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Anatase titania–vanadium polyphosphomolybdate as an efficient and reusable nano catalyst for the desulphurization of gas oil

MOHAMMAD ALI REZVANI[1]*, ABDOLLAH FALLAH SHOJAEI[2]
and FAROKHZAD MOHAMADI ZONOZ[3]

[1]Department of Chemistry, Faculty of Science, University of Zanjan, 45371-38791 Zanjan, Iran, [2]Department of Chemistry, Faculty of Science, University of Guilan, 419961-3769 Rasht, Iran and [3]Department of Chemistry, Hakim Sabzevari University, Sabzevar, 397, Iran

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Abstract: $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ nanocomposite has been synthesized by a reaction of $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ with titanium tetraisopropoxide at 100 °C *via* the sol–gel method. The crushed nano layer of the anatase phase was 20 nm in nature and the fixing of $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ decreased its size. This nano polyphosphomolybdate was shown to be able to oxidatively desulphurize simulated gas oil with a high S conversion (more than 98 %). In the present work, the efficient oxidative desulphurization of gas oil and simulated gas oil using the formic acid/hydrogen peroxide system is reported. This system provides an efficient, convenient and practical method for scavenging sulfur compound.

Keywords: polyoxometals; desulfurization; anatase; gas oil; nanocomposite.

INTRODUCTION

The catalytic function of heteropolyacids (HPAs) has attracted much attention because of their uncommon ability to accept an electron without deformation of their structure or reversible reduction.[1–4] Keggin type polyoxoanions have been widely studied as homogeneous and heterogeneous catalyst for the oxidation of organic compounds, whereas the application of Wells–Dawson type polyoxoanions is mostly limited to homogeneous or gas phase applications and only a few of them have demonstrated catalytic activity in the heterogeneous form.[5–7] Generally, Keggin structures show more acidity and catalytic activity among the heteropolyacids.[8] These solid acids are usually insoluble in non-polar solvents but highly soluble in polar ones. They can be used in bulk or supported forms in both homogeneous and heterogeneous systems.[9] Further catalytically important subclasses of the Keggin compounds are the mixed-addenda vanadium

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[*] Corresponding author. E-mail: marezvani2010@gmail.com

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(V) substituted HPAs with the general formula $H_{3+n}PM_{12–n}V_nO_{40}$ (M = Mo and W; n = 1 to 6). The best known of these HPAs is the 10-molybdo-2-vanadophosphoric acid $H_5PV_2Mo_{10}O_{40}$). This compound contains a central PO_4 tetrahedron, surrounded by 12 MO_6 ($10MoO_6$ + $2VO_6$) octahedra arranged in four M_3O_{13} group-edge-sharing octahedra. The edge-sharing M_3O_{13} groups are linked to each other and to the central tetrahedron by shared corners. $H_5PV_2Mo_{10}O_{40}$ has been extensively used as an effective redox catalyst in homogeneous oxidation processes.[10] There are fewer reports regarding the application of $H_5PV_2Mo_{10}O_{40}$ as an acid catalyst for organic transformations for the simple reason that V^{5+} is the most strongly oxidizing element and can be readily reduced to V^{4+} with concomitant oxidation of an organic substrate. In fact, the introduction of V^{5+} into the Keggin framework shifts its catalytic activity from acid-dominated to redox-dominated. Deep desulphurization of transportation fuels has become an important research subject due to the increasingly stringent regulations and fuel specifications in many countries for the purpose of environmental protection.[11–13] In the conventional hydrodesulphurization (HDS) process, it is difficult to remove alkyl-substituted dibenzothiophenes, such as 4,6--dimethyldibenzothiophene, which are refractive to HDS due to steric hindrance. In order to produce ultralow sulfur diesel fuel using the HDS process, higher temperature, higher pressure, larger reactor volume and catalysts that are more active are required. Therefore, alternative desulphurization techniques have been widely investigated, among which oxidative desulphurization (ODS) is considered to be one of the promising new methods for super deep desulphurization of fuel oil.[12–14] Various oxidants have been used in ODS, such as NO_2, O_3, H_2O_2 and solid oxidizing agents.[11–16] Among these oxidants, H_2O_2 is mostly chosen as an oxidant, as only water is produced as a byproduct. Peracids produced *in situ* from organic acids catalysts and H_2O_2 are reported to be very effective for rapid oxidation of sulfur compounds in fuel oils under mild conditions. 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 have been synthesized and applied as effective catalyst in organic reactions.[17–19] Supporting the 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 semiconductor material that has received intense scrutiny for a broad range of applications, thanks to its intriguing physicochemical properties, as well as being cheap, abundant, and reasonably nontoxic. TiO_2, also a widely used catalyst and catalyst support is known to enhance the catalytic activity in many cases because of the strong interaction between the active phase and the support.[17]

