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## PAPER

## Influence of porous MOF support in the catalytic performance of Eu-polyoxometalate based materials: desulfurization of model diesel<sup>†</sup>

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Carlos M. Granadeiro,<sup>a</sup> Lucie S. Nogueira,<sup>a</sup> Diana Julião,<sup>a</sup> Fátima Mirante,<sup>a</sup> Duarte Ananias,<sup>b</sup> Salete S. Balula<sup>\*a</sup> and Luís Cunha-Silva<sup>\*a</sup>

An aluminum 2-aminoterephthalate based metal-organic framework (MOF) material was applied for the first time to prepare highly efficient heterogeneous catalysts in desulfurization processes. Sandwich-type  $[\text{Eu}(\text{PW}_{11}\text{O}_{39})_2]^{12-}$  polyoxometalate (POM) was supported on Al(III) and Cr(III) MIL-type MOFs,  $\text{NH}_2\text{-MIL-53}(\text{Al})$  and  $\text{MIL-101}(\text{Cr})$ , and extensive characterization confirmed the incorporation of the POM on the two supports. The catalytic performance of the two composite materials, POM/MIL(Al) and POM/MIL(Cr), was evaluated in the oxidative desulfurization (ODS) of a model oil containing some of the most common refractory sulfur compounds in diesel. Both composite materials have shown to be active and robust heterogeneous catalysts for the efficient removal of sulfur-containing compounds from model diesel, and the influence of the solid support on the catalytic performance of the active species was further assessed. The POM/MIL(Al) revealed notable catalytic performance, since complete desulfurization was obtained after 2 h of reaction. Furthermore, this remarkable heterogeneous catalyst revealed to be stable and recyclable for various catalytic cycles.

### 1. Introduction

The production of sulfur-free fuels is one of the most active scientific areas as a consequence of the global effort to reduce the hazardous emissions of transportation fuels for environmental preservation and healthcare purposes.<sup>1, 2</sup> Hydrodesulfurization (HDS) is the commonly used technology for the removal of sulfur compounds from fuel. However, some drawbacks have been associated with this process such as the high cost of operation as well as the difficulty in removing the heterocyclic sulfur compounds in fuel (for example, thiophene and DBT derivatives).<sup>3, 4</sup> Consequently, there is an urgent need for the development of novel, cheaper and more efficient methods for the production of sulfur-free fuels.<sup>5, 6</sup> Several alternative and/or complementary

desulfurization methods have been investigated, such as adsorptive desulfurization (ADS) that uses highly porous materials to remove the sulfur compounds from fuels by adsorption.<sup>7-9</sup> Oxidative desulfurization (ODS) is one of the most promising techniques for the deep desulfurization of fuels since it operates under mild conditions and the refractory sulfur compounds are easily converted by oxidation.<sup>2, 10, 11</sup> The ODS process comprises two steps: (i) oxidation of the organosulfur compounds to the corresponding sulfoxides and/or sulfones, and (ii) the removal of the oxidized compounds by extraction, adsorption or distillation.<sup>12-14</sup> Several ODS approaches have been described for the production of sulfur-free fuels, generally using  $\text{H}_2\text{O}_2$  as the oxidant, and including ODS systems based on formic acid, acetic acid, polyoxometalates (POMs) and ionic liquids.<sup>10, 15-17</sup>

Our research group has been designing novel heterogeneous catalysts for ODS applications through the incorporation/immobilization of catalytically active POMs in solid supports.<sup>18-22</sup> The three-dimensional structure, chemical robustness and accessible porosity of metal-organic frameworks (MOFs) make them suitable candidates to act as solid supports in the heterogenization process.<sup>23, 24</sup> Among the vast amount of reported MOFs, the MIL-type materials (Materials of Institute Lavoisier) comprise some of the most

<sup>a</sup> REQUIMTE / LAQV & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal. E-mail: sbalula@fc.up.pt, l.cunha.silva@fc.up.pt; Tel: +351 220402576; Fax: +351 220402659

<sup>b</sup> CICECO, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.

