

Article

Ionic Liquid-Based Polyoxometalate Incorporated at ZIF-8: A Sustainable Catalyst to Combine Desulfurization and Denitrogenation Processes

Dinis F. Silva ^{1,†} , Alexandre M. Viana ^{1,†}, Isabel Santos-Vieira ² , Salete S. Balula ^{1,*} 
and Luís Cunha-Silva ^{1,*} 

¹ 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@fc.up.pt (A.M.V.)

² CICECO—Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal; ivieira@ua.pt

* Correspondence: sbalula@fc.up.pt (S.S.B.); l.cunha.silva@fc.up.pt (L.C.-S.)

† These authors contributed equally to this work.

Abstract: An effective and sustainable process capable of simultaneously execute desulfurization and denitrogenation of fuels is in fact an actual necessity in the refinery industry. The key to achieve this goal is the parallel oxidation of sulfur and nitrogen compounds present in fuels, which is only achieved by an active and recovered catalyst. A novel heterogeneous catalyst was successfully prepared by the encapsulation of an imidazolium-based polyoxometalate (POM) into a ZIF-8 framework ([BMIM]PMo₁₂@ZIF-8). This composite material revealed exceptional catalytic efficiency to concurrently proceed with the oxidative desulfurization and denitrogenation of a multicomponent model fuel containing various sulfur and nitrogen compounds. A complete removal of all these compounds was achieved after only one hour and the catalyst system was able to be reused for ten consecutive cycles without loss of efficiency. In fact, an ionic liquid POM was incorporated in the ZIF-8 for the first time, and this composite compound was originally applied as a catalyst for simultaneous oxidative desulfurization and denitrogenation processes.

Keywords: zeolitic imidazolate frameworks; polyoxomolybdate; desulfurization; oxidative catalysis; ionic liquid; hydrogen peroxide; 1-Butyl-3-methylimidazolium cation



Citation: Silva, D.F.; Viana, A.M.; Santos-Vieira, I.; Balula, S.S.; Cunha-Silva, L. Ionic Liquid-Based Polyoxometalate Incorporated at ZIF-8: A Sustainable Catalyst to Combine Desulfurization and Denitrogenation Processes. *Molecules* **2022**, *27*, 1711. <https://doi.org/10.3390/molecules27051711>

Academic Editors: Antonio Caballero and Simonetta Fornarini

Received: 19 January 2022

Accepted: 1 March 2022

Published: 5 March 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Fuel consumption and combustion is known to cause emissions of SO_x and NO_x which are harmful to the environment [1,2]. Consequently, regulations have been put in place to limit the amount of sulfur and nitrogen present in commercial fuels. To meet these parameters, the fuel industry resorts to hydrotreating processes such as hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) [3]. However, these techniques are considerably unsustainable since they demand high economic and energetic costs, and they require high temperature (>350 °C) and pressure (up to 6MPa) conditions [3,4]. While N-based compounds are the most difficult to extract by HDN, the removal by HDS of some S-based compounds, such as benzothiophene derivatives, has also proven to be a difficult task [3–5].

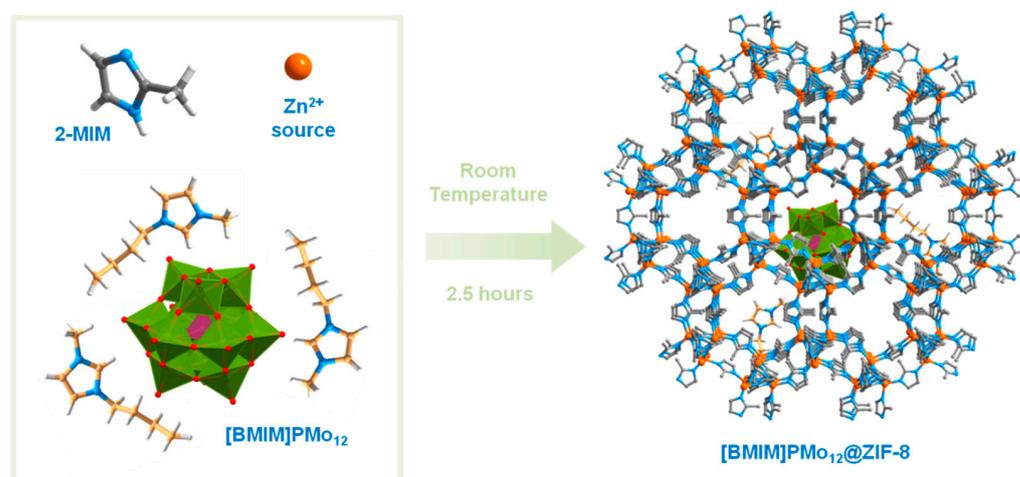
Oxidative desulfurization (ODS) and oxidative denitrogenation (ODN) have been presented as low-cost, eco-friendly and efficient alternatives to HDS and HDN, respectively [6–9]. These processes occur under lower temperatures, at atmospheric pressure and with the aid of a green oxidant and a suitable catalyst [10–12]. Currently, one of the challenges associated with the scale-up of ODS/ODN processes relates to catalysts durability and reutilization [13,14].

Polyoxometalates (POMs) are molecular clusters of transition metal oxide anions, with their negative charge being balanced by counter-cations. Keggin-type heteropolyoxometalates $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ have a central heteroatom (X e.g., B, Si, P) that provides a higher structural stabilization, thermal stability and reduction-oxidation properties [15,16].

Keggin POMs are known for their potential of application in homogeneous oxidative catalytic systems, such as ODS and ODN [15,17–19]. One of the approaches employed to overcome the usual drawbacks associated with homogeneous catalysis, like poor recyclability potential, is their encapsulation or incorporation in a suitable porous material.

Zeolitic imidazolate frameworks (ZIFs) are a subclass of Metal-Organic Frameworks (MOFs) that have been studied and described as highly porous and crystalline materials with a wide range of potential application [20,21]. ZIFs have a 3D structure with imidazolate ligands linked with tetrahedral transition metal cations, such as Zn^{2+} and Co^{2+} , to give diverse frameworks with interesting mechanical, chemical and thermal stability, good biocompatibility and tuneable pore environments [22,23]. ZIF-8 is a well-known robust structure characterized by its high surface area (S around $1410\text{ m}^2\text{ g}^{-1}$) and pore volume (V around $0.546\text{ cm}^3\text{ g}^{-1}$) [24–26]. These properties allow ZIF-8 to be a promising host structure for the heterogenization of homogeneous catalysts like Keggin POMs.

