]–TiO$_2$), as a catalyst, were mixed with 2 mL H$_2$O$_2$/acetic acid (peroxyacetic acid) (hydrogen peroxide/acetic acid molar ratio of 1.0) in a flask. The flask was immersed in the heating bath and stirred at 500 rpm for 2 h. After completion of the oxidation, the mixture was cooled to room temperature and 10 ml acetonitrile (MeCN) was added to extract the oxidized sulphur compounds. The two phases of MeCN and *n*-heptane were separated. The sulphur content in model sulphur compounds before and after the reaction was determined using X-ray fluorescence spectroscopy using a Tanaka X-ray fluorescence spectrometer RX-360 SH (ASTM D-4294 method). The ASTM D-4294 method covers the measurement of sulphur in fuels, such as diesel, naphtha, kerosene, residuals, lubricating base oils, hydraulic oils, jet fuels, crude oils, gasoline (all unleaded), and other distillates. Compared to other test methods for sulphur determination, the D-4294 test method has high throughput, minimal sample preparation, good precision, and is capable of determining sulphur over a wide range of concentrations. The equipment specified is in most cases less costly than that required for alternative methods. In the case of petroleum materials that contain suspended water, it is recommended that the water be removed before testing or that the sample be thoroughly homogenized and im-

mediately tested. The interference is greatest if the water creates a layer over the transparent film as it will attenuate the X-ray intensity for sulphur. One such method to accomplish the removal of water is to centrifuge the sample first under ambient sealed conditions, taking care that the sample integrity is not compromised.
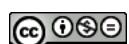
Oxidative desulphurization (ODS) of gas oil

Oxidative desulphurization of the gas oil was accomplished in the same manner as used for the oxidation of the model sulphur compounds, *i.e.*, gas oil (sulphur 2300 ppm S, 10 ml) with 0.06 mmol catalyst and H_2O_2/acetic acid (hydrogen peroxide/acetic acid molar ratio of 1.0) at a temperature of 60 °C. After completion of the oxidation, the oxidized sulphur in the gas oil was extracted with acetonitrile at room temperature. The acetonitrile/oil ratio used was 1/2 by volume. The biphasic mixture was separated by decantation. The oil phase was separated and weighed to calculate % recovery of oil. The sulphur content in the oil before and after reaction was determined using an X-ray fluorescence spectrometer (ASTM D4294 method).

RESULT AND DISCUSSION

Effect of the catalyst structure

The effect of the nature of the catalyst on the oxidative desulphurization of DBT using hydrogen peroxide/acetic acid as the oxidant is shown in Table III. The sandwich type polyoxometalate-anatase nanoparticle catalyst $(Bu_4N)_7H_3$ $[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2$ and the unsupported $(Bu_4N)_7H_3[P_2W_{18}Cd_4]$ catalyst were very active systems for the oxidation of the model compound, while other studied polyoxometalates systems were much less active. It was shown that the order of the oxidation reactivity of the catalyst in the presence of hydrogen peroxide/acetic acid was: $(Bu_4N)_7H_3[P_2W_{18}Cd_4]$–$TiO_2$ > $(Bu_4N)_7H_3[P_2W_{18}Cd_4]$ > $(NH_4)_{10}[P_2W_{18}Cd_4]$ > $K_{10}[P_2W_{18}Cd_3Zn]$ > $K_{10}[P_2W_{18}Cd_2Zn_2]$ > $K_{10}[P_2W_{18}CdZn_3]$ > $K_{10}[P_2W_{18}Zn_4]$ > $K_6[P_2W_{21}O_{71}]$ > $K_{10}[P_2W_{20}O_{70}]$ > $K_{14}[P_2W_{19}O_{69}]$.

