Efficient oxidation of thiophene derivatives with homogeneous and heterogeneous MTO/H_2O_2 systems: A novel approach for, oxidative desulfurization (ODS) of diesel fuel

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ABSTRACT

The oxidation of benzothiophene (BTs) and dibenzothiophene (DBTs) derivatives, of model fuel (MF) and authentic diesel fuel (ADF) with homogeneous and heterogeneous rhenium catalysts and H_2O_2 has been studied to design an alternative environmentally benign oxidative desulfurization process (ODS), for oil industry. The quantitative conversion of both BTs and DBTs derivatives was obtained in several of the cases investigated, to afford the corresponding sulfones as the only recovered products in very high yield. Excellent results in terms of both conversion of substrates and yields of sulfones were also obtained during oxidation of MF and ADF. Heterogeneous rhenium catalysts were stable systems to be used for several runs without any appreciable reduction of reactivity and selectivity.

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1. Introduction

Organosulfur compounds in fuel oils are known to have a negative impact onto the environment because of SO_x emissions from their combustion exhausts [1]. As a consequence, removal of sulfur (S) is becoming a worldwide challenge, also due to more and more stringent regulations [2]. Hydrodesulfurization (HDS) is the process most widely used in refineries to remove thiols, sulfides and disulfides from crude fuel oils [3]. However, this process achieves only limited performances, being not able to get ultra low sulfur levels, because of the presence of refractory S-containing aromatic compounds [4]. These compounds are predominantly alkyl-substituted benzothiophenes (BTs) and dibenzothiophenes (DBTs). In particular, 4,6-dimethyldibenzothiophene (DMDBT) is the most resistant substrate towards HDS, due to the hindered nature of the sulfur atom, that makes the approach to the catalyst surface difficult [5]. For this reason removal of BTs and DBTs by the

HDS technology requires highly energy-demanding conditions. As an alternative to the other desulfurization processes, oxidative desulfurization (ODS) is considered the most promising technology [6]. In this case, organosulfur compounds are oxidized to the corresponding sulfoxides and sulfones, which are successively removed by extraction with polar solvents. To date, a series of oxidants have been used in the ODS processes, such as nitric acid (HNO_3), t-butyl-hydroperoxide (TBHP) [7a], superoxides [7b], peracids [8], and ozone [9]. Among the stoichiometric reagents, hydrogen peroxide (H_2O_2) is preferentially chosen as primary oxidant [4,5,10] due to its environmental benign properties. Activation of H_2O_2, however, invariably requires the presence of an efficient catalyst. In the last years, methyltrioxorhenium (CH_3ReO_3, MTO) [11] showed interesting catalytic properties being H_2O_2 the oxygen atom donor [12]. In these reactions the active catalytic forms are monoperoxorhenium [$MeRe(O)_2(O_2)$] and bisperoxorhenium [$MeRe(O)(O_2)_2$] complexes and/or their adducts with solvent molecules [13]. In this context, oxidation of sulfides [14], disulfides [15], and sulfoxides [16] to corresponding sulfones has been studied, using MTO and H_2O_2 or urea-hydrogen peroxide adduct (UHP) under homogeneous conditions [17]. Despite of these efforts, the oxidation of thiophenes has received only a low attention. In 1996, *Espenson* reported that the MTO/H_2O_2 system

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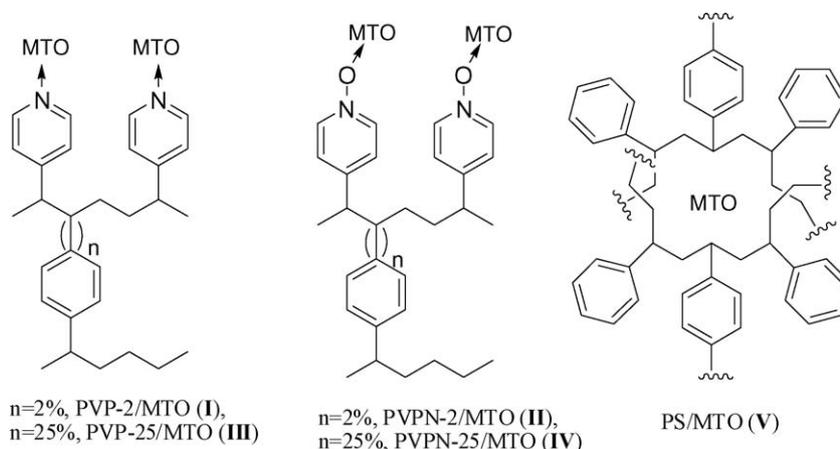saladino@unitus.it (R. Saladino).

