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$(N(But)_4)_5H_4PV_6Mo_6O_{40}$ as an efficient catalyst for the oxidative desulphurisation of gasoline

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Abstract: The oxidative desulphurization (ODS) of gasoline and model compounds that exist in gasoline with hydrogen peroxide using $(N(But)_4)_5H_4PV_6Mo_6O_{40}$ as a scavenger was studied. This Keggin-type polyoxometalate was shown to be able to scavenge hydrogen sulphide and mercaptans in high yields. This system provides an efficient, convenient and practical method for scavenging sulphur compounds. This quaternary ammonium Keggin-type polyoxometalate ($(N(But)_4)_5H_4PV_6Mo_6O_{40}$) that has a lipophilic cation can act as a phase transfer agent and better transfer the peroxometal anion into the organic phase. The oxidation reactivity of the catalysts depends on the type of the counter-cation: $((C_4H_9)_4N)^+ > NH_4^+ > K^+$.

Keywords: Keggin-type polyoxometalate; counter-cation; mercaptan; gasoline; demercaptanization.

INTRODUCTION

In the past decade, clean fuels research, including demercaptanization and desulphurization, has become an important subject of environmental catalysis studies worldwide.[1–5] Mercaptans are a kind of organic sulphide that widely exist in petroleum products. They cause foul odours and deteriorate the finished products. Due to their acidity, mercaptans are corrosive to metals, which is harmful to storage and usage of oil products.[5–7] Therefore, it is necessary to remove them, either by transforming them to innocuous disulphides or by their extraction.[7–11] In continuation of on-going research on the syntheses and application of polyoxometalate in organic reactions,[12–21] herein, the applicability of quaternary ammonium Keggin-type molybdovanadophosphate ($(N(But)_4)_5H_4PV_6Mo_6O_{40}$) for the efficient desulphurization of gasoline in the preparation of ultra-clean fuels is reported. This quaternary ammonium Keggin-type molybdovanadophos-

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phate, ($(N(But)_4)_5H_4PV_6Mo_6O_{40}$), that has a lipophilic cation can act as a phase transfer agent and transfer the peroxometal anion into the organic phase. 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.[12–14] 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 investigations have demonstrated catalytic activity in the heterogeneous form.[14–17] Generally, Keggin structures show more acidity and catalytic activity among the heteropolyacids.[14] 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.[19] Further catalytically important subclasses of the Keggin compounds are the mixed-addenda vanadium-substituted HPAs with the general formula $H_{3+n}PM_{12-n}V_nO_{40}$ (M = = Mo or W; n = 1 to 6). In fact, V^{n+} is the most strongly oxidizing element and can be readily reduced to $V^{(n-1)+}$ with the concomitant oxidation of an organic substrate. The introduction of V^{n+} into the Keggin framework shifts its catalytic activity from acid-dominated to redox-dominated. Various oxidants have been used in oxidative desulfurization (ODS), such as NO_2, O_3, H_2O_2 and solid oxidizing agents.[11] Among these oxidants, H_2O_2 is mostly chosen as an oxidant, as only water is produced as a by-product. Peracids produced *in situ* from organic acid catalysts and H_2O_2 were reported to be very effective for the rapid oxidation of sulphur compounds in fuel oils under mild conditions. The catalytic activity of ($(N(But)_4)_5H_4PV_6Mo_6O_{40}$) was tested on the oxidative desulphurization of gasoline and model sulphur compounds that exist in gasoline, *i.e.*, benzothiophene (BT) and thiophene (T), with formic acid/hydrogen peroxide as the oxidizing reagent. The catalyst could be easily separated and reused at the end of the reaction without significant loss in its catalytic activity, which suggests that the catalyst is stable under different conditions.

EXPERIMENTAL

All reagents and solvents used in this work were available commercially and used as received, unless otherwise indicated. The model compounds and chemicals, including thiophene (T) and benzothiophene (BT), solvent (*n*-heptane) for the experiments and analysis and hydrogen peroxide (30 vol. %) were obtained from Aldrich. Typical actual gasoline (density 0.7918 g mL^{-1} at 15 °C, total sulphur content 0.391 wt. %) was used and details of its properties are given in Table I.

Preparation of the catalysts

Several heteropolyoxometalate catalysts: $(NH_4)_5H_4PV_6W_6O_{40}$, $(NH_4)_6HPV_4W_8O_{40}$ and $(NH_4)_5H_4PV_6Mo_6O_{40}$, *etc.*, used for comparison, were prepared according to literature procedures.[17,22] Details of the preparation of the catalysts are given in the Supplementary material to this paper.