In continuation of ongoing research into the synthesis and application of polyoxometalates (POM) and anatase,[18–26] anatase TiO_2 crushed nano leaf coupled by a sandwich type polyoxometalate was fabricated at 100 ° C *via* the sol–gel method under oil bath conditions. The chemical characterization of this fabrication was accomplished by means of elemental analysis, IR, ^{31}P- and ^{113}Cd-NMR spectroscopy, and XRD and TEM analyses. The catalytic performance of these homogenous and heterogeneous catalysts were tested on the oxidative desulphurization of model sulfur compounds, *i.e.*, benzothiophene (BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) and gas oil, using formic acid/hydrogen peroxide as the oxidizing reagent. The POM–TiO_2 nanocomposite presented much higher catalytic activity than those of unsupported polyoxometalates. The catalyst could be easily separated and reused at the end of the reaction without significant loss of its catalytic activity, which suggests that the catalyst is stable under different conditions.

EXPERIMENTAL

All employed reagents and solvents were commercially available and used as received, unless otherwise indicated. The model compounds and chemicals, including BT, DBT, 4-MDBT and 4,6-DMDBT, solvent (*n*-heptane) for the experiments and analyses and hydrogen peroxide (30 vol. %) were obtained from Aldrich Chemical Company. Preparation of the $H_5PV_2Mo_{10}O_{40}$ catalyst and other mixed heteropolyacids and salts were based on a literature procedure with modifications.[20,21] Titanium (IV) tetra-isopropoxide and glacial acetic acid were obtained from Merck Chemical Company. Gas oil (density 0.8361 g mL^{-1} at 15 °C, total sulfur content 0.98 wt. %) was supplied from the terminal of the North Iranian Oil Company (Table I).

TABLE I. Properties of the actual gas oil; abbreviations: 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	Results
1	Specific gravity at 60/60, °F	ASTM D1298	0.8365
2	Density at 15 °C, g cm^{-3}	ASTM D1298	0.8361
3	API GR. 60/60, °F	Calculated	37.66
4	Flash point, °C	ASTM D93	142
5	Water content, vol. %	ASTM D4006	0.025
6	Total sulfur content, wt. %	ASTM D4294	0.98
7	Cloud point, °C	ASTM D2500	–4
8	Color 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
13	Initial boiling point (IBP), °C	ASTM D86	157.8
14	10 % Distillation, °C	ASTM D86	194.6

TABLE I. Continued

Entry	Properties of gas oil	Method	Results
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 (FBP), °C	ASTM D86	384.9
19	Distillation residue, vol. %	ASTM D86	1.5
20	Distillation loss, vol. %	ASTM D86	1
21	Distillation recovery, vol. %	ASTM D86	97.5