**Fig. 1.** Sketches of heterogeneous rhenium catalysts based on MTO.

can be used for the oxidation of thiophenes to sulfones in water-acetonitrile mixture, by way of their sulfoxide intermediates [18]. The rate constant for the oxidation of thiophenes was smaller than those of aliphatic sulfides. Moreover, the rate constant for the conversion of sulfide to sulfoxide increased in the presence of electron-donating substituents, whereas the opposite trend was found for the oxidation of sulfoxide to sulfone. To the best of our knowledge, to date no data are reported on the oxidation of thiophene derivatives with MTO under heterogeneous conditions. The use of heterogeneous catalysts in the ODS process is of particular relevance under the environmental point of view, because it reduces the leaching of metal in the waste and can favour the recovery and reuse of the catalyst itself for successive transformations. Recently, heterogeneous rhenium catalysts based on the anchorage of MTO on commercially available and low cost resins, such as poly(4-vinylpyridine) (PVP) and poly(4-vinylpyridine)-N-oxide (PVPN) [2% or 25% cross-linked with divinylbenzene (PVP-2/MTO **I**, PVPN-2/MTO **II**, PVP-25/MTO **III** and PVPN-25/MTO **IV**, respectively; Fig. 1)], or by physical microencapsulation of MTO on polystyrene (2% cross-linked with divinylbenzene, PS/MTO **V**, Fig. 1), have been prepared. These catalysts are efficient and selective systems in a large variety of oxidative reactions, maintaining their stability for successive recycling experiments

[19,20]. We report here on the efficient and selective oxidation of BTs and DBTs derivatives with homogeneous and heterogeneous MTO catalysts and H_2O_2 in dichloromethane, n-octane and in a complex model of fuel oil (MF). Treatment of an authentic sample of diesel fuel (ADF), under optimized experimental conditions, will be also reported (see Scheme 1).

2. Experimental

2.1. Materials and equipments

Methyltrioxorhenium, H_2O_2 (35% aqueous solution), PVP 2% or 25% cross-linked with divinylbenzene, polystyrene (PS) 2% cross-linked with divinylbenzene and the thiophene derivatives as 2-methylbenzothiophene **1** (2MeBT), 3-methylbenzothiophene **2** (3MeBT), dibenzothiophene **3** (DBT), 4,6-dimethyldibenzothiophene **4** (DMDBT), and 4,6-diethyldibenzothiophene **5** (DEDBT) were obtained from a commercial source (Aldrich). All commercial products and solvents such as dichloromethane, n-octane, N,N-dimethylformamide (DMF), n-hexadecane, were of the highest grade available and were used without further purification. 4-Methyl-6-isobutyldibenzothiophene **6** (MiBuDBT) and 4,6-diisobutyldibenzothiophene **7** (DiBuDBT) were prepared according to a
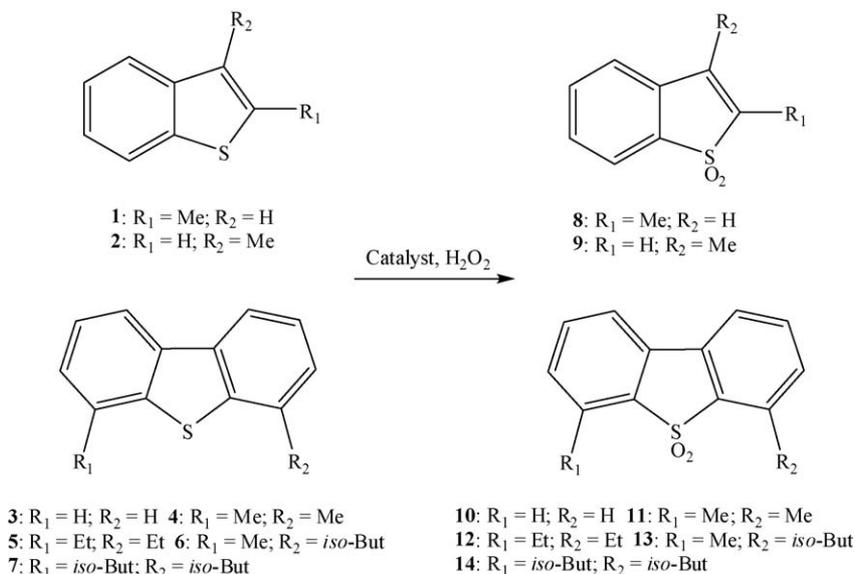
Scheme 1.