TABLE I. Properties of the examined gasoline before and after oxidative desulphurization, ODS, by $(N(But)_4)_5H_4PV_6Mo_6O_{40}$; IBP – initial boiling point; FBP – final boiling point

Entry	Properties of gasoline		Unit	Method	Before ODS	After ODS[a]
1	Density by hydrometer at 15 °C		g mL^{-1}	ASTM D 1298	0.7918	0.7912
2	Total sulphur by X-ray analysis		wt.%	ASTM D 4294	0.391	0.014
3	Mercaptans		ppm	ASTM D 3227	39	3
4	Salt		ptb	ASTM D 3230	16	14
5	Water content by distillation		vol. %	ASTM D 4006	Nil.	Nil.
6	Distillation	IBP*	°C	ASTM D 86	43.9	43.6
		FBP[#]			208.5	208.1
		10	vol. %		68.3	67.1
		50			114.2	112.2
		90			184.3	183.6
		95			206.1	205.8

[a]Condition for desulphurization: 20 mL of gasoline, 0.1 g catalyst, 2 mL oxidant, 10 mL of extraction solvent, time = 1 h, and temperature = 40 °C

Catalyst characterization

The chemical characterization of the prepared catalysts was accomplished by means of elemental analysis and IR spectroscopy. Elemental analysis results were obtained by Integra XL inductively coupled plasma spectrometer. The Fourier transform infrared (FTIR) spectra of the solid samples were recorded in KBr pellets on a Thermo-Nicolet-is 10 instrument in the wavenumber range 400–4000 cm^{-1}.

Catalytic tests

Oxidative desulphurization of simulated gasoline using the formic acid/H_2O_2 system. Some typical thiophenes and benzothiophenes, which represent easy and hard to remove sulphur species in gasoline, were selected to evaluate the catalysts and the reactivity of the thiophenes and benzothiophenes in the oxidation reaction. Stock solutions of the model sulphur compound were made by dissolving T or BT in *n*-heptane to give a final sulphur concentration of 500 ppm. Then, performic acid (1:1 mixture of formic acid and hydrogen peroxide) was added to 5 mL of a stock solution. The resulting solution was heated to the required temperature (0–50 °C) in a water bath under stirring. After attaining the desired temperature, a sample was removed and catalyst was added to the remaining solution to initiate the reaction. Stirring was continued for a further 1 h. After cooling to room temperature, the biphasic mixture was separated by decantation and the organic phase saved for analysis.

Oxidative desulphurization of gasoline using the formic acid/H_2O_2 system. In the same manner as for the oxidation of the model sulphur compounds but using actual gasoline (sulphur 391 ppm) except 20 mL of gasoline was used. After the oxidation was finished, the mixture was cooled down to room temperature and 10 mL acetonitrile (MeCN) was added to extract the oxidized sulphur compounds. The observed biphasic system was separated by decantation and weighed to calculate % recovery of gasoline. (Through three times reaction: 98, 97 and 95 %).

Determination of the total sulphur and mercaptan sulphur contents

Determination of the contents of total sulphur and mercaptan sulphur in the gasoline and simulated gasoline samples before and after reaction were determined by X-ray fluorescence spectroscopy using a Tanaka RX-360 SH X-ray fluorescence spectrometer following the ASTM D-4294 and ASTM D-3227 standard test methods. Details of the ASTM D-4294 method are discussed in the Supplementary material to this paper.

Recycling of the catalyst

At the end of the oxidative desulphurization of the model sulphur compounds and gasoline, 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, the desulphurization reaction of gasoline and model compounds was performed in the presence of fresh and recovered catalyst.

RESULT AND DISCUSSION

Catalysis characterization

The chemical compositions of the vanadium-containing catalysts are given in Table II.

