

Article

Efficient Oxidative Desulfurization Processes Using Polyoxomolybdate Based Catalysts

Carlos M. Granadeiro ^{1,2}, Pedro M. C. Ferreira ¹, Diana Julião ^{1,2}, Luís A. Ribeiro ¹, Rita Valença ³, Jorge C. Ribeiro ³, Isabel S. Gonçalves ², Baltazar de Castro ¹, Martyn Pillinger ², Luís Cunha-Silva ¹, and Salete S. Balula ^{1,*}

- ¹ REQUIMTE/LAQV & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal; cgranadeiro@fc.up.pt (C.M.G.); up201408026@fc.up.pt (P.M.C.F.); diananetojuliao@hotmail.com (D.J.); laribeir@fc.up.pt (L.A.R.); bcastro@fc.up.pt (B.d.C.); l.cunha.silva@fc.up.pt (L.C.-S.)
- ² Department of Chemistry, CICECO—Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal; igoncalves@ua.pt (I.S.G.); mpillinger@ua.pt (M.P.)
- ³ Galp Energia, Refinaria de Matosinhos, 4452-852 Leça da Palmeira, Matosinhos, Portugal; rita.valenca@galp.com (R.V.); jorge.ribeiro@galp.com (J.C.R.)
- * Correspondence: sbalula@fc.up.pt; Tel.: +351-220-402-576

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Abstract: This work proposes an efficient desulfurization system to produce low sulfur diesel under sustainable and moderate experimental conditions. Treatment of a real diesel with a sulfur content of 2300 ppm led to 80% desulfurization after 2 h. The processes used conciliate liquid-liquid extraction and sulfur oxidative catalysis. The catalytic performance of the commercial Keggin-polyoxomolybdate $H_3[PMo_{12}O_{40}]$ (PMo₁₂) was strategically increased by simple cation exchange, using a long carbon chain (ODAPMo₁₂, ODA = CH₃(CH₂)₁₇(CH₃)₃N), and by its incorporation into the Metal-Organic Framework (MOF) NH₂-MIL-101(Cr), forming a new active heterogeneous PMo₁₂@MOF composite catalyst. Activity of both catalysts was similar; however, the solid catalyst could be easily recovered and reused, and its stability was confirmed after multiple continuous cycles.

Keywords: real diesel; ionic liquid; oxidative desulfurization; benzothiophene derivatives; hydrogen peroxide

1. Introduction

The reduction of sulfur content in fuels is a major environmental concern [1]. International policies have adopted increasingly strict requirements to eliminate the hazardous emissions of sulfur oxides [2]. Therefore, the production of sulfur-free fuels has become of major interest in both academic and industrial research [3]. Extractive and catalytic oxidative desulfurization (ECODS) is considered the most promising complementary method to conventional desulfurization technology used in refineries [4]. By combining extractive and oxidative steps, ECODS allows the removal of the refractory sulfur compounds in fuel under mild conditions [5,6].

Polyoxometalates (POMs) are large inorganic clusters with vast structural diversity that have been used for a wide range of applications, such as catalysis, luminescence, magnetism and medicine [7]. In particular, POMs have been extensively used in acid and oxidative catalysis owing to their tunable acidity, solubility and redox potentials [8]. The Keggin $[XM_{12}O_{40}]^{n-}$ anions are the most studied in oxidative desulfurization most likely due to their commercial availability [9]. Despite the great number of reports with Keggin tungstates, the application of the corresponding polyoxomolybdates in ODS is

relatively rare [10–13]. Qiu et al. evaluated the activity of quaternary ammonium salts of $H_3[PMo_{12}O_{40}]$ (PMo₁₂) in the ODS of straight-run diesel [10]. The results showed that the carbon chain length of the surfactant influenced the desulfurization performance, with the catalyst containing a longer carbon chain being able to remove 93% of sulfur after 2 h of reaction. Composites prepared by intercalation of different heteropolyanions in a hydrotalcite-type compound were tested as heterogeneous catalysts in the ECODS process of model and real diesel [11]. The best performance was attained with a PMo₁₂-based catalyst (98% of sulfur removal), although a considerable amount of oxidant was used ($H_2O_2/S = 20$).