modified published procedure [21]. ADF sample was obtained from a commercial italian source, having a density of 0.713 g/mL, 0.34% w/w of total sulfur, 73 ppm of total nitrogen (N), and 18% w/w of total aromatic fractions. A sample of this diesel was added with equimolar amounts of BTs **1–2** and DBTs **3–7** and directly used in the ODS experiments. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 MHz spectrometer. The reaction mixtures were analyzed by a Hewlett Packard 6890 series gas chromatograph equipped with a FID, using a 30 m × 0.32 mm × 0.25 μm film thickness (cross-linked 5% phenylmethylsiloxane) column, and helium as carrier gas. The identification of the peaks by gas-chromatography mass-spectrometry (GC–MS) has been performed by means of a Varian 2000 GC–MS instrument, using the same column. Yields and conversions have been quantified using n-hexadecane as internal standard or, when necessary, after flash-chromatographic purification (silica gel, 230–400 mesh). Product yields are calculated on the basis of substrate conversion. They may be termed, in the strict sense, as selectivities in the main reaction product. Reaction products were characterized by comparison of their NMR and MS spectra with authentic samples.

2.2. Preparation of supported catalysts I–V

The preparation of PVPN resins and of supported catalysts has been performed as previously reported [22]. Briefly, MTO (256 mg, 1.0 mmol) was added to a suspension of the appropriate resin (0.2 g, loading factor (LF) = 5.0, defined as mmol of MTO per gram of resin) in ethanol (4.0 mL for PVP or PVPN resins) or, respectively, in THF (4.0 mL for PS resin). The mixture was kept under stirring for 1 h (12 h for PS resin). The solvent was removed by filtration, and the catalyst washed with ethyl acetate and finally dried under high vacuum. In each case, MTO showed to be completely bound to the polymer, as confirmed by spectroscopic and atomic absorptions analyses of the residues obtained after evaporation of the organic layers. The catalysts were used without any further purification.

2.3. Preparation of model fuel sample

A sample of MF was prepared by adding equimolar amounts (in the range of 0.01–0.03 mmol) of each substrate **1–7** into n-octane (from 1.5 to 2.0 mL), in order to obtain a total sulfur concentration of 2.8 mg/mL, that is indicative of a real sample. The solution was then submitted to the homogeneous and heterogeneous catalytic oxidative conditions, as described below.

2.4. Preparation of synthetic diesel fuel (SDF) sample

1.5 mL of ADF sample was added with equimolar amounts (0.02 mmol) of each substrate **1–7**, in order to evaluate more precisely the ODS reactivity of BTs and DBTs, to gain a total sulfur concentration of 3.8 mg/mL. The SDF sample was then submitted to the homogeneous and heterogeneous catalytic oxidative conditions, as described below.

2.5. Oxidative desulfurization under homogeneous conditions. General procedure

To a solution of substrate (0.1 mmol), MF or SDF samples (see above for the molar composition of MF or SDF mixtures) and n-hexadecane as internal standard (5 μL) in 1.5 mL of the appropriate solvent (Table 1), MTO (5% w/w with respect to substrate, unless otherwise specified) and H_2O_2 (2.5 equiv.; 5.0 equiv. in the case of SDF), were added under stirring. The solution was allowed to react at the appropriate temperature and for the selected reaction time (see Tables 1, 2 and 5 and Fig. 2). The reaction progress was regularly monitored by GC–MS analyses of

Table 1
Oxidation of thiophene derivatives 1–7 with MTO/H_2O_2, at r.t., under homogeneous conditions[a].

Entry	Substrate	Solvent	Time (h)	Conversion (%)	Product (yield, %)[b]
1	**1**	CH_2Cl_2	5	>99	**8** (>99)
2	**2**	CH_2Cl_2	6	>99	**9** (>99)
3	**3**	CH_2Cl_2	4	>99	**10** (>99)
4	**4**	CH_2Cl_2	4	>99	**11** (>99)
5	**5**	CH_2Cl_2	3	>99	**12** (>99)
6	**6**	CH_2Cl_2	3	>99	**13** (>99)
7	**7**	CH_2Cl_2	3	>99	**14** (>99)
8	**1**	n-Octane	5	>99	**8** (>99)
9	**2**	n-Octane	5	>99	**9** (>99)
10	**3**	n-Octane	3	>99	**10** (>99)
11	**4**	n-Octane	3	>99	**11** (>99)
12	**5**	n-Octane	2	>99	**12** (>99)
13	**6**	n-Octane	2	>99	**13** (>99)
14	**7**	n-Octane	2	>99	**14** (>99)

[a] MTO (5% w/w), 2.5 equiv. of H_2O_2.
[b] Yields are calculated on the substrate, conversion.

Table 2
Oxidation of thiophene derivatives 1–7 with MTO/H_2O_2, at 50 and 70 °C, under homogeneous conditions[a].