In previous works from our research group, several ionic liquid phosphomolybdates revealed to be efficient homogeneous catalysts for ODS/ODN processes [17,27,28]. Thus, following our scientific and technological interest in the development of POM@MOF-based catalysts, [29–39] the 1-Butyl-3-methylimidazolium phosphomolybdate, $[BMIM]_3PMo_{12}O_4$, was incorporated in a porous ZIF-8 support to prepare a robust heterogeneous catalyst suitable for simultaneous ODS/ODN catalytic systems, $[BMIM]PMo_{12}@ZIF-8$ (Scheme 1).



Scheme 1. Representation of the preparation of the $[BMIM]PMo_{12}@ZIF-8$ compound by a “bottle-around-the ship” approach and using a sustainable room temperature synthetic strategy (one-pot and in situ).

2. Results and Discussion

2.1. Materials Characterization

ZIF-8 and derived $[BMIM]_3PMo_{12}@ZIF-8$ composite material were prepared through a straightforward room temperature procedure adapted from a synthesis method described elsewhere [24]. The obtained solid compounds were isolated, dried, and characterized by powder X-ray diffraction (PXRD), Fourier-transform infrared (FT-IR) spectroscopy, as well as scanning electron microscopy with electron dispersive X-ray spectroscopy (SEM/EDS). The PXRD patterns obtained for the prepared pristine MOF sample ZIF-8 (Figure 1a) agree with previously reported diffractograms for this crystalline structure, showing all characteristic diffraction peaks with expected relative intensities [40]. $[BMIM]_3PMo_{12}@ZIF-8$ revealed an equivalent single-phase diffraction pattern which points to the successful formation of the MOF as a host framework. Infrared spectra of both samples show every

absorption band expected from ZIF-8 (Figure 1b): weak and strong (C-N) ring bond vibration bands are observable from 600 up to 1500 cm^{-1} , weak (C=N) bond vibration bands can be seen around 1580 cm^{-1} , and very strong (Zn-N) coordination bond vibration bands are registered around 420 cm^{-1} [41]. In the acquired spectra for $[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8$, a group of additional medium intensity absorption bands are clearly observable in the interval from 775 to 975 cm^{-1} . These can be attributed to different (Mo=O) and (Mo-O) bond vibrations associated with the encapsulation of the POM in the MOF vacancies [28]. Also, a weak absorption band can be seen around 1080 cm^{-1} which can be related to a (P-O) bond vibration.

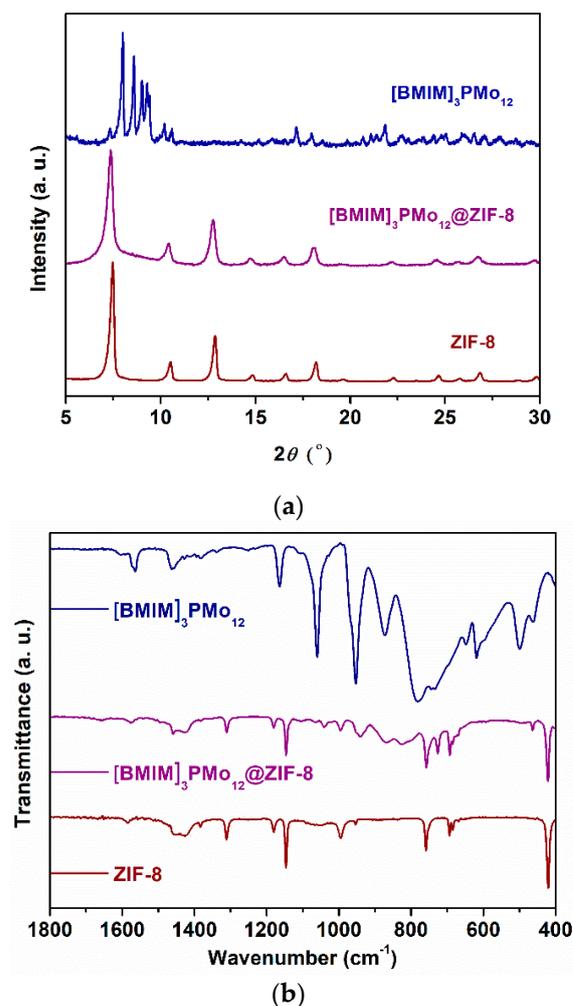


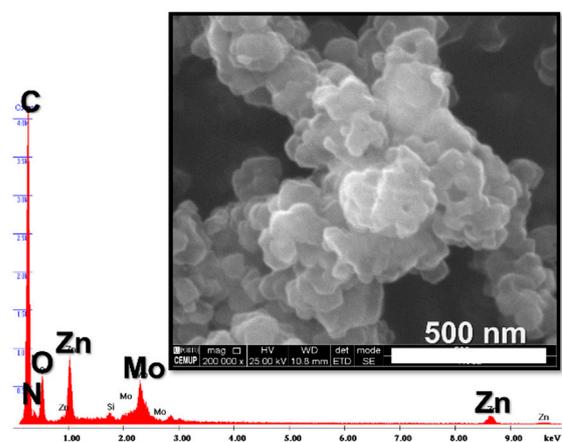
Figure 1. PXRD patterns (a) and FT-IR spectra (b) recorded for the pristine ZIF-8 compound and composite $[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8$.

SEM micrographs obtained for pristine ZIF-8 (Figure 2a) show aggregated particles with regular rhombic dodecahedron morphology and uniform size distribution around 100 nm. For $[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8$, similar sized particles with decreased degree of morphological regularity and apparent increased degree of aggregation are observable (Figure 2b). In these, the uniform distribution of Mo is revealed by EDS analysis, suggesting good dispersion of $[\text{BMIM}]_3\text{PMo}_{12}$ on the ZIF-8 support.

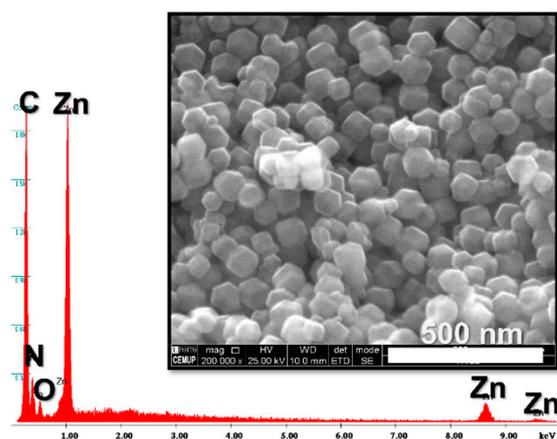
2.2. Catalytic Desulfurization/Denitrogenation Studies

Combined ODS/ODN catalytic experiments were performed under in a biphasic system using 1-butyl-3-methylimidazole hexafluorophosphate ($[\text{BMIM}]\text{PF}_6$) and multicomponent S and N model fuel. The efficiency of desulfurization and denitrogenation was

determined by the periodical analysis of a multicomponent model fuel phase. Pristine ZIF-8 showed no intrinsic catalytic activity towards either the ODS or ODN processes.