TABLE III. Effect of different catalysts in the oxidative desulphurization of DBT; conditions for desulphurization: 5 ml of DBT model oil (500 ppm S), 0.06 mmol catalyst, 2 ml H_2O_2/ /acetic acid, 5 ml extraction solvent, time 2 h and temperature 60 °C

Entry	Catalyst	DBT/ca-talyst	Oxi-dant/DBT	Residual sulphur, ppm	Sulphur removal, %
1	$(Bu_4N)_7H_3[P_2W_{18}Cd_4]$–$TiO_2$	100	10	8.4	98.32
2	$(Bu_4N)_7H_3[P_2W_{18}Cd_4]$	30	10	38.8	92.24
3	$(NH_4)_{10}[P_2W_{18}Cd_4]$	20	15	72.8	85.44
4	$K_{10}[P_2W_{18}Cd_2Zn_2]^a$	20	15	84.8	83.04
5	$K_{10}[P_2W_{18}CdZn_3]^a$	20	10	105.8	78.84
6	$K_{10}[P_2W_{18}Zn_4]^a$	20	10	148.2	70.36
7	$K_6[P_2W_{21}O_{71}]^b$	25	15	163.8	67.24
8	$K_{10}[P_2W_{20}O_{70}]^b$	25	15	171.35	65.73
9	$K_{14}[P_2W_{19}O_{69}]^b$	25	15	172.9	65.42

[a]synthesis of the catalyst is given in the literature;[2,19] [b]synthesis of the catalyst is given in the literature[3,14]

Reactivity of various sulphur compounds

The effect of the different soluble catalysts and $(Bu_4N)_7H_3$ $[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2$ in oxidative desulphurization of different sulphurs compounds are given in Table IV. The oxidation reactivity decreased in the order of DBT > 4,6-DMDBT > 4-MDBT > BT. BT exhibited the lowest reactivity, which was related to the different electron density on the sulphur atom. The difference in electron density on the sulphur atom of DBT and 4,6-DMDBT is very small. The oxidation reactivity was governed by the steric hindrance of the methyl groups, which become on obstacle for the approach of the sulphur atom to the catalytically active sites. The electron density for 4,6-DMDBT is the highest, but its oxidation reactivity was lower than DBT, this is due to the steric effect from the alkyl groups at the 4 and 6 positions.

TABLE IV. Effect of different catalysts in the oxidative desulphurization of various sulphur compounds; condition for desulphurization: 2 ml H_2O_2/acetic acid as the oxidant, 0.1 mmol catalyst, 5 ml acetonitrile as the extraction solvent, time 2 h and temperature 60 °C

Entry	Catalyst	Sulphur removal, %			
		DBT	4-MDBT	4,6-DMDBT	BT
1	$(Bu_4N)_7H_3[P_2W_{18}Cd_4]$–$TiO_2$	98.5	95.5	96	89
2	$(Bu_4N)_7H_3[P_2W_{18}Cd_4]$	92	90	91	84
3	$(NH_4)_{10}[P_2W_{18}Cd_4]$	86	87	87	79
4	$K_{10}[P_2W_{18}Cd_2Zn_2]$ [b]	85	86	85	77
5	$K_{10}[P_2W_{18}CdZn_3]$ [b]	83	85	84	75
6	$K_{10}[P_2W_{18}Zn_4]$ [b]	80	81	80	73
7	$K_6[P_2W_{21}O_{71}]$ [c]	75	73	73	72
8	$K_{10}[P_2W_{20}O_{70}]$ [c]	74	71	72	70
9	$K_{14}[P_2W_{19}O_{69}]$ [c]	70	69	71	68

[a]Synthesis of the catalyst is given in the literature;[2,19] [b]synthesis of the catalyst is given in the literature[3,14]

Oxidative desulphurization (ODS) of gas oil

The results of the oxidative desulphurization of oil gas are given in Table V. According to the obtained data, the total sulphur content (Entry 1) and the content of mercaptans (Entry 2) were much lower after the oxidation process, while numerous other properties of the gas oil remained unaffected. From the results obtained in this work, it was demonstrated that the nano mercaptan scavenger $((Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2)$ can catalyze the oxidative desulphurization reaction in 2 h and can reduce the total sulphur content of gas oil from 0.98 to 0.087 wt. % and also reduce the content of mercaptans from 286 to 10 ppm.