Entry	Substrate	Time (h)	Temp. (°C)	Conversion (%)	Product (yield, %)[c]
1	**1**	5[b]	50	>99	**8** (>99)
2	**2**	5[b]	50	>99	**9** (>99)
3	**3**	3[b]	50	>99	**10** (>99)
4	**4**	2	50	>99	**11** (>99)
5	**5**	1	50	>99	**12** (>99)
6	**6**	1	50	>99	**13** (>99)
7	**7**	1	50	>99	**14** (>99)
8	**1**	4	70	>99	**8** (>99)
9	**2**	4	70	>99	**9** (>99)
10	**3**	2	70	>99	**10** (>99)
11	**4**	1	70	>99	**11** (>99)
12	**5**	0.5	70	>99	**12** (>99)
13	**6**	0.5	70	>99	**13** (>99)
14	**7**	0.5	70	>99	**14** (>99)

[a] MTO (5% w/w), 2.5 equiv. of H_2O_2, n-octane.
[b] Time values are, approximated by excess (the exact values being 4.7, 4.5 and 2.75 h, for entries 1–3, respectively).
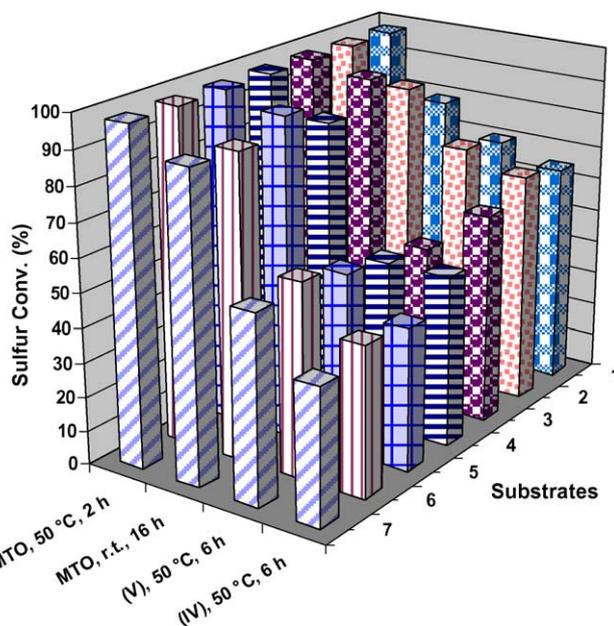[c] Yields are calculated on substrate conversion.

Fig. 2. Oxidation of a DF sample, by homogeneous and heterogeneous catalysis. Conditions: MTO (5% w/w), IV or V (5% w/w of MTO, LF = 5.0); 5.0 equiv. of H_2O_2; 1.5 mL of a DF, sample having a total S concentration of 3.8 mg/mL. Catalysts and H_2O_2 ratios are referred to overall S content of DF sample.

periodically withdrawn samples (1 μL samples were taken out the reaction solution), until the substrate was entirely consumed. As the reaction was over, a small amount of MnO_2 (2.0 mg) was added, at r.t., to eliminate the excess of oxidant (the reaction mixture was found to be unchanged after the MnO_2 treatment). After each experiment, excepts when dichloromethane was used as the reaction solvent, the sulfone was recovered from the reaction medium by extraction with DMF (1.5 mL). When dichloromethane was used, the sulfone was recovered after filtration and solvent evaporation. The organic layers were analyzed by GC–MS.

2.6. Oxidative desulfurization under heterogeneous conditions. General procedure

To a solution of substrate (0.1 mmol), MF or SDF samples (see above for the molar composition of MF or SDF mixtures) and *n*-hexadecane (5 μL) in *n*-octane (1.5 mL), the appropriate heterogeneous catalyst (5% w/w of MTO with respect to substrate; $LF = 5.0$) and H_2O_2 (4.0 equiv., added in two steps to reduce thermal decomposition [23]; 8.0 equiv. in the case of SDF) were added under stirring. The solution was heated at 70 °C (max. 50 °C, for SDF) and allowed to react for the selected time (see Tables 3–5 and Fig. 2). The reaction progress was regularly monitored by GC–MS analyses of periodically withdrawn samples (1 μL samples were taken out the reaction solution), until the substrate was entirely consumed. After filtration for the recovery of catalyst a little amount of MnO_2 (2.0 mg) was added, at r.t., to eliminate the excess of oxidant (the reaction mixture was found to be unchanged after the MnO_2 treatment). Then 1.5 mL of DMF were added to the mixture, in order to recover the sulfone (insoluble in *n*-octane and soluble in the SDF sample). The biphasic mixture was stirred for 30 min, filtered and, after separation, each organic layers was analyzed by GC–MS. In the case of the SDF sample, the GC–MS analysis of extracting DMF solvent phase, showed no presence of any precious hydrocarbon fraction initially present in the original sample, before the ODS treatment.

