

## Research Article

# Novel Oxidative Desulfurization of a Model Fuel with H<sub>2</sub>O<sub>2</sub> Catalyzed by AlPMo<sub>12</sub>O<sub>40</sub> under Phase Transfer Catalyst-Free Conditions

Márcio José da Silva and Lidiane Faria dos Santos

Chemistry Department, Federal University of Viçosa, Campus Universitário, Avenida PHRolfs, S/N, Viçosa, MG 36570-000, Brazil

Correspondence should be addressed to Márcio José da Silva; silvamj2003@ufv.br

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A novel process was developed for oxidative desulfurization (ODS) in the absence of a phase transfer catalyst (PTC) using only Keggin heteropolyacids and their aluminum salts as catalysts. Reactions were performed in biphasic mixtures of isooctane/acetonitrile, with dibenzothiophene (DBT) as a model sulfur compound and hydrogen peroxide as the oxidant. Remarkably, only the AlPMo<sub>12</sub>O<sub>40</sub>-catalyzed reactions resulted in complete oxidation of DBT into DBT sulfone, which was totally extracted by acetonitrile, reducing the sulfur content of isooctane from the 1000 ppm to <1 ppm. Ranking of catalyst efficiency is as follows: AlPMo<sub>12</sub>O<sub>40</sub> > H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> > AlPW<sub>12</sub>O<sub>40</sub> > H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. The absence of a PTC, acidic organic peroxides, and the use of hydrogen peroxide, an environmentally benign oxidant, make up the positive aspects of AlPMo<sub>12</sub>O<sub>40</sub>-catalyzed ODS reactions. In these reactions, high rates of DBT removal (*ca.* 100%) were achieved within a short time (*ca.* 2 hours) and under mild reaction conditions.

## 1. Introduction

Demand for the production and use of more environment-friendly fuels are increasing due to the introduction of the legislative regulations requiring rigid control of green-house gas emissions [1]. Nowadays, many countries are introducing stringent regulations to reduce sulfur content in liquid fuels to ultralow levels, making the development of deep desulfurization processes an important research goal [2]. Among the main industrial processes for the sulfur removal of liquid fuels, the most important is referred as hydrodesulfurization (HDS) and operates with oxide-supported heterogeneous metal catalysts, typically Co- (or Ni-) promoted Mo/Al<sub>2</sub>O<sub>3</sub>, under high temperatures (593–653 K) and hydrogen pressures (3–7 MPa) [3]. The HDS process is an efficient technology used by the petroleum refining industries to remove aliphatic and acyclic sulfur compounds present in the liquid fuels. However, due to the high stereo hindrance and as consequence of proximity between the values of C–S and C–H bond energy, some sulfured aromatic compounds such as

dibenzothiophene (DBT) and their derivatives are especially refractory to the HDS processes [4]. Moreover, the lower sulfur level achieved by the HDS process is still high when compared to the futures legal exigencies (*ca.* 50–15 ppm) [5]. Consequently, the development of processes for the fuels production with low sulfur content is a great challenge to overcome [6]. Alternative processes to HDS, in which high temperatures or hydrogen pressures are avoided, have been proposed, and the main examples are the biodesulfurization [7], selective adsorption [8], and ionic-liquid extraction [9]. Oxidative desulfurization (ODS) appears as a promising technology because it presents significant advantages over those processes. ODS processes are highly efficient and selective for a broad range of substrates under mild conditions (*ca.* 313–373 K and 0.1–0.2 MPa), working within short reaction times (1–2 hours) and requiring only a simple extraction with polar solvent [10]. In the ODS processes several different oxidants have been used; however, hydrogen peroxide is the most frequently employed. Hydrogen peroxide is a benign environmental oxidant, commercially available at affordable cost,

which has been used as oxidant in reactions with different metal catalysts [11]. Moreover, it is easier to be handled and less corrosive than other organic peroxides oxidants.

