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Removing Simultaneously Sulfur and Nitrogen from Fuel under a Sustainable Oxidative Catalytic System

Dinis F. Silva [†], Alexandre M. Viana [†] , Fátima Mirante, Baltazar de Castro, Luís Cunha-Silva 
and Salette S. Balula ^{*} 

LAQV/REQUIMTE & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal; josedinis.silva@fc.up.pt (D.F.S.); up201405091@edu.fc.up.pt (A.M.V.); fatima.mirante@fc.up.pt (F.M.); bcastro@fc.up.pt (B.d.C.); l.cunha.silva@fc.up.pt (L.C.-S.)

^{*} Correspondence: sbalula@fc.up.pt; Tel.: +351-220-402-576

[†] These authors contributed equally for the research work.

Abstract: An effective process to remove nitrogen-based compounds from fossil fuels without harming the process of sulfur removal is an actual gap in refineries. A success combination of desulfurization and denitrogenation processes capable of completely removing the most environmental contaminants in diesel under sustainable conditions was achieved in this work, applying polyoxometalates as catalysts, hydrogen peroxide as oxidant, and an immiscible ionic liquid as an extraction solvent. The developed process based in simultaneous oxidative desulfurization (ODS) and oxidative denitrogenation (ODN) involved initial extraction of sulfur and nitrogen compounds followed by catalytic oxidation. Keggin-type polyoxomolybdates revealed much higher reusing capacity than the related polyoxotungstate. Effectively, the first catalysts practically allowed complete sulfur and nitrogen removal only in 1 h of reaction and for ten consecutive cycles, maintaining the original catalyst and ionic liquid samples.

Keywords: desulfurization; denitrogenation; oxidative catalysis; hydrogen peroxide; Polyoxometalate; ionic liquids



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1. Introduction

Long-term energy outlooks agree that fossil fuels will remain the dominant energy for at least more two decades, since the demand for energy is increasing with the growth of the world's population, economy, and increasing living standards. At present, fossil fuels cover ~88% of the energy requirement in the world [1]. The inevitable drawbacks of the current fossil fuel consumption are related to the environment degradation and public health. In the transportation sector, fossil fuels will be the main energy source for the near future. Motor vehicles powered on fossil fuels are among the major sources of air pollution in urban areas [2,3]. Fuels such as fuel oil, jet fuel, gasoline, diesel, etc., contain various pollutants, with the sulfur- and nitrogen-based organic compounds (SCs and NCs, respectively) as the majority of the contaminants [4]. The utilization of fossil fuels without purification poses a devastating effect on the environment and humans, mainly because of the emission of sulfur oxides (SO_x) and nitrogen oxides (NO_x) from SCs and NCs, respectively [5,6]. The global impact of SO_x emissions resulting from the burning of fossil fuels has led to the imposition of environmental restrictions for the sulfur level in transportation fuels (10 ppm in EU) [7,8].

The standard industrial methods for the removal of sulfur and nitrogen-based compounds from crude oils are hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) [9,10]. HDS is an effective process that needs high temperature (>350 °C) and pressure (up to 6 MPa), and also requires high amounts of hydrogen consumption [11–13]. SCs and NCs in fuels are converted to hydrogen sulfide and ammonia, respectively, via

the catalytic reduction with H₂ [14]. In the HDS process, NCs severely affect the catalyst and cause corrosion of the refinery equipment due to their high reactivity [14–16]. Therefore, it is essential to remove NCs before the desulfurization treatment of fuel, or preferably, to remove NCs and SCs simultaneously by an alternative process, capable of depth desulfurization and denitrogenation, reducing the impact of fuels on the environment by decreasing NO_x and SO_x emissions. Oxidative desulfurization (ODS) and oxidative denitrogenation (ODN) processes have been the focus of promising research in recent years due to their efficiency for removal of the most refractory S and N-content present in fuels [10,17,18]. This technology conciliates oxidative catalysis and liquid-liquid extraction steps [15,16]. Consequently, the efficiency of combined ODS/ODN processes depends of the catalyst performance and the ability of the extraction solvent. The sustainability and the cost-effectiveness of the process can be assured by the use of recovered and recyclable catalysts and the application of environmental-friendly solvents, such as ionic liquids [19,20]. The former are able to behave as an extraction solvent and also as an immobilization medium for the homogeneous catalyst, containing catalyst and substrate in the same liquid phase [21,22]. Hydrogen peroxide is generally the preferred oxidant to use in these processes due to its high active oxygen content and the fact that water is the sole by-product [23,24]. Our research group has been dedicated to the design of efficient catalysts for ODS based on polyoxometalates (POMs) [18,25–29]. POMs are polyanions incorporating various transition metals and are well-known by their structural diversity and potential in several areas of application [30]. In general, POMs are powerful catalysts for a great variety of oxidative reactions. In particular, Keggin-type POMs ([Xⁿ⁺M₁₂O₄₀]⁽⁸⁻ⁿ⁾⁻) (X: block p or d heteroatom) have been successfully used as efficient catalysts in ODS processes [31–35]. However, the investigation combining ODS and ODN is in a primitive stage and only one publication could be found in the literature demonstrating the ability of POMs as catalysts in this mixed systems [36].