We have been developing POM-based catalysts for application in the oxidative desulfurization of fuels [12–14]. In this work, phosphomolybdic acid (PMo₁₂), a quaternary ammonium salt of PMo₁₂ consisting of a cationic surfactant (trimethyloctadecylammonium, ODA), and a POM@MOF composite material have been prepared and evaluated in the ECODS process of a multicomponent model diesel. The MOF used was the amino-functionalized chromium terephthalate, NH₂-MIL-101(Cr), and to the best of our knowledge this is the first report of the incorporation of PMo₁₂ in this support. The reusability and stability of the most promising catalyst were evaluated for consecutive ECODS cycles. The good performance of the catalyst prompted its application in the desulfurization of an untreated real diesel.

2. Results and Discussion

2.1. Catalyst Characterization

The FT-IR spectra of PMo₁₂ and ODAPMo₁₂ display the bands associated with the POM stretching modes, namely the bands assigned to v_{as} (P–O) vibrations at 1063 cm⁻¹, terminal v_{as} (Mo=O) at 956 cm⁻¹, corner-sharing v_{as} (Mo–Ob–Mo) at 879 cm⁻¹, and edge-sharing v_{as} (Mo–Oc–Mo) at 796 cm⁻¹ (Figure 1) [15,16]. For ODAPMo₁₂, the spectrum displays the typical bands of the organic cation, which can be assigned to v_{as} (C-H) and v_{s} (C-H) stretches located at 2920 and 2850 cm⁻¹, respectively, as well as a δ (C-H) bending mode at 1464 cm⁻¹ [17]. The PMo₁₂@MOF spectrum (Figure 1B) shows the characteristic bands of the amino-functionalized MIL-101(Cr) support [18] together with the bands associated with the PMo₁₂ stretching modes (v_{as} (P–O) at 1061 cm⁻¹ and v_{as} (Mo=O) at 958 cm⁻¹). Elemental analysis of PMo₁₂@MOF for the Mo content revealed a POM loading of 0.122 mmol·g⁻¹. The presence of amine groups in the MOF structure leads to a high POM loading since it allows a more efficient immobilization of the anionic PMo₁₂ via electrostatic interactions. Similar results have been reported for the incorporation of the phosphotungstate Keggin analogue in amine-functionalized MIL-101(Cr) [19].



Figure 1. FT-IR spectra of (**A**) the homogeneous catalysts and (**B**) the NH₂-MIL-101(Cr) (MOF) support and the corresponding $PMo_{12}@MOF$ composite before and after catalysis (ac).

The powder XRD pattern of the $PMo_{12}@MOF$ composite exhibits a similar profile to the pattern of the MOF support, suggesting the preservation of the MOF crystalline structure in the final composite (Figure 2). The position and intensity of the peaks in both XRD patterns are in good agreement with previously reported data for NH₂-MIL-101(Cr) [18,20–22].

The SEM images of PMo₁₂@MOF (Figure 3) show the typical morphology of NH₂-MIL-101(Cr) composed of cubic micro-crystals [18,19,23]. Energy dispersive X-ray spectroscopy revealed the presence of chromium from the support as well as phosphorous and molybdenum from the impregnated POM (Figure 4).



Figure 2. Powder XRD patterns of NH₂-MIL-101(Cr) (MOF) and the corresponding PMo₁₂@MOF composite before and after catalysis (ac).



Figure 3. SEM images of the PMo₁₂@MOF composite material before (top) and after (bottom) catalytic utilization (PMo₁₂@MOF-ac) at different magnifications: (left) \times 25,000 and (right) \times 50,000.



Figure 4. EDS spectra of the PMo12@MOF composite material (left) before and (right) after catalytic use.

