



Catalytic oxidative/extractive desulfurization of model and untreated diesel using hybrid based zinc-substituted polyoxometalates



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ABSTRACT

The desulfurization efficiency of various hybrid zinc-substituted polyoxometalates ($[PW_{11}Zn(H_2O)O_{39}]^{5-}$, abbreviated as $PW_{11}Zn$) was here investigated for the first time and optimized using sustainable systems conciliating successfully the liquid–liquid extraction and the oxidative catalytic process. Initially, the desulfurization studies were performed using a model diesel containing a mixture of the most refractory sulfur compounds and later extended to an untreated real diesel. In both cases, acetonitrile was used as extraction solvent and aqueous H_2O_2 as oxidant. High level of desulfurization was achieved using model and untreated diesels after few hours. The quaternary ammonium catalysts (TBAPW₁₁Zn and ODAPW₁₁Zn) showed higher catalytic desulfurization efficiency than the ionic liquid catalyst (BMIPW₁₁Zn). The TBAPW₁₁Zn behaved as a homogeneous catalyst immobilized in the extraction solvent, while the ODAPW₁₁Zn with the long carbon chain behaved as a heterogeneous catalyst capable to be recovered from the system. Both quaternary ammonium catalysts showed to be successfully reused/recycled for various consecutive desulfurization cycles.

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1. Introduction

Adverse environmental effects associated to sulfur oxides released during the combustion process of fuels, forced government authorities to establish sulfur limits content in fuels to ultra low levels (<10 ppm). As result, ultra-deep desulfurization of fuels has drawn researchers attention and become an important task for oil refining industries [1,2]. Hydrodesulfurization (HDS) is the current process implemented in the refineries, in spite of its operation under severe conditions (high temperature and pressure and consumes large amounts of hydrogen), and the low efficiency associated with the removal of refractory sulfur compounds, such as dibenzothiophenes and its derivatives [3,4]. The oxidative desulfurization (ODS) is considered one of the most promising alternative or supplementary processes offering several advantages over HDS, such as mild reaction conditions (no requiring hydrogen and operates under atmospheric pressure), high selectivity and economic viability [5]. By means of this procedure, in the presence of an oxidant and appropriate catalyst, sulfur containing compounds in diesel are converted in sulfoxide and/or sulfone which are easily

separated from oil by liquid–liquid extraction with polar solvents or by adsorption [5–7]. In the ODS system, H_2O_2 was the mostly chosen oxidant, because it only produced water as a byproduct. Several catalysts have been used together with H_2O_2 as oxidant, such as various acids [8–11], metallic ionic liquids (ILs) [12–15], homogeneous and heterogeneous polyoxometalate (POM) catalysts [16–21], and some few solid catalysts including activated carbon [22,23], titanium micro/mesoporous silica materials [24–26], homogeneous and heterogeneous rhenium catalyst [27], VO_x/Al_2O_3 [28], WO_x/ZrO_2 [29,30] and Mo/Al_2O_3 [31]. Among these catalysts, POMs have been highlighted with special interest because they have showed high sulfur removal efficiency due to their unique features [32–34]. POMs belong to a large class of metal–oxygen cluster anions which presents various structures, including the Keggin type that represents the most employed in catalysis, since it has unique acid strength, oxidation potential and thermal stability [35–37]. Furthermore, the catalytic activity of Keggin POM compounds $C_n[XM_{12}O_{40}]^{p-}$ is strongly influenced by the nature of the counter-cation C, the central atom X and metal M [35–37]. Organic–inorganic hybrid materials based on Keggin-type POMs and various organic cations have gradually become worldwide attention, especially for the application in ODS processes [38–45]. The modification of POMs with organic

