

RESEARCH PAPER

Synthesis and Characterization of TBA-PV₂Mo₁₀@PVA as an Efficient and Reusable Heterogeneous Catalyst for Oxidative Desulfurization of Gasoline

Mohammad Ali Rezvani*, Maryam Shaterian, Nasrian Khalafi

Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran

ARTICLE INFO

Article History:

Received 10 November 2018

Accepted 26 January 2019

Published 01 April 2019

Keywords:

Gasoline

Heterogeneous Catalyst

Nanocomposite

Oxidative Desulfurization

Polyoxometalate

ABSTRACT

To prepare ultra-clean gasoline fuel, a new nanocomposite TBA-PV₂Mo₁₀@PVA was introduced as an efficient and green catalyst for oxidative desulfurization (ODS) process. The nanocomposite was successfully prepared by reaction of tetrabutylammonium bromide (TBA), H₅PMo₁₀V₂O₄₀, and poly vinyl alcohol (PVA) at room temperature *via* sol-gel method under oil-bath condition. The synthesized TBA-PV₂Mo₁₀@PVA was characterized by FT-IR, XRD, UV-vis, SEM and ³¹P NMR spectroscopy. The catalytic activity of catalyst was tested on the ODS of gasoline in the presence of CH₃COOH/H₂O₂ (1/1 volume ratio) as oxidant system and results were compared with model sulfur compounds (MSCs). After 2 h, the results were shown that the removal of total sulfur content could be reduced to 97% at the temperature of 35 °C. The main factors affecting the desulfurization efficiency, including catalyst dosage and temperature were investigated in detail. In addition, the kinetic parameters of oxidation of MSCs, reaction mechanism, and reusability of catalyst were discussed. The TBA-PV₂Mo₁₀@PVA nanocatalyst was separated and reused conveniently at the end of the reaction for five times. The excellent performance of this catalytic oxidation system can be a promising rout to achieve ultra-clean gasoline.

How to cite this article

Rezvani MA, Shaterian M, Khalafi N. Synthesis and Characterization of TBA-PV₂Mo₁₀@PVA as an Efficient and Reusable Heterogeneous Catalyst for Oxidative Desulfurization of Gasoline. J Nanostruct, 2019; 9(2): 349-364.

DOI: 10.22052/JNS.2019.02.017

INTRODUCTION

Sulfur-containing compounds are undesirable in gasoline and diesel fuels because of the emission of SO_x gases leading to air pollution. In order to protect the human health and reduce the environmental hazards, environmental regulations that tend to limit the sulfur levels to very lower ones have already been introduced in many countries during the last few decades (1). The specifications present a new and challenging task for the crude oil and its derivation refining industry. Much attention has been paid to low level sulfur approaching requirements for the deep desulfurization technologies currently (2-4). Hydrodesulfurization (HDS) can remove aliphatic and acyclic sulfur

compounds quite efficiently when adopted at an industrial scale. HDS is a catalytic chemical process to obtain ultra-low sulfur fuel which needs high temperature and pressure, large reactor tower and more active catalysts (5-7). Because of high hydrogen consumption, decreased catalysts life and low yield of products, HDS is very costly. Therefore, alternative desulfurization techniques have been investigated widely, among which oxidative desulfurization (ODS) is considered to be one of the promising new methods for super high desulfurization of petroleum oil. As a part of our ongoing efforts for developing the synthesis and application of POMs (8-12), herein we report the synthesis of TBA-PV₂Mo₁₀@PVA nanocomposite

* Corresponding Author Email: marezvani@znu.ac.ir

as a high-performance nanocatalyst for the elimination of organic sulfur compounds. To the best of our knowledge, it is the first reported results of the application of this catalyst for desulfurization of gasoline.

Polyoxometalates (POMs) are well-defined oxoanionic clusters of early transition metals that have attracted growing interest for the development of advanced functional materials (13-16). POMs are a type of intriguing catalysts that can be applied for a wide range of technologically relevant applications owing to reasonably high thermal stability, and reversible electron transfer ability under mild conditions (14). Furthermore, polyoxometalates have several advantages, including high flexibility in the modification of the acid strength, non-toxicity, environmental compatibility, ease of handling, and experimental simplicity (14-16). Keggin-type of POMs have been widely studied as heterogeneous and homogeneous catalyst for the oxidation of organic compounds (16,17). However, the application of this type of catalysts still suffers from some drawbacks, mainly the low surface area (1–10 m²/g) leading to the low efficiency and the high solubility, causing recycling difficulty and environmental problem (18). To overcome these disadvantages there is a need to invent a supported and heterogeneously active forms of POM (18,19). Organic polymers due to their excellent toughness and durability are suitable candidates as matrices for assembling polyoxometalates (20).

In this investigation, polyvinyl alcohol (PVA) is used to play this important and useful role as great matrices. TBA-PV₂Mo₁₀@PVA has lipophilic cation which acts as a good phase transfer agent and transfers the peroxometal anion into organic phase. A phase transfer between the aqueous phase containing the oxidants and catalyst and the organic phase containing the oil limits the overall efficiency. This aspect of the process can be improved by using a phase transfer agent that facilitates the transfer of reagents between the two immiscible phases. A new approach to phase transfer catalysis uses surfactant based or amphiphilic catalysts, which combine together a polyoxoanion and a quaternary ammonium cation. However, the organic-inorganic hybrid nanocomposite is successfully designed by reaction of TBA-PV₂Mo₁₀ and PVA *via* sol gel method under oil-bath condition as a phase transfer catalyst for ODS of gasoline. In typical

oxidation reactions, the mixture of H₂O₂/CH₃COOH is used as oxidant and polar CH₃CN applied as an extraction solvent for removing the oxidized products. In addition, the influences of different parameters on the desulfurization efficiency are investigated in detail.

MATERIALS AND METHODS

Materials and characterization methods

All chemicals and solvents were commercially available and used as received. Benzothiophene (BT) and thiophene (Th), n-heptane, hydrogen peroxide (H₂O₂, 30 vol.%), and acetic acid (CH₃COOH, 99.7%), acetonitrile (CH₃CN), sodium tungstate dihydrate (Na₂WO₄·2H₂O), disodium hydrogen phosphate (Na₂HPO₄) and tetrabutylammonium bromide (TBAB) were purchased from Sigma–Aldrich company. Several heteropolyoxometalates catalysts were prepared according to procedures published in literature (11, 12). Typical real gasoline was used with the following specification: density 0.7863 g/mL at 15 °C, total sulfur content 0.287 wt.%.

Fourier transform infrared spectroscopy (FT-IR) studies were done on a Thermo-Nicolet-is 10 spectrometer, using KBr disks in the range 400–4000 cm⁻¹. Ultraviolet–visible (UV–vis) spectra were measured with a double beam Thermo-Heylos spectrometer in the range of 200–400 nm. Measurements were performed by using quartz cuvettes. Powder X-ray diffraction (XRD) analysis were collected between 2θ = 5°–80° at room temperature on a Bruker D8 advance powder X-ray diffractometer with a Cu-Kα (λ = 0.154 nm) radiation source. The surface morphologies were examined by scanning electron microscope (SEM) by LEO 1455 VP equipped with an energy dispersive X-ray (EDX) spectroscopy apparatus. ³¹P NMR spectrums were recorded on Bruker Ultra Shield 250 MHz. The total sulfur and mercaptan content in gasoline before and after treatment were determined using X-ray fluorescence with a TANAKA X-ray fluorescence spectrometer RX-360 SH.

Synthesis of tetrabutylammonium divanadododecamolibdophosphate (TBA-PV₂Mo₁₀)

H₅PV₂Mo₁₀O₄₀ was synthesized according to published literature [12]. In summary, in 50 mL of boiling water sodium metavanadate (12.2 g, 100 mmol) was dissolved and mixed with (3.55 g, 25 mmol) of Na₂HPO₄ in 50 mL of water. The solution

was cooled and 5 mL of concentrated sulfuric acid (17M, 85 mmol) was added to it. The solution was developed a red color. Na₂MoO₄·2H₂O (60.5 g, 250 mmol) was dissolved in 100 mL of water and added to the red solution with vigorous stirring. Concentrated sulfuric acid (42 mL, 17 M, 714 mmol) was added to it, slowly. The hot solution was cooled to room temperature. The 10-molybdo-2-vanadophosphoric acid was extracted with 500 mL of ethyl ether. Air was passed through the heteropoly etherate (bottom layer) to free it of ether. The solid remaining behind was dissolved in water, concentrated to first crystal formation, as already described. The large red crystals that formed were filtered, washed with water, and air dried. By addition of solid potassium carbonate, the pH is adjusted between 6 and 7. By addition of solid potassium chloride (2.2 g, 40 mmol) an orange potassium salt (2.5 g, 45 mmol) is precipitated and recrystallized in water. Then, the remaining solid was dissolved in 55 mL of warm distilled water.