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chemically robust and thermally stable frameworks with permanent and accessible pores.<sup>25-27</sup>

The preparation of MOF-based heterogeneous catalysts through the immobilization of the sandwich-type [Eu(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>11-</sup> anion in two different MIL-type frameworks, MIL-101(Cr) and NH<sub>2</sub>-MIL-53(Al), is reported in this work. The resulting composite materials, POM/MIL(Cr) and POM/MIL(Al), were tested as heterogeneous catalysts in the ODS process for the desulfurization of a multicomponent model diesel using H<sub>2</sub>O<sub>2</sub> as the oxidant. The influence of the solid support on the final catalytic performance of the composites was evaluated. The immobilization of the POM has led to a significant enhancement of the overall desulfurization performance. To the best of our knowledge this is the first work reporting the preparation of a composite material using an aluminum 2-aminoterephthalate MOF as the solid support and its application in catalytic desulfurization processes. Moreover, this is also the first report describing the preparation of heterogeneous catalysts based on POM/NH<sub>2</sub>-MIL-53(Al) and the successful application in oxidative catalytic systems using H<sub>2</sub>O<sub>2</sub>. In fact, the use of NH<sub>2</sub>-MIL-53(Al) in the heterogeneization of catalytically active POMs is still practically unexplored as only one example can be found in the literature, in particular for application in the aldol condensation of acetaldehyde.<sup>28</sup>

## 2. Experimental section

### 2.1. Materials and methods

All the reagents used in the preparation of the composite materials, namely chromium(III) nitrate nonahydrate [Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Aldrich, 99%], aluminum chloride hexahydrate [AlCl<sub>3</sub>·6H<sub>2</sub>O, Aldrich, 99%], benzene-1,4-dicarboxylic acid [Aldrich, 98%], 2-aminobenzene-1,4-dicarboxylic acid [HO<sub>2</sub>C-C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>-CO<sub>2</sub>H, Aldrich, 99%], hydrofluoric acid [Aldrich, 40-50%] and N,N-dimethylformamide [DMF, (CH<sub>3</sub>)<sub>2</sub>NCHO, Aldrich, >99%] were used as received without further purification. Dibenzothiophene [DBT, C<sub>12</sub>H<sub>8</sub>S, Aldrich], 1-benzothiophene [1-BT, C<sub>8</sub>H<sub>6</sub>S, Aldrich], 4-methyldibenzothiophene [4-MDBT, C<sub>13</sub>H<sub>10</sub>S, Aldrich], 4,6-dimethyldibenzothiophene [4,6-DMDBT, C<sub>14</sub>H<sub>12</sub>S, Aldrich], thiophene [C<sub>4</sub>H<sub>4</sub>S, Aldrich], acetonitrile [MeCN, Panreac] and H<sub>2</sub>O<sub>2</sub> 30% (Aldrich) were also used as received. Elemental analyses were performed by ICP-MS on a Varian 820-MS and C, N and H analyses were executed on a Leco CHNS-932, both techniques were carried out in the University of Santiago de Compostela. Infrared absorption spectra were obtained on a Jasco 460 Plus spectrometer, using KBr pellets. FT-Raman spectra were recorded on a RFS-100 Bruker FT-spectrometer, equipped with a Nd:YAG laser with excitation wavelength of 1064 nm and the laser power set to 350 mW. Powder X-ray diffraction analyses were collected at room temperature on a X'Pert MPD Philips diffractometer, equipped with an X'Celerator detector and a flat-plate sample

holder in a Bragg-Brentano para-focusing optics configuration (45 kV, 40 mA). Intensity data were collected by the step-counting method (step 0.04°), in continuous mode, in the range ca. 3.5 ≤ 2θ ≤ 50°. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) studies were performed at "Centro de Materiais da Universidade do Porto" (CEMUP, Porto, Portugal) using a scanning electron microscope JEOL JSM 6301F operating at 15 kV equipped with an energy-dispersive X-ray spectrometer Oxford INCA Energy 350. The samples were studied as powders and were previously subjected to gold sputtering. GC-FID analysis were carried out in a Varian CP-3380 chromatograph to monitor the catalytic reactions, equipped with a fused silica Supelco capillary columns SPB-5 (30m × 0.25mm i.d.; 25 μm film thickness). The hydrogen was used as the carrier gas (55 cms<sup>-1</sup>).

### 2.2. Synthesis and preparation of the materials

**2.2.1. Sandwich-type polyoxometalate.** The potassium salt of the Keggin-type POM [Eu(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>11-</sup> (herein referred as POM) was prepared according to a previously described procedure by our group.<sup>29</sup> Briefly, an aqueous solution of EuCl<sub>3</sub>·6H<sub>2</sub>O was slowly added to an aqueous solution of the lacunary [PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup> in a 1:2 stoichiometric ratio. After stirring for 1h at 90 °C, the solid was recovered by filtration and dried in a desiccator over silica gel. The identity of the POM was confirmed by FT-IR, FT-Raman, <sup>31</sup>P NMR spectroscopy, elemental and thermal analyses.

