



# Efficient eco-sustainable ionic liquid-polyoxometalate desulfurization processes for model and real diesel



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## ABSTRACT

This work presents a successful recycling system based in homogeneous polyoxometalate catalysts to desulfurize model and real diesels. Various Keggin-type polyoxometalates entrapped in a room temperature ionic liquid (RTIL) phase were investigated. The desulfurization process here proposed conciliates efficiently an extraction and an oxidative catalytic process under sustainable and moderate conditions ( $\text{H}_2\text{O}_2$  as oxidant,  $50^\circ\text{C}$ ). The ionic liquid acts as an extraction solvent and also as an effective immobilization medium for the active homogeneous catalysts. The zinc-polyoxometalates presented high stability and high capacity to be recycled for various consecutive cycles with no loss of desulfurization efficiency. Complete desulfurization of model diesel was achieved at short reaction time (3 h). Under the same experimental conditions, 80% of sulfur was removed from real diesel ( $S_{\text{initial}} = 2300 \text{ ppm}$ ).

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## 1. Introduction

The fuel desulfurization is an important area of the petroleum refining industry and has become an environmental concern at global level due to the emissions of  $\text{SO}_x$  produced by the combustion of the sulfur-containing compounds. To prevent the environmental pollution many countries have proposed more stringent environmental regulations on sulfur level in fuels. The actual industrial method applied is the hydrodesulfurization (HDS) that promotes an efficient extraction of thiols, sulfides and disulfides from fuels using severe conditions (large catalyst amount, high temperature and pressure and excessive hydrogen consumption). In fact, the need to remove the most refractory sulfur compounds from liquid fuels (such as alkyl-substituted benzothiophenes and dibenzothiophenes turns the HDS process less sustainable and economically less attractive [1,2]. Therefore, new methodologies that improve an efficient removal of refractory sulfur-containing compounds under mild conditions are a priority in industry to decrease the cost of treating fuels. These methods include oxidative desulfurization (ODS), bio-desulfurization, adsorption and extractive desulfurization. The ODS process consists on the oxidation of the organosulfur compounds to the corresponding sulfoxides and/or sulfones which can be easily removed from fuel medium by sol-

vent extraction and/or adsorption. Therefore, the conciliation of catalytic oxidation and solvent extraction and/or adsorption constitutes a promising desulfurization process [3–7]. The liquid–liquid extraction process can occur before the oxidation step, during the oxidative stage or/and after the oxidation of sulfur-compounds. The room temperature ionic liquids (RTILs) possess sustainable properties such as, non-volatility, thermal stability and ability to be recycled, making them advantageous solvents and extractants, comparatively to flammable and volatile organic solvents, for desulfurization processes that conciliate liquid extraction and catalytic oxidation (ECODs) [6–10].

Transition-metal oxygen anion clusters referred to as polyoxometalates (POMs) are constituted by early transition metal cations (W, Mo, V, Nb, Ta and Ti) and oxide anions. The unique properties of POMs make them of fundamental and practical interest. POMs have single physical and chemical properties, e.g., strong Brønsted acidity, strong oxidizing agents, an unmatched range of molecular structures, efficient adsorbents, green catalysts, and redox activity. Their properties as green catalysts are due mainly to their sustainable synthesis procedures and also their compatibility with some environmentally friendly oxidants, such as  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  [11]. Other advantages of POMs are their high solubility and stability in RTILs media [5,10,12,13]. POMs have demonstrated to be active catalysts for ODS processes, mainly using model diesels containing aromatic sulfur-compounds [4,13–18]. The most used POMs in ODS processes are mainly Keggin  $[\text{XM}_{12}\text{O}_{40}]^{n-}$ , Lindqvist  $[\text{M}_5\text{O}_{19}]^{p-}$  and Anderson-type  $[\text{M}_7\text{O}_{24}]^{q-}$  ( $\text{M} = \text{W}, \text{Mo}$  and  $\text{V}$ ) [14,16,19–21]. The

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research line of our group have been focused on the application of Keggin-type POMs in ODS processes to treat model and real diesels [10,23–26]. A special attention has been given to the zinc-substituted polyoxotungstate  $[PW_{11}Zn(H_2O)O_{39}]^{5-}$  due to the high oxidative catalytic desulfurization performance obtained with this POM. An effort has been made to immobilize this active POM in different solid supports to form robust recyclable catalysts; however, some stability limitations have been found [4,10,23].