2.2. Oxidative Desulfurization of Model Diesel

The desulfurization performance of the catalysts was evaluated in the ECODS process of a model diesel prepared by dissolving the refractory sulfur compounds most commonly found in diesel, namely BT, DBT, 4-MDBT and 4,6-DMDBT, in *n*-octane to give a total sulfur concentration of 2000 ppm. An ionic liquid (IL) and H₂O₂ were chosen as extraction solvent and oxidant, respectively. This choice was based on the negligible vapor pressure of ILs when compared with the conventional volatile organic solvents and to the fact that H₂O₂ only produces water as by-product. In particular, the IL [BMIM][PF₆] was selected due to the desulfurization efficiency achieved in previous ECODS systems [24–26]. The ECODS process begins with an initial extraction step by stirring the biphasic system for 10 min at 50 °C, which promotes the transfer of the sulfur compounds from the model diesel to the IL. Afterwards, the addition of oxidant initiates the catalytic step during which the sulfur compounds in the extraction solvent are oxidized to sulfoxides and/or sulfones. This leads to a continuous transfer of non-oxidized sulfur compounds from the model diesel to the IL phase. The individual desulfurization of each component at the end of initial extraction follows the order: BT > DBT > 4-MDBT > 4,6-DMDBT (Table 1). Similar results have been previously reported and are explained by the different molecular diameters as well as steric hindrance by the methyl groups in DBT derivatives [24,26,27].

Table 1. Results obtained for the initial extraction of each refractory sulfur compound from the model diesel to the extractant phase using PMo₁₂, ODAPMo₁₂ and PMo₁₂@MOF catalysts. Desulfurization (Des) was determined considering the initial sulfur concentration in diesel (Sinitial): Des=(Sinitial-S)/Sinitial x 100.

Catalyst	Desulfurization (%)			
	BT	DBT	4-MDBT	4,6-DMDBT
-	57	49	32	20
PMo ₁₂	57	52	37	25
ODAPMo ₁₂	59	49	31	11
PMo ₁₂ @MOF	63	51	37	29

The results obtained in the desulfurization of the model diesel using the three different catalysts are compared in Figure 5. At the end of the initial extraction, the system using the $PMo_{12}@MOF$ catalyst allowed the highest desulfurization percentage of 45%. Most likely, this result is due to

the presence of an extensive porous framework for NH₂-MIL-101(Cr) that contributes to a higher degree of contact between the phases [14,28]. After the addition of H_2O_2 , the ODAPMo₁₂ and PMo12@MOF catalysts exhibit similar desulfurization profiles with remarkable efficiency. After just 40 min of ECODS process, both catalysts allowed approximately 1690 ppm of sulfur to be removed, corresponding to a desulfurization of 85%. Moreover, only 2 h of the catalytic stage are necessary to achieve practically complete desulfurization of the model diesel (96 and 95% using ODAPMo₁₂ and PMo₁₂@MOF, respectively). Some examples can be found in the literature for PMo₁₂-based catalysts and their application in oxidative desulfurization [10,11,29–31]. A composite material consisting of PMo₁₂ immobilized in the copper-based MOF HKUST-1 gave similar desulfurization values (for a model diesel using H_2O_2 as the oxidant) to those found in the present work, although Rafiee et al. used a higher temperature and H_2O_2/S ratio [31]. In another report, NH₂-MIL-101(Cr) was used as a support to incorporate the tungsten analogue Keggin anion [19]. The resulting PW₁₂@MOF proved to be an efficient and recyclable catalyst for ODS, allowing the complete conversion of DBT after 1 h during six cycles. This ECODS system used mild conditions identical to those used here, but was evaluated with a single-component model oil rather than a multicomponent model diesel containing a mixture of sulfur compounds more difficult to oxidize than DBT. ODS of the sulfur components follows the order: DBT > 4-MDBT > 4,6-DMDBT > BT as previously reported for POM-catalyzed ODS systems with H₂O₂ [28,32–34]



Figure 5. Desulfurization of a multicomponent model diesel in a biphasic system (diesel/[BMIM][PF₆]) showing the initial extraction (before the dashed line) and the catalytic stage (after the dashed line) using PMo₁₂, ODAPMo₁₂ and PMo₁₂@MOF as catalysts at 50 °C.