(a)



(b)

Figure 2. SEM micrographs and corresponding EDS spectra obtained for ZIF-8 (a) and [BMIM]₃PMo₁₂@ZIF-8 (b).

[BMIM]₃PMo₁₂@ZIF-8 was applied as a heterogeneous catalyst in combined ODS/ODN processes, and its catalytic behaviour was compared to the homogeneous active center [BMIM]₃PMo₁₂ (Figure 3). It was observed for both catalytic systems, besides an initial propensity towards ODN aided by a superior extraction step and a higher catalytic efficiency towards ODS. After the first hour of the combined processes, near complete sulfur and nitrogen removal were achieved (Figure 3a). Homogeneous and heterogeneous catalysts used to treat the same model fuel under the same experimental conditions (Figure 3b) presented similar catalytic efficiency, since similar profiles for sulfur and nitrogen compounds were obtained. In both homogeneous and heterogeneous catalytic systems, the removal rates of each compound present in the multicomponent model fuel follow the order: IND > QUI > DBT > MDBT > DMDBT ~ BT. Identical results were obtained and previously discussed by our research group using homogeneous phosphomolybdate catalysts incorporating different organic cations [27].

The heterogeneous [BMIM]₃PMo₁₂@ZIF-8 catalyst and the ionic liquid extraction phase ([BMIM]PF₆) were reused for ten consecutive combined ODS/ODN cycles (Figure 4). This procedure allowed the sustainability and increased the cost-efficiency of the fuel treatment process. It is possible to observe that the combined ODS/ODN efficiency is maintained or even slightly increased after the fifth cycle. This increases after the fifth cycle

is promoted by the increases of ODS. In fact, a near total desulfurization of the model fuel was observed from the fifth to the tenth cycle (always higher than 98.5%), in detriment of denitrogenation (which stabilizes around 82%). Therefore, these results confirm the potential of the reutilization of the $[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8/[\text{BMIM}]\text{PF}_6$ system combining the ODS and the ODN processes. Recently, our research group used a heterogeneous catalyst having the phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}$) as an active center immobilized into porous MOF-808 support ($\text{H}_3\text{PMo}_{12}@MOF-808$) [30]. Similar results were obtained for simultaneous ODS and ODN processes (near complete desulfurization and denitrogenation achieved after 1 h); however, using the $\text{H}_3\text{PMo}_{12}@MOF-808$ catalyst, this presented a loss of activity for the ODS process after the fourth cycle. The superior maintenance of activity in reusing ODS/ODN processes with $[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8$ catalyst can be related to the structural properties of MOF support (pore and windows size and/or metal center nature). Other studies in the literature using $\text{PMo}_{12}@MOFs$ catalysts only performed a single ODS process, needing higher quantities of catalysts or using other less sustainable oxidants [13,42,43].

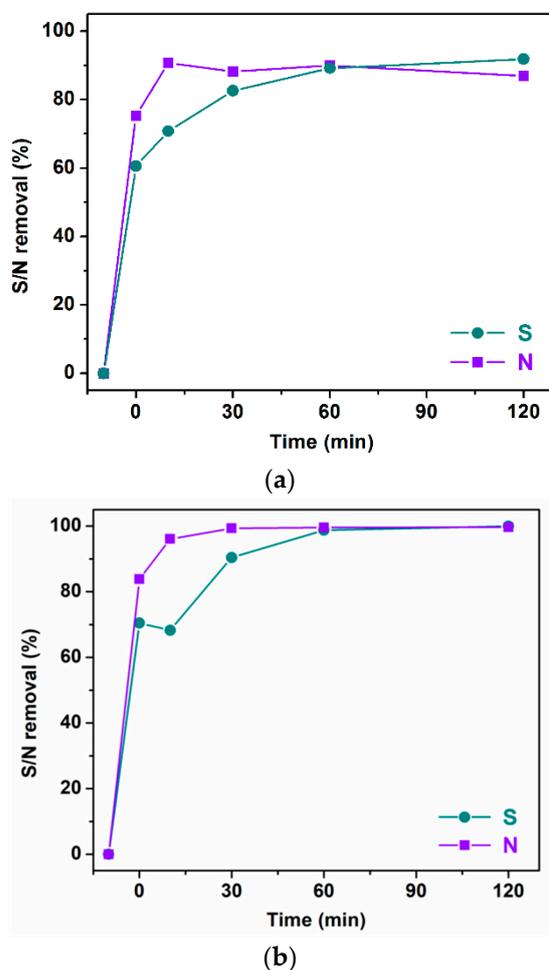


Figure 3. Desulfurization and denitrogenation of a multicomponent model fuel (BT, DBT, MDBT, DMDBT, IND, QUI) catalysed by the heterogeneous $[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8$ (a) and the homogeneous $[\text{BMIM}]_3\text{PMo}_{12}$ (b), using $[\text{BMIM}]\text{PF}_6$ as extraction solvent and H_2O_2 as oxidant.

The stability of the catalyst after the first and tenth cycles was investigated by analysing the recovered solid by PXRD and SEM/EDS (after being washed and dried). Furthermore, the resultant model fuel and the extraction phases were analysed by ^{31}P NMR to verify the occurrence of possible PMo_{12} leaching. The post-catalytic PXRD characterization of the recovered catalyst (Figure 5) shows that $[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8$ undergoes structural

transformations during its catalytic use, evidenced by clear differences between the diffraction patterns of the catalyst before and after being subjected to the ODS/ODN experiments. Interestingly, a considerable structural transformation is verified from the first catalytic cycle, where the typical crystalline phase of the ZIF-8 changes, suggesting that the support materials suffer structural modification from the beginning of the reaction. Furthermore, the results obtained by ^{31}P NMR showed no signal attributable to $[\text{BMIM}]_3\text{PMo}_{12}$, which suggests that there was no leaching of the $[\text{BMIM}]_3\text{PMo}_{12}$ active center.