Preparation of the catalyst

$(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ was prepared as follows: Sodium metavanadate (12.2 g, 100 mmol) was dissolved by boiling in 50 mL of water and then mixed with 3.55 g (25.0 mmol) of Na_2HPO_4 in 50 mL of water. After the solution had cooled, concentrated sulfuric acid (5 mL, 17 M, 85 mmol) was added, whereby the solution developed a red color. Then, $Na_2MoO_4 \cdot 2H_2O$ (60.5 g, 250 mmol) dissolved in 100 mL of water was added to the red solution under vigorous stirring, followed by the slow addition of a solution of 1.0 g (3.7 mmol) of tetrabutylammonium bromide in 5.0 mL of H_2O. The mixture was stirred at 60 °C for 3 h. The formed white precipitate was filtered off, recrystallized from acetonitrile and diethyl ether, and air dried.[21]

Preparation of the nanocatalyst

The $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ nanoparticle was prepared as follows: titanium tetraisopropoxide was added into glacial acetic acid with stirring. Next, a solution of $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ in water was added drop-wise. The mixture was stirred to dissolve any solid. Then, the sol was heated to 100 °C under oil bath conditions until a homogenous $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ hydrogel was formed. Finally, the gel was filtered, washed with deionized water–acetone and dried in oven at 50 °C overnight.[17]

Oxidative desulphurization (ODS) of simulated gas oil using the formic acid/H_2O_2 system

Some typical benzothiophenes and dibenzothiophenes, which represent easy, hard and very hard to remove sulfur species in gas oil, were selected to evaluate the catalysts and the reactivity of the benzothiophenes and dibenzothiophenes in the oxidation reaction. The water bath was first heated up and stabilized to the desired reaction temperature (25–80 °C). A 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, mixed with 2 mL formic acid/H_2O_2 (performic acid, formic acid/hydrogen peroxide mole ratio of 1) was added into the flask. The flask was immersed in a heating bath and stirred at 500 rpm for 2 h. The biphasic mixture was separated by decantation. It reached the reaction temperature in about 15 min. After withdrawing the first sample, 0.1 g of the nanocomposite ($(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$) catalyst was added to the flask to initiate the reaction. The sulfur concentration of the sample was determined using a Tanaka Scientific RX--360 SH X-ray fluorescence spectrometer (ASTM D-4294 method and D-3227).

ASTM D-4294. This test method covers the measurement of sulfur in hydrocarbons, such as diesel, naphtha, kerosene, residuals, lubricating base oils, hydraulic oils, jet fuels, crude oils, gasoline (all unleaded) and other distillates. Compared to the other test methods for sulfur determination, the test method D-4294 has a high throughput, minimal sample preparation, good precision, and is capable of determining sulfur 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 immediately tested. The interference is greatest if the water creates a layer over the transparent film, as this would attenuate the X-ray intensity for sulfur. 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. The results are given in Table II.

TABLE II. Oxidative desulphurization of gas oil by $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$

Entry	Properties of gas oil	Before ODS	After ODS[a]	After ODS[b]
1	Total sulfur content, wt. %	0.98	0.068	0.072
2	Density at 15 °C, g cm^{-3}	0.8361	0.8358	0.8364
3	Mercaptans, ppm	286	8	11
4	Flash point, °C	142	142	142
5	Water content, vol. %	0.025	0.025	0.025
6	Cloud point, °C	–4	–4	–4
7	Color test	1.5	1.5	1.5
8	Viscosity KIN at 50 °C, CST	2.8	2.7	2.5
9	Pour point, °C	–9	–9	–9
10	Distillation IBP, °C	157.8	156.9	157.5
11	Distillation FBP, °C	384.9	382.6	384.0

[a]Conditions for the desulphurization: 5 mL of gas oil (9800 ppm S), 0.1 g nano-catalyst, 2 mL oxidant, 5 mL extraction solvent, time = 2 h, temperature = 80 °C; [b]reuse of the catalyst in the desulphurization of gas oil