Then, aqueous solution of tetrabutylammonium bromide (Bu₄NBr) (1.8 mmol) was added dropwise, with vigorous stirring. The solid formed was filtered off, recrystallized with acetonitrile, ether and air dried (Fig. 1). The resultant (((n-C₄H₉)₄N)₄K[PMo₁₀V₂O₄₀]) solid is designated as TBA-PV₂Mo₁₀.

Synthesis of the TBA-PV₂Mo₁₀@PVA nanocatalyst

Preparation of TBA-PV₂Mo₁₀@PVA via sol-gel method under oil-bath condition is as follows: 0.1 g of PVA was dissolved in 35 mL of hot distilled water and the temperature was fixed at 60 °C. Then, aqueous solution of 0.04 g mL⁻¹ of TBA-PV₂Mo₁₀ in water was added drop wise in it. The mixture was stirred to dissolve any solid. Then, the sol was heated to 65 °C under oil bath condition until a hydrogel TBA-PV₂Mo₁₀@PVA was formed. Finally, the gel was filtered, washed with deionized water-acetone and dried in oven at 50 °C for 2 h. (Fig. 2).

ODS of model fuel

The ODS process of model fuel was carried out in a round-bottom flask equipped with a magnetic

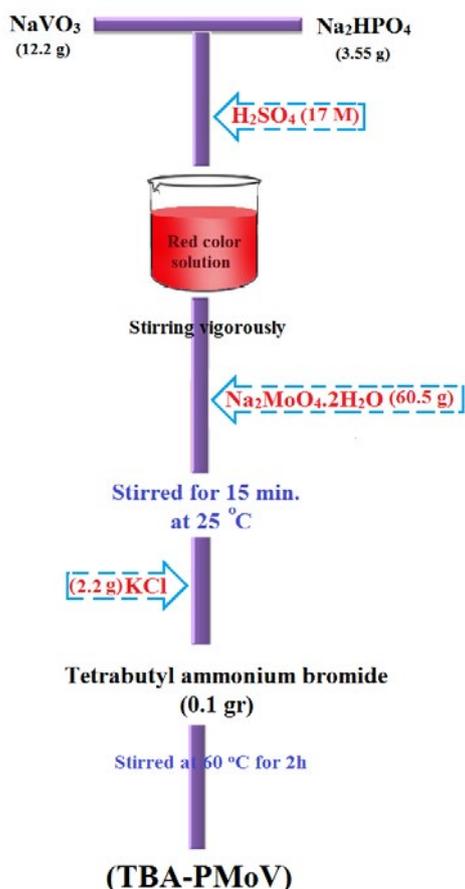


Fig. 1. Schematic illustration of synthesis of TBA-PMoV.

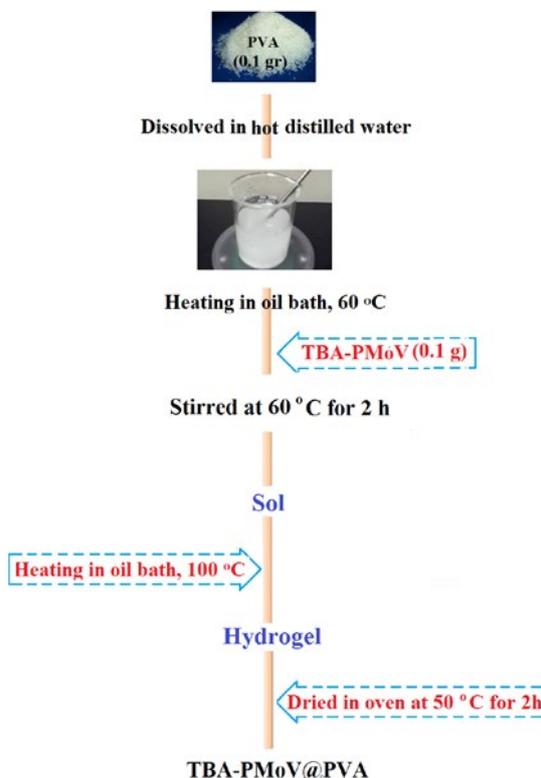


Fig. 2. Schematic illustration of synthesis of TBA-PV₂Mo₁₀@PVA.

stirrer and a thermometer. Some of the MSCs such as BT or Th was dissolved in n-heptane as a model fuel to evaluate the catalytic performance of TBA-PV₂Mo₁₀@PVA and the reactivity of mercaptans in the oxidation reaction. First, the water bath was heated and stabilized to a certain temperature (25-40 °C). 4 mL CH₃COOH/H₂O₂ in the volume ratio of 1/1 was added and mixed with 50 mL of the model sulfur compound (Th or BT). 0.1 g of TBA-PV₂Mo₁₀@PVA was added to the flask as a catalyst. The flask was immersed in a heating bath and stirred at 500 rpm for 2 h. The biphasic was formed and separated by decantation. After the decantation, the upper phase (model fuel) was withdrawn and the remained MSCs in model fuel were analyzed by GC-FID (Agilent 6890). The conversion of BT in the model fuel was used to calculate the removal of MSCs. The oxidized MSCs was characterized by GC-MS (Varian cp-1200 quadrupole MS), HP5890 Series II with 5972 Series MS detector. The results indicated a perfect match of the mass spectrum of the product with the standard benzothiophene sulfone. Also the total sulfur concentration of the model gasoline before and after ODS was determined using a Tanaka Scientific RX-360 SH X-ray fluorescence spectrometer (ASTM D-4294 method). The desulfurization (%) of real gasoline fuel was calculated by the following equation, where S₀ is the sulfur concentration in the original fuel, and S_t is the sulfur concentration in the treated oil.

$$\% \text{Desulfurization} = (S_0 - S_t) / S_0 \times 100 \quad (1)$$

The concentrations of the MSCs (BT) in the treated model fuel were determined from

their peak areas in the GC-FID chromatograms using a calibration curve obtained with the peak areas of their standard concentrations. The change in concentration was calculated as conversion (%) using equation (2), in which C₀ is initial concentration of BT, and C_t is the final concentration of BT after time t.

$$\% \text{Conversion} = (C_0 - C_t) / C_0 \times 100 \quad (2)$$

ODS of real gasoline

For ODS of real fuel, 50 mL gasoline was added to two-necked round bottom flask. The temperature of solution fixed at 35°C. Then, 0.1 g of TBA-PV₂Mo₁₀@PVA was added to the solution and strongly stirred by a magnetic stirrer. A mixture of CH₃COOH: H₂O₂ (4 mL) in ratio of 1/1 was added drop wise in 2 h, while it has been stirring vigorously. When the ODS has been finished the mixture was cooled down to room temperature and then 10 mL of CH₃CN was added to extract the oxidized MSCs. The acetonitrile/oil ratio used was 1/5 by volume. The biphasic mixture was separated by decantation. The oil phase was separated and weighed to calculate present of gasoline (for three times reaction: 98, 97 and 96%). The total sulfur and mercaptan content in gasoline before and after ODS were determined using standard test method (ASTM D-4294 and D-3227). Results are showed in Table 1.

RESULTS AND DISCUSSION

Characterization of materials

The identification of specific chemical bands and functional groups of the synthesized samples was characterized using FT-IR spectroscopy to

Table 1. Oxidation desulfurization of gasoline by TBA-PV₂Mo₁₀@PVA.