This work reports an innovative combined ODS/ODN system catalyzed by hybrid-POMs and by applying an ionic liquid that acts as extraction solvent (1-butyl-3-methylimidazole hexafluorophosphate ([BMIM]PF₆)). The reusability and the stability of the catalyst were further investigated.

2. Materials and Methods

2.1. Reagents and Solvents

Phosphomolybdic acid (H₃PMo₁₂O₄₀·xH₂O, for microscopy), sodium phosphomolybdate (Na₃PMo₁₂O₄₀·xH₂O, technical), tetradecane (C₁₄H₃₀, >99%), 1-butyl-3-methylimidazole hexafluorophosphate (C₈H₁₅F₆N₂P, >97%, [BMIM]PF₆), hydrogen peroxide (H₂O₂, aq. 30%), dibenzothiophene (C₁₂H₈S, 98%, DBT), 4-methyldibenzothiophene (C₁₃H₁₀S, 96%, MDBT), quinoline (98 %, QUI), and indole (>99%, IND) were obtained from Sigma-Aldrich. Benzothiophene (C₈H₆S, >95%, BT), phosphotungstic acid (H₃PW₁₂O₄₀·xH₂O, 98%), and 1-butylpyridinium bromide (>99%, BPyBr) were acquired from Fluka. *N*-octane (C₈H₁₈, >99%) and 4,6-dimethyldibenzothiophene (C₁₄H₁₂S, 95%, DMDBT) were acquired from Acros Organic. None of these were subject to further treatment or purification.

2.2. Characterization Methods and Instrumentation

Fourier-transformed Infrared (FT-IR) spectra were acquired between 400 and 4000 cm⁻¹ on a Bruker Tensor 27 Spectrometer using KBr pellets, and all the representations are shown in arbitrary unities of transmittance. Solution ³¹P nuclear magnetic resonance (NMR) spectra were recorded in CD₃CN or D₂O at 162 MHz with a Bruker Avance III 400 spectrometer, and the chemical shifts are given with respect to external 85% H₃PO₄. Catalytic reactions were periodically monitored by GC-FID analysis carried out in a Bruker 430-GC-FID chromatograph (Germany). Hydrogen was used as carrier gas (55 cm.s⁻¹) and fused silica Supelco capillary columns SPB-5 (30 m × 0.25 mm i.d.; 25 μm film thickness) were used.

2.3. [BPy]₃ Salts Preparation

[BPy]₃PMo₁₂O₄₀ ([BPy]PMo₁₂) and [BPy]₃PW₁₂O₄₀ ([BPy]PW₁₂) were prepared following an experimental procedure adapted from previously reported methods [34,35]. Briefly, [BPy]Br (2.5 mmol) was dissolved in 2.5 mL of deionized water, and an aqueous solution of phosphomolybdic or phosphotungstic acid (0.5 mmol) in deionized water (2.5 mL) was added dropwise under magnetic stirring at room temperature. The mixture was left stirring for 30 min, after which the precipitate was filtrated, washed thoroughly with deionized water, and dried in a desiccator overnight. FT-IR (cm⁻¹, KBr): ν ([BPy]PMo₁₂) = 3435 (w), 3126 (w), 3085 (w), 3065 (w), 2964 (w), 2930 (w), 2874 (w), 1632 (m), 1486 (m), 1465 (vw), 1384 (vw), 1314 (vw), 1169 (w), 1063 (s), 956 (s), 878 (m), 796 (s), 683 (m), 596 (vw), 502 (w); ν ([BPy]PW₁₂) = 3456 (w), 3127 (w), 3085 (w), 3065 (w), 2964 (w), 2930 (w), 2874 (w), 1632 (m), 1486 (m), 1462 (vw), 1385 (vw), 1319 (vw), 1168 (w), 1080 (s), 978 (s), 896 (m), 804 (s), 683 (m), 596 (vw), 524 (m). ³¹P NMR (162 MHz, CD₃CN, 25 °C): δ ([BPy]PMo₁₂) = -2.39 ppm; δ ([BPy]PW₁₂) = -13.89 ppm.