Oxidative desulphurization (ODS) of gas oil using the formic acid/H_2O_2 system

In the same manner as the oxidation of the model sulfur compounds but using actual gas oil (sulfur 2300 ppm, 10 mL) with 0.1 g nanocatalyst ($(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$), 2 mL formic acid/$H_2O_2$ (formic acid/hydrogen peroxide mole ratio of 1) and temperature 80 °C. After completion of the oxidation, the oxidized sulfur 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 gas oil (for three times reaction: 98, 96 and 95 %). The sulfur content in the oil before and after reaction was determined using X-ray fluorescence spectrometer (ASTM D--4294 method). According to data in Table II, after the oxidation process, the total sulfur content (Entry 1) and content of mercaptans (Entry 2) were much lower, while numerous other properties of gas oil showed in Table II remained unaffected. From the results obtained in this work, it was demonstrated that the nanocomposite ($(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$) could catalyze the oxidative desulphurization reaction in 2 h and could reduce the total sulfur content in the gas oil from 0.98 to 0.068 wt. % and reduce content of mercaptans from 286 to 8 ppm. The addition of formic acid enhanced the conversion.

Recycling of the catalyst

At the end of the oxidative desulphurization of the model sulfur compounds and gas oil, the catalyst was filtered 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, we carried out the desulphurization reaction of gas oil and model compounds in the presence of fresh and recovered catalyst (Table II). Even after three runs for the reaction, the catalytic activity of

($(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$) was almost the same as that of freshly used catalyst. The results are summarized in Table II.

RESULT AND DISCUSSION

Characterization of synthesized catalysts

The XRD pattern corresponding to pure TiO_2 was found to match with that of fully anatase phase. No peaks from any impurities or the rutile phase were observed, which indicates the high purity of the obtained powders. The sharp diffraction peaks confirmed that the obtained TiO_2 was of high crystallinity. When $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ was bound to the TiO_2 surface, $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$, all of signals corresponding to $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ had disappeared and the final pattern matched that of fully anatase phase of TiO_2 (JCPDS No. 21-1272), which was most likely because $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ formed only a thin coating on the TiO_2 surface and thus the majority of the observed signals were due to the crystal phases of anatase TiO_2. A TEM image of the obtained fully anatase phase of TiO_2 as a crushed nano leaf indicate an average size of about 25 nm. After modification of anatase with $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$, a significant change in the morphology and size occurred. In the TEM image, most of the obtained powders consisted of nano particles with an average size of about 10 nm but there were some nano rods. In ultraviolet light regions, which are shorter than 332 nm, pure nano-TiO_2, the band gap energy of which corresponds to around 320 nm (3.60 eV), shows the highest absorbance because of charge-transfer from the valence band (mainly formed of the 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d t_2g orbitals of Ti^{4+}).[17] In addition, $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ showed an absorbance maximum at 230 nm attributed to charge transfer (CT) from O 2p to W 5d of the Keggin units at the W–O and W–O–W bonds. The $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ nanocomposite showed strong and broad optical absorption in the range from 220 to 330 nm, and a red shift is observed compared with the parent $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$, and a blue shift compared with anatase. The above UV–Vis results indicate that the introduction of $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ into TiO_2 framework has an influence on the coordination environment of crystalline TiO_2.[17,20]

Catalytic results

Effect of the oxidation system on the oxidative desulphurization of gas oil or simulated gas oil. In this study, many types of oxidative systems, such as H_2O_2/organic acids, H_2O_2/POMs, H_2O_2/POMs–TiO_2, were investigated. Formic acid, benzoic acid, oxalic acid, acetic acid, H_2SO_4 and H_2CO_3 were selected to acidify the system, and were added into the gas oil or simulated gas oil solutions in a mole ratio of 1:1 with 30 % H_2O_2. The reactions were performed at 80 °C for 2 h. The results given in Table III show that the oxidation reactivities of the inorganic acids, H_2SO_4 and H_2CO_3, were lower than those of the organic acids because the inorganic acids are insoluble in the gas oil and simulated gas oil solutions.