TABLE II. Characteristic IR vibrations (ν_{as} / cm^{-1}) and elemental analysis data for the vanadium-containing polyoxmetalate catalysts

Catalyst	P–O$_a$	Mo–O$_d$	Mo–O$_b$–Mo	Mo–O$_c$–Mo	Composition, %					
					P		Mo		V	
					Found	Cal.	Found	Cal.	Found	Cal.
$H_4PMo_{11}VO_{40}$	1053	954	875	741	1.26	1.29	46.5	44.1	3.35	2.13
$H_5PMo_{10}V_2O_{40}$	1052	952	873	740	1.33	1.31	40.6	40.4	6.91	4.31
$H_9PV_6Mo_6O_{40}$	1042	947	865	732	1.75	1.76	39.2	32.7	16.3	17.4

FTIR spectroscopy is an extensively used tool for the characterization of polyoxometalates as this technique provides finger printing in the structural elucidation of the Keggin structure.[12,14] The FTIR spectra of different polyoxometalates salts showed the common characteristic absorption peaks ranging from 500 to 1100 cm^{-1} that correspond to the oxometalate anion configurations (Table II).

The peak ranges (Table II) characteristic for POM are: 730–765 cm^{-1}, octahedral corner sharing M–O$_c$–M; 860–885 cm^{-1}, octahedral bridge/edge sharing M–O$_b$–M; 940–965 cm^{-1}, terminal M–O and 1040–1070 cm^{-1}, P–O configurations.[12,14] These configurations collectively account for Keggin type polyoxometalates. The oxygen atoms of the Keggin structure can be subdivided into four different types, *i.e.*, O$_a$, inner oxygen; O$_c$, corner-sharing oxygen; O$_b$, edge-sharing oxygen and O$_d$, terminal oxygen. These exhibit four well-defined infrared bands that can be applied for the identification and discrimination of different heteropolyacid catalysts. The four classes of oxygen atoms can be described as follows: the central oxygen X–O$_a$ establishes a connection between the central heteroatom of the XO_4 tetrahedron and the transition metal atoms of a trimetallic

MO_3 structure. The M–O_b–M oxygen atoms connect two M_3O_{13} units by corner sharing. Furthermore, M–O_c–M oxygen links two transition metal atoms by edge sharing of two MO_6 units and finally the terminal oxygen atom M–O_d binds to only one transition metal atom.[8,14,22]

Effect of the catalyst structure on the oxidative desulphurization

The effect of the nature of the catalyst on the oxidative desulphurization of gasoline using formic acid/H_2O_2 as the oxidant is shown in Tables III and IV. The amount of each catalyst was constant throughout the series. The Keggin type polyoxometalate catalyst $(N(But)_4)_5H_4PV_6Mo_6O_{40}$ was a very active system for the oxidation of gasoline, while the other studied polyoxometalates systems were much less active. This system ($(N(But)_4)_5H_4PV_6Mo_6O_{40}$) with a phase transfer or emulsion catalyst comprising a quaternary ammonium salt-based polyoxometalate was shown to be a very active system for oxidative desulphurization of gasoline. This quaternary ammonium Keggin-type molybdovanadophosphate ($(N(But)_4)_5H_4PV_6Mo_6O_{40}$) that has a lipophilic cation could better act as phase transfer agent and better transfer the peroxometal anion into the organic phase. That is, the oxidation reactivity of the catalysts depends on the type of countercation: $((C_4H_9)_4N)^+ > NH_4^+ > K^+$. It was shown that the order of the oxidation reactivity of the catalyst in the presence of hydrogen peroxide/formic acid was: $((N(But)_4)_5H_4PV_6Mo_6O_{40} > (N(But)_4)_4HPMo_{10}V_2O_{40} > (NH_4)_5H_4PV_6Mo_6O_{40} > K_5H_4PV_6Mo_6O_{40} > H_5PMo_{10}V_2O_{40} > H_4PMo_{11}VO_{40}$. From the result of Table III, the catalytic activity of $R_{3+n}PM_{12-n}V_nO_{40}$ (R = H, K, NH_4 or $N(But)_4$; M = Mo or W; n = 0 to 6) was in the order of $n = 6 >\ldots> n = 0$. The results show that the catalytic activity of $((N(But)_4)_5H_4PV_6Mo_6O_{40}$ was much higher than those of the other polyoxometalates. In fact, V^{n+} is the most strongly oxidizing element and can be readily reduced to $V^{(n-1)+}$ with the concomitant oxidation of an organic substrate. The introduction of V^{n+} into the Keggin framework shifts the catalytic activity from acid-dominated to redox-dominated.