2.4. Simultaneous Desulfurization and Denitrogenation Processes (ODS/ODN)

ODS/ODN studies were performed with a multicomponent Model Diesel containing SCs and NCs prepared with BT, DBT, MDBT, DMDBT, Q, and I in *n*-octane (500 ppm of sulfur or 300 ppm of nitrogen from each compound). The reactions were carried out under air in a closed borosilicate vessel with a magnetic stirrer and were immersed in a thermostatically controlled liquid paraffin bath at 70 °C. ODS/ODN reactions were performed in a biphasic system composed of the Model Diesel and [BMIM]PF₆ as extraction solvent. In a representative experiment, a certain amount of the catalyst equivalent to 3 μ mol of POM was added to 0.75 mL of [BMIM]PF₆ and 0.75 mL of Model Diesel, and this mixture was stirred for 10 min at 70 °C. The oxidative catalytic step was then initiated with the addition of aqueous H₂O₂ 30 % (75 μ L) to the reaction mixture. Tetradecane was used as a standard in the periodical monitorization of the sulfur content by gas chromatography (GC) analysis. At the end of each reaction, the processed Model Diesel phase was removed and substituted by a fresh volume. Both catalyst and [BMIM]PF₆ solvent were reused in the subsequent catalytic cycle, under identical reaction conditions and with the addition of a new portion of H₂O₂. The experimental error associated with the combined ODS/ODN efficiency was calculated by performing at least three repeated reactions (see Figure S1 in Supporting Information), and it was found to be approximately 5% to ODS and 4% to ODN.

3. Results and Discussion

3.1. Catalysts Synthesis and Characterization

The catalysts [BPy]PMo₁₂ and [BPy]PW₁₂ are POM salts previously reported by our group [34,35]. These were prepared by replacing the protons of phosphomolybdic or phosphotungstic acid through a simple acid-base reaction with [BPy]Br in water. [Na]₃PMo₁₂O₄₀ ([Na]PMo₁₂) is a commercially available salt. Characterization results by FT-IR and ³¹P NMR spectroscopies obtained for these compounds are displayed in Figure 1. All infrared spectra generally display the expected bond vibration absorption band pattern. For phosphomolybdic salts, strong intensity bond vibration bands around 1064, 960, 880, and 794 cm⁻¹ are registered for [BPy]PMo₁₂ corresponding to ν_{as} (P—O_a), ν_{as} (Mo—O_d), ν_{as} (Mo—O_b—Mo), and ν_{as} (Mo—O_c—Mo), respectively [37–39]. For [Na]PMo₁₂, ν_{as} (Mo—O_b—Mo) seems to be expressed in a pair of bands observed at 904 and 862 cm⁻¹, hinting at variable oxidation states for Mo. Phosphotungstate in [BPy]PW₁₂ is similarly expressed by strong intensity ν_{as} (P—O_a), ν_{as} (W—O_d), ν_{as} (W—O_b—W), and ν_{as} (W—O_c—W) bond vibration absorption bands at 1080, 976, 892, and 802 cm⁻¹, correspondingly. The infrared spectra of both [BPy]₃ salts contain weak bands at 3126, 3085, and 3065 cm⁻¹ corresponding to ν (C—H) aromatic bond vibrations, as well as at 2964, 2930, and 2874 cm⁻¹ attributed to the ν (C—H) of the aliphatic chain, a medium intensity band at 1632 cm⁻¹ corresponding to ν (C=N) vibrations that is typical of the quaternary nitrogen atom in a heterocyclic ring.

Several weak/medium bands in the range 1580–1100 cm^{-1} are observed due to aromatic $\nu(\text{C—N})$, $\nu(\text{C—C})$, and $\delta(\text{C—H})$ vibrations. A strong band at 1485 cm^{-1} is attributable to the conjugation of $\nu(\text{C=C})$ and $\nu(\text{C=N})$ bonds, typical of pyridinium salts. The strong one at 682 cm^{-1} corresponds to the aromatic out-of-plane hydrogen deformation [40]. ^{31}P NMR analysis reveals the typical chemical shifts for each structure [34,35]. The spectrum recorded for $[\text{Na}]\text{PMo}_{12}$ registers two single peaks attributed to a different content of Na cations in the POM structure.