TABLE III. Effect of different acids in the presence of hydrogen peroxide and $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ in the oxidative desulfurization of different sulfur compounds; conditions for the desulfurization: 2 mL acid/H_2O_2 as oxidant, 0.1 mmol nanocatalyst ($(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$), 5 mL DMF as extraction solvent, time 2 h, temperature 80 °C

Entry	Acid used	Conversion, %			
		DBT	4-MDBT	4,6-DMDBT	BT
1	Formic acid	98	96	97	94
2	Benzoic acid	94	90	94	90
3	Oxalic acid	92	86	92	92
4	Acetic acid	97	96	97	93
5	H_2SO_4	79	75	78	72
6	H_2CO_3	77	73	77	71

The order of the oxidative reactivity of the different acids in the presence of hydrogen peroxide and $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ was:

formic acid > acetic acid > benzoic acid > oxalic acid > H_2SO_4 > H_2CO_3

Effect of types of the sulfur compound on the desulphurization of simulated gas oil. The reactivities of different sulfur-containing compounds, including benzothiophene (BT), 4-methyldibenzothiophene (4-MDBT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), were investigated for oxidetive desulphurization using hydrogen peroxide and formic acid. The electron densities of the thiophene derivatives varied between 5.696 (thiophene) and 5.760.[16] Thiophene is usually oxidized with difficulty because of its low electron density. BT (electron density 5.739) and the other model compounds with higher electron densities were oxidized to form their corresponding sulfones. The apparent rate constants (*k*) for these oxidations decreased as follows: 4,6-DMDBT > 4-MDBT > > DBT > BT.[16] This result indicates that the rate constant increased with increasing electron density. The oxidation reactivities decreased according to DBT > > 4-MDBT > 4,6-DMDBT, and the same reactivity trend was found for ODS. The apparent activation energies of DBT, 4-MDBT, and 4,6-DMDBT oxidation were 53.8, 56.0, and 58.7 kJ mol^{-1}, respectively. These results indicate that DBT oxidation was achieved under mild reaction conditions and it was easy to increase the reaction temperature or reaction time to achieve high conversions, even for the least reactive 4,6-DMDBT that showed a lower reactivity compared with DBT, as methyl substituents were present at the 4 and 6 positions on the DBT rings. In addition, the formic acid/H_2O_2 and polyoxometalates/H_2O_2 biphasic catalytic systems have completely different reactivity orders for the oxidation of DBTs because of the important role of the molecular size of the catalyst.[18] For the formic acid catalyzed reaction, the formic acid can interact with sulfur without any steric hindrance from alkyl groups. Therefore, the reactivity trend obtained in the formic acid catalyzed reactions reflected the intrinsic oxidative reactivity of the DBTs. Phosphotungstic compounds convert to polyoxoperoxo complexes in the presence of hydrogen peroxide.[18,19] The tungsten atom in this polyoxoperoxo species is in a highly crowded rigid structure. The effects of different catalysts in the oxidative desulphurization of different sulfur-containing compounds are listed in Table IV. The alkyl groups of dialkyl DBT likely sterically hinder the polyoxoperoxo species from interacting with DBT *via* the sulfur atom to form a transition state. Therefore, the oxidation reactivity trend in polyoxometalates/H_2O_2 in a biphasic catalytic system imply the presence of steric hindrance because of the alkyl groups. These results suggest that there is little steric hindrance in the amphiphilic compounds. The oxidation reactivity decreased in the order of DBT > 4,6-DMDBT > 4-MDBT > BT. BT exhibited the lowest reactivity, and this was related to the different electron density on the sulfur atom. Difference in electron density on the sulfur atom is for DBT and 4,6-DMDBT very small. The oxidation reactivity was governed by the strict hindrance of the methyl groups, which become an obstacle for the approach of the sulfur atom to the catalytically active spaces. The electron density for 4,6-DMDBT is the highest, but its oxidation reactivity is lower than DBT, this is due to the steric effect from the alkyl groups at the 4 and 6 position.