Entry	Properties of gasoline	Unit	Method	Before ODS	After ODS ^a
1	Density by hydrometer @ 15 °C	g/mL	ASTM D1298	0.7992	0.7990
2	Water content by distillation	vol. %	ASTM D4006	Nil	Nil
3	Sediment by extraction	vol. %	ASTM D473	0.01	0.01
4	Total sulfur content	Wt. %	ASTM D4294	0.398	0.012
5	Pour point	°C	ASTM D97	-12	-12
6	Mercaptans	ppm	ASTM D3227	87	3
7	Total acidity	mg KOH/g	ASTM D664	0.13	0.12
8	Salt	ptb	ASTM D3230	18	16
		IBP		44.4	44.1
		FBP		205.3	204.5
9	Distillation	10	ASTM D 86	67.6	67.1
		50		112.7	112.2
		90		179.5	179.1
		95		205.3	204.8

^a Condition for desulfurization: 50 ml of gasoline, 4 mL oxidant, 10 mL of extraction solvent, time = 2 h, and temperature = 35 °C, catalyst= TBA-PV₂Mo₁₀@PVA..

Abbreviation: API GR.; API gravity (API-American Petroleum Institute); API = 141.5/Specific gravity - 131.5.

confirm their successful incorporation. The FT-IR spectra of different POMs salts showed the common characteristic absorption peaks ranging from 500 to 1100 cm⁻¹ corresponded to POM anion configurations, and the peaks ranging from 1450 to 3000 cm⁻¹ showed the pattern of quaternary ammonium salts (Fig. 3). The peaks of POM in 560-590 cm⁻¹, 765-796 cm⁻¹, 860-885 cm⁻¹, 940-965 cm⁻¹, and 1060-1075 cm⁻¹ related to the symmetric vibrations of O–Mo–O, octahedral bridge/edge sharing Mo–O_c–Mo, octahedral corner sharing Mo–O_b–Mo, terminal Mo–O_d, and P–O configurations, respectively (14-16). These configurations collectively account for the Keggin type POMs. The absorption peaks in the range of 1450-1475 cm⁻¹ indicated the C–H bending vibrations for CH₂ and the peaks at 640 cm⁻¹ showed N–H bending vibrations. The adoption

bands at 2850 and 2915 cm⁻¹ represented the stretching vibrations of C–H for CH₂ and CH₃ (16). From FT-IR spectra shown in Fig. 3, it can understand that there is a clear and notable difference among TBA-PV₂Mo₁₀ powder, PVA and TBA-PV₂Mo₁₀@PVA nanocomposite. As presented in Table 2, characteristic bands of TBA-PV₂Mo₁₀ on PVA, compared to pure TBA-PV₂Mo₁₀, which shows a blue- or red-shift indicate the electrostatic and hydrogen-bond interactions between TBA-PV₂Mo₁₀ and PVA. According to this table Mo-O corner-sharing band experiences a red shift and show it is involved in the interaction with hydrogen on the PVA and formed a hydrogen bond.

Fig. 4 shows the UV-vis spectra of pure PVA, TBA-PV₂Mo₁₀ and TBA-PV₂Mo₁₀@PVA as comparative data to confirm the changes on pure TBA-PV₂Mo₁₀ after introducing PVA. The UV-vis spectra of PVA

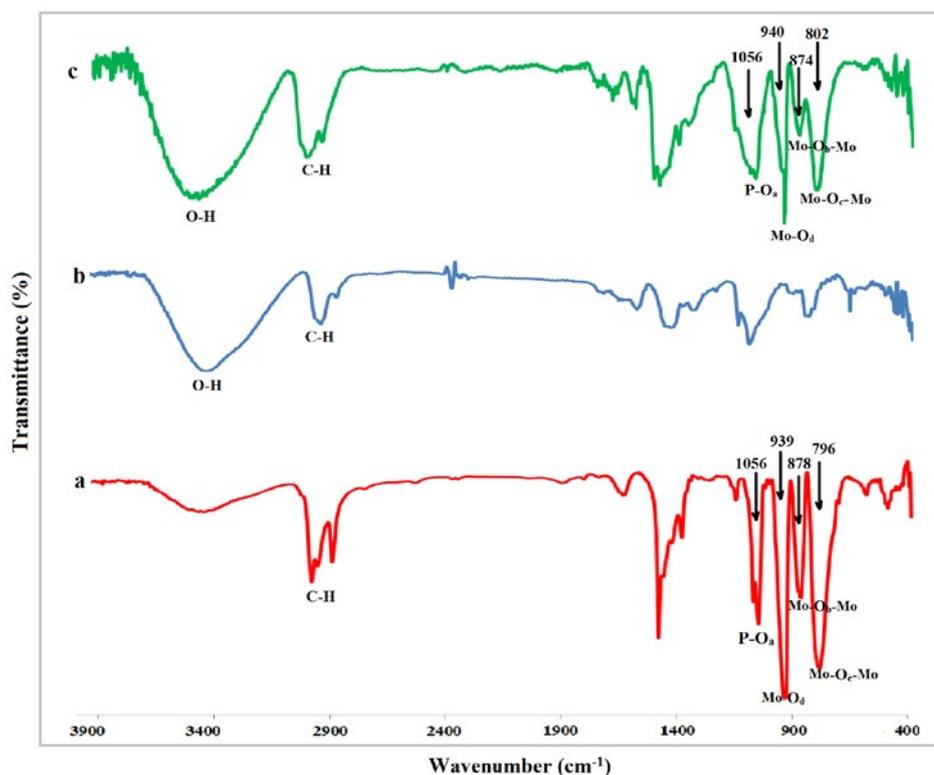


Fig. 3. FT-IR spectra of (a) PV₂Mo₁₀, (b) PVA and (c) TBA-PV₂Mo₁₀@PVA.

Table 2. FT-IR related to Keggin TBA-PMoV and TBA-PV₂Mo₁₀@PVA.

Compound	Wavenumber (cm ⁻¹)			
	ν (Mo–O _c –Mo)	ν (Mo–O _b –Mo)	ν (Mo–O _d)	ν (P–O _a)
TBA-PV ₂ Mo ₁₀ @PVA	802	874	940	1056
TBA-PV ₂ Mo ₁₀	796	878	939	1056

(a), TBA-PV₂Mo₁₀ (b), and TBA-PV₂Mo₁₀@PVA (c) (Fig. 4), showed strong absorption peak at 214 nm which assigned to oxygen-to-vanadium or O⁻² to Mo⁺⁶ charge-transfer transition of PV₂Mo₁₀, 213 nm for TBA-PV₂Mo₁₀@PVA and 270 nm for PVA which indicated TBA-PV₂Mo₁₀@PVA blue shift towards PVA and red shift towards TBA-PV₂Mo₁₀. Excitation of the oxygen to metal charge transfer band of TBA-PV₂Mo₁₀ in near UV light region results in the charge transfer from an O⁻² to Mo⁺⁶, forming the O⁻¹ and Mo⁺⁵. By introducing TBA-PV₂Mo₁₀ on PVA, corresponding to (a, b), the intensity of bands decreased so can persuade us that interaction between them completed and spectra of PVA overlapped TBA-PV₂Mo₁₀. This confirmative state made us to use TBA-PV₂Mo₁₀@PVA during the ODS process of gasoline.

The surface morphology of TBA-PV₂Mo₁₀@PVA nanocomposite was investigated by SEM. A typical SEM picture of the as prepared TBA-PV₂Mo₁₀@PVA catalyst is shown in Fig. 5. From Fig. 5(a), the blank PVA film is observed to be relatively flat surface and Fig. 5(b) shows TBA-PV₂Mo₁₀ consist of very small agglomerated nanoparticle. This

picture (Fig. 5 c) shows non regular morphology. Nanocomposite TBA-PV₂Mo₁₀@PVA is made and the estimated particle sizes are seen to be nano-scale. The SEM images, Fig. 5(c), of TBA-PV₂Mo₁₀@PVA present the self-assembly of TBA-PV₂Mo₁₀ with PVA. The structures of the nanocomposite TBA-PV₂Mo₁₀@PVA conform that the rate of stirring as well as the given temperature is optimum, which led to appropriate nanoshape. The presence of Keggin type of TBA-PV₂Mo₁₀ on PVA, as substrate, indicates an interaction between them that was according to our expectations and can satisfy to be as an efficient catalyst for next project.