When necessary, the sulfones were quantitatively recovered after evaporation of DMF.

2.7. Catalyst recycling experiments

After the first run, the catalyst was recovered by filtration, washed with *n*-hexane and acetone and dried under vacuum for 1 h. More runs were then performed, working under optimized experimental conditions.

Table 3
Oxidation of thiophene derivatives 1–7 with supported MTO catalysts **I** and **II**[a].

Entry	Substrate	Catalyst	Conversion (%)	Product (yield, %)[b]
1	**1**	PVP-2/MTO, **I**	64	**8** (>99)
2	**2**	PVP-2/MTO, **I**	59	**9** (>99)
3	**3**	PVP-2/MTO, **I**	51	**10** (>99)
4	**4**	PVP-2/MTO, **I**	54	**11** (>99)
5	**5**	PVP-2/MTO, **I**	32	**12** (>99)
6	**6**	PVP-2/MTO, **I**	13	**13** (>99)
7	**7**	PVP-2/MTO, **I**	15	**14** (>99)
8	**1**	PVPN-2/MTO, **II**	68	**8** (>99)
9	**2**	PVPN-2/MTO, **II**	86	**9** (>99)
10	**3**	PVPN-2/MTO, **II**	60	**10** (>99)
11	**4**	PVPN-2/MTO, **II**	76	**11** (>99)
12	**5**	PVPN-2/MTO, **II**	70	**12** (>99)
13	**6**	PVPN-2/MTO, **II**	65	**13** (>99)
14	**7**	PVPN-2/MTO, **II**	72	**14** (>99)

[a] Catalysts **I** or **II** (5% w/w of MTO, $LF = 5.0$), 4.0 equiv. of H_2O_2, *n*-octane, 70 °C, 24 h.
[b] Yields are calculated on substrate conversion.

Table 4
Oxidation of thiophene derivatives 1–7 with supported MTO catalysts **III–V**[a].

Entry	Substrate	Catalyst	Conversion (%)	time (h)	Product (yield, %)[b]
1	**1**	PVP-25/MTO, **III**	>99	24	**8** (>99)
2	**2**	PVP-25/MTO, **III**	>99	24	**9** (>99)
3	**3**	PVP-25/MTO, **III**	>99	24	**10** (>99)
4	**4**	PVP-25/MTO, **III**	80	24	**11** (>99)
5	**5**	PVP-25/MTO, **III**	55	24	**12** (>99)
6	**6**	PVP-25/MTO, **III**	50	24	**13** (>99)
7	**7**	PVP-25/MTO, **III**	45	24	**14** (>99)
8	**1**	PVPN-25/MTO, **IV**	>99	10	**8** (>99)
9	**2**	PVPN-25/MTO, **IV**	>99	10	**9** (>99)
10	**3**	PVPN-25/MTO, **IV**	>99	4	**10** (>99)
11	**4**	PVPN-25/MTO, **IV**	>99	4	**11** (>99)
12	**5**	PVPN-25/MTO, **IV**	>99	4	**12** (>99)
13	**6**	PVPN-25/MTO, **IV**	>99	4	**13** (>99)
14	**7**	PVPN-25/MTO, **IV**	>99	4	**14** (>99)
15	**1**	PS/MTO, **V**	>99	5	**8** (>99)
16	**2**	PS/MTO, **V**	>99	5	**9** (>99)
17	**3**	PS/MTO, **V**	>99	4	**10** (>99)
18	**4**	PS/MTO, **V**	>99	2	**11** (>99)
19	**5**	PS/MTO, **V**	>99	2	**12** (>99)
20	**6**	PS/MTO, **V**	>99	1	**13** (>99)
21	**7**	PS/MTO, **V**	>99	1	**14** (>99)

[a] Catalysts **III–V** (5% w/w of MTO, $LF = 5.0$), 4.0 equiv. of H_2O_2, *n*-octane, 70 °C.
[b] Yields are calculated on substrate conversion.

Table 5
Oxidation of model fuel oil by homogeneous and heterogeneous MTO catalysts[a].