Although the ODAPMo₁₂ and PMo₁₂@MOF catalysts exhibited similar desulfurization performances, the latter was considered as the better catalyst overall. The efficiency of H_2O_2 usage was also calculated for the systems using both catalysts and similar result was obtained with 95% of efficiency. ODAPMo₁₂ behaves as a homogeneous catalyst, probably due to the low number of surfactant molecules acting as cations (only three molecules). Therefore, the heterogeneous nature of PMo₁₂@MOF, which allows the catalyst to be recovered and isolated from the system, confers a very important advantage over the homogeneous ODAPMo₁₂.

Different control experiments have been performed, such as a blank experiment without catalyst, the adsorptive capacity of the composite (without oxidant) and using only the MOF support as catalyst (Figure 6). In all cases, the results show that there is no significant catalytic contribution as the desulfurization practically stops after the oxidant addition.



Figure 6. Kinetic profiles for the desulfurization of a multicomponent model diesel in a biphasic system (diesel/[BMIM][PF₆]) using the MOF support, a blank experiment (without any catalyst) and the adsorptive capacity of $PMo_{12}@MOF$ (without oxidant) at 50 °C.

The reusability of $PMo_{12}@MOF$ was investigated in consecutive ECODS cycles (Figure 7). At the end of each cycle, the model diesel was removed, and the extracting phase was reused. A new ECODS cycle was prepared by adding an equal volume of model diesel and a new portion of oxidant after the initial extraction stage. This method promotes the low cost of the process by avoiding the waste of ionic liquid in a recycling process. The first two cycles exhibit similar performances, achieving 96% of sulfur removal after 3 h of the catalytic stage. Interestingly, the third cycle reached a desulfurization of 100% for the same period of time. This slight increase in desulfurization could be due to the presence of active species in the extraction phase that remained from the previous cycles. The desulfurization values after the initial extraction (10 min) are similar along the cycles, which suggests that the increasing amount of oxidized sulfur compounds in the IL phase does not lead to solvent saturation.



Figure 7. Desulfurization data of a multicomponent model diesel for three consecutive cycles using the ECODS system with PMo₁₂@MOF at 50 °C.

The mechanism involved in the ECODS process starts with the formation of peroxo-POM active species by nucleophilic attack of H_2O_2 on Mo^{VI} atoms [12,29,34] The sulfur compounds are then oxidized into the corresponding sulfoxides by these active species which in turn are regenerated into the initial Mo^{VI} -species. Sulfoxides can suffer a new nucleophilic attack leading to the formation of sulfones.

2.3. Oxidative Desulfurization of Real Diesel

The PMo₁₂@MOF composite was used in the desulfurization of an untreated real diesel containing 2300 ppm of sulfur. An initial treatment was performed consisting of nine liquid-liquid extractions

using 1:1 (v/v) diesel:MeCN at 50 °C, which promoted a lowering of the sulfur content to 714 ppm (69% desulfurization; additional extractions did not lower the S content any further). Afterwards, the treated diesel sample was used in an ECODS cycle under similar experimental conditions to the ones described for the model diesel (1:1 diesel/[BMIM][PF₆]). At the end of this step, a final extraction with MeCN or with [BMIM][PF₆] was performed to remove the oxidized products (the total ratio extraction solvent/real diesel used was 11:1). After only 2 h at 50 °C, an additional 250 ppm of sulfur had been removed leading to an overall desulfurization of 80%. For comparison, an ECODS cycle with the initial untreated diesel (S = 2300 ppm) was performed and, for the same period of time, led to the removal of 1377 ppm of sulfur, corresponding to a desulfurization of 60%. The initial treatment therefore plays a crucial role in the desulfurization process since when combined with ECODS it allows a much lower sulfur content to be reached. The MeCN used for the initial extraction cycles could be recovered by distillation and reused.