In the present work, POMs with different structures (Keggin-type and sandwich-type), were immobilized in a RTIL phase (POMs@BMIMPF<sub>6</sub>, BMIMPF<sub>6</sub> means 1-butyl-3-methylimidazolium hexafluorophosphate). The POM@BMIMPF<sub>6</sub> presents a bi-functionality of liquid–liquid desulfurization associated to a simple extraction and an oxidative catalytic desulfurization of model and real diesels. Furthermore, the POM@RTIL system demonstrated to be capable to be recycled and stable for various consecutive ODS cycles.

## 2. Experimental

### 2.1. Materials and methods

All the reagents, 1-butyl-3-methylimidazolium hexafluorophosphate (Sigma-Aldrich), tetra-*n*-butylammonium bromide (Merck), sodium tungstate dehydrate (Sigma-Aldrich), sodium phosphate dehydrate (Aldrich), zinc acetate di-hydrated (M&B), sodium metavanadate (Sigma-Aldrich), phosphotungstic acid (Sigma-Aldrich), 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), hydrogen peroxide (30%, Sigma-Aldrich) were used as received without further purification.

Elemental analysis for C, N and H were executed on a Leco CHNS-932, performed at University of Santiago. Hydration waters contents were determined by thermogravimetric analysis between 20 and 800 °C in air at heating rate of 5 °C min<sup>-1</sup>, using a Shimadzu TGA-50 thermobalance. Infrared absorption spectra were recorded for 400–4000 cm<sup>-1</sup> region on a Perkin Elmer spectrum BX FTIR spectrometer, a resolution of 4 cm<sup>-1</sup> and 64 scans. <sup>31</sup>P NMR spectra were recorded for liquid solutions using a Bruker Avance III 400 spectrometer at 400 MHz at room temperature. The chemical shifts are given with respect to external 85% H<sub>3</sub>PO<sub>4</sub>. The desulfurization processes using model diesel were monitored by a Bruker 430 GC-FID using hydrogen as carried gas (55 cm<sup>3</sup> s<sup>-1</sup>) and fused silica Supelco capillary columns SPB-5 (30m × 0.25 mm i.d.; 25 μm film thickness). The sulfur content in real diesel was measured by ultraviolet fluorescence test method in Galp Energia, using 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.

### 2.2. Synthesis and characterization of POMs

#### 2.2.1. Zinc-substituted POM (PW<sub>11</sub>Zn)

The tetra-*n*-butylammonium (TBA) salts of zinc-substituted TBA<sub>4</sub>H[PW<sub>11</sub>Zn(H<sub>2</sub>O)O<sub>39</sub>].5H<sub>2</sub>O [PW<sub>11</sub>Zn, TBA=(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N] was prepared based on following a reported procedure [26]. The compound was characterized by elemental and thermogravimetric analysis, infrared spectroscopy (FT-IR) and <sup>31</sup>P NMR spectroscopy, which confirmed the successful preparation. Anal. Calculated (%) for C<sub>64</sub>H<sub>157</sub>N<sub>4</sub>O<sub>45</sub>PW<sub>11</sub>Zn (3821.55): C, 20.02; H, 4.17; N, 1.46; found: C, 20.95; H, 4.18; N, 1.49. TGA showed a mass loss of 2.6% in the range of 40–130 °C (calcd, for loss of 5 hydrated H<sub>2</sub>O molecules: 2.4%), in the range of 130–225 °C the mass loss was 0.35% (calcd,

for loss 1 coordinated water molecule:0.47%).<sup>31</sup>P (400 MHz, CD<sub>3</sub>CN, 298 K): δ = -10.65 ppm. FT-IR (cm<sup>-1</sup>): 2960 (s), 2936 (s), 1642 (m), 1484 (s), 1380 (m), 1054 (s), 952 (vs), 884 (s), 800 (vs), 592 (s), 514 (m).