In general, the ODS process can operate with heterogeneous or homogeneous catalysts, in systems with one or two liquid phases, respectively [12]. Normally, homogeneous catalysts in biphasic systems requires an additional presence of phase transfer catalyst (PTC), which notably increases mass transfer across the polar-apolar phase interface. Among the catalysts employed, heteropolyacids arise as versatile multi-electronic oxidants and acidic catalysts, which have been frequently used in numerous reactions in liquid phase. Actually, the use of heteropolyacid catalysts and PTC (i.e., tetrabutylammonium bromide) in ODS reactions was recently described [13]. Alternatively, aiming to avoid the use of PTC, tungsten polyoxometalate catalysts containing organic cations (i.e., tetrabutylammonium) were synthesized and successfully applied on the ODS reactions of gas oil samples [14]. Heteropolyacid catalysts have been also employed in ODS reactions with hydrogen peroxide where organic acids are the solvent [15]. However, it results in the formation of a highly corrosive oxidant (i.e., peracetic acid), which can provoke the undesirable reactor corrosion [15].

In this work, we wish to present a novel application of aluminum dodecamolybdophosphate ( $\text{AlPMo}_{12}\text{O}_{40}$ ), an efficient and water-tolerant Lewis acid, as catalyst for the ODS reactions. The reactions were performed in absence of PTC, using hydrogen peroxide as oxidant in  $\text{CH}_3\text{CN}$  solutions. Isooctane was the model gasoline. This catalyst was easily prepared from cheap and commercially available chemicals, and to the best of our knowledge, this is the first report of using  $\text{AlPMo}_{12}\text{O}_{40}$  as a catalyst in ODS reactions. Catalytic activities of the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  Keggin heteropolyacids and their respective aluminum salts were assessed.

## 2. Experimental Section

**2.1. Chemicals.** Dibenzothiophene and heteropolyacids catalysts ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) were acquired from Sigma-Aldrich (all they with 99%). Aluminum nitrate (Merck, 99%) was used without prior treatment. An aqueous  $\text{H}_2\text{O}_2$  solution (ca. 34% wt., Vetec, Brazil) was the oxidant employed in all reactions, and its concentration was determined by titration against a  $\text{KMnO}_4$  solution. Acetonitrile and isooctane (Sigma-Aldrich, 99%) were used as received.

**2.2. Synthesis and Characterization of Catalysts.** The  $\text{AlPMo}_{12}\text{O}_{40}$  and  $\text{AlPW}_{12}\text{O}_{40}$  salts were synthesized according to procedures published in the literature [16]. Herein, both catalysts ( $\text{AlPW}_{12}\text{O}_{40}$  or  $\text{AlPMo}_{12}\text{O}_{40}$ ) were prepared by the addition of  $\text{Al}(\text{NO}_3)_3$  aqueous solution at a rate of  $1.0 \text{ mL}\cdot\text{min}^{-1}$  to an aqueous solution of heteropolyacid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$  or  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ), under constant agitation and at room temperature. Then, the solution was stirred at ambient pressure, and the temperature was maintained at temperature  $80^\circ\text{C}$  for 24 hours; complete evaporation of water resulted in the desired salt as a white ( $\text{AlPW}_{12}\text{O}_{40}$ ) or yellow ( $\text{AlPMo}_{12}\text{O}_{40}$ ) powder. These Keggin heteropolyacid salts are easily handled, nonhygroscopic, noncorrosive, and

water stable compounds, which makes them suitable catalysts for large-scale use [17]. Aluminum heteropolyacid salts are known products and were characterized by comparison of their physical data with that reported in the literature [16, 17].

FT-IR spectra of the catalysts were performed in the solid phase (KBr pellet samples), and a measuring range of  $400\text{--}4000 \text{ cm}^{-1}$  in a Varian model 660 FT-IR spectrophotometer. The contents of W and Mo in solution were determined by UV-visible spectroscopy with the aid of calibration curves (Micronal AJX Model 6100PC double beam UV-visible spectrophotometer and quartz cells with 1.0 cm path length were employed for the analysis).

**2.3. Kinetic Studies and Reaction Monitoring.** Catalytic tests were carried out during two hours in a 50 mL three-necked glass flask equipped with a reflux condenser at room pressure. Typically, a biphasic mixture of isooctane (10 mL) containing DBT (ca. 1000 ppm, 3.19 mmol) and  $\text{CH}_3\text{CN}$  (10 mL) containing  $\text{H}_2\text{O}_2$  (34% wt., 17.6 mmol) were magnetically stirred and heated to the  $60^\circ\text{C}$  temperature. Then, the heteropoly catalyst (5 mol%; 0.1595 mmol) was added to the mixture and the reaction started. Reaction progress was accomplished by GC analysis in a Varian gas chromatograph GC-450 instrument with flame ionization detector and Carbowax capillary column (30 m length, 0.25 mm i.d., and 0.25 mm film thickness).