TABLE IV. Effect of different catalysts on the oxidative desulphurization of different sulfur compounds; conditions for the desulphurization: 2 mL H_2O_2/formic acid as oxidant, 0.1 mmol catalyst, 5 mL DMF as extraction solvent, time 2 h, temperature 80 °C

Entry	Catalyst	Conversion, %			
		DBT	4-MDBT	4,6-DMDBT	BT
1	$(Bu_4N)_4H[PMo_{10}V_2O_{40}]–TiO_2$	98	96	97	94
2	$(Bu_4N)_4H[PMo_{10}V_2O_{40}]$	93	92	93	90
3	$H_5PMo_{10}V_2O_{40}$	92	91	92	89
4	$H_4PMo_{11}VO_{40}$	91	90	91	88
5	$H_6PMo_9V_3O_{40}$	91	88	90	87
6	$H_3PMo_{12}O_{40}$	90	88	90	86
7	$H_3PW_{12}O_{40}$	90	87	90	85
8	$H_4SiW_{12}O_{40}$	86	84	86	82
9	H_{14} $[NaP_5W_{30}O_{110}]$	81	77	80	74
10	$Na_3PMo_{12}O_{40}$	80	75	80	72
11	$Na_3PW_{12}O_{40}$	78	74	77	70
12	$(NH_4)_3H[PMo_{11}VO_{40}]$	78	72	78	68
13	$H_6P_2Mo_{18}O_{62}$	74	71	73	70
14	$H_6P_2W_{18}O_{62}$	70	67	70	65

Effect of the catalyst structure

The effects of the catalyst structure on the oxidation of the simulated gas oil by formic acid/H_2O_2 are presented in Table IV. BT, DBT, 4-MDBT and 4,6-

DMDBT were taken as model compounds. The amount of each catalyst used was the same. POM–TiO_2 nanocomposite presented a much higher catalytic activity than that of the unsupported polyoxometalates. The $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ nanoparticle was a very active catalyst system for the oxidation of the model compound, while other polyoxometalate systems were much less active. In the series of Keggin-type polyoxometalates, $H_5[PMo_{10}V_2O_{40}]$ showed the highest catalytic activity. In general, heteropoly salt-type catalysts were less efficient than the heteropolyacids. The Keggin-type polyoxometalates lead to more effective reactions in comparison with the Wells–Dawson-type polyoxometalates. Moreover, $H_6[P_2Mo_{18}O_{62}]$ was more effective than $H_6[P_2W_{18}O_{62}]$, which may be due to the difference in the reduction potentials of tungsten and molybdenum. However, the results indicate that the highest yield of oxidation was obtained when the oxidation of the substrates was realized with the $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ as catalyst.

Effect of the amount formic acid

Effect of the amount of formic acid on the oxidative desulphurization of different sulfur compounds was studied and the results are given in Table V. In the formic acid catalyzed reaction, the formic acid can interact with sulfur without any steric hindrance from alkyl groups. Therefore, the reactivity trend obtained in the formic acid catalyzed reactions reflects the intrinsic oxidation reactivity of the DBTs., The % sulfur removal of the simulated gas oil increased with increasing formic acid. It could be seen that a formic acid/H_2O_2 mole ratio of 1.0 (98 % conversion of DBT) was better than the other mole ratio. Therefore, in all the subsequent experiments, this formic acid/DBT mole ratio was used. The fuel mixed with H_2O_2/formic acid (performic acid) and the oxidative reaction occurred below 100 °C under atmospheric pressure. This was followed by liquid/ /liquid extraction to obtain a fuel with a low sulfur and an extract with a high sulfur content. Finally, the low sulfur fuel may require additional treatment. The extraction solvent was then removed from the extract for reuse and the concen-

TABLE V. Effect of formic acid amount on the oxidative desulphurization of different sulfur compounds using $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ as catalyst; conditions for the desulphurization: 2 mL H_2O_2/formic acid as oxidant, 0.1 mmol nanocatalyst, 5 mL DMF as extraction solvent, time 2 h, temperature 80 °C

Entry	Formic acid/sulfur compound mole ratio	Conversion, %			
		DBT	4-MDBT	4,6-DMDBT	BT
1	0.25	48	45	48	39
2	0.5	68	62	67	59
3	0.75	84	82	84	78
4	1	98	96	97	94
5	1.25	96	94	96	87
6	1.5	91	85	89	82

trated extract was made available for further processing to remove sulfur and to produce hydrocarbons.