Entry	Substrates	Catalyst	Conversion (%)	Time (h)	Products (yield, %)[b]
1	**1-7**	MTO	>99	1	**8-14** (>99)
2	**1-7**	PVPN-25/MTO, **IV**	>99	2	**8-14** (>99)
3	**1-7**	PS/MTO, **V**	>99	2	**8-14** (>99)

[a] Catalysts: MTO (5% w/w), **IV** or **V** (5% w/w of MTO, $LF = 5.0$); 2.5 equiv. of H_2O_2 (4.0 equiv. for entries 2–3, added in two steps); 1.5 mL of MF having a total S concentration of 2.8 mg/mL; 70 °C. Catalysts and H_2O_2 ratios are referred to the total S content.
[b] Yields are calculated on the substrate conversion.

3. Results and discussion

3.1. Oxidation under homogeneous conditions

The oxidation of a series of thiophene derivatives, namely 2MeBT, 3MeBT, DBT DMDBT, DEDBT, MiBuDBT and DiBuDBT, was performed under homogeneous conditions (5% w/w of MTO with respect to the substrate) in two selected reaction solvents, dichloromethane (CH_2Cl_2) and *n*-octane, with a small excess of H_2O_2 (2.5 equiv., 35% aqueous solution) at r.t. The results of the oxidation reactions are showed in Scheme 1 and in Table 1. Irrespective of the substrate, the thiophene derivatives were oxidized to the corresponding sulfones **8–14**, with quantitative conversion and yields in CH_2Cl_2 after 3–6 h (Table 1, entries 1–7). No traces of sulfoxide derivatives were detected in the reaction mixtures by GC–MS analyses. In the absence of the catalyst, conversion of substrate lower than 3% was observed. In accordance with the general order of reactivity reported for thiophenes during ODS process [10b,10c], DBTs **3–7** showed to be more reactive than BTs **1–2** (Table 1, entries 3–7 versus 1–2). The oxidation of thiophene derivatives **2–7** was more efficient in *n*-octane than in CH_2Cl_2 (see, for example, Table 1, entry 4 versus 11). An exception was observed in the case of 2MeBT **1**, which showed similar reactivity in both solvents (Table 1, entry 1 versus 8).

In order to evaluate the role of the temperature on the reaction efficiency, the oxidation of **1–7** was also performed in *n*-octane at 50 and 70 °C. As shown in Table 2, the reactivity of the MTO/H_2O_2

system increased by increasing the reaction temperature, to afford the quantitative conversion of DBTs **5–7** in only 0.5 h at 70 °C (Table 2 entries 12–14). This effect was also observed in the case of BTs **1–2**, the sulfones **8–9** being quantitatively obtained after 4 h (Table 2, entries 8–9). These results are in agreement with data reported in literature [24]. Moreover, no relevant differences in terms of reactivity were observed in the case of BTs **1–2** and DBT **3**, by increasing the temperature from r.t. to 50 °C, having observed, at 50 °C, only a very slight decrease of the reaction times required for the quantitative oxidation of substrates (compare Table 1, entries 8–10 with Table 2, entries 1–3).

It is worth to note that, in the case of **3–7**, the presence of alkyl substituents on the 4- and 6-positions of the aromatic ring increases the reactivity, probably due to inductive releasing effects. Indeed, with the increase of electron density on sulfur atom, as it occurs in substrates **3–7** with respect to **1–2**, an increase of the reactivity toward sulfur oxidation is observed [25]. On the other hand, the substituents steric effects were absolutely not relevant under our experimental conditions. This is of particular interest, since the previously reported catalytic systems for ODS process, containing vanadium or tungsten metals, showed to be sensible to steric effects [10a,23].

3.2. Oxidation under heterogeneous conditions

Next, we evaluated the efficacy of the methyltrioxorhenium based heterogeneous catalysts as PVP-2/MTO **I**, PVPN-2/MTO **II**, PVP-25/MTO **III**, PVPN-25/MTO **IV** and PS/MTO **V** [22]. The structures of catalysts **I–V** are reported in Fig. 1.

Treatment of compounds **1–7** with catalysts **I–II** and H$_2$O$_2$ in n-octane at 70 °C afforded sulfones **8–9** in quantitative yields and acceptable substrate conversion (Table 3). It is worth to note that, differently from what observed during the oxidation under homogeneous conditions, BTs **1–2** were oxidized with comparable efficiency as DBTs **3–4**, with the same reaction times (Table 3, entries 1 and 2 versus 3 and 4). Moreover, in the oxidation of **5–7** with catalyst **I**, the presence of alkyl substituents on the aromatic ring significantly reduces their reactivity, probably due to the major relevance of the steric hindrance of the substrate during the approach to the catalytic site. A different behaviour was observed with catalyst **II**, where high conversions of **5–7** have been observed (Table 3, entries 8–14 versus 1–7).