**2.4. Products Identification.** Mass spectrometry analyses were carried in a Shimadzu GC17A gas chromatograph coupled to a Shimadzu MS-QP 5050A mass spectrometer. Chromatographic conditions were as follows: helium was the carrier gas at flow rate of  $1.0 \text{ mL}\cdot\text{min}^{-1}$ ; the temperature profile was  $180^\circ\text{C}$  for 1 min,  $10^\circ\text{C}\cdot\text{min}^{-1}$  up to  $240^\circ\text{C}$ , hold time of 5 min; the GC injector and MS ions source were maintained at  $260\text{--}270^\circ\text{C}$ , respectively; and the MS detector operated in the electronic impact mode at 70 eV with a scanning range of  $m/z$  50–400. The chromatography standards were obtained from Supelco.

## 3. Results and Discussion

**3.1. General Aspects.** Heteropoly compounds are widely applied as catalysts due to their varied composition and physical-chemical features. Moreover, heteropolyacid compounds are easily synthesized and exhibit the possibility for introducing elements into their structures that are necessary to acquire the desired properties [18]. However, data on the use of heteropolyacid salts in ODS reactions is still scarce. The present study, therefore, investigated the effects of total replacement of acidic hydrogen in heteropolyacid structure by aluminum cations. The heteropoly salts catalytic activity in ODS reactions was assessed using DBT as the model sulfur compound and hydrogen peroxide as the oxidant, in isooctane/acetonitrile biphasic mixtures in the absence of PTC.

**3.2. Catalysts Characterization.** In general, polyoxometalate synthesis routes are linear, and the reactions of formation of their salts occur with high yields [18, 19]. Herein, the synthesis

of both  $\text{AlPW}_{12}\text{O}_{40}$  and  $\text{AlPMo}_{12}\text{O}_{40}$  catalysts were directly performed, with yields exceeding *ca.* 98%. The results obtained via elemental analysis (i.e., Mo and W percentage were determined by UV-Visible spectroscopy) indicated that the molar content of these elements is that corresponding to the salts  $\text{AlPMo}_{12}\text{O}_{40}$  and  $\text{AlPW}_{12}\text{O}_{40}$ . Figure 1 shows FT-IR spectra of molybdenum and tungsten catalysts which allowed to prove the presence of the Keggin anion structure in the salts synthesized.

The  $\text{PM}_{12}\text{O}_{40}^{3-}$  ( $M = \text{W}$  or  $\text{Mo}$ ) Keggin anion structure is well known; it has tetrahedral  $\text{PO}_4$  groups surrounded by four  $\text{Mo}_3\text{O}_{13}$  groups formed by octahedral edge-sharing [19, 20]. In the heteropolyacids Keggin structure, there are four types of oxygen atoms which are distinguishable via FT-IR spectroscopy, responsible for the fingerprint bands of the Keggin ion (*ca.*  $1200\text{--}700\text{ cm}^{-1}$ ). Figure 1 shows the characteristic absorption bands for the stretching of the bonds  $\nu(\text{P-O})$ ,  $\nu_{\text{ass}}(\text{M-O-M})$ , and  $\nu(\text{M-O})$  (with  $M = \text{W}$  or  $\text{Mo}$ ), present in the FT-IR spectra of the tungsten or molybdenum compounds used as catalysts, demonstrating that the Keggin structure remained intact. However, it can be observed that the  $\text{Mo-O}$  bonds were more affected by replacement of the  $\text{H}^+$  cations by the  $\text{Al}^{3+}$  cations than the  $\text{W-O}$  bonds. In general, on the  $\text{AlPMo}_{12}\text{O}_{40}$  FT-IR spectrum there was a small displacement for a region of lower wave number of the band corresponding to  $\text{Mo=O}$  stretching when comparatively to the same stretching on the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  FT-IR spectrum. The same occurred with stretching of the  $\text{P=O}$  bond. Conversely, when comparing the  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{AlPW}_{12}\text{O}_{40}$  infrared spectra, a different behavior can be observed; stretching of the  $\text{W=O}$  and  $\text{P-O}$  bonds underwent a slight shift to a higher wave number. These results are in agreement with those found in the literature [19]. Previously, Deltcheff et al. reported that the  $\text{M-O}$  stretching frequency decreases while the cation size increases; those authors attributed this fact to a weakening of anion-anion interactions of the electrostatic type [20]. However, in the present study, this effect was more pronounced on the molybdenum catalysts.