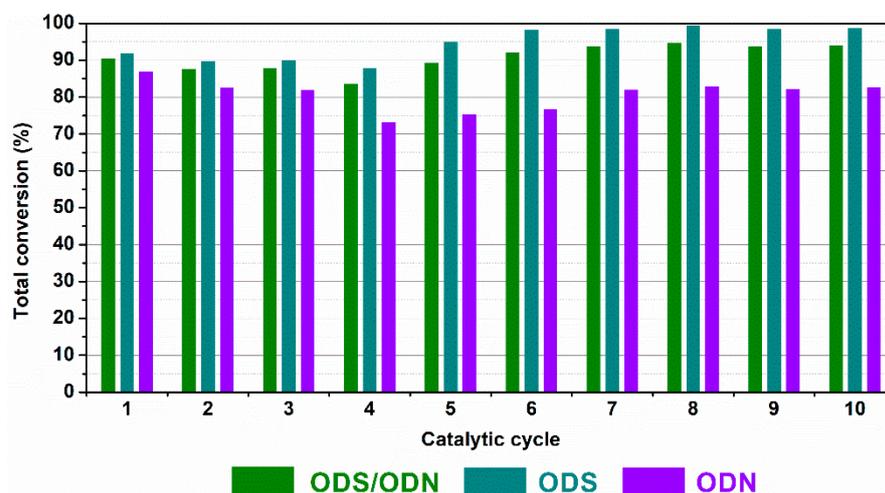


Figure 4. Reutilization performance of $[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8$ over 10 cycles combining desulfurization and denitrogenation processes to treat a multicomponent model fuel (BT, DBT, MDBT, DMDBT, IND, QUI), using $[\text{BMIM}]\text{PF}_6$ as extraction solvent and H_2O_2 as oxidant.

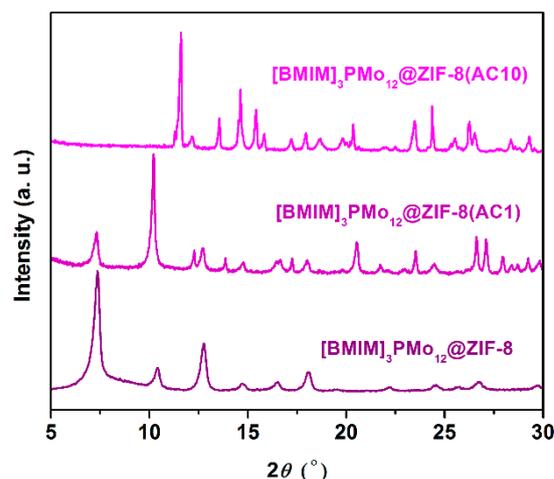
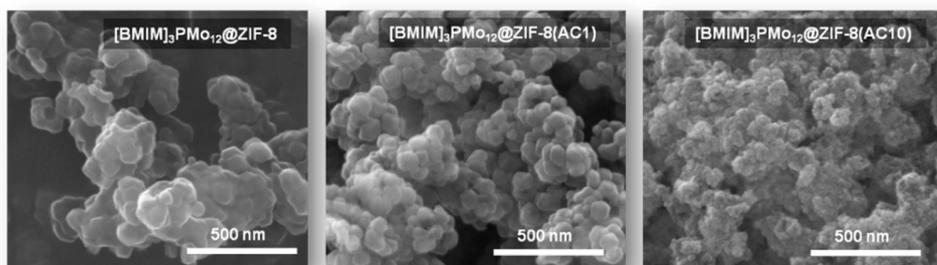


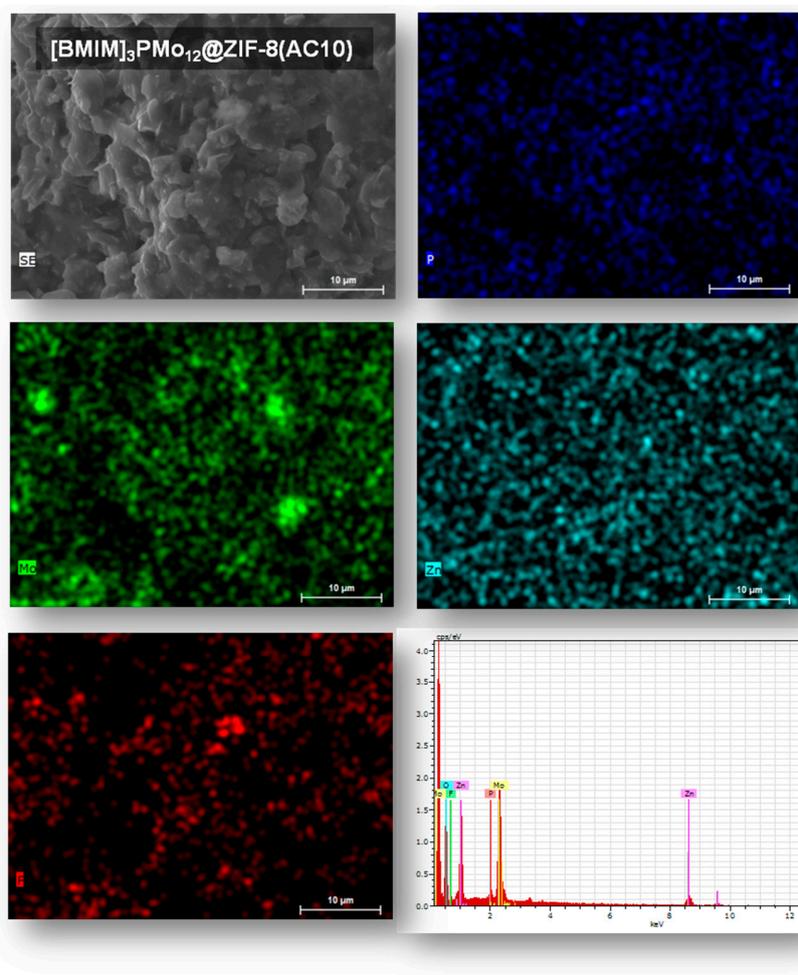
Figure 5. Powder XRD patterns of the $[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8$ material before catalytic utilization, isolated after the 1st ($[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8(\text{AC}1)$) and after the 10th catalytic cycle.

The SEM images obtained after the first and the tenth ODS/ODN cycles are present in Figure 6a. After the first cycle the composite still presents particles with regular rhombic dodecahedron morphological regularity as observed in the composite before catalytic use. However, after the tenth ODS/ODN cycle, the composite presents a not well defined morphology without uniform particles. This result corroborates with the previous XRD data also performed for this tenth cycle (Figure 6b). Nevertheless, EDS elemental mappings and spectra (Figure 5) still confirm the maintenance of a uniform distribution of the main elements of the composite even after the tenth cycle, namely Molybdenum, Phosphorus (from the $[\text{BMIM}]_3\text{PMo}_{12}$) and Zinc (from de ZIF-8). EDS dates were further used as Zn/Mo ratio to compare the content for the initial composite and for the composite recovered after

the first and the tenth catalytic cycles. The ratio Zn/Mo increased from 1.32 to 2.91 from the initial composite to the same recovered after the first catalytic cycle, and consequently to 3.7 after the tenth cycle. These results indicate the occurrence of Mo leaching during the reutilization process. However, the active $[\text{BMIM}]_3\text{PMo}_{12}$ was not detected by ^{31}P NMR analysis, probably due to the decomposition of Keggin polyoxomolybdate structures during the catalytic reaction. This POM decomposition probably forms smaller sized polyoxomolybdate fragments that can leach from the ZIF-8 structure.