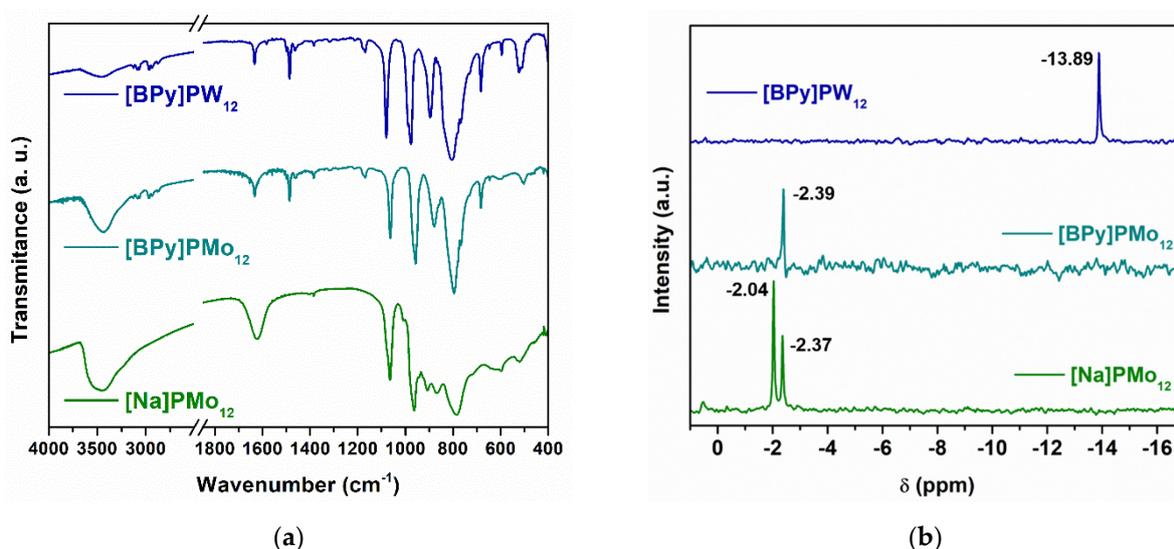


Figure 1. (a) FT-IR spectra showed in the wavenumber regions 4000–2500 cm^{-1} and 1800–400 cm^{-1} , and (b) ^{31}P NMR spectra showed in the chemical shifts ranging from 1 to -17 ppm, obtained for $[\text{Na}]\text{PMo}_{12}$, $[\text{BPy}]\text{PMo}_{12}$, and $[\text{BPy}]\text{PW}_{12}$.

3.2. ODS/ODN Catalytic Studies

All ODS/ODN studies were performed at 70 $^{\circ}\text{C}$ in a biphasic liquid-liquid system based on $[\text{BMIM}]\text{PF}_6$ as extraction solvent and an immiscible multicomponent S/N Model Diesel containing the most representative refractory sulfur and nitrogen content present in fuels, namely benzothiophene (BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (MDBT), and 4,6-dimethyldibenzothiophene (DMDBT) from SCs, and indole (IND) and quinoline (QUI) from NCs. Catalytic systems based on $[\text{Na}]\text{PMo}_{12}$, $[\text{BPy}]\text{PMo}_{12}$, and $[\text{BPy}]\text{PW}_{12}$ were composed by equal volumes of Model Diesel and $[\text{BMIM}]\text{PF}_6$ (750 μL) and an equivalent of 3 μmol of active catalyst. The simultaneous desulfurization and denitrogenation processes occurred in two main steps; at first, an initial extraction of SCs and NCs was transferred from the Model Diesel to the $[\text{BMIM}]\text{PF}_6$ extraction phase (during 10 min at 70 $^{\circ}\text{C}$ under stirring). A time longer than 10 min did not increase the initial extraction of SCs and NCs. In the next step, the oxidative catalytic stage was initiated by the addition of aq. H_2O_2 (30%). The performance of catalysts $[\text{Na}]\text{PMo}_{12}$, $[\text{BPy}]\text{PMo}_{12}$, and $[\text{BPy}]\text{PW}_{12}$ in simultaneous ODS/ODN reactions was evaluated and the experimental results are displayed in Figure 2. All these catalysts behaved as homogenous catalysts presented only in the $[\text{BMIM}]\text{PF}_6$ phase, since the ^{31}P NMR analysis did not present any phosphorus signal. The combined desulfurization/denitrogenation profiles demonstrate that $[\text{Na}]\text{PMo}_{12}$ and $[\text{BPy}]\text{PMo}_{12}$ have similar catalytic performance, achieving near total conversion after 1 h of reaction (98.7 and 97.9%, respectively). On the other hand, using the $[\text{BPy}]\text{PW}_{12}$ catalyst, near complete ODS/ODN was achieved faster than the analogous $[\text{BPy}]\text{PMo}_{12}$ catalyst. These results indicate that the nature of the cation in the POM catalyst does not seem to have an important influence in its catalytic performance. On the other hand, a distinct combined ODS/ODN profile was found using polyoxotungstate and polyoxomolybdate, where the first showed to be the most effective, guaranteeing total desulfurization and denitrogena-