The role of the support on the oxidation of **1–7** was then evaluated by the study of the efficiency of catalysts **III** and **IV**, which are characterized by the highest value of the reticulation grade.

As a general observation, **III** and **IV** were more efficient than **I** and **II** (compare data of Table 4 with those of Table 3), catalyst **IV** being the most reactive systems to give sulfones 8–14 in quantitative conversion and yields (Table 4, entries **8–14**). Again, in the oxidation of DBTs **5–7** with **III**, the presence of substituents on the aromatic ring decreases the substrate reactivity. These data suggest that the reactivity of sterically hindered thiophenes can be controlled by the oxidation state of the support, that is poly(4-vinylpyridine) versus poly(4-vinylpyridine N-oxide). This effect may be in part ascribed to the different structure of the active site in these two families of catalysts. In fact, in the case of **I** and **III**, X-ray diffraction analysis showed that coordination of the rhenium atom occurs at the two nitrogen atoms of neighbouring pyridine rings, to form an octahedral complex with high steric hindrance at the metal site which interferes with the substrate approach [22a]. As to the role of the reticulation grade of the support, as well as that of the oxidation state of the pyridine moieties on the intrinsic reactivity and selectivity of the heterogeneous MTO catalysts, they have been previously discussed in detail for the oxidation of alkanes, alkenes and phenol derivatives [22,26]. Finally, the

microencapsulated catalyst **V** revealed to be the most reactive system to give sulfones **8–14** in quantitative conversion and yields, with reaction times that are relatively short for an heterogeneous process (Table 4, entries 15–21). Note that the chemoselectivity of **V** was similar to that of MTO. Indeed, **V** was not affected at all by the steric hindrance of the substrates, as confirmed by the high conversion observed for DBTs 5–7.

3.3. Oxidative desulfurization of model fuel

The efficacy of catalysts MTO, **I–IV** and **V** for the ODS process was further investigated by the study of a more complex system closely reproducing the authentic fuel oil, named model fuel oil. The MF was prepared by adding equimolar amounts of **1–7** to n-octane, to gain an overall sulfur content of 2.8 mg/mL, which is typical of a real fuel sample [5,23,27]. The MF was oxidized with a slight molar excess of H$_2$O$_2$, at 70 °C in the presence either of MTO or of the selected catalysts **IV** and **V**. The conversion of thiophene derivatives in the mixture and the yields of produced sulfones was evaluated for each component by GC–MS analysis (the oxidation test was repeated three times). The average reaction times and overall conversions are reported in Table 5. The oxidation of MF with MTO proceeded with high efficiency, to give quantitative conversions of **1–7** and quantitative yields of the sulfones **8–14**, in only 1 h of reaction time. Similar results were obtained with catalysts **IV** and **V** (Table 5, entries 2–3 versus 1). It is worth to note that compounds **1–7** were oxidized at a faster rate in MF than as isolated substrates (compare data on Table 5 with those in Tables 3 and 4). Probably, once they are present as a mixture, synergic effects or autocatalysis could be operative, to facilitate the substrates oxidation.

Catalysts **IV** and **V** showed to be stable systems under the experimental conditions used in the oxidation of MF (Table 6). Very remarkable appeared the stability of catalyst **IV**, which was recovered and recycled five times (run no. 6) without any appreciable loss in reactivity and selectivity (Table 6, entry 1). Anyway, a slight decrease of the reactivity, after the third recycling step (run no. 4), was observed with **V** (Table 6, entry 2).

3.4. Oxidative desulfurization of SDF

Encouraged by the results obtained in the oxidation of MF, we also studied the desulfurization of SDF containing BTs **1–2** and DBTs **3–7** (to gain 3.8 mg/mL of total sulfur content). Homogeneous MTO and catalysts **IV** and **V**, under the previously optimized experimental conditions, have been used. Again, the conversion of compounds **1–7** and the yield of the formed sulfones were evaluated by GC–MS (the oxidation reaction was repeated three times). The average reaction times and overall conversions are reported in Fig. 2. Initially, SDF was oxidized with an excess of H$_2$O$_2$ (5.0 equiv.) and MTO (5.0% w/w with respect to total amount of sulfur) at r.t. After 16 h, compounds **1–7** were converted to the corresponding sulfones **8–14** as the only recovered products, with values of conversion ranging from 79% to 95%. As expected, the reactivity of the system increased by increasing the temperature; noteworthy, a quantitative conversion of substrates **1–7** and quantitative yields of sulfones **8–14** were obtained at 50 °C, after only 2 h of reaction times (Fig. 2). Temperatures higher than 50 °C were not investigated since the oxidation of SDF performed at temperatures higher than 70–80 °C is characterized by the appearance of decomposition products [3]. Oxidations with heterogeneous catalysts **IV** and **V** were performed under similar experimental conditions. In these cases, **1–7** were converted in acceptable yields, BTs **1–2** being the most reactive substrates. Oxidation was selective, and **8–14** were the only recovered products beside the residual substrate (Fig. 2). This trend of

Table 6
Stability of catalysts **IV** and **V** in the oxidation of MF[a].