The powder nanostructures were investigated by X-ray diffraction (XRD) measurement (25). XRD patterns of TBA-PV₂Mo₁₀, PVA and TBA-PV₂Mo₁₀@PVA are shown in Fig. 6 and were collected in the range 2θ = 5°–70° and continuous scan mode. XRD patterns (a), (b) and (c) in Fig. 6 corresponded to TBA-PV₂Mo₁₀, PVA and TBA-PV₂Mo₁₀@PVA respectively. It is obviously seen that in the XRD patterns of kegginn type POM special peak has appeared. The existence of sharp peaks in 5°–10° can prove the structure of synthesized TBA-

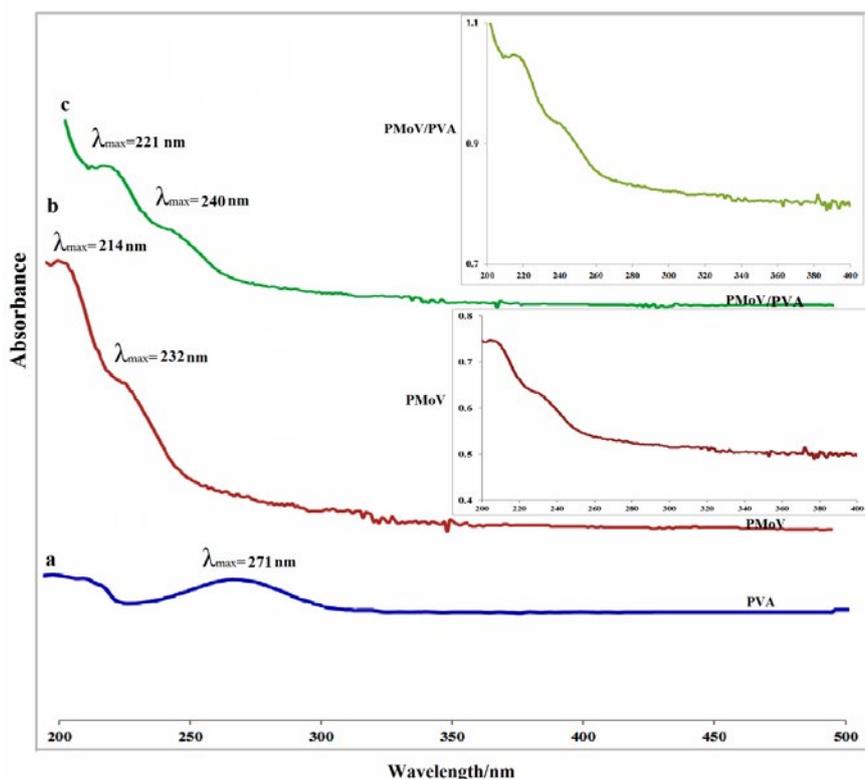


Fig. 4. UV-vis spectra of (a) PV₂Mo₁₀, (b) PVA and (c) TBA-PV₂Mo₁₀@PVA.

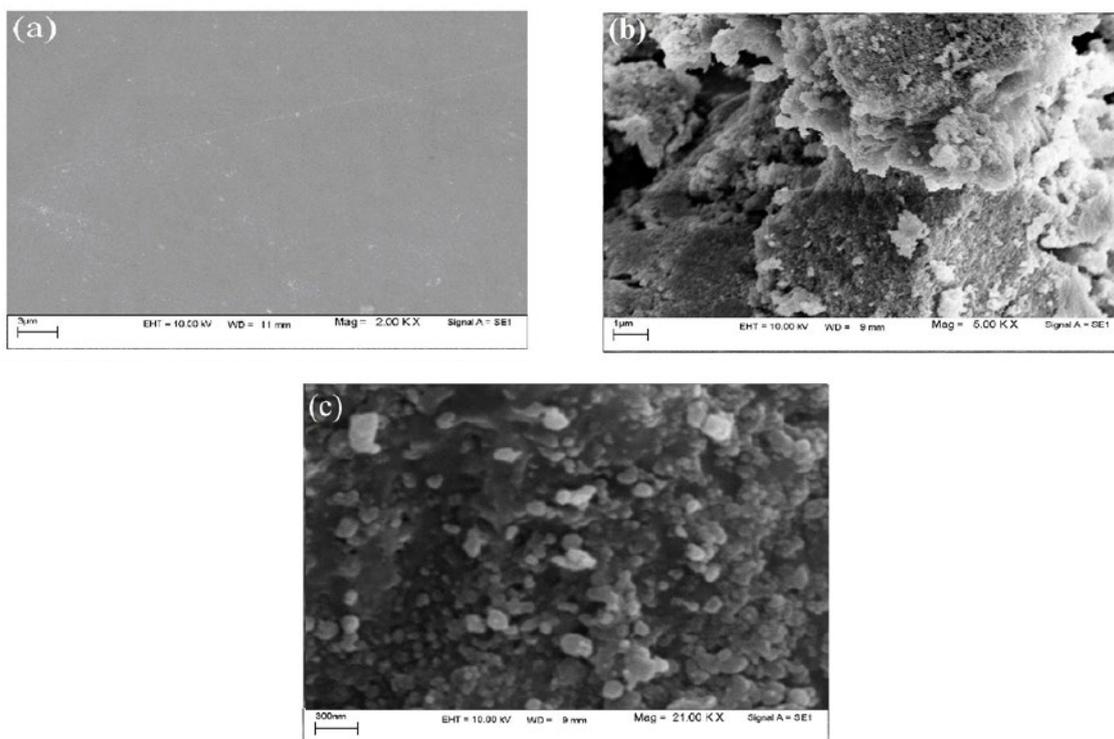


Fig. 5. SEM images of (a) PVA film (3 μm), (b) PV₂Mo₁₀ (1 μm), and (c) TBA-PV₂Mo₁₀@PVA (300 nm).

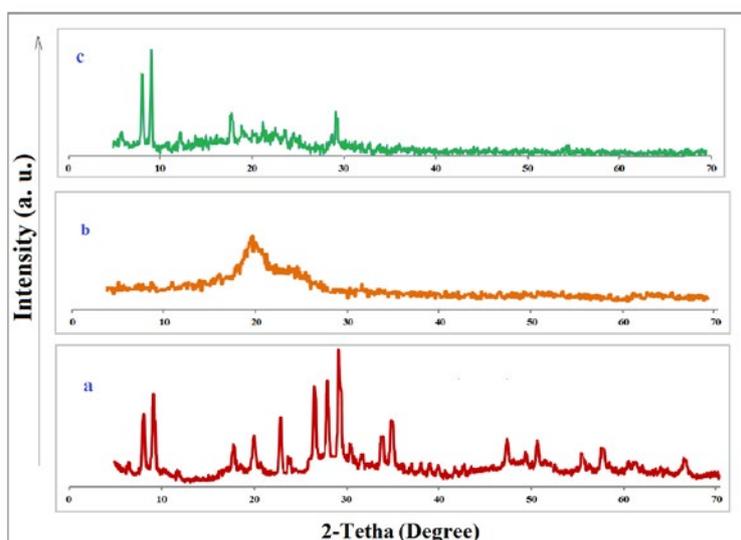


Fig. 6. XRD pattern of (a) PV₂Mo₁₀, (b) PVA, and (c) TBA-PV₂Mo₁₀@PVA.

PV₂Mo₁₀ as a Keggin type POM. Besides, the peaks at 15°-20° and 30° are important to be sure about the structure. According to previous reporting, the XRD pattern of pure PVA must have a sharp peak in 19.8° (21). Fig. 6 consists of required information of PVA and TBA-PV₂Mo₁₀. It can be seen that the

diffraction of PVA is overlapped by TBA-PV₂Mo₁₀ so the intensity around 20° is decreased. Therefore, TBA-PV₂Mo₁₀ has immobilized on PVA with a good interaction between them. Scherer equation ($D = 0.89\lambda/\beta\cos\theta$) was used to calculate the nano crystallite size by XRD radiation of wavelength

from measuring full width at half maximum of peaks in radian located at any 2θ in the pattern. The mean crystal size obtained was around 21 nm.

Nuclear magnetic resonance (NMR) of the different active nuclei constituting POM is considered to be a very powerful method to clear their molecular structures both in solution and in the solid state. The ³¹P NMR spectrum of TBA-PV₂Mo₁₀ and TBA-PV₂Mo₁₀@PVA in DMSO at ~25 °C was a clear single line spectrum at -3.9 ppm due to the internal phosphorus atom, thereby confirming the compound's purity (it suggested that no other P-related impurities present), as shown in Fig. 7. According to Fig. 1-5 it is proved that TBA-PV₂Mo₁₀ is put on polymer matrixes thus the useful nanocatalyst is synthesized in its efficient way for developing the next step which is desulfurization of gasoline.