(a)



(b)

Figure 6. (a) SEM micrographs of $[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8$ before catalytic utilization, isolated after the 1st ($[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8(\text{AC}1)$) and after the 10th catalytic cycle; (b) SEM micrographs and corresponding EDS elemental mapping and spectra for the sample $[\text{BMIM}]_3\text{PMo}_{12}@ZIF-8$ isolated after the 10 catalytic cycles.

A scarce number of reported works can be found studying a simultaneously oxidative desulfurization and oxidative denitrogenation of fuels using heterogeneous catalysts. Aghbolagh et al. used a copper based catalyst TBAPMo₁₁Cu@CuO that presented high efficiency (>90%) for S and N oxidation; however, low efficiency for the extraction of oxidized products was found using an organic inadequate extraction solvent [44]. Other work presented by Ishihara et al. used MoOx impregnated into aluminium oxide as a catalyst. In this case a high catalytic efficiency was found using tert-butyl hydroperoxide as an oxidant [45]. This oxidant presents a lower viability to be used in an industrial process and, also, the recycle capacity of the catalyst was not discussed. The work reported by Palomeque-Santiago using WOx on ZrO₂ still presents an ODS/ODN efficiency of 97%; however, the recycle capacity and the stability of the catalyst was not presented in this study either [14]. Recently, our research group has been reporting the application of PMo₁₂@MOF-808 as a catalyst for simultaneous ODS/ODN processes [30]. While showing a high catalytic efficiency, this catalyst decreases its activity after the first three or four catalytic cycles. Compared with these few published works, the [BMIM]₃PMo₁₂@ZIF.8 catalyst presents identical high efficiency and high recycle capacity, although its structural transformation is probably necessary to maintain its activity for at least 10 consecutive ODS/ODN cycles.

3. Experimental section

3.1. Materials and Methods

Phosphomolybdic acid (H₃PMo₁₂O₄₀·xH₂O, for microscopy), 2-methylimidazole (C₄H₆N₂, 99.0%, 2-MIM), tetradecane (C₁₄H₃₀, >99.0%), 1-butyl-3-methylimidazole hexafluorophosphate (C₈H₁₅F₆N₂P, >97%, [BMIM]PF₆), hydrogen peroxide (H₂O₂, aq. 30%), dibenzothiophene (C₁₂H₈S, 98%, DBT) and 4-methyldibenzothiophene (C₁₃H₁₀S, 96%, MDBT), quinoline (98%, QUI) and indole (>99%, IND) were obtained from Sigma-Aldrich. *N,N*-dimethylformamide (C₃H₇NO, 99.99%, DMF), methanol (CH₃OH, analytical reagent grade) and ethanol (C₂H₅OH, >99.8%, EtOH) were purchased from Fisher. Acetonitrile (CH₃CN, >99.5%, MeCN), 1-butyl-3-methylimidazolium bromide (C₈H₁₅N₂Br, >97%, [BMIM]Br) and benzothiophene (C₈H₆S, >95%, BT) were acquired from Fluka. Zinc(II) nitrate tetrahydrate (Zn(NO₃)₂·4H₂O, >98.5%) was obtained from Merck. *N*-octane (C₈H₁₈, >99.0%) and 4,6-dimethyldibenzothiophene (C₁₄H₁₂S, 95%, DMDBT) were acquired from Acros Organic. None of these was the subject of further treatment or purification.

Fourier-transform infrared (FT-IR) spectra were acquired on the attenuated total reflectance (ATR) operation mode of a PerkinElmer FT-IR System Spectrum BX spectrometer, and all the representations are shown in arbitrary unities of transmittance. Elemental analyses (CHN) were performed using a ThermofinniganFlash EA 112 series (University of Santiago de Compostela, Spain). Powder X-ray diffraction (PXRD) patterns were obtained at room temperature on a Rigaku Geigerflex diffractometer operating with a Cu radiation source ($\lambda_1 = 1.540598 \text{ \AA}$; $\lambda_2 = 1.544426 \text{ \AA}$; $\lambda_1/\lambda_2 = 0.500$) and in a Bragg-Brentano $\theta/2\theta$ configuration (45 kV, 40 mA). Intensity data were collected by a step-counting method (step 0.026°), in continuous mode, in the $3 \leq 2\theta \leq 50^\circ$ range, and all the re-presentations are shown in arbitrary unities of intensity. Scanning electron microscopy (SEM) and electron dispersive X-ray spectroscopy (EDS) analysis were performed in a FEI Quanta 400 FEG ESEM high resolution scanning electron microscope equipped with an EDAX Genesis X4M spectrometer working at 15 kV. Samples were coated with a Au/Pd thin film by sputtering using a SPI Module Sputter Coater equipment. ³¹P nuclear magnetic resonance (³¹P NMR) spectra were acquired in CD₃CN at 162 MHz with a Bruker Avance III 400 spectrometer, and the chemical shifts are given with respect to external 85% H₃PO₄. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to quantify the Mo concentration, resorting to a PerkinElmer Otima 4300 DV. Catalytic reactions were periodically monitored by GC-FID analysis carried out in a Bruker 430-GC-FID chromatograph. 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.

3.2. Materials Preparation

3.2.1. [BMIM]₃PMo₁₂

This phosphomolybdate salt was prepared following a procedure adapted from a method previously reported [17]. [BMIM]Br (2.5 mmol) was dissolved in 2.5 mL of deionized water. To this, an aqueous solution of phosphomolybdic 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. FTIR (cm⁻¹): ν ([BMIM]₃PMo₁₂) = 3150 (w), 3098 (w), 2965 (w), 1603 (vw), 1564 (w), 1463 (w), 1383 (vw), 1338 (vw), 1250 (vw), 1164 (m), 1060 (s), 953 (s), 872 (m), 781 (s), 744 (s), 619 (m), 500 (m), 463 (m). ³¹P NMR (162 MHz, CD₃CN, 25 °C) δ = -2.38 ppm. Anal.Calc. for (C₈H₁₅N₂)₃PMo₁₂O₄₀(2239.88): C, 13.20; H, 1.99; N, 3.72; Found: C,13.19; H, 2.01; N, 3.72.

3.2.2. ZIF-8 and [BMIM]₃PMo₁₂@ZIF-8

These materials were prepared following an experimental procedure adapted from previously reported methods [24]. For the ZIF-8, an initial solution of Zn(NO₃)₂·4H₂O (2.5 mmol) in MeOH (25 mL) was magnetically stirred for 15 min. Then, a solution of 2-MIM (19.8 mmol) in MeOH (25 mL) was slowly added. The resulting reactional mixture was magnetically stirred for 2.5 h, at ambient temperature, after which the resulting material was isolated by centrifugation, washed five times with MeOH and dried at 60 °C under vacuum overnight. For [BMIM]₃PMo₁₂@ZIF-8, a solution of [BMIM]₃PMo₁₂ (100 mg) in DMF (5 mL) was added to the first one and the mixture was left to stir for 15 min before the addition of the 2-MIM solution.