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units has been applied as an efficient strategy to achieve POMs-based hybrid catalysts with higher catalytic efficiency, recovery and reusability capacity. Different organic groups such as ILS [38,41,43,46–48], organic polymers [49–51] and surfactants with different carbon-chain lengths [33,39,44,45,52–58] have been applied, leading to an improved catalytic activity and possibility to be recycled. The cationic surfactant octadecyldimethylammonium (ODA) with the long alkyl chain attached to the POM active center catalyst, may act as a dynamic trap to improve the probability of interaction between the substrate, oxidant and the catalyst center, what will promote the catalytic efficiency [33,39,44,45,55,56,58,59]. The formed POM amphiphilic structures based on surfactant molecules not only increase the catalyst activity but also provide easy and fast catalyst recovery from reaction system [33,39,44,45,55,56,58,59]. On the other hand, the high-valence POMs anions have been employed as counter negative ions for ILS, producing new catalytic ILS. Some studies in the literature demonstrate that the resulting ILS based POMs are highly active catalysts, possible to be recovery and reusable [43,60]. Some of these ILS based POMs were synthesized from imidazole ILS, such as 3-methylimidazolium [2,38,41,43,61–63]. However, only a couple of examples were reported in the literature using ILS based POMs for ODS systems [64,65].

Recently, our research group reported the efficiency of zinc-substituted POM ($[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}]^{5-}$, abbreviated as PW_{11}Zn) for olefin oxidation. In these studies the catalytic performance of PW_{11}Zn was investigated when this active center was encapsulated into MIL-101(Cr) support [66] or encapsulated into silica nanoparticles [16]. In the present work, different hybrid organic- PW_{11}Zn compounds have been prepared with the cationic surfactant ODA and the cation 1-butyl-3-methylimidazolium (BMIM) to form BMIPW₁₁Zn ionic liquid. The catalytic performance of these hybrid PW_{11}Zn based compounds was investigated in the desulfurization of a model diesel and also in an untreated diesel supplied by Galp Energia.

2. Experimental section

2.1. Materials and methods

All the reagents, 1-butyl-3-methylimidazolium bromide (Fluka), trimethyloctadecylammonium (ODA) bromide (Aldrich), tetra-*n*-butylammonium bromide (Merck), sodium tungstate dehydrate (Aldrich), sodium phosphate dehydrate (Aldrich), zinc acetate di-hydrated (M&B), hydrochloric acid (Fisher Chemicals), 4,6-dimethyldibenzothiophene (Alfa Aesar GmbH & Co kg), dibenzothiophene (Aldrich), 1-benzothiophene (Fluka), *n*-octane (VWR international S.A.S.), ethyl acetate (Merck), acetonitrile (Fisher Chemical), 1-butyl-3-methylimidazolium hexafluorophosphate (Sigma-Aldrich), H₂O₂ 30% (Aldrich) were used as received without further purification.

Elemental analysis for C, N, and H were performed on a Leco CHNS-932 at the University of Santiago de Compostela. Hydration water contents were determined by thermogravimetric analysis performed in air between 20 °C and 800 °C, at heating rate 5 °C min⁻¹, using a TGA-50 Shimadzu thermobalance. Infrared absorption spectra were recorded for 400–4000 cm⁻¹ region on a Perkin Elmer Spectrum 100 series with ATR accessory, with resolution of 4 cm⁻¹ and 64 scans. ³¹P spectra were collected for liquid solutions using a Bruker Avance III 400 spectrometer and chemical shifts are given with respect to external 85% H₃PO₄. Solid state ³¹P MAS NMR spectra were recorded with a 7 T (300 MHz) AVANCE III Bruker spectrometer under a magic angle spinning of 10 Hz at room temperature. The catalytic reactions were monitored in a Bruker 430-GC-FID gas chromatograph, with hydrogen as carried

gas (55 cm³ s⁻¹) and a Supelco capillary column SPB-5 (30 m × 250 μm id.; 25 μm film thickness) was used. Sulfur content in real diesel was measured by ultraviolet fluorescence test method in Galp Energia, using a Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry, using a OXFORD LAB-X, LZ 3125. The sulfur content in real diesel was analyzed by Shimadzu GC-FPD gas chromatograph, with helium as carrier gas and a TRB-1 column (50 m, ID = 0.32) was used.