#### 2.2.2. Zinc-sandwich POM ((PW<sub>9</sub>)<sub>2</sub>Zn<sub>4</sub>)

The tetra-*n*-butylammonium (TBA) salts of zinc-sandwich TBA<sub>7</sub>H<sub>3</sub>[(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>Zn<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>].9H<sub>2</sub>O[(PW<sub>9</sub>)<sub>2</sub>Zn<sub>4</sub>, TBA=(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N] was prepared according reported procedure [27]. The compound was characterized by elemental and thermogravimetric analysis, infrared spectroscopy (FT-IR) and <sup>31</sup>P NMR spectroscopy, that confirmed the successful preparation. Anal. Calculated (%) for C<sub>112</sub>H<sub>277</sub>N<sub>7</sub>O<sub>79</sub>P<sub>2</sub>W<sub>18</sub>Zn<sub>4</sub> (6619.10): C, 20.32; H, 4.22; N, 1.48; found: C, 19.64; H, 3.91; N, 1.39. TGA showed a mass loss of 2.5% in the range of 20–100 °C (calcd, for loss of 9 hydrated H<sub>2</sub>O molecules: 2.4%), in the range of 100–200 °C the mass loss was 0.56% (calcd, for loss 2 coordinated water molecule:0.54%).<sup>31</sup>P (400 MHz, CD<sub>3</sub>CN, 298 K): δ = -3.69 ppm. FT-IR (cm<sup>-1</sup>): 2960 (m), 2874 (m), 1636 (m), 1560 (m), 1482 (w), 1036 (vs), 964 (vs), 942 (s), 882 (s), 824 (m), 764 (w), 726 (s), 584 (w), 500 (m).

#### 2.2.3. Keggin POM (PW<sub>12</sub>)

The tetra-*n*-butylammonium (TBA) salts of the Keggin POM TBA<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> [PW<sub>12</sub>, TBA=(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N] was prepared by the addition of a slight excess of TBA to an aqueous solution of the commercial H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, followed by its recrystallization in the minimum amount of boiling water. The compound was characterized by elemental analysis, infrared spectroscopy (FT-IR) and <sup>31</sup>P NMR spectroscopy. Anal. Calculated (%) for C<sub>48</sub>H<sub>108</sub>N<sub>3</sub>O<sub>40</sub>PW<sub>12</sub> (3604.42): C, 15.99; H, 3.02; N, 1.16. Found: C, 16.10; H, 2.90; N, 1.02. TGA showed no mass loss in the range from 20 to 200 °C, which indicates the absence of hydrated and coordinated water molecules.<sup>31</sup>P (400 MHz, CD<sub>3</sub>CN, 298 K): δ = -13.9 ppm. FT-IR (cm<sup>-1</sup>): 2964 (m), 2876 (w), 2362 (w), 1470 (m), 1380 (m), 1078 (vs), 972 (vs), 892 (s), 806 (vs), 594 (m), 518 (s).

#### 2.2.4. Vanadium-mixed addenda POM (PW<sub>11</sub>V)

The tetra-*n*-butylammonium salts of vanadium mixed addenda POM TBA<sub>4</sub>[PW<sub>11</sub>VO<sub>40</sub>].7H<sub>2</sub>O [PW<sub>11</sub>V, TBA=(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N] was prepared according with the method described in the literature [28]. The compound was characterized by different techniques, such as elemental and thermogravimetric analysis, infrared spectroscopy (FT-IR), <sup>31</sup>P and <sup>51</sup>V NMR spectroscopy. Anal. Calculated (%) for C<sub>64</sub>H<sub>158</sub>N<sub>4</sub>O<sub>47</sub>PW<sub>11</sub>V (3840.093): C, 19.8; H, 4.54; N, 1.44. Found: C, 28.5; H, 5.86; N, 2.06; 5.12. TGA showed a mass loss of 3.3% in the range of 30–100 °C (calcd, for loss of 7 hydrated H<sub>2</sub>O molecules: 3.3%).<sup>31</sup>P and <sup>51</sup>V (400 MHz, CD<sub>3</sub>CN, 298 K): δ = -13.61 ppm and -549.35 ppm, respectively. FT-IR (cm<sup>-1</sup>): 3436 (m), 2960 (s), 2874 (s), 2342 (m), 1622 (m), 1502 (s), 1482 (m), 1382 (s), 1250 (w), 1152 (w) 1096 (vs), 1070 (vs), 962 (vs), 884 (vs), 800 (vs), 594 (w), 502 (m).

### 2.3. Oxidative desulfurization (ODS) studies

#### 2.3.1. Model diesel

The ODS studies were performed using a model diesel formed by the dissolution of different aromatic sulfur compounds present in real diesel: dibenzothiophene (DBT), 1-benzothiophene (1-BT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), in *n*-octane (500 ppm or 0.0156 mol dm<sup>-3</sup> of each sulfur compound). The desulfurization studies were performed using a biphasic liquid–liquid 1:1 (v/v) of model diesel/RTIL system. 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF<sub>6</sub>) was the RTIL used. Various POMs were studied as homogeneous catalysts dissolved in the RTIL phase (5 μmol in 0,75 mL of RTIL). All experiments were carried out under air (atmospheric pressure) in a closed borosilicate 5 mL reaction

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