3.3. Oxidative Desulfurization and Denitrogenation (ODS/ODN)

ODS and ODN studies were performed with a model fuel prepared with a group of compounds representative of the most refractory sulfur and nitrogen content in diesel, namely benzothiophene (BT), dibenzothiophene (DBT), 4-methylthiophene (MDBT), 4,6-dimethylthiophene (DMDBT), quinoline (QUI) and indole (IND), dissolved in n-octane (500 ppm of sulfur or 300 ppm of nitrogen from each compound). Aqueous hydrogen peroxide was used as an oxidizing agent. The reactions were carried out under air in a closed borosilicate vessel with a magnetic stirrer and immersed in a thermostatically controlled liquid paraffin bath at 70 °C. ODS/ODN reactions were performed in a biphasic system composed by the model fuel and [BMIM]PF₆ as extraction solvent with ratio 1:1 (v/v). The simultaneous desulfurization and denitrogenation experiments were performed in two main separated steps; initially an extraction of sulfur and nitrogen compounds was transferred from model fuel to the extraction phase just by stirring the biphasic system. Then, the oxidative catalytic step was initiated by adding the oxidant. In a representative experiment, a certain amount of heterogeneous catalyst equivalent to 3 mmol of active POM ([BMIM]PMo₁₂) was added to 0.75 mL of [BMIM]PF₆ and 0.75 mL of model fuel. 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 GC analysis. At the end of each reaction, the model fuel phase was removed and substituted with an equal volume of fresh model fuel, after which a subsequent catalytic cycle was started, under identical reaction conditions. After 10 catalytic cycles, the catalyst was recovered by centrifugation, washed carefully for three times with MeCN and EtOH, and dried at 60 °C under vacuum overnight.

4. Conclusions

A novel composite prepared by the encapsulation of the ionic liquid polyoxomolybdate [BMIM]₃PMo₁₂ into a ZIF-8 framework was successfully isolated and characterized. Furthermore, the isolated material [BMIM]₃PMo₁₂@ZIF-8 was used as heterogeneous catalyst to simultaneously remove sulfur and nitrogen from a model fuel via oxidation. In a

competitive oxidative environment, this catalyst showed high efficiency and the absence of active centre leaching during ten consecutive model fuel treatments. Complete desulfurization and denitrogenation were achieved after only one hour, which is comparable with the catalytic performance of the corresponding homogeneous catalyst, [BMIM]₃PMo₁₂. Remarkably, the structural transformation of the [BMIM]₃PMo₁₂@ZIF-8 observed from the first catalytic cycle seems too crucial for the high catalytic performance of this solid, in particular for the preservation of the catalytic activity during the ten reaction cycles. Despite the interesting result reported, further systematic studies will be needed to achieve a more complete understanding of the nature of the structural transformation.

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 I.S.-V.; writing—original draft preparation, A.M.V. and S.S.B.; writing—review and editing, S.S.B. and L.C.-S.; supervision, S.S.B. and L.C.-S.; project administration, S.S.B. and L.C.-S.; funding acquisition S.S.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research work received financial support from Portuguese national funds (FCT/MCTES, Fundação para a Ciência e a Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the strategic projects UIDB/50006/2020 (for LAQV / REQUIMTE) and UIDB/50011/2020 and UIDP/50011/2020 (for CICECO). Parts of this work were performed with funds from the European Union (FEDER funds through COMPETE POCI-01-0145-FEDER-031983) and FCT/MCTES by National Funds to the R&D project GlyGold (PTDC/CTM-CTM/31983/2017).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: More data can be obtained by request to the authors.

Acknowledgments: L.C.-S. and S.S.B. thank FCT/MCTES for funding through the Individual Call to Scientific Employment Stimulus (Ref. CEECIND/00793/2018 and Ref. CEECIND/03877/2018, respectively). The position held by I.S.-V. (Ref. 197_97_ARH-2018) was funded by national funds (OE), through FCT, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of article 23 of the Decree-Law 57/2016 of 29 August, changed by Law 57/2017 of 19 July. AMV thanks FCT/MCTES and ESF (European Social Fund) through POCH (Programa Operacional Capital Humano) for his PhD grant (Ref. SFRH/BD/150659/2020).

Conflicts of Interest: The authors declare that they have no conflict of interest.

Sample Availability: Samples of the compounds can be available by request from the authors.

References

1. Ajdari, S.; Normann, F.; Andersson, K. Evaluation of Operating and Design Parameters of Pressurized Flue Gas Systems with Integrated Removal of NO_x and SO_x. *Energy Fuels* **2019**, *33*, 3339–3348. [[CrossRef](#)]
2. Besenic, T.; Mikulic, H.; Vujanovic, M.; Duic, N. Numerical modelling of emissions of nitrogen oxides in solid fuel combustion. *J. Environ. Manag.* **2018**, *215*, 177–184. [[CrossRef](#)] [[PubMed](#)]
3. Prado, G.H.C.; Rao, Y.; de Klerk, A. Nitrogen Removal from Oil: A Review. *Energy Fuels* **2016**, *31*, 14–36. [[CrossRef](#)]
4. Wang, B.; Zheng, P.; Fan, H.; Meng, Q.; Duan, A.; Chen, Z.; Xu, C. Insights into the effect of solvent on dibenzothiophene hydrodesulfurization. *Fuel* **2021**, *287*, 119459. [[CrossRef](#)]
5. Ribeiro, S.; Granadeiro, C.M.; Silva, P.; Almeida Paz, F.A.; de Biani, F.F.; Cunha-Silva, L.; Balula, S.S. An efficient oxidative desulfurization process using terbium-polyoxometalate@MIL-101(Cr). *Catal. Sci. Technol.* **2013**, *3*, 2404–2414. [[CrossRef](#)]
6. Aghbolagh, Z.S.; Khorrami, M.R.K.; Rahmatyan, M.S. Sum of ranking differences in studies on high performance of catalytic oxidative denitrogenation and desulfurization of model fuel using efficient organic–inorganic hybrid nanocatalyst. *J. Iran. Chem. Soc.* **2022**, *19*, 219–230. [[CrossRef](#)]
7. Bhadra, B.N.; Jhung, S.H. Oxidative desulfurization of liquid fuel with tungsten-nitride@porous carbon, derived from MAF-6(Zn) loaded with phosphotungstic acid and melamine. *Chem. Eng. J.* **2021**, *419*, 129485. [[CrossRef](#)]
8. Shafiq, I.; Hussain, M.; Shafique, S.; Rashid, R.; Akhter, P.; Ahmed, A.; Jeon, J.-K.; Park, Y.-K. Oxidative desulfurization of refinery diesel pool fractions using LaVO₄ photocatalyst. *J. Ind. Eng. Chem.* **2021**, *98*, 283–288. [[CrossRef](#)]
9. Subhan, S.; Yaseen, M.; Ahmad, B.; Tong, Z.; Subhan, F.; Ahmad, W.; Sahibzada, M. Fabrication of MnO₂ NPs incorporated UiO-66 for the green and efficient oxidative desulfurization and denitrogenation of fuel oils. *J. Environ. Chem. Eng.* **2021**, *9*, 105179. [[CrossRef](#)]