TABLE III. Effect of different catalysts on the ODS of gasoline and simulated gasoline conversion; conditions for desulphurization: 5 mL of model gasoline (200 ppm S) or 20 mL of gasoline, 0.1 mmol catalyst, 2 mL performic acid, 10 mL extraction solvent, time 1 h and temperature 40 °C

Entry	Catalyst	Ratio		Conversion, %		
		BT/catalyst	Oxidant/BT	Thiophene	BT	Gasoline
1	$(N(But)_4)_5H_4PV_6Mo_6O_{40}$	100	10	98	97	97
2	$(NH_4)_5H_4PV_6Mo_6O_{40}$	30	10	92	90	91
3	$K_5H_4PV_6Mo_6O_{40}$	30	15	86	85	85
4	$H_5PMo_{10}V_2O_{40}$	30	15	85	85	84
5	$(N(But)_4)_4HPMo_{10}V_2O_{40}$	50	10	94	94	94
6	$H_4PMo_{11}VO_{40}$	20	15	84	83	83
7	$H_3PMo_{12}O_{40}$	20	15	81	81	81

TABLE IV. Effect of different catalysts on the ODS of gasoline; conditions for desulphurization: 20 mL of gasoline, 0.1 g catalyst, 2 mL oxidant, 10 mL of extraction solvent, time 1 h, temperature 40 °C

Entry	Catalyst	Total sulphur removed, %		Mercaptans removed, %	
		With H_2O_2	Without H_2O_2	With H_2O_2	Without H_2O_2
1	$(N(But)_4)_5H_4PV_6Mo_6O_{40}$	97	45	94	38
2	$(NH_4)_5H_4PV_6Mo_6O_{40}$	91	40	89	30
3	$K_5H_4PV_6Mo_6O_{40}$	85	38	84	33
4	$H_5PMo_{10}V_2O_{40}$	84	37	82	31
5	$(N(But)_4)_4HPMo_{10}V_2O_{40}$	94	41	90	36
6	$H_4PMo_{11}VO_{40}$	83	34	81	30
7	$H_3PMo_{12}O_{40}$	81	33	80	30
8	$N(But)_4Br$	33	16	34	15
9	None	22	–	21	–

Effect of catalyst dosage

Another factor that should be considered is the catalyst dosage. It was found that the catalyst dosage had a marked influence on the process efficiency (Table V). Under otherwise identical conditions, without catalyst, 24 % of the thiophene and 23 % of the benzothiophene were removed from the *n*-heptane phase and 23 % of the sulphur from actual gasoline in 60 min by oxidation. The percent conversions in actual gasoline in the presence of $((N(But)_4)_5H_4PV_6Mo_6O_{40}$ were found to be 64, 87.5 and 97 %, corresponding to catalyst amount of 0.06, 0.08 and 0.1 g, respectively. Thus, the desulfurization efficiency increased rapidly with increasing catalyst dosage.

TABLE V. Effect of catalyst dosage on the ODS of gasoline and simulated gasoline conversion; conditions for desulphurization: 20 mL of gasoline, catalyst, $(N(But)_4)_5H_4PV_6Mo_6O_{40}$, 2 mL oxidant, 10 mL of extraction solvent, time 1 h, temperature 40 °C

Entry	Amount of catalyst, g	Reactant		
		Thiophene	Benzothiophene	Actual gasoline
1	0	24	23	22
2	0.02	38	36	35
3	0.04	45	43	42
4	0.06	67	65	64
5	0.08	89	87	87
6	0.1	98	97	97
7	0.11	98	97	97
8	0.12	98	97	97

Influence of quaternary ammonium cation on the catalytic activity

Countercation with quaternary ammonium salts with lipophilic cation could act as a phase transfer agent and could transfer the peroxometal anion into the organic phase. An amphiphilic catalyst with a proper quaternary ammonium cation could form metastable emulsion droplets in gasoline with an aqueous H_2O_2 solution, demonstrating high oxidative activity, and could be separated after reaction through centrifugation. For example, $[N(C_4H_9)_4]^+$ is a proper quaternary ammonium cation (Tables III–V). Other cations were tested and it was found that $[N(C_4H_9)_4]^+$ forms metastable emulsion droplets in gasoline more readily than do NH_4^+ and K^+.

Effect of temperature on the oxidative desulfurization of gasoline or simulated gasoline

The reaction was carried out at different temperatures under the same conditions using $((N(But)_4)_5H_4PV_6Mo_6O_{40}$ as the catalyst and formic acid/H_2O_2 as the oxidant. The results, given in Table VI, show that yields of the products are a function of temperature. The percent conversions of sulphur in the solutions of the model compounds and in actual gasoline increased with temperature and time. The percent conversion of sulphur in the simulated fuel at 40 °C was higher than that at 30 °C. At 40 °C in 60 min, 97 % conversion of sulphur was obtained.