**2.2.2. Solid supports MIL-101(Cr) and amino-MIL-53(Al).** The chromium terephthalate was prepared according to the method of Férey et al.<sup>25</sup> A mixture containing chromium(III) nitrate (2 mmol), benzene-1,4-dicarboxylic acid (2 mmol), hydrofluoric acid (100 μL) and H<sub>2</sub>O (10 mL) was stirred for 10 min at room temperature, placed in an autoclave and heated at 493 K for 9 h in an electric oven. After cooling, the solid was recovered by filtration and purified through a double DMF and double ethanol treatments. The amino-MIL-53(Al) was prepared following the procedure reported by Kapteijn and co-workers.<sup>27, 30</sup> A mixture containing aluminum chloride hexahydrate (1.1 mmol), 2-aminobenzene-1,4-dicarboxylic acid (1.5 mmol) and DMF (15 mL) was stirred for 10 min at room temperature, placed in an autoclave and heated at 403 K for 72 h. The yellow solid was recovered by centrifugation and washed with acetone by stirring for 30 min at room temperature. Afterwards, the solid was purified with methanol under reflux overnight.

**2.2.3. Composite materials.** The composite materials were prepared through an impregnation procedure previously reported by our group.<sup>31, 32</sup> The preparation of the POM/MIL(Cr) composite has already been reported by our group.<sup>31</sup> For the preparation of the POM/MIL(Al) composite, an aqueous solution of the POM (10 mM) was added to the amino-MIL-53(Al) solid support (160 mg) and stirred at room

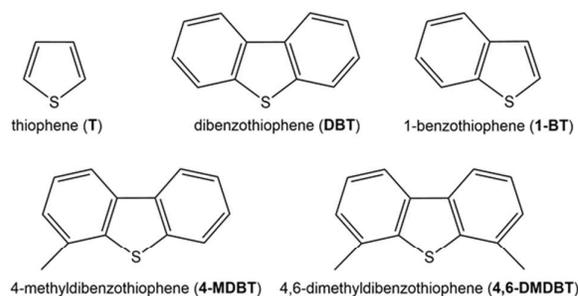
temperature for 5 days. The resulting solid was filtrated, washed thoroughly with water and dried in a desiccator over silica gel.

**POM/MIL(Cr):** Anal. found (%): W, 7.15; loading of  $\text{Eu}(\text{PW}_{11}\text{O}_{39})_2$ :  $0.018 \text{ mmol.g}^{-1}$ . Selected FT-IR ( $\text{cm}^{-1}$ ): 3410, 2976, 2925, 1628, 1558, 1543, 1508, 1431, 1400, 1304, 1277, 1159, 1090, 1049, 1020, 953, 881, 831, 808, 783, 746, 714, 663, 584, 526, 418; selected FT-Raman ( $\text{cm}^{-1}$ ): 3072, 1613, 1512, 1495, 1458, 1179, 1144, 1044, 984, 970, 872, 812, 631, 500, 467.

**POM/MIL(Al):** Anal. found (%): W, 1.72; loading of  $\text{Eu}(\text{PW}_{11}\text{O}_{39})_2$ :  $0.0043 \text{ mmol.g}^{-1}$ . Selected FT-IR ( $\text{cm}^{-1}$ ): 3498, 3386, 1687, 1585, 1498, 1439, 1402, 1340, 1309, 1261, 1242, 1165, 1124, 1012, 958, 906, 889, 854, 841, 814, 773, 754, 700, 650, 606, 552, 471; selected FT-Raman ( $\text{cm}^{-1}$ ): 3385, 3076, 2928, 1618, 1580, 1470, 1402, 1339, 1273, 1260, 1235, 1163, 1130, 986, 970, 839, 810, 776, 693, 660, 587, 537, 483, 438.

### 2.3. Catalytic studies: Oxidative desulfurization (ODS) processes

The ODS studies were performed using a model diesel containing thiophene (T), dibenzothiophene (DBT), 1-benzothiophene (1-BT), 4-methylidibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in n-octane to make a stock solution with approximately 500 ppm of each sulfur compound (chemical structures of all the refractory sulfur compounds studied in this work are depicted in Scheme 1). The ODS processes were carried out under air (atmospheric pressure) in a closed borosilicate 5 mL reaction vessel equipped with a magnetic stirrer and immersed in a thermostated oil bath at 70 °C. In a typical ODS reaction, the catalyst (1  $\mu\text{mol}$  of POM or the equivalent amount of composite material) was added to the biphasic system (0.5 mL MeCN + 0.5 mL model diesel) and the initial extraction was performed by stirring the system at 70 °C for 10 min. After this