2.2. Synthesis of hybrid zinc-substituted POMs

$\text{K}_5[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}] \cdot n\text{H}_2\text{O}$ (KPW_{11}Zn) was prepared by following a previously described procedure [67]. Na₂HPO₄ (1.8 mmol) and Na₂WO₄·2H₂O (20 mmol) were dissolved in 40 ml of water, the mixture was heated at 90 °C for 4 h and the pH was adjusted to 4.8 with HCl 4 M. Zinc acetate (2.4 mmol) was then added and the pH was corrected to 4.8. An excess of potassium chloride was added and the formed solid was filtered, washed and dried at room temperature. The successful preparation of KPW_{11}Zn was confirmed by FT-IR and ³¹P NMR spectroscopies (see Supporting Information).

$(\text{C}_4\text{H}_9)_4\text{N}][\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}] \cdot 4\text{H}_2\text{O}$ ($\text{TBAPW}_{11}\text{Zn}$, TBA = (C₄H₉)₄N)) was prepared following the procedure described in the literature [68,69]. Elemental and thermogravimetric analysis, vibrational spectra (FT-IR) and ³¹P NMR data confirmed the successful preparation of $\text{TBAPW}_{11}\text{Zn}$ (see Supporting Information).

$(\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3)_5[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}] \cdot 4\text{H}_2\text{O}$ ($\text{ODAPW}_{11}\text{Zn}$) was prepared for the first time adapting a procedure reported in the literature [55]. A solution of trimethyloctadecylammonium (ODA) bromide (5 mmol dissolved in 20 mL of ethanol) was added dropwise to the aqueous solution of previously prepared KPW_{11}Zn (1 mmol in 40 mL), with continuous stirring for 2 h. The mixture was filtered and the obtained solid was dried in vacuum at 60 °C. The hybrid compound was characterized by elemental and thermogravimetric analysis, vibrational spectroscopy (FT-IR) and solid-state ³¹P NMR data (see Supporting Information).

$(\text{BMI})_5[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}] \cdot 4\text{H}_2\text{O}$ ($\text{BMIPW}_{11}\text{Zn}$, BMI stands for 1-butyl-3-methylimidazolium, C₈H₁₅N₂) was prepared adapting a procedure reported in the literature [65]. An aqueous solution of 1-*n*-butyl-3-methylimidazolium bromide (5 mmol) was added dropwise to the aqueous solution of KPW_{11}Zn (1 mmol) at room temperature under constant stirring during 2 hours. The resulting precipitate was washed with distilled water, filtered and dried under vacuum at 60 °C overnight. Elemental and thermogravimetric analysis, vibrational spectra (FT-IR) and NMR data confirmed the successful preparation of $\text{BMIPW}_{11}\text{Zn}$ (see Supporting Information).

2.3. Oxidative desulfurization process (ODS) using a model diesel

The ODS experiments were carried out under air (atmospheric pressure) in a closed borosilicate 5 mL reaction vessel equipped with a magnetic stirrer, and immersed in a thermostatic oil bath at 50 °C. Hydrogen peroxide (30 wt%) was used as oxidant. A model diesel was prepared by dissolving the most refractory sulfur compounds in diesel (dibenzothiophene, **DBT**, 1-benzothiophene, **1-BT**, and 4,6-dimethyldibenzothiophene, **4,6-DMDBT**, approximately 500 ppm of each) in *n*-octane. ODS experiments were performed in the absence and in the presence of acetonitrile as extraction solvent. In the last case, equal volume of model diesel and MeCN was used to prepare the biphasic liquid-liquid system. An initial extraction of sulfur compounds from model diesel to the extraction solvent was analyzed. The biphasic system was stirred for 10 min until the initial extraction equilibrium was reached, an aliquot from the upper model diesel phase was taken and analyzed by GC. After this stage, the oxidant H₂O₂ was added to the system.

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