tion after just 1 h of reaction. The removal rates of each component of the S/N Model Diesel are the following: IND > QUI > DBT > MDBT > DMDBT ~ BT. The removal of NCs is largely achieved during the initial extraction step. The difference in removal rates between IND and QUI relates to the higher basicity of the proton-donor present in IND [41,42]. During the oxidation catalytic step (after the 10 min), the difference of reactivity between the SCs can be explained by the decrease in electron density on the sulfur atom, which hinders oxidation [18]. The nature of the obtained oxidized products was identified by the analysis of the extraction phase, since, in the model diesel phase, no oxidized products were found. The oxidized products of sulfur compounds were the corresponding sulfones. Only vestigial amounts of sulfoxide from BT were found. From the QUI oxidation, the quinoline N-oxide was identified.

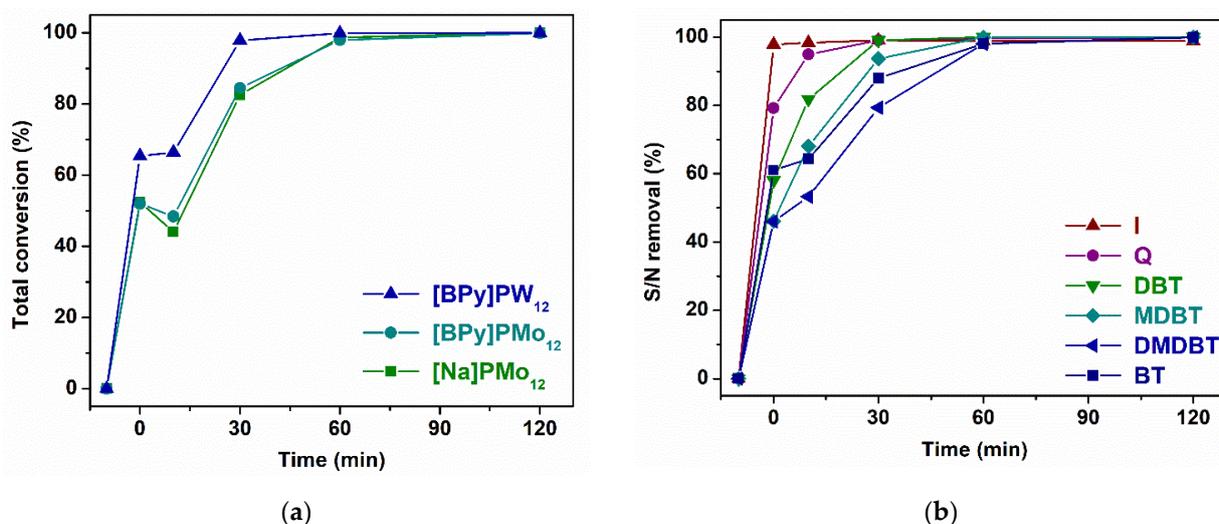


Figure 2. (a) Combined denitrogenation and desulfurization profiles catalyzed by the various POMs, using a biphasic S/N Model Diesel/[BMIM]PF₆ system, H₂O₂ as oxidant, at 70 °C; (b) denitrogenation and desulfurization profile of each SCs and NCs present in the Model Diesel, using [Na]PMo₁₂ catalyst.

Figure 3 displays the denitrogenation and the desulfurization profiles of the combined ODS/ODS processes. These results demonstrated that complete denitrogenation is achieved faster than desulfurization, since higher extraction of NCs occurred during the first 10 min of the process, which is associated to the higher oxidative facility of NCs than SCs. Figure 3 also compares the desulfurization profiles that occurred in a combined ODS/ODN process and a single ODS process, i.e., using a Model Diesel containing only SCs. These experiments were performed using the same reactional conditions. Without duties, the desulfurization profiles are similar in combined S/N and single S processes. These results indicate that the conciliation of extraction and oxidative catalytic steps did not result in a competitive S and N removal process, and these may occur in parallel, sharing the oxidant and the catalyst action. This is a remarkable advantage compared to the combined hydrodesulfuration/hydrodenitrogenation processes [14].