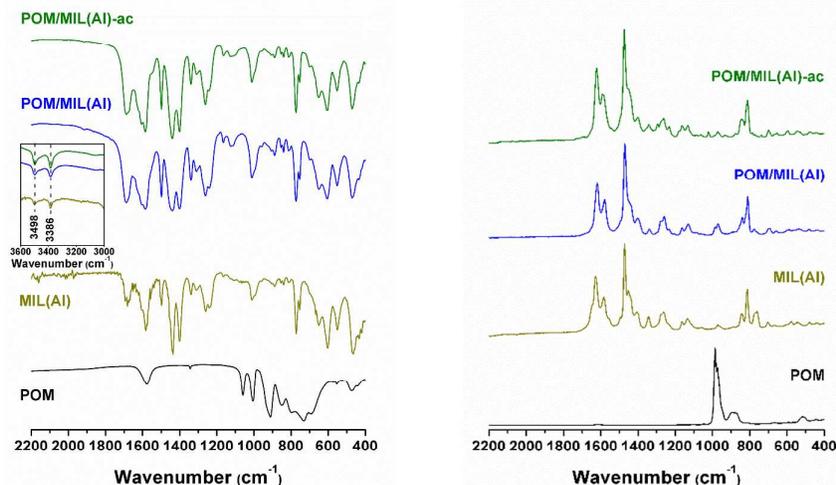
**Scheme 1** Chemical structures of the refractory sulfur compounds in the model diesel.

time, the catalytic step was initiated by the addition of the oxidant  $\text{H}_2\text{O}_2$  (90  $\mu\text{L}$ ;  $\text{H}_2\text{O}_2/\text{S}$  molar ratio = 23). Aliquots were taken directly from the n-octane phase with a microsyringe to quantify the sulfur content periodically. This quantification was performed by GC analysis, using tetradecane diluted with ethyl acetate as external standard. For the recyclability tests, the catalyst was recovered by filtration at the end of each cycle, washed thoroughly with MeCN, and dried at room temperature to be used in a new cycle under identical experimental conditions.

## 3. Results and discussion

### 3.1. Catalysts characterization

The composites were prepared following an impregnation method previously described by our group using aqueous solutions of the POM.<sup>31,32</sup> The preparation of the POM/MIL(Cr) composite has been already reported<sup>31</sup> and its full characterization is presented in the ESI. POM/MIL(Al) composite, which resulted from the immobilization of the POM in the amino-MIL-53(Al) framework, was characterized by a myriad of techniques including FT-IR, FT-Raman, elemental analysis, powder X-ray diffraction (XRD), scanning electron



**Fig. 1** FT-IR (left side) and FT-Raman (right side) spectra of the isolated POM, the aluminum  $\text{NH}_2$ -MIL-53(Al) support material [MIL(Al)] and corresponding composite before [POM/MIL(Al)], and after catalysis [POM/MIL(Al)-ac].

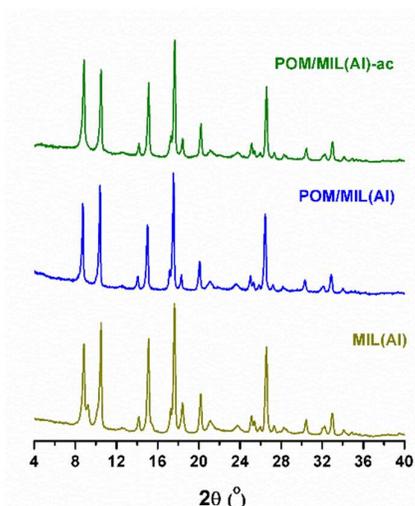


Fig. 2 Powder XRD patterns of the  $\text{NH}_2$ -MIL-53(Al) support material and corresponding POM/MIL(Al) composite before and after catalysis (ac).

microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Fig. 1 (left side) compares the FT-IR spectra of the solid support with the corresponding composite material before and after catalytic use. The spectrum of POM/MIL(Al) is mainly composed by the typical bands of amino-MIL-53 materials assigned to the terephthalate linkers stretches.<sup>33-35</sup> The spectrum also displays bands arising from the amino moieties including the asymmetric and symmetric stretches of primary amines located at  $3487$  and  $3375\text{ cm}^{-1}$ , respectively (Fig 1 - inset).<sup>27, 30</sup> Unlike the FT-IR spectrum of POM/MIL(Cr) (Fig. S1 in ESI), the presence of the POM is not so clear in the case of POM/MIL(Al). Nevertheless, an additional band ( $1124\text{ cm}^{-1}$ ) can be observed in the spectrum which is assigned to the  $\nu_{\text{as}}(\text{P-O})$  stretching mode of the immobilized heteropolyanion. The