10. Bhadra, B.N.; Song, J.Y.; Uddin, N.; Khan, N.A.; Kim, S.; Choi, C.H.; Jhung, S.H. Oxidative denitrogenation with TiO₂@porous carbon catalyst for purification of fuel: Chemical aspects. *Appl. Catal. B Environ.* **2019**, *240*, 215–224. [[CrossRef](#)]
11. Mondol, M.M.H.; Bhadra, B.N.; Jhung, S.H. Molybdenum nitride@porous carbon, derived from phosphomolybdic acid loaded metal-azolate framework-6: A highly effective catalyst for oxidative desulfurization. *Appl. Catal. B Environ.* **2021**, *288*, 119988. [[CrossRef](#)]
12. Subhan, S.; Muhammad, Y.; Sahibzada, M.; Subhan, F.; Tong, Z. Studies on the Selection of a Catalyst–Oxidant System for the Energy-Efficient Desulfurization and Denitrogenation of Fuel Oil at Mild Operating Conditions. *Energy Fuels* **2019**, *33*, 8423–8439. [[CrossRef](#)]
13. Abazari, R.; Esrafil, L.; Morsali, A.; Wu, Y.; Gao, J. PMo₁₂@UiO-67 nanocomposite as a novel non-leaching catalyst with enhanced performance durability for sulfur removal from liquid fuels with exceptionally diluted oxidant. *Appl. Catal. B Environ.* **2021**, *283*, 119582. [[CrossRef](#)]
14. Palomeque-Santiago, J.F.; López-Medina, R.; Oviedo-Roa, R.; Navarrete-Bolaños, J.; Mora-Vallejo, R.; Montoya-de la Fuente, J.A.; Martínez-Magadán, J.M. Deep oxidative desulfurization with simultaneous oxidative denitrogenation of diesel fuel and straight run gas oil. *Appl. Catal. B Environ.* **2018**, *236*, 326–337. [[CrossRef](#)]
15. Kozhevnikov, I.V. Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-Phase Reactions. *Chem. Rev.* **1998**, *98*, 171–198. [[CrossRef](#)]
16. Samaniyan, M.; Mirzaei, M.; Khajavian, R.; Eshtiagh-Hosseini, H.; Streb, C. Heterogeneous Catalysis by Polyoxometalates in Metal–Organic Frameworks. *ACS Catal.* **2019**, *9*, 10174–10191. [[CrossRef](#)]
17. Mirante, F.; Gomes, N.; Branco, L.C.; Cunha-Silva, L.; Almeida, P.L.; Pillinger, M.; Gago, S.; Granadeiro, C.M.; Balula, S.S. Mesoporous nanosilica-supported polyoxomolybdate as catalysts for sustainable desulfurization. *Microporous Mesoporous Mater.* **2019**, *275*, 163–171. [[CrossRef](#)]
18. Patel, A.; Narkhede, N.; Singh, S.; Pathan, S. Keggin-type lacunary and transition metal substituted polyoxometalates as heterogeneous catalysts: A recent progress. *Catal. Rev.* **2016**, *58*, 337–370. [[CrossRef](#)]
19. Sun, M.; Zhang, J.; Cao, C.; Zhang, Q.; Wang, Y.; Wan, H. Significant effect of acidity on catalytic behaviors of Cs-substituted polyoxometalates for oxidative dehydrogenation of propane. *Appl. Catal. A Gen.* **2008**, *349*, 212–221. [[CrossRef](#)]
20. Moggach, S.A.; Bennett, T.D.; Cheetham, A.K. The effect of pressure on ZIF-8: Increasing pore size with pressure and the formation of a high-pressure phase at 1.47 GPa. *Angew. Chem. Int. Ed. Engl.* **2009**, *48*, 7087–7089. [[CrossRef](#)]
21. Tanaka, H.; Ohsaki, S.; Hiraide, S.; Yamamoto, D.; Watanabe, S.; Miyahara, M.T. Adsorption-Induced Structural Transition of ZIF-8: A Combined Experimental and Simulation Study. *J. Phys. Chem. C* **2014**, *118*, 8445–8454. [[CrossRef](#)]
22. Park, K.S.; Ni, Z.; Côté, A.P.; Choi, J.Y.; Hyang, R.; Uribe-Romo, F.J.; Chae, H.K.; O’Keefe, M.; Yaghi, O.M. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10186–10191. [[CrossRef](#)] [[PubMed](#)]
23. Phan, A.; Doonan, C.J.; Uribe-Romo, F.J.; Knobler, C.B.; O’Keefe, M.; Yaghi, O.M. Synthesis, Structure, and Carbon Dioxide Capture Properties of Zeolitic Imidazolate Frameworks. *Acc. Chem. Res.* **2010**, *43*, 58–67. [[CrossRef](#)] [[PubMed](#)]
24. Mukhopadhyay, S.; Debgupta, J.; Singh, C.; Kar, A.; Das, S.K. A Keggin Polyoxometalate Shows Water Oxidation Activity at Neutral pH: POM@ZIF-8, an Efficient and Robust Electrocatalyst. *Angew. Chem. Int. Ed.* **2018**, *57*, 1918–1923. [[CrossRef](#)] [[PubMed](#)]
25. Venna, S.R.; Jasinski, J.B.; Carreon, M.A. Structural Evolution of Zeolitic Imidazolate Framework-8. *J. Am. Chem. Soc.* **2010**, *132*, 18030–18033. [[CrossRef](#)]
26. Zareba, J.K.; Nyk, M.; Samoć, M. Co/ZIF-8 Heterometallic Nanoparticles: Control of Nanocrystal Size and Properties by a Mixed-Metal Approach. *Cryst. Growth Des.* **2016**, *16*, 6419–6425. [[CrossRef](#)]
27. Silva, D.F.; Viana, A.M.; Mirante, F.; de Castro, B.; Cunha-Silva, L.; Balula, S.S. Removing Simultaneously Sulfur and Nitrogen from Fuel under a Sustainable Oxidative Catalytic System. *Sustain. Chem.* **2021**, *2*, 382–391. [[CrossRef](#)]
28. Mirante, F.; Gomes, N.; Corvo, M.C.; Gago, S.; Balula, S.S. Polyoxomolybdate based ionic-liquids as active catalysts for oxidative desulfurization of simulated diesel. *Polyhedron* **2019**, *170*, 762–770. [[CrossRef](#)]
29. Balula, S.S.; Granadeiro, C.M.; Barbosa, A.D.S.; Santos, I.; Cunha-Silva, L. Multifunctional catalyst based on sandwich-type polyoxotungstate and MIL-101 for liquid phase oxidations. *Catal. Today* **2013**, *210*, 142–148. [[CrossRef](#)]
30. Fernandes, S.C.; Viana, A.M.; de Castro, B.; Cunha-Silva, L.; Balula, S.S. Synergistic combination of the nanoporous system of MOF-808 with a polyoxomolybdate to design an effective catalyst: Simultaneous oxidative desulfurization and denitrogenation processes. *Sustain. Energy Fuels* **2021**, *5*, 4032–4040. [[CrossRef](#)]
31. Gao, Y.; Mirante, F.; de Castro, B.; Zhao, J.S.; Cunha-Silva, L.; Balula, S.S. An Effective Hybrid Heterogeneous Catalyst to Desulfurize Diesel: Peroxotungstate@Metal–Organic Framework. *Molecules* **2020**, *25*, 5494. [[CrossRef](#)] [[PubMed](#)]
32. Granadeiro, C.M.; Barbosa, A.D.S.; Ribeiro, S.; Santos, I.; de Castro, B.; Cunha-Silva, L.; Balula, S.S. Oxidative catalytic versatility of a trivacant polyoxotungstate incorporated into MIL-101(Cr). *Catal. Sci. Technol.* **2014**, *4*, 1416–1425. [[CrossRef](#)]
33. Granadeiro, C.M.; Barbosa, A.D.S.; Silva, P.; Paz, F.A.A.; Saini, V.K.; Fires, J.; de Castro, B.; Balula, S.S.; Cunha-Silva, L. Monovacant polyoxometalates incorporated into MIL-101(Cr): Novel heterogeneous catalysts for liquid phase oxidation. *Appl. Catal. A-Gen.* **2013**, *453*, 316–326. [[CrossRef](#)]
34. Granadeiro, C.M.; Nogueira, L.S.; Juliao, D.; Mirante, F.; Ananias, D.; Balula, S.S.; Cunha-Silva, L. Influence of a porous MOF support on the catalytic performance of Eu-polyoxometalate based materials: Desulfurization of a model diesel. *Catal. Sci. Technol.* **2016**, *6*, 1515–1522. [[CrossRef](#)]