2.4. Catalyst Stability

The stability of the catalyst PMo₁₂@MOF was investigated by recovering and characterizing the solid after catalytic use (PMo₁₂@MOF-ac). The FT-IR spectrum of PMo₁₂@MOF-ac (Figure 1B) still exhibits the main absorption bands of the support and the POM. In particular, the presence of the bands ascribed to POM vibrations, namely v_{as} (P–O) and v_{as} (Mo=O) stretches, at the same wavelengths suggests that the Keggin structure is preserved after the ECODS process. The crystalline structure of NH₂-MIL-101(Cr) seems to be preserved on the evidence of powder XRD (Figure 2), since the patterns before and after catalysis show the MOF main peaks at the same positions and intensities. The SEM images of PMo₁₂@MOF (Figure 3) showed that the morphology of the sample was maintained while EDS analysis (Figure 4) revealed an identical chemical composition before and after catalysis.

3. Experimental Section

3.1. Materials and Methods

The following chemicals and reagents were purchased from commercial suppliers and used without further purification: phosphomolybdic acid (H₃PMo₁₂O₄₀·nH₂O, Sigma-Aldrich, St. Louis, MO, USA, 99.9%), trimethyloctadecylammonium bromide (Sigma-Aldrich, 98%), chromium(III) nitrate nonahydrate (Sigma-Aldrich, 99%), 2-aminobenzene-1,4-dicarboxylic acid (Aldrich, St. Louis, MO, USA, 99%), sodium hydroxide (Fluka, \geq 98%), (3-aminopropyl)triethoxysilane (Sigma-Aldrich, 99%), tetraethyl orthosilicate (Aldrich, 98%), ethanol (VWR, \geq 99.5%), *N*,*N*-dimethylformamide (Merck, Kenilworth, NJ, USA, 99.8%), ammonia (Merck, 25% aq.), dibenzothiophene (Sigma-Aldrich, 98%), 1-benzothiophene (Fluka, 95%), 4-methyldibenzothiophene (Sigma-Aldrich, 96%), 4,6-dimethyldibenzothiophene (Alfa-Aesar, Haverhill, MA, USA, 97%), *n*-octane (Sigma-Aldrich, 98%), 1-butyl-3-methylimidazolium hexafluorophosphate (Aldrich, 97%), tetradecane (Aldrich, 99%), acetonitrile (Merck, 99.5%) and hydrogen peroxide (Sigma-Aldrich, 30% w/v aq).

Elemental analysis for C, N, and H was performed on a Leco CHNS-932 at the University of Santiago de Compostela. Infrared spectra were recorded in the 400–4000 cm⁻¹ region on a Jasco 460 Plus Spectrometer using KBr pellets. ³¹P NMR spectra were collected for liquid solutions using a Bruker Avance III 400 spectrometer and chemical shifts are given with respect to external 85% H₃PO₄. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) studies were performed at the "Centro de Materiais da Universidade do Porto" (CEMUP, Porto, Portugal) using a JEOL JSM 6301F scanning electron microscope operating at 15 kV equipped with an Oxford INCA Energy 350 energy-dispersive X-ray spectrometer. The samples were studied as powders and were previously subjected to gold sputtering. Powder X-ray diffraction analyses were collected at ambient temperature in Bragg-Brentano para-focusing geometry using a Rigaku Smartlab diffractometer, equipped with a D/teX Ultra 250 detector and using Cu-K- α radiation (K α_1 wavelength 1.54059 Å), 45 kV, 200 mA, in continuous mode, step 0.01°, speed 15°/min, in the range $1 \le 2\theta \le 50^\circ$. GC-FID

analyses were carried out in a Bruker 430-GC-FID gas chromatograph using hydrogen as the carrier gas (55 cm³s⁻¹) and fused silica SPB-5 Supelco capillary columns (30 m × 0.25 mm i.d.; 25 µm film thickness). The analysis of sulfur content of the treated diesel was performed by Galp Energia by ultraviolet fluorescence using Thermo Scientific equipment, with a TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125.