FT-Raman spectrum of POM/MIL(Al) (Fig. 1 – right side) displays the typical bands of the solid support<sup>36</sup> as well as two extra bands ( $986$  and  $970\text{ cm}^{-1}$ ) associated to the  $\nu_{\text{as}}(\text{W=O})$  stretching modes of the POM. Elemental analysis also confirm the presence of the POMs in the composite materials showing a POM loading of  $0.0043$  and  $0.018\text{ mmol/g}$  of POM/MIL(Al) and POM/MIL(Cr), respectively.

The powder XRD patterns of the solid supports MOFs and the respective POM-containing composites are shown at Fig. 2. The XRD pattern of the POM/MIL(Al) composite is mainly composed by the diffraction peaks of the amino-MIL-53(Al) MOF. The location and intensity of the peaks in the obtained XRD patterns is consistent with the data previously reported for the amino-MIL-53(Al).<sup>33, 35, 37</sup> Similarly, the POM/MIL(Cr) pattern is composed by the typical diffraction peaks of the solid support and is consistent with the reported data for POMs incorporated in MIL-101(Cr).<sup>19, 31</sup> The high resemblance observed between the patterns of the two composites before and after the immobilization of the POM suggests that the crystalline structure of both MOFs is retained in the respective final composite material. The isolated POM and the composite materials were studied by solid-state  $^{31}\text{P}$  MAS NMR spectroscopy (Fig. S3 in ESI). The spectrum of POM/MIL(Al) exhibits a broader and upfield shift when compared with the  $^{31}\text{P}$  signal of the POM. Such a result is in good agreement with previously reported data for immobilized POMs in amino-functionalized MILs due to the strong POM-MOF interaction.<sup>38</sup> On the other hand, the immobilization of the POM in the non-functionalized MIL-101(Cr) framework only leads to a slightly shifted  $^{31}\text{P}$  signal as previously described.<sup>32</sup>

The morphology and chemical composition of the POM/MIL(Al) composite were evaluated using SEM/EDS techniques (Fig. 3 and Fig. S4 in ESI). The SEM studies show that the POM/MIL(Al) exhibits the typical morphology of the amino-MIL-53(Al)<sup>33</sup> composed by

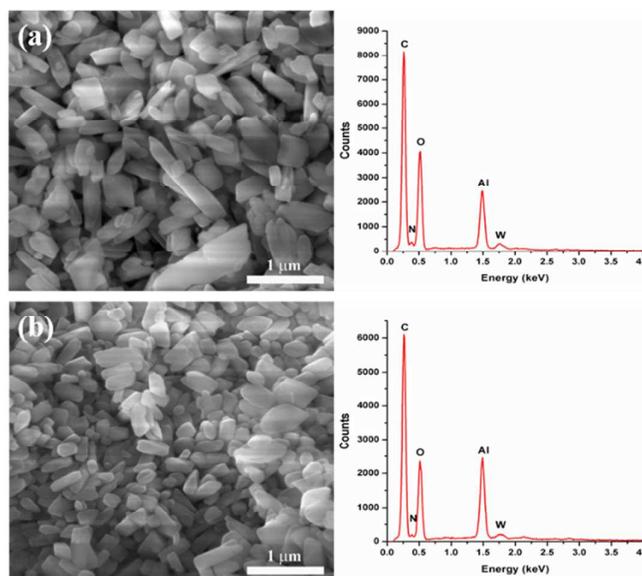


Fig. 3. SEM images and EDS spectra of POM/MIL(Al) composite material: (a) as-synthesized and (b) after catalysis.

longer micro-crystals than the characteristic cubic micro-crystals observed for MIL-101(Cr) composites<sup>19, 32</sup>. The morphology of the initial amino-MIL-53(Al) support remains essentially unchanged after the immobilization procedure. The corresponding EDS spectrum of POM/MIL(Al) clearly displays the Al and N elements from the MOF framework as well as W which further confirms the incorporation of the POM in the final composite material.