**3.3. Effect of Heteropoly Catalysts on PTC-Free ODS Reactions of DBT with  $\text{H}_2\text{O}_2$  in Isooctane/ $\text{CH}_3\text{CN}$  Biphasic Mixtures.** Quaternary ammonium salts have been fairly used as PTC in oxidative desulfurization reactions with  $\text{H}_2\text{O}_2$  [13, 14, 21]. In these cases, an organic peracid formed from the reaction of solvent (i.e., formic or acetic acid) and the peroxide reactant (i.e., hydrogen peroxide or *t*-butyl hydroperoxide) is the real oxidant [22]. Nevertheless, Trakarnpruk and Rujiraworawut assessed the ODS reactions of gas oil samples with  $\text{H}_2\text{O}_2$  in HOAc solutions, catalyzed by polyoxometalates in absence of PTC. Those authors found two significance results: at first, the tungsten catalysts were more active than molybdenum catalysts [23]. Secondly, DBT conversions obtained in the reactions catalyzed by the heteropolyacids or even by their sodium salts (i.e.,  $\text{Na}_2\text{HPMo}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) were almost equal. Although being efficient, those ODS reactions have a considerable disadvantage: the use of peracids as oxidant, which are little attractive at industrial scale due to its high corrosiveness.

Herein, we investigated the activity of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  heteropolyacids and their aluminum salts in PTC-free conditions, using nonacidic solvent ( $\text{CH}_3\text{CN}$ ),  $\text{H}_2\text{O}_2$  as oxidant, and DBT as model sulfur compound (Table 1). This way, we avoided the use of corrosive organic peracids and also circumventing the laborious PTC synthesis.

The results obtained herein were different than those reported in the literature [23]. Indeed, the use of  $\text{CH}_3\text{CN}$  and mainly the presence of aluminum cations affected drastically the behavior of the heteropolyacid catalysts. However, it is important to note that the higher activity of tungsten catalysts comparatively than molybdenum catalysts, which is described in the literature, was dependent on HOAc excess used (DBT: $\text{H}_2\text{O}_2$ :HOAc molar ratio equal to 1:10:10) [23]. Thus, because HOAc was not used, this effect was not observed.

Although peroxotungstate species (i.e.,  $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$ ) have been described as the active catalytically intermediates in those reactions, an increase on HOAc concentration also resulted in a consequent increase on peracetic acid concentration, which is another oxidant species stronger than  $\text{H}_2\text{O}_2$  [22, 23]. Actually, because the reactions were performed in absence of organic acids (Table 1), this behavior was not observed herein. The literature described a higher oxidative activity of molybdenum polyoxoperoxo species comparatively than tungsten species on the oxidation of other organic substrates in polyoxometalate/ $\text{H}_2\text{O}_2$  systems [24].

In general, the oxidation of DBT into DBT sulfone by hydrogen peroxide typically involves the formation of DBT sulfoxide as an intermediate, as is displayed in Figure 2. Under the conditions studied and independent of the catalyst employed, the DBT was exclusively converted into DBT sulfone and no formation of DBT sulfoxide was observed throughout the reactions. Moreover, no DBT conversion was detected in the absence of heteropoly catalysts under the same reaction conditions (Table 1).

In Figure 3, the kinetic curves obtained from ODS of DBT catalyzed by heteropoly compounds are displayed.

Experiments performed in the absence of the catalyst showed that there was no reaction even after a long reaction time (*ca.* 24 h; omitted by simplification). Conversely, when in the presence of tungsten catalysts, the reaction proceeded smoothly and DBT was oxidized into DBT sulfone with maximum conversion of 24% after a three hour reaction (Figure 2). However, the molybdenum heteropoly catalysts were the most effective. The DBT was completely removed from the isooctane phase conducting  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed ODS reactions for 340 minutes (not shown in Figure 2 for simplification). When catalyzed by  $\text{AlPMo}_{12}\text{O}_{40}$ , all the reactions proceeded well in short reaction times (*ca.* 180 min) resulting in total oxidation of DBT into DBT sulfone at high rates; consequently, the content of DBT in the isooctane phase was reduced to less than 1 ppm (Table 1, Figure 1).