3.2. Catalyst Synthesis

The salt $(C_{18}H_{37}N(CH_3)_3)_3$ [PMo₁₂O₄₀]·nH₂O (ODAPMo₁₂) [17], the amino-functionalized MOF NH₂-MIL-101(Cr) [18], and the composite material PMo₁₂@NH₂-MIL-101(Cr) [19,20] were prepared by following literature procedures or adaptions thereof.

3.2.1. Quaternary Ammonium Salt (ODA) of PMo₁₂O₄₀

 $(C_{18}H_{37}N(CH_3)_3)_3$ [PMo₁₂O₄₀]·nH₂O (ODAPMo₁₂) was prepared following the reported procedure [17]. A solution of trimethyloctadecylammonium (ODA) bromide (5 mmol dissolved in 20 mL of EtOH) was added dropwise to an aqueous solution of H₃[PMo₁₂O₄₀]·nH₂O (1 mmol in 40 mL) and the mixture was stirred for 2.5 h at room temperature. The solid was vacuum filtered, washed with deionized water and dried in a desiccator over silica gel. Anal. Found (%): C, 33.18; H, 6.41; N, 1.86; Calcd. (%) (C₁₈H₃₇N(CH₃)₃)₃[PMo₁₂O₄₀] (2760.02): C, 27.41; H, 5.04; N, 1.52. ³¹P (161.9 MHz, CD₃CN, 25 °C): $\delta = -2.36$ ppm. FT-IR (cm⁻¹): $\nu = 3455$ (s), 3032 (w), 3016 (w), 2920 (vs), 2850 (s), 1630 (m), 1487 (w), 1464 (m), 1396 (w), 1063 (vs, ν_{as} (PO₄)), 956 (vs, ν_{as} (Mo=O)), 879 (s, ν_{as} (Mo-O_b-Mo)), 796 (vs, ν_{as} (Mo-O_c-Mo)), 719 (w), 669 (w), 659 (w), 615 (w), 602 (w), 503 (m), 460 (w), 418 (w).

3.2.2. Solid Support NH₂-MIL-101(Cr)

The amino-functionalized metal-organic framework was obtained based on a described method [18]. An aqueous solution containing $Cr(NO_3)_3 \cdot 9H_2O$ (1 mmol), 2-aminobenzene-1,4-dicarboxylic acid (1 mmol) and NaOH (2.6 mmol) in 6 mL H₂O was prepared and transferred to a microwave reaction vessel and left to stir for 10 min. The reaction vessel was then placed in a microwave synthesis oven and irradiated for 1 h at 150 °C. The resulting green precipitate was left to cool to room temperature, and then collected by centrifugation and washed with DMF (25 mL) under stirring for 30 min at room temperature followed by washing with EtOH (25 mL) under continuous reflux and stirring for 24 h at 80 °C. The support material was characterized by FT-IR spectroscopy and SEM/EDS analysis. FT-IR (cm⁻¹): ν = 3405 (vs), 2925 (w), 1655 (w), 1616 (w), 1558 (vs), 1496 (w), 1421 (sh), 1373 (vs), 1251 (m), 1151 (w), 1105 (w), 956 (w), 899 (w), 829 (m), 771 (m), 667 (w), 509 (s), 418 (w).

3.2.3. PMo₁₂@NH₂-MIL-101(Cr) Composite Material

The composite material was prepared by using a method previously described by our group [19,20]. An aqueous solution of $H_3[PMo_{12}O_{40}] \cdot nH_2O$ (10 mM) was added to the solid support NH₂-MIL-101(Cr) (0.0984 g), and the mixture was stirred at room temperature for 72 h. The obtained solid was filtered under vacuum, washed with deionized water and dried in a desiccator over silica gel. The composite was characterized by ICP, FT-IR spectroscopy, powder XRD, and SEM/EDS analysis. Anal. Found (%): Mo, 14.3%; Cr, 10.9%; P, 0.32%. Loading of $H_3PMo_{12} = 0.122 \text{ mmol} \cdot g^{-1}$. FT-IR (cm⁻¹): $\nu = 3446$ (vs), 2960 (w), 2925 (w), 2854 (w), 1621 (vs), 1593 (sh), 1496 (m), 1433 (s), 1385 (vs), 1340 (w), 1259 (s), 1165 (w), 1061 (m), 1005 (w), 958 (w), 891 (w), 808 (w), 767 (m), 667 (m), 602 (m), 542 (w), 496 (w), 463 (w), 449 (w), 384 (w), 372 (w).