### 3.2. Oxidative desulfurization (ODS) processes

The ODS processes were carried out using a multicomponent model diesel containing thiophene (T), dibenzothiophene (DBT), 1-benzothiophene (1-BT), 4-methylthiophene (4-MDBT) and 4,6-dimethylthiophene (4,6-DMDBT) in n-octane. The ODS studies were carried out in a biphasic system composed by equal amounts of the model diesel and an immiscible organic solvent (acetonitrile). The comparison of the catalytic performance of both catalysts, POM/MIL(Al) and POM/MIL(Cr), in the desulfurization of the multicomponent model diesel, demonstrate that the best results were achieved using the POM/MIL(Al) composite with only 1.9 ppm of sulfur content present after 2 h of reaction (99.9 % of desulfurization) (Fig. 4). For the same period of time, the POM/MIL(Cr) has removed 82.0 % of sulfur compounds from the model diesel. The catalytic performance of the homogeneous POM was also evaluated in the ODS process for comparison and the results are summarized in Table 1. The results show that the immobilization of the POM in both solid supports has led to an enhancement of the catalytic activity as previously observed for other POM/MOFs catalytic systems in ODS processes.<sup>18, 22</sup>

The individual desulfurization percentage for each compound using the heterogeneous catalysts after the initial extraction stage (10 min) and 2 h of reaction is represented in Fig. 5. For POM/MIL(Al), the desulfurization of the studied refractory sulfur components decreases in the order: T > DBT > 4-MDBT > 4,6-DMDBT > 1-BT as previously reported for ODS systems catalyzed by POMs using H<sub>2</sub>O<sub>2</sub> as oxidant.<sup>5, 15, 18, 20, 22</sup> The higher desulfurization performance of T is related with the higher electron density on the sulfur atom, while 1-BT (least reactive) exhibits the lowest electron density among the studied refractory sulfur compounds.<sup>39</sup> DBT and its derivatives

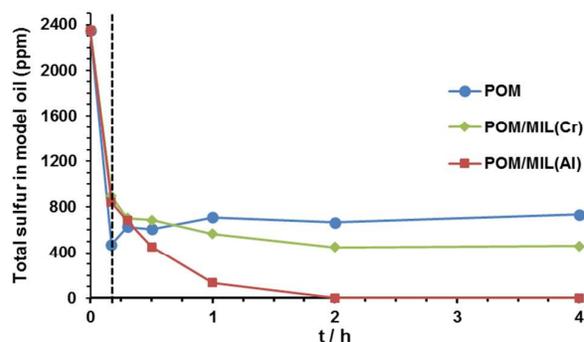


Fig. 4 Desulfurization of the multicomponent model diesel showing the initial extraction stage (before the dashed line) and the catalytic stage (after the dashed line) in the presence of the homogeneous POM and the heterogeneous POM/MIL(Al) and POM/MIL(Cr) catalysts at 70 °C, using acetonitrile as extraction solvent.

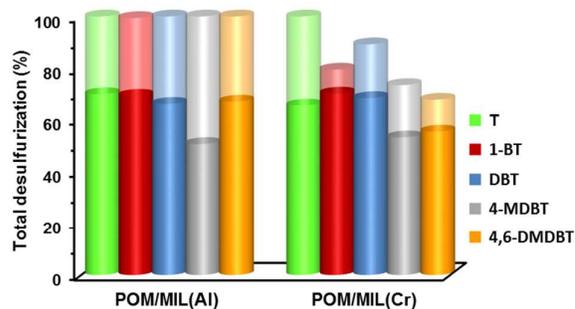


Fig. 5 Percentage of each sulfur compound removed from the model diesel in the presence of the heterogeneous POM/MIL(Al) and POM/MIL(Cr) catalysts after 10 min (darker part) and 2 h (entire bars) of reaction.

exhibit very similar electron density on the sulfur atom (5.758, 5.759 and 5.760 for DBT, 4-MDBT and 4,6-DMDBT, respectively).<sup>40</sup> Therefore, the competitive desulfurization between them is ruled by the steric hindrance of the methyl groups. The presence of methyl groups in position 4 and/or 6 of the DBT ring hinders the interaction of the sulfur atom with the catalytic active species and oxidant.<sup>15, 21, 41</sup> Regarding the ODS system catalyzed by POM/MIL(Cr) composite, the desulfurization efficiency of all studied sulfur compounds is

Table 1. Desulfurization (%) and sulfur content (ppm) in model diesel after 2 h of reaction.