Moreover, in all reactions it was observed that any of the heteropoly catalysts promoted the disproportionation of hydrogen peroxide, suggesting that it remained stable throughout the time reaction. This is a welcome result; when a system  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /tetraoctylammonium bromide/ $\text{H}_2\text{O}_2$  is

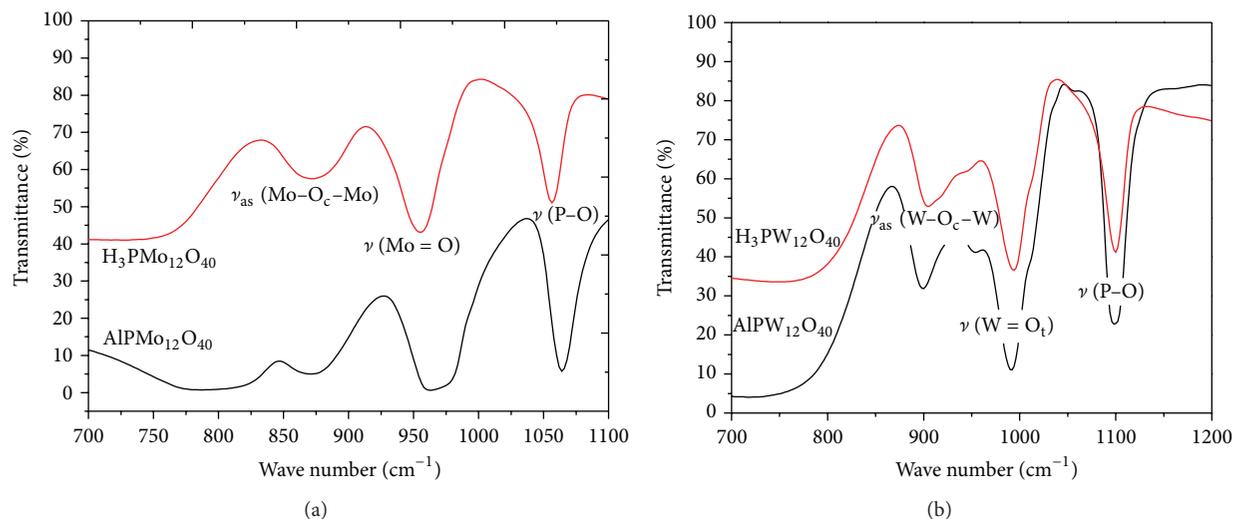


FIGURE 1: FT-IR spectra of molybdenum (a) and tungsten (b) catalysts used in ODS reactions.

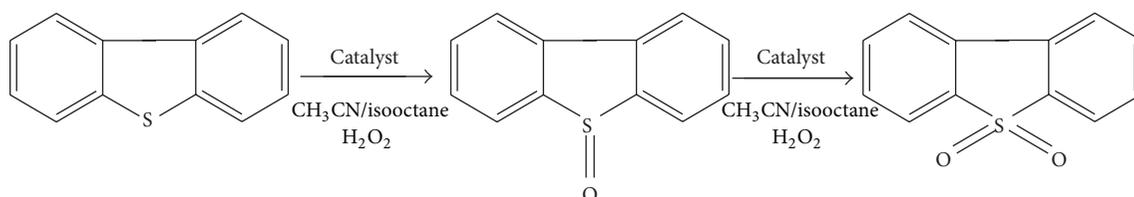


FIGURE 2: Oxidation of DBT into DBT sulfone by hydrogen peroxide.

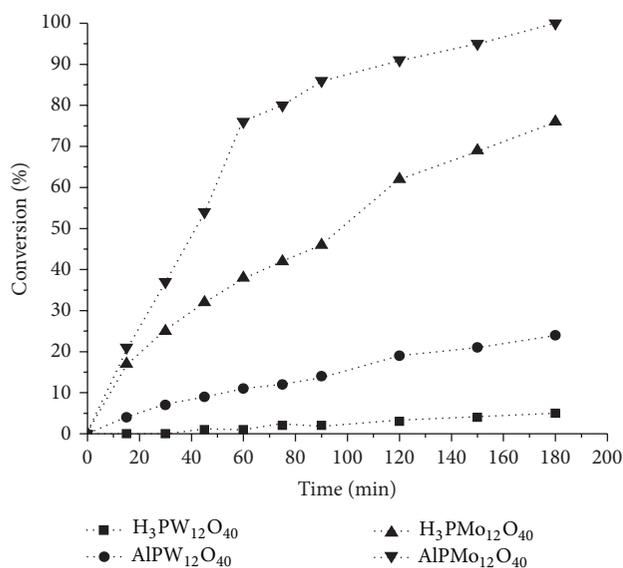


FIGURE 3: Kinetic curves obtained from ODS of DBT catalyzed by heteropoly compounds.