General desulfurization process

A model oil was made by adding Th and BT into *n*-heptane solvent, with a total sulfur concentration of 500 mg/L. The MSCs are mixed with CH₃OOH/H₂O₂ and TBA-PV₂Mo₁₀@PVA then the ODS takes place at 35 °C under atmospheric pressure. This is followed by a polar liquid extraction (CH₃COOH) to obtain gasoline with low sulfur. H₂O₂ first reacts with organic acid (CH₃COOH) quickly and generates peracid (CH₃COOOH). CH₃COOOH can efficiency converts MSCs to sulfones without forming a substantial amount of residual product. The nanocatalyst accepted the active oxygen from the oxidant H₂O₂ to form new oxoperoxo species mediate. The role of the metal atoms, W or V, is to form peroxy-metal species which are able to activate the H₂O₂ and peracid molecules. The

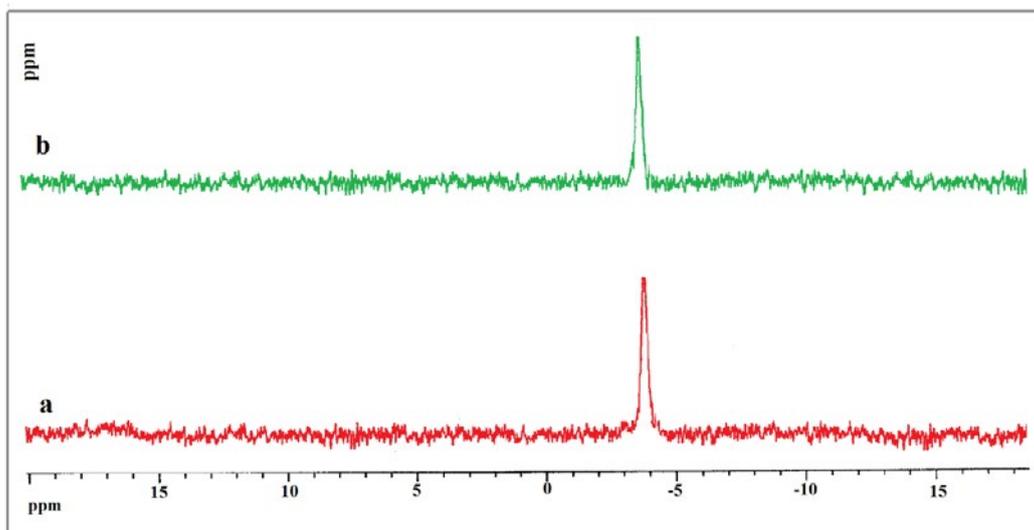


Fig. 7. ³¹P NMR of (a) PV₂Mo₁₀ and (b) TBA-PV₂Mo₁₀@PVA.

Table 3. Effect of different catalyts on the ODS of real gasoline.^a

Entry	Catalyst	Removal (%)			
		Total sulfur content		Mercaptans	
		With H ₂ O ₂	Without H ₂ O ₂	With H ₂ O ₂	Without H ₂ O ₂
1	TBA- PV ₂ Mo ₁₀ @PVA	97	42	97	41
2	TBA- PV ₂ Mo ₁₀	90	36	88	35
3	H ₅ PMo ₁₀ V ₂ O ₄₀	83	34	85	34
4	(NH ₄) ₅ PV ₂ Mo ₁₀ O ₄₀	81	33	84	33
5	K ₅ PV ₂ Mo ₁₀ O ₄₀	80	33	83	32
6	H ₃ PMo ₁₂ O ₄₀	78	32	78	31
7	H ₃ PW ₁₂ O ₄₀	78	32	77	31
8	H ₄ SiW ₁₂ O ₄₀	77	31	77	30
9	PVA	26	17	25	16
10	(N(tBu) ₄) ₄ Br	22	16	22	15
11	None	21	16	21	15

^a Condition for desulfurization : 50 mL of gasoline, 0.1 g catalyst, 4 mL acetic acid/H₂O₂, 10 mL of extraction solvent, time = 2 h, and temperature = 35 °C.

cation with carbon chain transferred oxoperoxo species to the substrates (Th or BT) and made the ODS process accomplish completely. This mechanism involves in the first step the easy formation of the peroxometalate species (27).

ODS of real gasoline

From the results of Table 1, after oxidation process, total sulfur content (Entry 4) and content of mercaptans (Entry 6) were very low, while other properties of gasoline remained unaffected. Also, it was demonstrated that the mercaptan scavenger, TBA-PV₂Mo₁₀@PVA, can catalyze the ODS process in 2 h and reduce total sulfur content of gasoline from 0.398 wt.% to 0.012 wt.% and also, reduce content of mercaptans from 87 ppm to 3 ppm.

Effect of the catalyst structure

As determined in previous work, the catalytic activity of the catalysts depends on the polyoxometalate anion and cation (6,7). The effect of the nature of the catalyst on the oxidative desulfurization of gasoline using CH₃COOH/H₂O₂ as the oxidant is shown in Tables 1 and 4. The amount of each catalyst was constant throughout the series. Blank experiment was performed in the absence of catalyst. Under these conditions, percent conversion was very low (22% in 2 h) at 35 °C (Table 3, entry 9). The results show that the catalytic

activity of TBA-PV₂Mo₁₀@PVA nanocomposite has presented much higher than other unsupported polyoxometalates (Fig. 8). Also in Fig. 8, the catalytic activity of supported and unsupported catalyst with H₂O₂ (3 and 4) and without H₂O₂ (1 and 2) were compared. The supported kegggin type polyoxometalate catalyst TBA-PV₂Mo₁₀ was very active systems for the oxidation of BT, while other studied polyoxometalates systems were very less active. This system TBA-PV₂Mo₁₀@PVA with a phase transfer or emulsion catalyst comprising a quaternary ammonium salt-based polyoxometalate is shown to be very active system for ODS of BT and real gasoline. This quaternary ammonium Keggin type which has lipophilic cation act as phase transfer agent and transfer the peroxometal anion into organic phase. That is, the oxidation reactivity of the catalysts depends on the type of counteraction: ((C₄H₉)₄N)⁺ > NH₄⁺ > K⁺. Also, the vanadium-substituted Keggin type polyoxometalate catalyst was very active systems for the ODS of gasoline.

Effect of Catalyst dosage

Another factor that should be concerned is the catalyst dosage. It was found that the catalyst dosage has a marked influence on the efficiency of process (Table 4). Under oxidation, without catalyst TBA-PV₂Mo₁₀@PVA (blank), 24% of

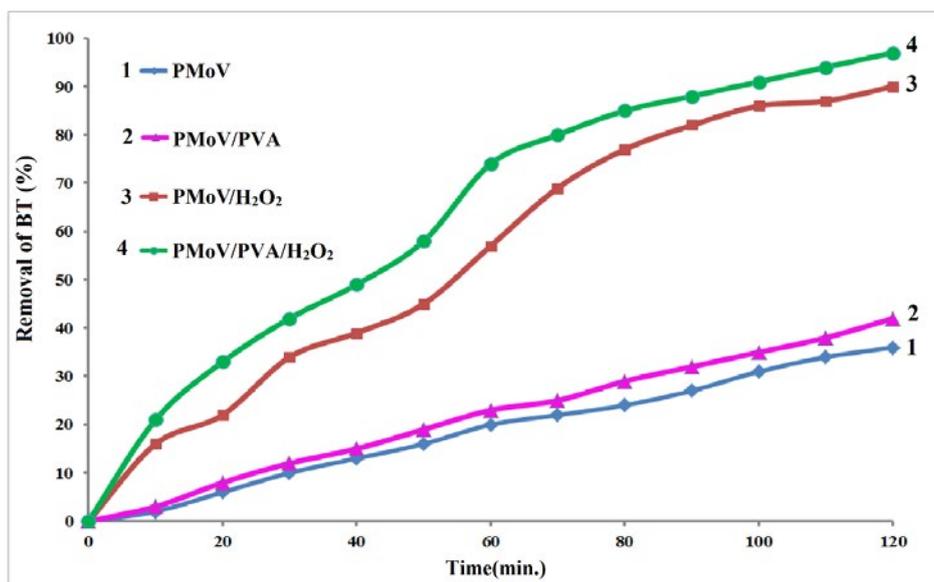


Fig. 8. Oxidation desulfurization of BT (500 ppm S) using (1) PMoV, (2) TBA-PV₂Mo₁₀@PVA, (3) PV₂Mo₁₀/H₂O₂, (4) PV₂Mo₁₀/PVA/H₂O₂ oxidation systems.



the Th, 23% of the BT and 23% of real gasoline are removed from the n-heptane phase in 120 min. Percent conversion of real gasoline in the presence of TBA-PV₂Mo₁₀@PVA were found to be 68%, 88% and 97%, corresponding to catalyst amount of 0.06, 0.08 and 0.1 gr respectively. Desulfurization efficiency increased rapidly with the increase of catalyst dosage (Fig. 9). The results indicate that, increasing the dosage of catalyst, more peroxy-polyoxo compound species can be formed and therefore deepens reaction. The increasing catalyst quantity (TBA-PV₂Mo₁₀@PVA) enhances the removal rate of sulfur because the concentration of the catalytically active species (Mo (O₂)_n^{-Q+}) increased. Results revealed that TBA-PV₂Mo₁₀@PVA is active for the oxidation of sulfur

compounds and more than 97% of the total sulfur removal was obtained during the ODS process. The results are summarized in Table 4.