35. Granadeiro, C.M.; Silva, P.; Saini, V.K.; Paz, F.A.A.; Pires, J.; Cunha-Silva, L.; Balula, S.S. Novel heterogeneous catalysts based on lanthanopolyoxometalates supported on MIL-101(Cr). *Catal. Today* **2013**, *218*, 35–42. [[CrossRef](#)]
36. Juliao, D.; Barbosa, A.D.S.; Peixoto, A.F.; Freire, C.; de Castro, B.; Balula, S.S.; Cunha-Silva, L. Improved catalytic performance of porous metal-organic frameworks for the ring opening of styrene oxide. *Crystengcomm* **2017**, *19*, 4219–4226. [[CrossRef](#)]
37. Juliao, D.; Gomes, A.C.; Pillinger, M.; Cunha-Silva, L.; de Castro, B.; Goncalves, I.S.; Balula, S.S. Desulfurization of model diesel by extraction/oxidation using a zinc-substituted polyoxometalate as catalyst under homogeneous and heterogeneous (MIL-101 (Cr) encapsulated) conditions. *Fuel Processing Technol.* **2015**, *131*, 78–86. [[CrossRef](#)]
38. Juliao, D.; Gomes, A.C.; Pillinger, M.; Valenca, R.; Ribeiro, J.C.; de Castro, B.; Goncalves, I.S.; Cunha Silva, L.; Balula, S.S. Zinc-Substituted Polyoxotungstate@amino-MIL-101(Al)—An Efficient Catalyst for the Sustainable Desulfurization of Model and Real Diesels. *Eur. J. Inorg. Chem.* **2016**, *32*, 5114–5122. [[CrossRef](#)]
39. Ribeiro, S.; Barbosa, A.D.S.; Gomes, A.C.; Pillinger, M.; Goncalves, I.S.; Cunha-Silva, L.; Balula, S.S. Catalytic oxidative desulfurization systems based on Keggin phosphotungstate and metal-organic framework MIL-101. *Fuel Processing Technol.* **2013**, *116*, 350–357. [[CrossRef](#)]
40. Pan, Y.; Liu, Y.; Zeng, G.; Zhao, L.; Lai, Z. Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) nanocrystals in an aqueous system. *Chem. Commun.* **2011**, *47*, 2071–2073. [[CrossRef](#)]
41. Kaur, H.; Mohanta, G.C.; Gupta, V.; Kukkar, D.; Tyagi, S. Synthesis and characterization of ZIF-8 nanoparticles for controlled release of 6-mercaptopurine drug. *J. Drug Deliv. Sci. Technol.* **2017**, *41*, 106–112. [[CrossRef](#)]
42. Granadeiro, C.M.; Ferreira, P.M.C.; Juliao, D.; Ribeiro, L.A.; Valenca, R.; Ribeiro, J.C.; Goncalves, I.S.; de Castro, B.; Pillinger, M.; Cunha-Silva, L.; et al. Efficient Oxidative Desulfurization Processes Using Polyoxomolybdate Based Catalysts. *Energies* **2018**, *11*, 1696. [[CrossRef](#)]
43. Chang, X.; Yang, X.F.; Qiao, Y.; Wang, S.; Zhang, M.H.; Xu, J.; Wang, D.H.; Bu, X.H. Confined Heteropoly Blues in Defected Zr-MOF (Bottle Around Ship) for High-Efficiency Oxidative Desulfurization. *Small* **2020**, *16*, 1906432. [[CrossRef](#)]
44. Shokri Aghbolagh, Z.; Khanmohammadi Khorrami, M.R.; Rahmatyan, M.S. Oxidative Desulfurization and Denitrogenation of Simulated Fuels Catalyzed by TBAPMo11Cu@CuO as a High-Performance and Recoverable Heterogeneous Phase-Transfer Catalyst. *Energy Fuels* **2020**, *34*, 16366–16380. [[CrossRef](#)]
45. Ishihara, A.; Wang, D.; Dumeignil, F.; Amano, H.; Qian, E.W.; Kabe, T. Oxidative desulfurization and denitrogenation of a light gas oil using an oxidation/adsorption continuous flow process. *Appl. Catal. A Gen.* **2005**, *279*, 279–287. [[CrossRef](#)]