TABLE VI. Effect of different temperatures on the ODS of gasoline and simulated gasoline conversion; conditions for desulphurization: 10mL simulated gasoline or 20 mL of gasoline, 0.1 g catalyst, 2 mL oxidant, 10 mL of extraction solvent, time 1 h

Entry	Temperature, °C	Reactant		
		Thiophene	Benzothiophene	Actual gasoline
1	25	82	81	80
2	30	86	85	84
3	35	90	88	87
4	40	98	97	97
5	45	98	97	97
6	50	97	96	97

Effect of different oxidation system on the oxidative desulphurization of gasoline

Effect of oxidation system on the oxidative desulfurization of gasoline was studied (Table VII). Hydrogen peroxide, $KMnO_4$ and $K_2Cr_2O_5$ were selected as oxidizing agents, which were used in the presence of an organic or inorganic acid, *i.e.*, formic acid, acetic acid, oxalic acid, benzoic acid, H_2SO_4 and H_2CO_3 to acidify the system. The results in Table VII showed that in the presence of the inorganic acids, H_2SO_4 and H_2CO_3, the oxidation reactivity was lower than in the presence of the organic acids. In actual gasoline, H_2SO_4 and H_2CO_3 cannot dissolve; thus, the sulphur removal from gasoline by inorganic acid/H_2O_2 was lower than the removal by the organic acid/H_2O_2 systems.

Effect of the amount of formic acid

Effect of the amount of formic acid on the oxidative desulphurization of different sulphur compounds was studied and the results are given in Table VIII. In

TABLE VII. Effect of different oxidation system on the ODS of gasoline; conditions for desulphurization: 20 mL of gasoline, 0.1 g $((N(But)_4)_5H_4PV_6Mo_6O_{40}$, 2 mL oxidant, 10 mL of extraction solvent, time 1 h, temperature 40 °C

Entry	Oxidant	Acid	Mercaptans removed, %	Total sulphur removed, %
1	H_2O_2	Formic acid	94	97
2	H_2O_2	Acetic acid	93	97
3	H_2O_2	Oxalic acid	89	92
4	H_2O_2	Benzoic acid	87	91
5	H_2O_2	H_2SO_4	80	79
6	H_2O_2	H_2CO_3	78	78
7	H_2O_2	–	86	85
8	$KMnO_4$	Formic acid	75	74
9	$KMnO_4$	Oxalic acid	74	73
10	$KMnO_4$	H_2SO_4	73	74
11	$KMnO_4$	–	76	76
12	$K_2Cr_2O_5$	Formic acid	76	74
13	$K_2Cr_2O_5$	Oxalic acid	73	74
14	$K_2Cr_2O_5$	H_2SO_4	74	73
15	$K_2Cr_2O_5$	–	77	76

TABLE VIII. Effect of formic acid amount on the ODS of gasoline and simulated gasoline conversion; conditions for the desulphurization: 20 mL of gasoline or 10 mL simulated gasoline, 2 mL H_2O_2/formic acid as oxidant, 0.1 g $(N(But)_4)_5H_4PV_6Mo_6O_{40}$, 2 mL oxidant, 10 mL of extraction solvent, time 1 h

Entry	Formic acid/sulphur compound mole ratio	Reactant		
		Thiophene	Benzothiophene	Actual 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

the formic acid catalyzed reaction, the formic acid can interact with sulphur without any steric hindrance from the alkyl groups. Therefore, the reactivity trend obtained in the formic acid catalyzed reactions reflects the intrinsic oxidation reactivity of the thiophenes. The % sulphur 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 thiophene) was better than the other mole ratios. Therefore, in all other experiments, this formic acid/thiophene mole ratio was used. In gasoline mixed with formic acid/H_2O_2 (performic acid), the oxidative reaction occurred below 50 °C under atmospheric pressure. This was followed by liquid//liquid extraction to obtain a gasoline with a low sulphur and an extract with a high sulphur content. Finally, the low sulphur gasoline may require additional treatment. The extraction solvent was then removed from the extract for reuse and the concentrated extract was made available for further processing to remove sulphur and to produce hydrocarbons.