Effect of temperature

The reaction was carried out at different temperatures under the same conditions by TBA-PV₂Mo₁₀@PVA as a catalysts and CH₃COOH/H₂O₂ as oxidant. The results are shown in Table 5 and Fig. 10. The results show that yields of products are a function of temperature. Percent conversion of sulfur in model fuel and in real gasoline has increased with temperature and time (Fig. 10). Percent conversion of sulfur in simulated fuel at 35 °C is higher than at 30 °C. 97% conversion of sulfur was obtained at 35 °C in 120 min. The

Table 4. Effect of catalyst dosage on the ODS of gasoline and MSCs. ^a

Entry	Amount of catalyst (g)	Removal (%)		
		Th	BT	Gasoline
1	0 (none)	24	23	23
2	0.02	40	39	38
3	0.04	51	49	48
4	0.06	72	70	69
5	0.08	90	88	88
6	0.1	98	97	97
7	0.11	98	97	97
8	0.12	98	97	97

^a Condition for desulfurization: 50 ml of gasoline, 4 mL oxidant, 10 mL of extraction solvent, time = 2 h, and temperature = 35 °C, catalyst= TBA-PV₂Mo₁₀@PVA.

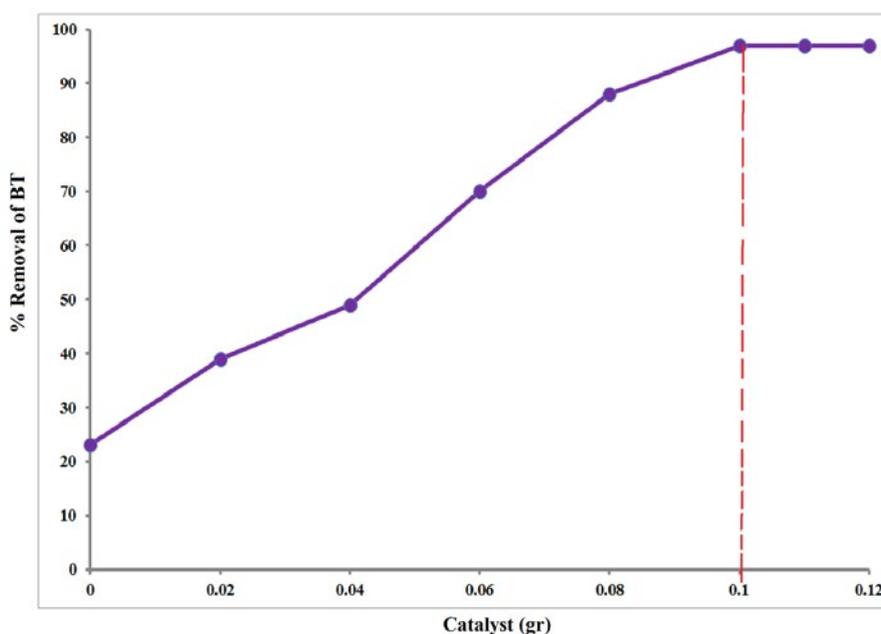


Fig. 9. Effect of catalyst dosage on BT removal.



effects of reaction time and temperature on benzothiophene oxidation are shown in Fig. 10 (a). At low temperature, the oxidative conversion of BT was very low, which increased gradually with increase in reaction time. At 25 and 30 °C, the BT conversion reached 72% and 84% after 120 min of reaction time, respectively. The oxidation rate of BT increased rapidly with increase in temperature. At 35 °C, 97% conversion was attained in 2 h. The oxidation of Th was also found to increase with

temperature and reaction time (Fig. 10(b)). At 25 and 30 °C, maximum conversions of 74% and 89% were attained in 2 h, while at 35 °C, more than 98% conversion of BT was achieved in 120 min reaction time.

Effect of different oxidative system on the ODS process

Effect of oxidative system on the ODS of gasoline was studied (Table 6). Hydrogen peroxide, KMnO₄

Table 5. Effect of different temperatures on the ODS of gasoline and MSCs. ^a

Entry	Temperature (°C)	Removal (%)		
		Th	BT	Gasoline
1	25	74	72	71
2	30	89	84	83
3	35	98	97	97
4	40	98	97	97

^a Condition for desulfurization: 50 ml of gasoline, 4 mL oxidant, 10 mL of extraction solvent, time = 2 h, and temperature = 35 °C, catalyst= TBA-PV₂Mo₁₀@PVA.

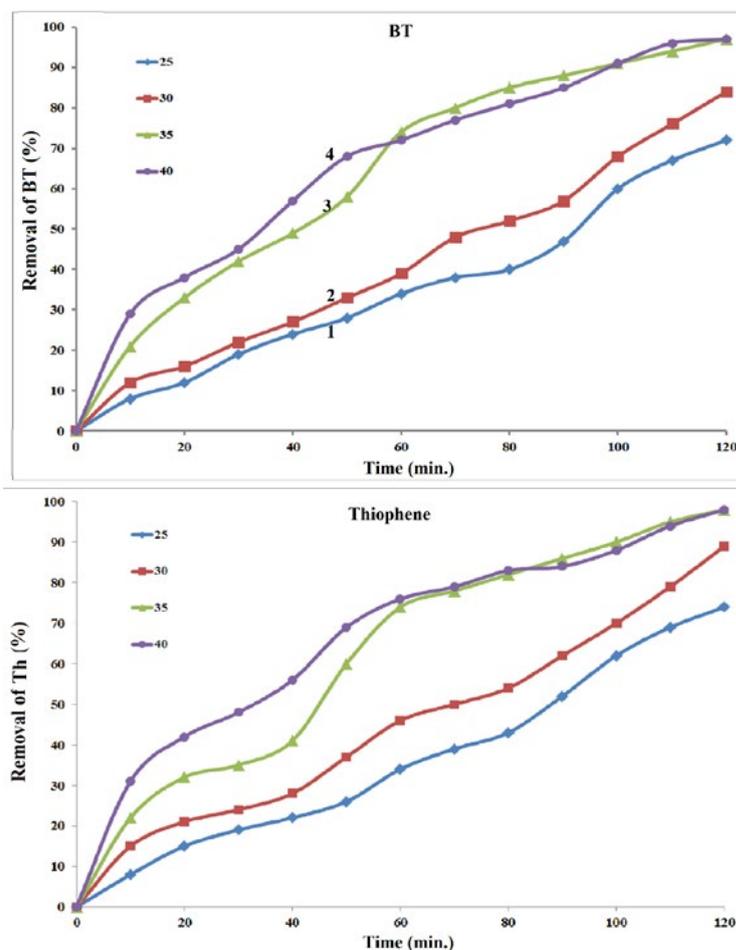


Fig. 10. Oxidation desulfurization of BT and Th (500 ppm S) at different temperature by TBA-PV₂Mo₁₀@PVA catalyst.



and K₂Cr₂O₅ were selected as oxidizing agents which were used in the presence of organic or inorganic acids such as; acetic acid, oxalic acid, benzoic acid, H₂SO₄ and H₂CO₃ to acidify the system. The results in Table 6 showed oxidation reactivity in inorganic acids, H₂SO₄ and H₂CO₃, are lower than organic acids. H₂SO₄ and H₂CO₃ cannot dissolve in real gasoline; therefore % sulfur removal of gasoline in inorganic acid/H₂O₂ was lower than organic acid/H₂O₂ system. Among these acids, HCOOH and CH₃COOH are inexpensive reagents. CH₃COOH has lesser toxicity than HCOOH. Thus, in the current study for ODS of gasoline the H₂O₂ in the presence of organic acid (CH₃COOH) were used as oxidants. The results are shown in Table 6, which indicates that the oxidation of real gasoline carried out in the presence of H₂O₂ without acetic acid resulted in a maximum of 78% conversion of all the sulfur compounds (entry 6). In the presence of acetic acid but no H₂O₂, the maximum conversion was 49% (entry 7). These results indicated that the oxidation of the sulfur compounds is governed by peracetic acid (CH₃COOOH), which is formed

by the reaction of H₂O₂ and CH₃COOH. In the absence of CH₃COOH or H₂O₂, no peracetic acid was formed and only H₂O₂ or CH₃COOH resulted in a low removal of total sulfur or mercaptan of real gasoline (entry 6 and 7).