used, the catalyzed decomposition of  $\text{H}_2\text{O}_2$  competes with DBT oxidation, and, therefore, the major cost involved in treating gas oils by ODS is the huge amount of hydrogen peroxide consumption [25].

On the other hand, the results in Table 1 strongly suggest that the replacement of hydrogen ions for aluminum cations

TABLE 1: ODS processes in the presence of different catalysts using DBT as the sulfur model compound in a biphasic mixture of isoctane/acetonitrile and  $\text{H}_2\text{O}_2$  as the oxidant<sup>a</sup>.

Run	Catalyst	Conversion <sup>b</sup> (%)
1	—	—
2	$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	76
3	$\text{AlPMo}_{12}\text{O}_{40}$	100
4	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	5
5	$\text{AlPW}_{12}\text{O}_{40}$	24

<sup>a</sup>Reaction conditions: DBT (3.19 mmol), catalyst (0.1595 mmol; 5 mol%),  $\text{H}_2\text{O}_2$  (2.0 mL; 30% w/w; 17.6 mmol), temperature of 60°C, isoctane/acetonitrile (20 mL), and 3-hour reaction. Conversions are the average of the results of three assays; experimental error was equal to 2%.

<sup>b</sup>Conversion into DBT sulfone determined by GC analyses.

promotes a significant improvement in heteropoly catalysts activity, in an extension much greater than those provoked by the sodium ions [23]. Thus, it can be concluded that either solvent as well as the  $\text{Al}^{3+}$  cations plays a key role in ODS reactions herein studied. The efficiency of aluminum-molybdenum-based catalysts was described previously, however, in heterogeneous phase. Molybdenum heteropoly catalysts supported on alumina successfully promoted the ultra-deep ODS of diesel sample with hydrogen peroxide [26].

**3.4. Discussions of Reaction Mechanism: the Role of  $\text{Al}^{3+}$  Cations.** It was found that peroxy- $\text{AlPMo}_{12}\text{O}_{40}$  oxidizes DBT

into DBT sulfone more efficiently than peroxy- $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ; the same occurs when based on tungsten catalysts. Thus, it may be reasonable to consider that the  $\text{Al}^{3+}$  cations have properties that favored some intermediate of this reaction. In general, it is accepted that peroxy oxidant is activated electrophilically via coordination to the high valent atom present on catalyst (molybdenum or tungsten). Indeed, our results suggested that its activation was also favored when heteropoly catalysts contained aluminum cations. The presence in the heteropolyacids structure of additional electrophilic sites allows (i.e.,  $\text{Al}^{3+}$  cations) the activation of peroxy to intermediate.

Sodium and aluminum ions have two main features that may affect differently the activity of heteropolyacid catalysts, the Lewis acidity and the electronegativity. The ratio of charge to ionic radius ( $elr$  (Å)) is an approximate measurement for the electron-withdrawing ability leading to the Lewis acidity of metal cations [27]. These aspects are summarized in Table 2.

In this sense,  $\text{Al}^{3+}$  and  $\text{Na}^+$  cations have ratio ( $elr$ ) equal to 4.5 and 0.8, respectively. Moreover, the Pauling electronegativity of these cations are equal to 10.6 and 2.9, for  $\text{Na}^+$  and  $\text{Al}^{3+}$  cations, respectively [28]. These data may be a reasonable explanation to fact that  $\text{Al}^{3+}$  cations affect much more drastically the catalytic activity of heteropolyacids than  $\text{Na}^+$  ions.