Entry	Catalyst	Conversion (%)[b]					
		Run no. 1	Run no. 2	Run no. 3	Run no. 4	Run no. 5	Run no. 6
1	PVPN25/MTO, **IV**	**1** >99 (>99)	>99 (>99)	>99 (>99)	>99 (>99)	94 (>99)	92 (>99)
		2 >99 (>99)	>99 (>99)	>99 (>99)	>99 (>99)	91 (>99)	89 (>99)
		3 >99 (>99)	>99 (>99)	>99 (>99)	>99 (>99)	98 (>99)	98 (>99)
		4 >99 (>99)	>99 (>99)	>99 (>99)	>99 (>99)	98 (>99)	98 (>99)
		5 >99 (>99)	>99 (>99)	>99 (>99)	>99 (>99)	98 (>99)	98 (>99)
		6 >99 (>99)	>99 (>99)	>99 (>99)	>99 (>99)	98 (>99)	98 (>99)
		7 >99 (>99)	>99 (>99)	>99 (>99)	>99 (>99)	98 (>99)	98 (>99)
2	PS/MTO, **V**	**1** >99 (>99)	>99 (>99)	92 (>99)	63 (>99)		
		2 >99 (>99)	>99 (>99)	82 (>99)	60 (>99)		
		3 >99 (>99)	>99 (>99)	>99 (>99)	75 (>99)		
		4 >99 (>99)	>99 (>99)	>99 (>99)	78 (>99)		
		5 >99 (>99)	>99 (>99)	>99 (>99)	74 (>99)		
		6 >99 (>99)	>99 (>99)	>99 (>99)	76 (>99)		
		7 >99 (>99)	>99 (>99)	>99 (>99)	79 (>99)		

[a] After the first reaction, catalyst was recovered by filtration; following runs were performed working under the same experimental conditions
[b] Yields of sulfones **8–14** (calculated on the substrate conversion) are given in parentheses.

reactivity is comparable to that previously observed in the comparative ODS study of a model mixture of thiophene, BT and DBT, under heterogeneous conditions, with different catalytic species [28].

Note that **IV** and **V** showed a lower reactivity in the oxidation of **1–7** in SDF than in MF, probably because of the occurrence of detrimental side-reactions due to the presence of complex mixture of organic components in the authentic sample. To prove this hypothesis, a filtered sample of SDF deriving from a previous ODS experiment was treated with a fresh amount of catalysts **IV** or **V**. Under these experimental conditions, quantitative conversion (>99%) of **1–7** was obtained, after only 4 h of reaction time. The ODS process discussed here does not introduce at the GC–MS analysis any significant change neither in the distribution nor in the intensity of paraffinic hydrocarbon peaks in comparison with the original sample, thus indicating that the latter compounds were not exposed to any negative effect.

4. Conclusions

Homogeneous and heterogeneous rhenium catalysts based on MTO are efficient systems for the activation of H_2O_2 in the ODS process at moderate temperatures. The quantitative conversion of both benzothiophene and dibenzothiophene derivatives was obtained in several of the studied cases, to afford the corresponding sulfones as the only recovered products in very high yields. In the case of MF synergic effects were observed, as confirmed by the higher efficiency in the oxidation of thiophene derivatives when they are present as a mixture rather than as a single substrate. Heterogeneous catalysts revealed to be stable systems, and underwent more runs without any appreciable reduction of reactivity and selectivity. The oxidation of thiophene derivatives in DF with MTO proceeded with high value of conversion and yields. Instead, a lower reactivity was observed with the heterogeneous catalysts IV and V, probably because of the occurrence of detrimental side-reactions. This drawback can be overcome by a sequential two steps treatment of the SDF sample. For what concerns the order of increasing reactivity observed during the ODS, in the case of homogeneous conditions the general observed trend was that of BT's < DBT's, being DBT's with larger alkyl chain the most reactive substrates. This trend was confirmed during homogeneous ODS of the SDF sample. A similar reactivity was observed for the heterogeneous catalysts II, IV and V, while more stringent steric requirements were operative in the case of

the catalysts I and III. In this latter case, BTs 1–2 showed to be more reactive than DBTs 3–7, suggesting the presence of a kinetic barrier in the approach of bulkier substrates to the catalyst.

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