Effect of the amount of acetic acid

Effect of the amount of acetic acid on the ODS of different sulfur compounds was studied and the results are given in Table 7. In the acetic acid catalyzed reaction, the acetic acid can interact with sulfur without any steric hindrance from alkyl groups. Therefore, the reactivity trend obtained in the acetic acid catalyzed reactions reflects the intrinsic oxidation reactivity of the BT. The percent sulfur removal of the mode fuel increased with increasing acetic acid. A mixture of acetic acid: H₂O₂ in ratio of 1:1 was better than the other mole ratio. Therefore, in all the subsequent experiments, this acetic acid/H₂O₂ mole ratio was used. The gasoline mixed with acetic acid/H₂O₂ (peracetic acid) and the oxidative reaction occurred below 40 °C under atmospheric pressure.

Table 6. Effect of different oxidation system on the ODS of gasoline and MSCs.^a

Entry	Oxidant	Acid	Removal (%)	
			Mercaptans	Total sulfur content
1	H ₂ O ₂	acetic acid	97	97
2	H ₂ O ₂	oxalic acid	89	97
3	H ₂ O ₂	benzoic acid	87	92
4	H ₂ O ₂	H ₂ SO ₄	85	91
5	H ₂ O ₂	H ₂ CO ₃	84	79
6	H ₂ O ₂	--	78	78
7	--	acetic acid	48	49
8	KMnO ₄	formic acid	86	85
9	KMnO ₄	oxalic acid	75	74
10	KMnO ₄	H ₂ SO ₄	74	73
11	KMnO ₄	--	73	74
12	K ₂ Cr ₂ O ₅	formic acid	84	76
13	K ₂ Cr ₂ O ₅	oxalic acid	76	74
14	K ₂ Cr ₂ O ₅	H ₂ SO ₄	73	74
15	K ₂ Cr ₂ O ₅	--	74	73

^a Condition for desulfurization: 50 ml of gasoline, 4 mL oxidant, 10 mL of extraction solvent, time = 2 h, and temperature = 35 °C, catalyst= TBA-PV₂Mo₁₀@PVA.

Table 7. Effect of acetic acid amount on the ODS of gasoline and MSCs.^a

Entry	acetic acid/sulfur compound volume ratio	Removal (%)		
		Th	BT	Gasoline
1	0.25	56	54	53
2	0.5	69	67	66
3	0.75	86	85	85
4	1.0	98	97	97
5	1.25	97	96	95
6	1.5	97	95	95

^a Condition for desulfurization: 50 ml of gasoline, 4 mL oxidant, 10 mL of extraction solvent, time = 2 h, and temperature = 35 °C, catalyst= TBA-PV₂Mo₁₀@PVA.

Mechanism of the oxidative desulfurization reaction

The mechanism of sulfide oxidation to sulfoxides using H₂O₂-organic acid is not studied sufficiently; however, the potential mechanism is a heterolytic electrophil interaction where H⁺X⁻ is a polar solvent (23). Based on this mechanism, hydrogen peroxide first reacts with organic acid (acetic acid) and produces peroxide acid (CH₃COOOH), and then the acid reacts with nonpolar sulfur compounds and generates relative sulfone or sulfoxide. The role of the metal atoms in TBA-PV₂Mo₁₀@PVA, M = W or Mo, is to form peroxo-metal species which are able to activate the H₂O₂ and peracid molecules. During the ODS process, the H₂O₂ can efficiently convert organic sulfur to sulfones without forming a substantial amount of residual product. TBA-PV₂Mo₁₀@PVA accepted

the active oxygen from the oxidant H₂O₂ to form new oxoperoxo species mediate. The cation with carbon chain transferred oxoperoxo species to the substrates (Th or BT) and made the oxidation reaction accomplish completely (Fig. 11).

Kinetics of BT oxidation

For better understand the catalytic oxidation of BT, reaction kinetics was examined. To the apparent consumption of BT, the constant rate was gained from the first-order kinetic model (Eq. (3)) as follows:

$$-\frac{dC}{dt} = kC \tag{3}$$

$$\int \frac{dC}{C} = \ln \frac{C}{C_o} = -kt \tag{4}$$

Table 8. Pseudo-first-order rate constants and correlation factors of the BT and Th.

Temperature (°C)	Rate constant k (min ⁻¹)		Correlation factor R ²	
	BT	Th	BT	Th
25	0.0086	0.009	0.9031	0.903
30	0.0115	0.013	0.8802	0.848
35	0.0249	0.025	0.9341	0.9052
40	0.0247	0.025	0.9548	0.9015

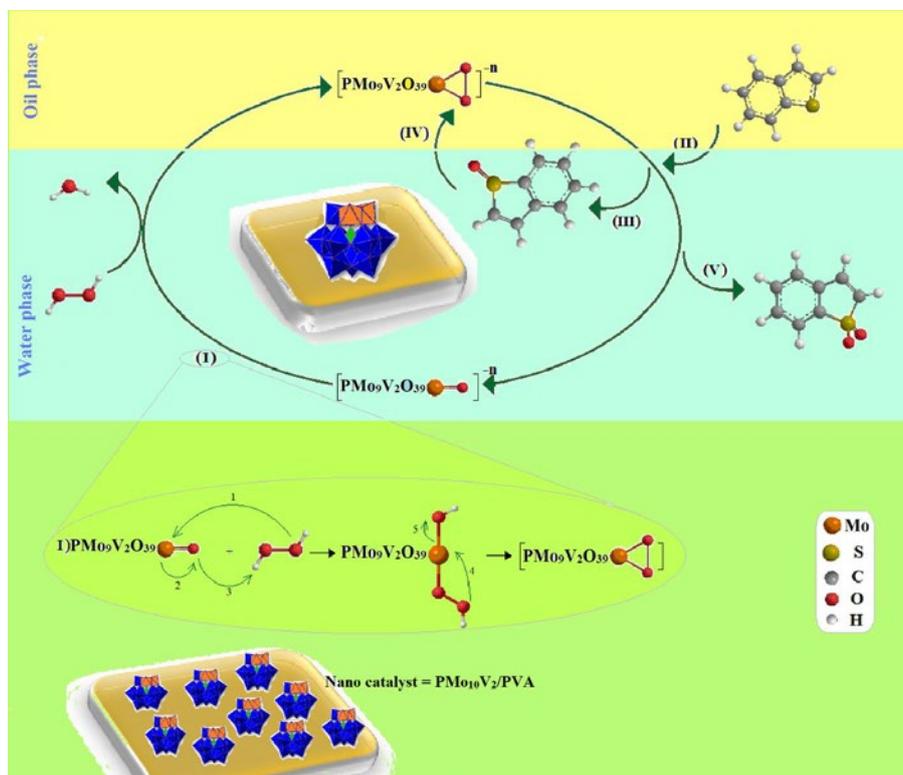


Fig. 11. Probable mechanism for the formation of peroxo-metal species and using H₂O₂ as the oxidant for oxidation of BT

$$C = C_0 e^{-kt} \quad (5)$$

Where:

$$k = Ae^{\frac{-E_a}{RT}} \quad (6)$$

Constant rate of BT was calculated using their initial concentrations at time zero (C_0) and time t reaction (C_t) in the plot of $\ln(C/C_0)$ or C/C_0 against t with use of Eq. (5), an exponential line (C/C_0) with slope k was gained (Fig. 12). The relationship between C and t can be applied to describe rate equations. With increasing reaction temperature from 25 to 35 °C removal of BT and thiophene and the constant rate reaction also increasing in 2 h (Table 8). The affiliation of the rate constant k on the reaction temperature can be expressed with the Arrhenius equation (Eq. (6)). A is the pre-exponential factor, E_a the apparent activation

energy, R and T are gas constant and the reaction temperature (K), respectively (21,28). Fig. 13 shown the Arrhenius plots and the calculated E_a values for the oxidation of BT and Th are 61.21 and 54.7 kJ/mol, respectively.