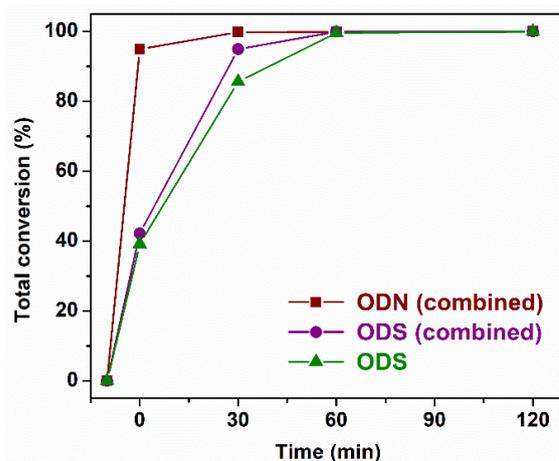


Figure 3. Denitrogenation and desulfurization profiles of a combined ODS/ODN process and also a desulfurization of a single ODS process (using a single Model Diesel containing BT, DMDBT, MDBT, and DBT), using $[\text{Na}]\text{PMo}_{12}$ catalyst, $[\text{BMIM}]\text{PF}_6$ extraction solvent, H_2O_2 as oxidant, at 70°C .

The recycling ability of each POM/ $[\text{BMIM}]\text{PF}_6$ catalytic system was accessed by consecutive reutilization cycles that consisted in the preservation of the POM/ $[\text{BMIM}]\text{PF}_6$ phase for various consecutive cycles. This reusing process is the desired sustainable procedure of using the same portion of catalyst and ionic liquid extraction solvent for consecutive combined ODS/ODN cycles. After each cycle, the treated S/N Model Diesel is removed from the system and replaced by a novel portion of S/N Model Diesel, as well the H_2O_2 oxidant. During the reutilization cycles, an interlayer aqueous phase increased in volume between the S/N Model Diesel and $[\text{BMIM}]\text{PF}_6$ phase due to the successive addition of aqueous oxidizing agent (Figure 4a). Figure 4b display the results obtained from reusing the three different POM/ $[\text{BMIM}]\text{PF}_6$ catalytic systems. These results were achieved after 1 h. The $[\text{BPy}]\text{PW}_{12}/[\text{BMIM}]\text{PF}_6$ system presented a decrease of catalytic efficiency, mainly after the 3rd cycle, since its combined ODS/ODN efficiency decreased from 98% from the 3rd cycle to 63% for the 4th cycle. In fact, the efficiency found for the 4th cycle was only attributed to the initial extraction step, indicating the absence of the oxidative catalytic performance of $[\text{BPy}]\text{PW}_{12}$ catalyst. In the 5th combined desulfurization/denitrogenation cycle, the catalyst did not promote any oxidative catalysis, and the initial extraction of the S/N compounds decreased to 46%. This decrease of S/N extraction is a consequence of absence of S/N oxidation, i.e., without decreasing non-oxidized SCs and NCs in the $[\text{BMIM}]\text{PF}_6$ phase, the extraction of more S/N from Diesel did not occur. Reusing experiments using the $[\text{BPy}]\text{PW}_{12}/[\text{BMIM}]\text{PF}_6$ system were not performed after the 5th cycle. On the other hand, using the polyoxomolybdate catalytic systems, i.e., $[\text{Na}]\text{PMo}_{12}$ and $[\text{BPy}]\text{PMo}_{12}$, the loss of the catalytic activity was not verified for ten consecutive combined ODS/ODN cycles and near complete removal of S/N from Model Diesel was achieved after 1 h. A small decrease in activity is only observed during the 10th cycle (93 and 98%, for $[\text{Na}]\text{PMo}_{12}$ and $[\text{BPy}]\text{PMo}_{12}$, respectively).