	S in model diesel (ppm) <sup>a</sup>	Desulfurization (%)					TOTAL
		T	1-BT	DBT	4-MDBT	4,6-DMDBT	
POM	662.2	100.0	73.2	72.6	60.8	63.0	73.9
POM/MIL(Cr)	451.9	100.0	79.5	89.3	73.5	67.9	82.0
POM/MIL(Al)	1.9	100.0	99.4	100.0	100.0	100.0	99.9

<sup>a</sup> Initial sulfur content in model diesel: 2348.2 ppm.

lower when compared with the POM/MIL(Al) ODS system. The different desulfurization efficiency observed for both ODS processes is mainly caused by the difference of activity of the heterogeneous catalysts since similar desulfurization percentages were achieved at the end of the initial extraction step (62.5% and 64.7% for POM/MIL(Cr) and POM/MIL(Al), respectively). This different activity may be related with the positions occupied by the POM molecules in each framework. The large windows in the cages of MIL-101(Cr) framework ( $\approx 12$  Å for the pentagonal and  $\approx 14.5 \times 16$  Å for the hexagonal windows)<sup>25</sup> allow the incorporation of very large molecules, including this Keggin-type anion as previously demonstrated.<sup>31</sup> On the other hand, the NH<sub>2</sub>-MIL-53(Al) framework is composed by one-dimensional diamond-shaped channels with significantly narrower free diameters ( $\approx 7.5$  Å).<sup>37</sup> As a result, in the POM/MIL(Al) composite, the POM is more likely to occupy more peripheral positions in the framework, resulting in more frequent substrate/oxidant interactions. The presence of the POM inside the MIL-101(Cr) cavities makes the diffusion of substrate/oxidant necessary which inevitably results in slower catalytic reactions.

The proposed ODS mechanism is well described in the literature for POM-catalyzed desulfurizations using H<sub>2</sub>O<sub>2</sub>.<sup>6, 18, 21, 41, 42</sup> The oxidation mechanism starts with the formation of hydroperoxy- or peroxy-POM active species by nucleophilic attack of the oxidant (H<sub>2</sub>O<sub>2</sub>) on the W<sup>VI</sup> atoms of POMs. These active species can oxidize the sulfur compounds, extracted from the model diesel phase into the polar organic phase, by nucleophilic attack producing the corresponding sulfoxide and regenerating the W<sup>VI</sup>-polyoxometalate species. The subsequent oxidation of the sulfide leads to the formation of sulfone. The oxidation occurring in the polar phase leads to the further extraction of sulfur compounds in the model oil phase in order to keep the extraction process in equilibrium.

The remarkable catalytic performance of POM/MIL(Al) has

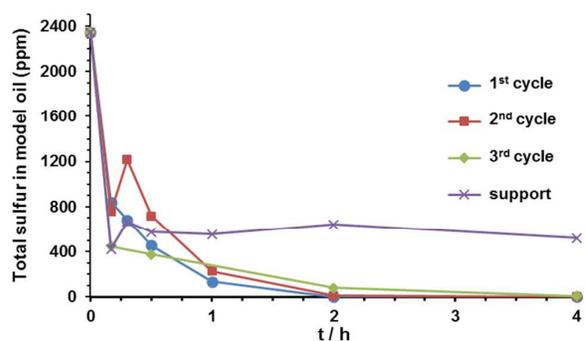


Fig. 6 Desulfurization profile of a multicomponent model diesel for three consecutive ODS cycles using the heterogeneous POM/MIL(Al) catalyst and acetonitrile as extraction solvent at 70 °C.

motivated the evaluation of its recyclability in consecutive ODS cycles. After each ODS cycle, the catalyst was recovered by filtration, washed thoroughly with acetonitrile, dried at room temperature and reused in a new ODS cycle under the same experimental conditions. The desulfurization performance of the model diesel using POM/MIL(Al) for the three consecutive ODS cycles is exhibited in Fig. 6. The isolated solid support, NH<sub>2</sub>-MIL-53(Al), was also evaluated in the ODS process under identical experimental conditions. The results show that the sulfur compound concentration remains constant after the initial extraction step. Indeed, no oxidation of sulfur compounds occurs during the catalytic stage which clearly identifies the POM as the active catalytic species. The high recycling ability of the composite can be observed from the very similar kinetic profiles obtained throughout the cycles. The obtained desulfurization performance data for the three ODS cycles is summarized in Table 2. The overall desulfurization order of the sulfur components in the model diesel remains the same in throughout the ODS cycles. A practically complete desulfurization is achieved after 2 h of reaction in all cycles (desulfurization percentages of 99.9, 99.4

Table 2. Desulfurization (%) and sulfur content (ppm) in model diesel in the presence of the POM/MIL(Al) heterogeneous catalyst for three consecutive ODS cycles.