The literature describes the crystallographic characterization of active catalyst species formed by the nucleophilic attack of hydrogen peroxide on metal atoms of the polyoxometalates [29]. These species are active oxygen transfer agents in the heteropolyacid-catalyzed oxidation reactions [29, 30]. Thus, in according to the literature and based on our experimental results, heteropoly compounds catalysts of W(IV) and more remarkably Mo(IV) probably act as oxygen transfer agents from  $\text{H}_2\text{O}_2$  to the sulfur compound, via an intermediate peroxy catalyst, which is more stable when  $\text{Al}^{3+}$  cations are present [29–31]. The higher stability of peroxide-Mo-Al intermediate is attributed to higher effect electron withdrawing of  $\text{Al}^{3+}$  cations, which are much more electronegative than  $\text{H}^+$  or  $\text{Na}^+$  cations (Table 2) [27, 28].

Generally, in the biphasic oxidation reactions the heteropolyacids catalysts is rapidly oxidized by the  $\text{H}_2\text{O}_2$  in the polar phase. When a PTC is used, the resulting peroxo-catalyst compound is transferred to the nonpolar phase by ion exchange with the PTC agent. However, no PTC catalyst was employed on this present study. Thus, we believed that the oxygen transfer step from peroxide to sulfur compound occurs via the peroxidized catalyst in the interface between isooctane and acetonitrile solvent (Figure 4).

Thereafter due the high solubility of sulfones in polar solvents, DBT sulfone is transferred to the  $\text{CH}_3\text{CN}$  phase resulting in the production of a sulfur-free isooctane phase. Currently, acetonitrile is an appropriate solvent because it is able to extract and solve the reaction products and exhibits a low surface tension, which facilitates the transfer of products and from the apolar phase to polar through of interface, increasing notably the mass transfer along the interphase [32]. However, it is important to note that  $\text{CH}_3\text{CN}$  is partially

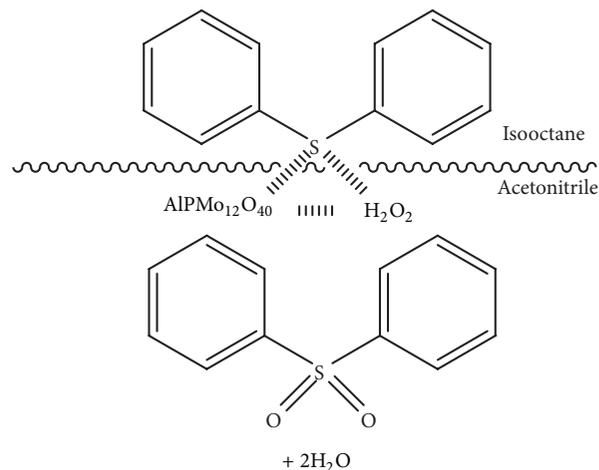


FIGURE 4:  $\text{AlPMo}_{12}\text{O}_{40}$ -catalyzed ODS of DBT with  $\text{H}_2\text{O}_2$ .

TABLE 2: Pauling electronegativity and ratio of charge to ionic radius ( $elr$  (Å)) of  $\text{Al}^{3+}$  and  $\text{Na}^+$  cations [27, 28].

Cation	Pauling electronegativity	Ratio of charge to ionic radius ( $elr$ (Å))
$\text{Al}^{3+}$	10.6	4.5
$\text{Na}^+$	2.9	0.8

solved in the apolar phase (i.e., octane; 0.2 mol/1 mol at 330 K); consequently, there are  $\text{CH}_3\text{CN}$  molecules present in the octane phase [33]. Probably, this partial solubility of the acetonitrile into isooctane phase is enough to allow the heteropoly catalysts to efficiently act on this system without a PTC.

## 4. Conclusions

This study consisted of investigating the catalytic activity of Keggin heteropolyacids substituted with aluminum, in ODS reactions using hydrogen peroxide as an oxidant and DBT as a model sulfur compound, in an acetonitrile/isooctane mixture. The ODS reactions were performed under acid-free conditions and in absence of a PTC. As far as we know, this is the first report on the use of aluminum heteropolyacid salts as catalysts in ODS reactions. The replacement of hydrogen cations by aluminum resulted in significant improvements to heteropolyacid activity. Tungsten and more remarkably molybdenum heteropoly salts containing aluminum reacted with hydrogen peroxide to form peroxocatalysts. Aluminum heteropoly salts were more active than their heteropolyacid precursors. Complete removal of the sulfur compound was obtained only when molybdenum catalysts (i.e.,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and mainly  $\text{AlPMo}_{12}\text{O}_{40}$ ) were used. It is intended that this novel, simple, and PTC-free protocol will be extended to the ODS of other substrates containing sulfur.

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