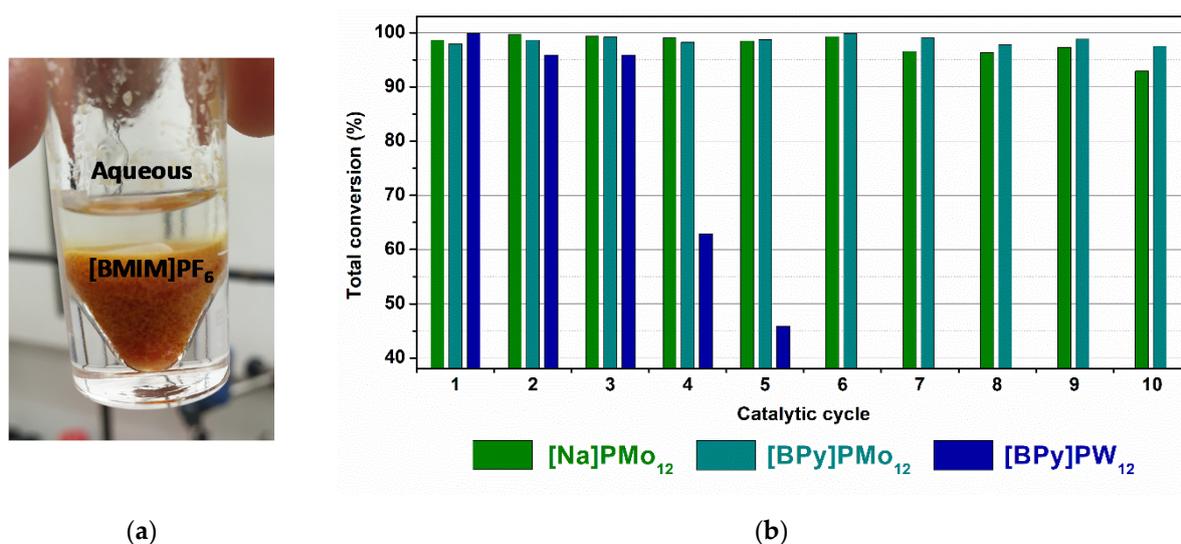


Figure 4. (a) Representation of the $[\text{Na}]\text{PMo}_{12}/[\text{BMIM}]\text{PF}_6$ system after ten consecutive ODS/ODS cycles. (b) Combined desulfurization/denitrogenation efficiency obtained after 1 h of reaction, when catalyst/ $[\text{BMIM}]\text{PF}_6$ system is reused for ten consecutive cycles, using catalysts $[\text{Na}]\text{PMo}_{12}$, $[\text{BPy}]\text{PMo}_{12}$, and $[\text{BPy}]\text{PW}_{12}$, with H_2O_2 as oxidant, at 70°C .

After the reusing cycles, the stability of the homogeneous POM catalysts was investigated by ^{31}P NMR. The immiscible aqueous and $[\text{BMIM}]\text{PF}_6$ phases (Figure 4b) were separated, analyzed, and the results are displayed in Figure 5. In general, all studied catalysts suffered structural transformations during the various reusing cycles. Furthermore, the structural transformations may alter solubility properties, since POM derivative peaks could be found in both the Ionic Liquid and aqueous phase. The structural modification of $\text{Na}[\text{PMo}_{12}]$ and $[\text{BPy}]\text{PMo}_{12}$ was not coincident, and different active POM derivative fragments were found in aqueous and $[\text{BMIM}]\text{PF}_6$ phases. On the other hand, the analysis of both phases obtained after the 5th cycle using the $[\text{BPy}]\text{PW}_{12}$ catalyst revealed similar distribution of POM transformed species. It ends up being implied that the structural transformations associated with $[\text{BPy}]\text{PW}_{12}$ catalytic activity ultimately led to its deactivation. In a future work, the stability and the facility of the recovery of these homogeneous catalysts will be treated by their immobilization in appropriate supporting materials.

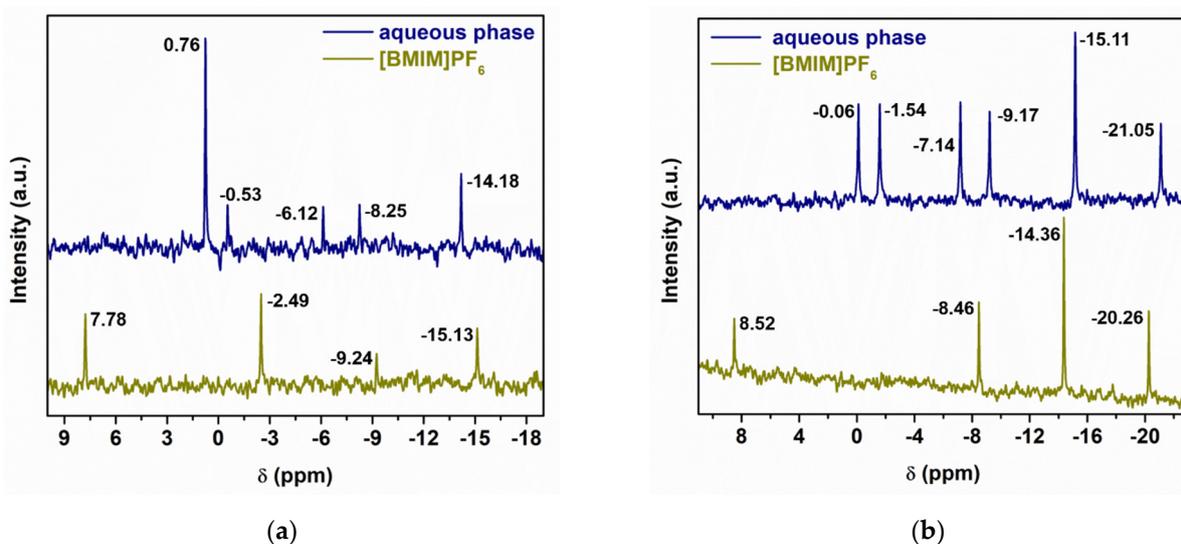


Figure 5. Cont.