POM/MIL(Al)	S in model diesel (ppm) <sup>a</sup>	Desulfurization (%)					
		T	1-BT	DBT	4-MDBT	4,6-DMDBT	TOTAL
<b>1<sup>st</sup> cycle</b>							
10 min	841.6	70.0	69.4	66.3	50.5	67.2	64.7
2 h	1.9	100.0	99.4	100.0	100.0	100.0	99.9
<b>2<sup>nd</sup> cycle</b>							
10 min	754.7	54.6	63.8	69.1	59.9	82.6	66.0
2 h	12.1	100.0	98.4	100.0	100.0	98.8	99.4
<b>3<sup>rd</sup> cycle</b>							
10 min	445.4	72.7	75.7	87.1	80.3	82.8	79.7
2 h	80.1	100.0	86.7	99.7	98.6	95.0	96.0

<sup>a</sup> Initial sulfur content in model diesel: 2348.2 ppm.

and 96.0 % for the first, second and third cycle, respectively). The extremely small decrease observed of desulfurization efficiency in the third cycle is probably related with tiny leaching of POM from the composite material. The decrease is more evident for the compounds more difficult to oxidize, namely 1-BT and 4,6-DMDBT with 86.7 and 95.0 % of sulfur removal, respectively, after 2 h of reaction (Table 2).

### 3.3. Catalyst materials stability

The structural robustness and chemical stability of the heterogeneous catalysts was evaluated by several characterization techniques. The catalysts were recovered after an ODS catalytic cycle, POM/MIL(Al)-ac and POM/MIL(Cr)-ac (ac stands for after catalysis), and studied by vibrational spectroscopy (FT-IR and FT-Raman), powder XRD and SEM/EDS.

The vibrational spectroscopy data of the POM/MIL(Al)-ac and POM/MIL(Cr)-ac (Fig. 1 and Fig. S1 in ESI) are similar to the corresponding ones before catalysis. Nevertheless, a small decrease of the bands associated with the POM vibrational modes is observed probably due to the occurrence of some leaching. The XRD patterns of the recycled composites exhibit identical profiles with the corresponding ones before catalysis (Fig. 2 and Fig. S2 in ESI). The patterns are composed by the main diffraction peaks of the solid supports, NH<sub>2</sub>-MIL-53(Al) and MIL-101(Cr), which remain unaltered regarding its position and relative intensity. Such an evidence points out to the preservation of the framework resisting to the collapse or degradation during the ODS catalytic cycle. The integrity of the composites after catalytic use was further confirmed by SEM/EDS (Fig. 3 and Fig. S4 in ESI). No significant morphologic changes are observed in the composites after catalytic use. The EDS spectra of both composites before and after catalysis (Fig. 3 and Fig. S4 in ESI) exhibit very similar profiles. The quantification of the aluminum and tungsten elements has led to a W/Al (wt%) ratio of 0.57 and 0.41 before and after catalysis, respectively. This small decrease is probably related with the slightly lower desulfurization efficiency observed in the ODS recycling tests.

## 4. Concluding remarks

In the present work, the sandwich-type [Eu(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>11-</sup> anion was immobilized in two different porous MIL-type materials, MIL-101(Cr) and NH<sub>2</sub>-MIL-53(Al), through a simple impregnation procedure. The resulting composites, POM/MIL(Cr) and POM/MIL(Al), were characterized by vibrational spectroscopy, powder XRD, elemental analyses, SEM and EDS indicating the immobilization of the POM in the MIL-frameworks and confirming the structural integrity of the MOFs in the final composite materials. The composites were evaluated as heterogeneous catalysts in the oxidative desulfurization of a multicomponent model diesel composed

by the most refractory sulfur compounds in diesel. The immobilization of the POM in both supports has led to a significant enhancement of the catalytic activity. In particular, the POM/MIL(Al) composite has proved to be a very efficient catalyst for ODS processes with the complete desulfurization of the model oil obtained after only 2 h of reaction, also confirming unequivocally the influence of the MOF support material in the catalytic performance of the composite materials. Moreover, the high recycling ability of POM/MIL(Al) was shown by the similar desulfurization profiles obtained in three consecutive ODS. The individual desulfurization performance of the model diesel components follows the general trend for POM-catalyzed ODS systems using H<sub>2</sub>O<sub>2</sub> as the oxidant. The integrity, stability and robustness of the composites after catalytic utilization was confirmed by several characterization techniques. Following the promising results obtained in this work, other POM/MOFs composites will be prepared and the influence of the MOF support in the desulfurization performance of ODS processes will be evaluated.

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