Effect of temperature on the oxidative desulphurization of gas oil or simulated gas oil

The reaction was carried out at different temperatures under the same conditions using $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ as the nanocatalyst and the formic acid/H_2O_2 system. The results are given in Table VI, from which it can be seen that the yields of the products were a function of temperature. Conversion of the sulfur compounds was increased at higher reaction temperatures and longer reaction times. The conversion of sulfur in the simulated gas oil was the highest at 80 °C, at which temperature, a conversion of sulfur of 98% was obtained. The catalytic activities of the $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ in the oxidation of DBT at different temperatures, 30–80 °C, were compared. At 80 °C, percent conversion was higher than that at 30 and 40 °C. In 120 min, up to 98 % removal of sulfur was obtained at 80 °C for the $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ catalyst, which was superior to the $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ catalyst, with which 94 % conversion was achieved.

TABLE VI. Effect of temperature on the oxidative desulfurization of different sulfur compounds (conversion, %) using $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ as catalyst; conditions for the desulphurization: 2 mL H_2O_2/formic acid as an oxidant, 0.1 mmol nanocatalyst, 5 mL DMF as an extraction solvent, time = 2 h

Entry	Temperature, °C	Compound			
		DBT	4-MDBT	4,6-DMDBT	BT
1	30	55	47	49	42
2	40	67	59	62	55
3	50	74	65	76	65
4	60	88	82	84	79
5	70	96	94	95	91
6	80	98	96	97	94

CONCLUSIONS

A $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ nanocomposite was synthesized at a low temperature *via* the sol–gel method under oil bath conditions. Fixing of $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ into TiO_2 decreases the particle size of the crushed nano leaf of the anatase phase. The $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$–$TiO_2$ nanocomposite was a very active catalyst system for the model compound oxidation, while unmodified $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ was much less active. The oxidation reaction was selective as only sulfone was detected. For this polyoxometalates/H_2O_2/formic acid system, the oxidation reactivity decreased in the following order: DBT > 4,6-DMDBT > BT. The percent conversion increased when the amounts of oxidant and catalyst were increased. The addition of formic acid enhanced the conversion.

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ИЗВОД

АНАТАЗНИ ОКСИД ТИТАНА–ВАНАДИЈУМ-ПОЛИФОСФОМОЛИБДАТ КАО ЕФИКАСАН И ПРАКТИЧАН НАНОКАТАЛИЗАТОР ЗА ДЕСУЛФУРИЗАЦИЈУ ГАСНОГ УЉА

MOHAMMAD ALI REZVANI[1], ABDOLLAH FALLAH SHOJAEI[2] и FAROKHZAD MOHAMADI ZONOZ[3]

[1]*Department of Chemistry, Faculty of Science, University of Zanjan, 45371-38791 Zanjan, Iran,*
[2]*Department of Chemistry, Faculty of Science, University of Guilan, 419961-3769 Rasht, Iran и*
[3]*Department of Chemistry, Hakim Sabzevari University, Sabzevar, 397, Iran*

Нанокомпозит $(Bu_4N)_4H[PMo_{10}V_2O_{40}]–TiO_2$ је синтетисан у реакцији $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$ и титан-тетраизопропоксида на 100 °C применом сол–гел методе. Дебљина слоја анатазне фазе, која износи 20 nm, се смањује додатком $(Bu_4N)_4H[PMo_{10}V_2O_{40}]$. За овај полифосфомолибдат је нађено да оксидује гасно уље са високим процентом конверзије (више од 98 %). У овом раду је приказана ефикасна оксидативна десулфуризација гасног уља помоћу система мравља киселина/водоник-пероксид. Овај систем омогућава ефикасан, погодан и практичан метод за везивање сумпорних једињења.

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