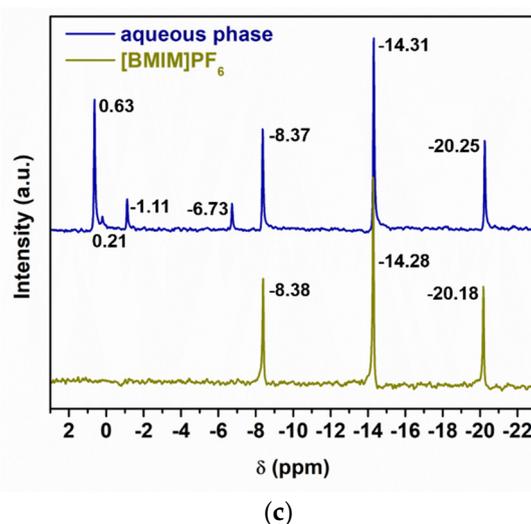


Figure 5. ^{31}P NMR spectra acquired in CD_3CN or D_2O for each $[\text{BMIM}]\text{PF}_6$ and aqueous phases present in the catalytic systems $[\text{Na}]\text{PMo}_{12}$ (10th cycle; a), $[\text{BPy}]\text{PMo}_{12}$ (10th cycle; b), and $[\text{BPy}]\text{PW}_{12}$ (5th cycle; c).

4. Conclusions

This work reported a novel efficient strategy capable of combining complete desulfurization and denitrogenation to treat a multicomponent S/N Model Diesel containing the most refractory elements present in Diesel. Keggin-type POMs showed to be active catalysts to perform parallel oxidative desulfurization (ODS) and oxidative denitrogenation (ODN) under sustainable conditions, i.e., using hydrogen peroxide as oxidant and an ionic liquid as extraction solvent ($[\text{BMIM}]\text{PF}_6$). Complete removal of sulfur and nitrogen compounds was achieved only after 1 h. Furthermore, a reusing test was performed by using the homogeneous POM catalyst and $[\text{BMIM}]\text{PF}_6$ for consecutive ODS/ODN cycles. The polyoxomolybdates $[\text{Na}]\text{PMo}_{12}$ and $[\text{BPy}]\text{PMo}_{12}$ showed high reusing capacity for ten consecutive cycles without any appreciable reduction of catalytic performance. The kinetic similarity obtained between these two polyoxomolybdates-based compounds indicated that the nature of the cation does not seem to influence its activity. The reusing capacity was drastically decreased when the polyoxotungstate $[\text{BPy}]\text{PW}_{12}$ was used and, in this case, only three consecutive ODS/ODN cycles were successfully performed. Lastly, the stability analysis of the POM catalysts after reusing cycles indicates that the polyoxomolybdate is in fact a precursor for the active catalytic species, since its Keggin structures are modified in other active compounds. On the other hand, the polyoxotungstate also suffered structural modification but into inactive species. Therefore, future work is already planned to prepare heterogeneous POM catalysts to avoid their fast structural modification and also to facilitate catalyst recovery.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/suschem2020022/s1>, Figure S1, Denitrogenation and desulfurization profiles of a combined ODS/ODN process, repeated three times for accuracy investigation, using a single Model Diesel containing BT, DMDBT, MDBT and DBT, QUI and IND, using $[\text{Na}]\text{PMo}_{12}$ catalyst, $[\text{BMIM}]\text{PF}_6$ extraction solvent, H_2O_2 as oxidant, at 70 °C.

Author Contributions: Conceptualization, S.S.B.; methodology, S.S.B.; validation, S.S.B. and L.C.-S.; formal analysis, S.S.B.; investigation, D.F.S., A.M.V. and F.M.; writing—original draft preparation, A.M.V. and S.S.B.; writing—review and editing, S.S.B. and L.C.-S.; supervision, B.d.C., S.S.B. and L.C.-S.; project administration, S.S.B. and L.C.-S.; funding acquisition, B.d.C. and S.S.B. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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