3.3. Oxidative Desulfurization Process Using a Model Diesel

The ODS studies were performed using a multicomponent model diesel with a sulfur content of 2000 ppm in *n*-octane. This solution was composed of various refractory sulfur compounds typically

present in fuels (approximately 500 ppm of each): dibenzothiophene (DBT), benzothiophene (BT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). The ODS reactions were performed in a 5 mL borosilicate vessel under atmospheric pressure, to which 3 μ mol of catalyst (homogeneous or heterogeneous containing 3 μ mol of active catalytic center, i.e., POM), model diesel (0.75 mL) and extraction solvent (0.75 mL) were added. An initial extraction was performed during 10 min at 50 °C with continuous stirring. After this time, the oxidant (0.30 mmol of 30% aq. H₂O₂) was added to the biphasic mixture, initiating the catalytic stage, in which the oxidation of the sulfur compounds to the corresponding sulfones and/or sulfoxides occurred. During the reaction, samples of the upper model diesel phase were periodically withdrawn and analyzed by gas chromatography. An external standard (tetradecane) was used to dilute the reaction samples. The reusability tests were performed by the removal of the model diesel phase after each cycle and adding fresh samples of model diesel and oxidant.

3.4. Oxidative Desulfurization Process of an Untreated Real Diesel

An untreated diesel (2300 ppm S) supplied by Galp Energia was treated using the best model diesel conditions, i.e., using the catalyst that showed the best catalytic performance and the most efficient amount of 30% aq. H_2O_2 . Two different experiments were performed, using the untreated diesel sample or performing an initial extraction treatment with MeCN. At the end of the process, samples were treated with equal amounts of MeCN to remove the oxidized sulfur compounds.

4. Conclusions

The desulfurization of multicomponent model and real diesels with sulfur contents between 2000 and 2300 ppm was successfully performed using moderate experimental conditions (low reaction temperature of 50 °C, low ratio $H_2O_2/S = 6$) in the presence of an IL as extraction solvent ([BMIM][PF₆]) and oxidant (H_2O_2). A commercial polyoxometalate ($H_3PMo_{12}O_{40}$) was used as active catalytic center; however, this homogeneous catalyst was modified by exchanging the cation for a long-chain alkylammonium ion, which conferred higher activity by promoting a higher interaction between sulfur-compounds, catalyst and oxidant. The catalytic performance of the commercial Keggin catalyst also increased when it was incorporated into a large-pore amine-functionalized MOF framework (NH₂-MIL-101(Cr)), forming a new heterogeneous catalyst PMo₁₂@MOF. The treatment of the real diesel by the solid catalyst resulted in the removal of 80% of the total sulfur after only 2 h of reaction. Furthermore, the solid catalyst and the IL extraction phase were successfully reused for consecutive cycles. After reuse, the solid catalyst was removed from the desulfurization system and its stability was confirmed by different characterization techniques. Due to the promising results obtained, the present oxidative desulfurization process will be applied to other liquid fuels.

Author Contributions: P.M.C.F. and D.J. performed all the experimental work related to the oxidative desulfurization experiments. P.M.C.F. was supervised by L.A.R. and S.S.B., and performed all the reactions using model diesel. D.J. was supervised by I.S.G. and S.S.B., and was responsible for the desulfurization tests using real diesel. C.M.G. (supervised by S.S.B. and M.P.) performed most of the catalyst preparation and characterization work. L.C.-S. (supervised B.d.C.) was responsible for the MOF preparation. R.V. and J.C.R. performed the sulfur content analysis of treated real diesel by XRF technique.

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