Recycling of the catalyst

At the end of the oxidative desulphurization of the model sulphur compounds and gas oil, the catalyst was filtered off and washed with dichloromethane. In order to determine whether the catalyst would succumb to poisoning

and lose its catalytic activity during the reaction, the reusability of the catalyst was investigated. For this purpose, desulphurization reaction of gas oil and the model compounds were performed in the presence of fresh and recovered catalyst. Even after three runs of the reaction, the catalytic activity of $(Bu_4N)_7H_3$ $[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2$ was almost the same as that of fresh catalyst. The results are summarized in Tables V and VI for the oxidative desulphurization DBT and gas oil, respectively.

TABLE V. Oxidative desulphurization of gas oil using $(Bu_4N)_7H_3[P_2W_{18}Cd_4]$–$TiO_2$

Entry	Properties of gas oil	Before ODS	After ODS[a]	After ODS[b]
1	Total sulphur content, wt. %	0.98	0.087	0.092
2	Density at 15 °C	0.8361	0.8362	0.83690
3	Mercaptans, ppm	286	10	9
4	Flash point, °F	142	142	142
5	Water content, vol. %	0.025	0.025	0.025
6	Cloud point, °C	–4	–4	–4
7	Colour test	1.5	1.5	1.5
8	Viscosity KIN at 50 °C. cSt.	2.8	2.7	2.6
9	Pour point, °C	–9	–9	–9
10	Initial boiling point, °C	157.8	156.9	157.2
11	Final boiling point, °C	384.9	383.8	385.2

[a]Condition for desulphurization: 5 ml of gas oil (2300 ppm S), 0.06 mmol catalyst, 2 ml oxidant, 5 ml of extraction solvent, time 2 h and temperature 60 °C; [b]reuse of the catalyst in the desulphurization of gas oil

TABLE VI. Reuse of $(Bu_4N)_7H_3[P_2W_{18}Cd_4]$–$TiO_2$ for the oxidative desulphurization of DBT

Run	Sulphur removal, %
1	96
2	94
3	95

CONCLUSIONS

The $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$–$TiO_2$ nanocomposite was synthesized at a low temperature *via* a sol–gel method under oil-bath conditions. Fixing of $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$ with TiO_2 decreased the particle size of the crushed nano leaf of the anatase phase. The $(Bu_4N)_7H_3[P_2W_{18}Cd_4]$–$TiO_2$ nanocomposite was a very active catalyst system for the oxidation of model sulphur compounds and gas oil, while unmodified $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$ showed much lower activities. For this polyoxometalates/H_2O_2/acetic acid system, the oxidation reactivity decreased in the following order: DBT > 4,6-DMDBT > BT. The percent conversion increased when the amount of oxidant and catalyst were increased. The addition of acetic acid enhanced the oxidation.
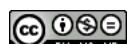
ИЗВОД

ДУБОКА ДЕСУЛФУРИЗАЦИЈА ПЛИНСКОГ УЉА И МОДЕЛ ЈЕДИЊЕЊА АНАТАЗНИМ НАНОКОМПОЗИТНИМ ПОЛИОКСОМЕТАЛАТОМ СЕНДВИЧ ТИПА КАО НОВИМ, ОБНОВЉИВИМ И НЕШКОДЉИВИМ ПРИМАОЦЕМ МЕРКАПТАНА

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Проучавана је оксидативна десулфуризација плинског уља и индивидуалних модел јединьења која се налазе у плинском уљу, водоник пероксидом/сирћетном киселином уз примену наночестица $(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]–TiO_2$ $((Bu_4N)_7H_3[P_2W_{18}Cd_4]–TiO_2))$ као примаоца меркаптана. Показано је да су ове наночестице сендвич-типа способне да вежу водоник-сулфид и меркаптане уз високе приносе. Додавање сирћетне киселине је побољшало конверзију. Овај систем омогућава ефикасан, погодан и практичан метод за везивање сумпорних јединьења. Наночестице $(Bu_4N)_7H_3[P_2W_{18}Cd_4]–TiO_2$ су се показале као врло активан катализаторски систем за оксидацију модел јединьења, док су се други полиоксометалатни системи показали много мање активним.

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