Influence of recycle times on oxidative desulfurization

At the end of the ODS of the MSCs and real gasoline, the catalyst was filtered and washed with dichloromethane. In order to determine whether TBA-PV₂Mo₁₀@PVA would succumb to poisoning and lose its catalytic activity during the reaction, the reusability of TBA-PV₂Mo₁₀@PVA was investigated. For this purpose, we carried out the desulfurization reaction of gasoline and model compounds in the presence of fresh and recovered TBA-PV₂Mo₁₀@PVA. The catalyst recovered after the reactions were characterized, in order to check the catalysts stability. Fig. 14 illustrates XRD

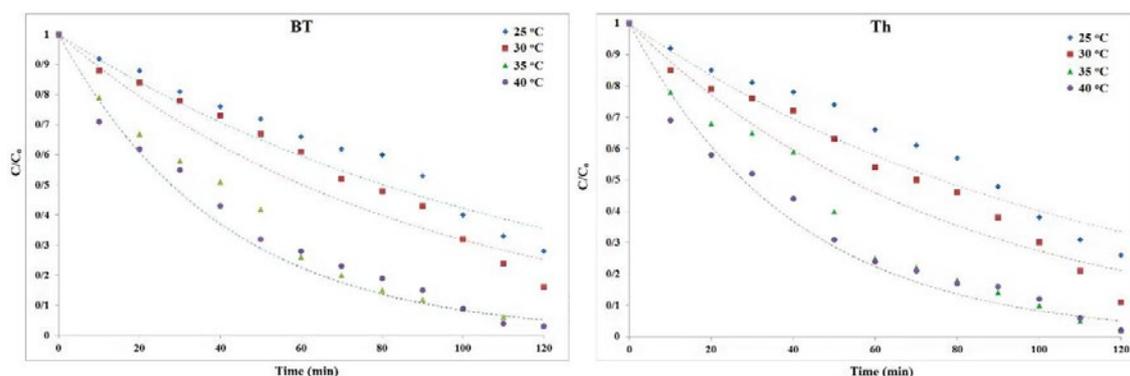


Fig. 12. Plots of C/C_0 for the oxidation of BT and Th with the TBA-PV₂Mo₁₀@PVA catalyst. (1): 25 °C, (2): 30 °C, (3): 35 °C and (4): 40 °C.

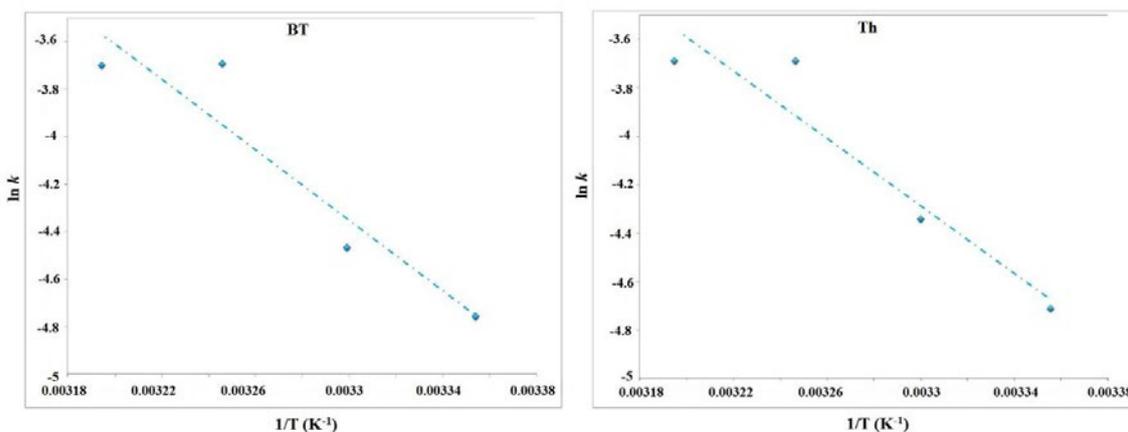


Fig. 13. Arrhenius plots for the oxidation of BT and Th with the TBA-PV₂Mo₁₀@PVA catalyst.

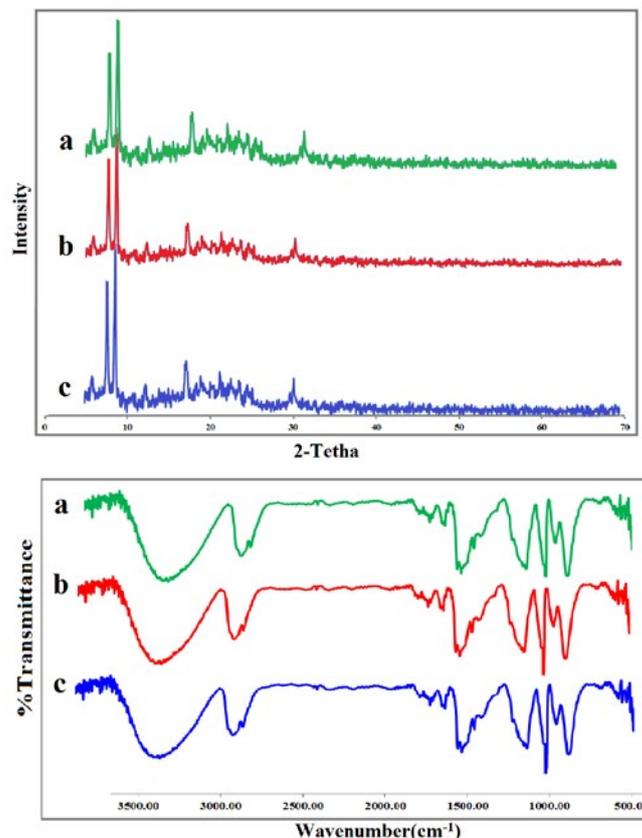


Fig. 14. Comparison of XRD pattern and IR spectrum of TBA-PV₂Mo₁₀@PVA (a) after first (b) third, and (c) fifth reuse.

Table 9. Reuse of the catalyst on the ODS of Th.^a

Entry	Removal (%)
1	97
2	96
3	95
4	94
5	93

^a Condition for desulfurization: 50 ml of model fuel (500 ppm S), 4 mL oxidant, 10 mL of extraction solvent, time = 2 h, and temperature = 35 °C, catalyst= TBA-PV₂Mo₁₀@PVA.

pattern and IR spectra of TBA-PV₂Mo₁₀@PVA after five catalytic cycles. Even after five runs for the reaction, the catalytic activity of TBA-PV₂Mo₁₀@PVA was almost the same as that of freshly used catalyst. The results are summarized in Table 9.

CONCLUSION

In conclusion, the TBA-PV₂Mo₁₀@PVA nanocomposite has been successfully prepared by immobilization of TBA-PV₂Mo₁₀ on PVA as a new nanocatalyst for ODS of gasoline. The catalytic activity of the catalyst was carried out on various MSCs and real gasoline. The organic sulfur

compounds were removed using the peroxy-metal intermediate complex as a catalytic enhancer in the present of H₂O₂/CH₃COOH as oxidant. The comparative experimental results were demonstrated that the desulfurization efficiency depended on the structure of the catalyst, nature of the sulfur molecules, reaction temperature, and dosage of the nanocatalyst. At the end, the heterogeneous nanocatalyst was reused up to five regeneration cycles. This work was introduced as a facile method for the synthesized phase transfer nanocatalyst TBA-PV₂Mo₁₀@PVA and its application in the ODS treatment to promote the quality of gasoline fuel. The TBA-PV₂Mo₁₀@PVA nanoparticle was very active catalyst system for desulfurization of the models compound, while unmodified TBA-PV₂Mo₁₀ showed much lower activity. This TBA-PV₂Mo₁₀@PVA/H₂O₂/CH₃COOH system provides an efficient, convenient and practical method for oxidative desulfurization of gasoline and the advantages of this method are nontoxic, mild condition and environmentally friendly.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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