Reusability of the catalyst

The catalyst from the first desulphurization was recovered from the reaction mixture by filtration, washed with dichloromethane and used for the next desulphurization. This was repeated a further three times. The results of the effectiveness of the reused catalyst are given in Table IX, from which it could be seen that the catalyst largely retained its activity on recycling.

TABLE IX. Reuse of the catalyst on the ODS of thiophene; conditions for desulphurization: 5 mL of model gasoline (200 ppm S), 0.1 mmol $(N(But)_4)_5H_4PV_6Mo_6O_{40}$, 2 mL formic acid/$H_2O_2$, 10 mL extraction solvent, time 1 h, temperature 40 °C

Entry	Isolated yield, %
1	98
2	96
3	96
4	95
5	94

General remark concerning the desulfurization process

A model gasoline was made by adding T and BT into *n*-heptane solvent, with a total sulphur concentration of 200 mg L^{-1}. The organic sulphur compounds were mixed with formic acid/H_2O_2 and $((N(But)_4)_5H_4PV_6Mo_6O_{40}$ and then the oxidation reaction occurred at 40 °C under atmospheric pressure. This was followed by a liquid extraction (acetonitrile) to obtain gasoline with a low sulphur content. Many oxidizing agents have been reported in ODS processes, whereby H_2O_2 was the main one. Hydrogen peroxide is one of the most attractive oxidants, mainly because it is environmentally clean and easily handled. Hydrogen peroxide first rapidly reacts with an organic acid to generate peracid. It should be noted that during the ODS process, H_2O_2 was used in the presence of formic acid as oxidants because formic acid, as an organic acid, reacts with H_2O_2 to *in situ* produce peracid, which can efficiency convert organic sulphur to sulphones without the formation of a substantial amount of residual product. The role of the metal atoms in $((N(But)_4)_5H_4PV_6Mo_6O_{40}$, M = V or Mo, was to form peroxo-metal species, which are able to activate the H_2O_2 and peracid molecules. $((N(But)_4)_5H_4PV_6Mo_6O_{40}$ accepted the active oxygen from the oxidant H_2O_2 to form new oxoperoxo species mediates. The cation with the carbon chain transferred oxoperoxo species to the substrates (T or BT) and enabled the oxidation reaction to be accomplished completely.

CONCLUSIONS

The system with ($(N(But)_4)_5H_4PV_6Mo_6O_{40}$), a phase transfer or emulsion catalyst comprising a quaternary ammonium salt-based polyoxometalate, was shown to be a very active system for the oxidative desulphurization of gasoline. This quaternary ammonium Keggin-type molybdovanadophosphate ($(N(But)_4)_5H_4PV_6Mo_6O_{40}$), which has a lipophilic cation, can act as phase transfer agent and transfer the peroxometal anion into the organic phase. That is, the oxidation reactivities of the catalysts depend on the type of countercation: $((C_4H_9)_4N)^+ > NH_4^+ > K^+$. In the present work, the efficient oxidative desulphurization of gasoline and simulated gasoline using the formic acid/hydrogen peroxide (peracid) system was reported. The system provides an efficient, convenient and practical method for scavenging sulphur compounds in gasoline.

SUPPLEMENTARY MATERIAL

The preparation of the V-containing catalysts and a discussion of the ASTM D-4294 standard method for the determination of sulphur compounds in gasoline are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding authors on request.

ИЗВОД

$(N(But)_4)_5H_4PV_6Mo_6O_{40}$ КАО ЕФИКАСАН КАТАЛИЗАТОР ЗА ОКСИДАТИВНУ ДЕСУЛФУРИЗАЦИЈУ БЕНЗИНА

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Испитивана је оксидативна десулфуризација (OSD) бензина и модел једињења која постоје у бензину са водник-пероксидом у присуству $(N(But)_4)_5H_4PV_6Mo_6O_{40}$. Показано је да ово полиоксометалатно једињење Кегиновог типа може да уклони водоник-сулфид и меркаптане у виском приносу. Овај систем омогућава ефикасан, погодан и практичан метод за елиминацију сумпорних једињења. Квартернерни амонијум-полиоксометалат Кегиновог типа, $(N(But)_4)_5H_4PV_6Mo_6O_{40}$, који има липофилни катјон има боље карактерстике као агенс за фазни трансфер и може боље да преведе пероксометални анјон у органску фазу. Тачније, оксидативна реактивност катализатора зависи од типа контракатјона: $((C_4H_9)_4N)^+ > NH_4^+ > K^+$.

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