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Additional Information

MIL-101 promotes the efficient aerobic oxidative desulfuration of dibenzothiophenes

Adrián Gómez-Paricio,^a Andrea Santiago-Portillo,^a Sergio Navalón,^a Patricia Concepción,^b Mercedes Alvaro^a and Hermenegildo García^{b,c,*}

MIL-101 promotes the aerobic oxidation in *n*-dodecane of dibenzothiophene (DBT) and its methyl-substituted derivatives to their corresponding sulfone with complete selectivity, without observation of the sulfoxide. DBT sulfones can be completely separated from *n*-dodecane by water extraction. MIL-101(Cr) without the need of pre-activation was found more convenient than the also-active MIL-101(Fe) analog. The reaction exhibits an induction period due to the diffusion inside the pore system of the solvent or oxygen and it is not observed if the MIL-101 sample is first contacted with the solvent at the reaction temperature for sufficiently long times. MIL-101 is reusable for at least five times without any sign of deactivation according to the time-conversion plots. Evidence by electron paramagnetic resonance spectroscopy detecting the hydroperoxide radical adduct with a spin trapping agent and Raman spectroscopy detection of superoxide supports that the process is an autooxidation reaction initiated by MIL-101 following the expected radical chain mechanism inside the MIL-101 cages.

Introduction

Metal organic frameworks (MOFs) are finding increasing application as heterogeneous catalysts, particularly for liquid phase reactions in which some MOFs exhibit a remarkable stability allowing their recovery and reuse in many consecutive runs.¹⁻⁷ MOFs are constituted by nodes of metal ions or small clusters of metal ions held in place by rigid bi- or multipodal organic linkers and offer in catalysis a large tunable porosity, a high density of active sites and a large variety on the transition metals that can be employed.^{1, 8, 9} Among the various MOFs that have been reported MIL-101 has been extensively used because it has shown a considerable robustness under catalytic conditions, it can be prepared reliably in sufficient quantities and it has a BET surface area above 2,000 m² g⁻¹ and a high metal content (~20 wt %).^{6, 10-12} There are in the literature some examples of the use of MOFs as catalysts to promote oxidation reactions although most of them use organic peroxides such as *tert*-butylhydroperoxide (TBHP)¹³⁻¹⁹ or H₂O₂^{19, 20} as terminal oxidants or as initiators when combined with molecular oxygen.^{16, 17, 21, 22} Interestingly, in a series of previous studies we have shown that MOFs are suited

catalysts for the aerobic oxidations of benzylic compounds²³ and thiols²⁴ or when combined with radical initiators such as N-hydroxyphthalimide (NHPI)²⁵⁻²⁷ or 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)²⁸ able to promote the aerobic oxidation of different substrates including saturated and unsaturated hydrocarbons,^{25, 27} alcohols²⁸ and amines.²⁶ The use of molecular oxygen as terminal oxidant replacing other reagents is very convenient from the point of view of the process greenness and for the economic competitiveness of the reaction.^{6, 29} In this context, in the present manuscript we report that dibenzothiophenes (DBTs) can be efficiently oxidized by molecular oxygen in the presence of MIL-101. DBT and its methyl-substituted derivatives are among the sulfur compounds present in gasoil and high boiling-point oil distillates and they are responsible for a large percentage of SO_x atmospheric pollution.³⁰ The tendency of legal regulations on fuel quality is to decrease the sulfur content (< 10 ppmw S, part per million weight of sulfur) and conventional hydrodesulfuration treatments in refining have to be supplemented with additional treatments to remove in higher degree sulfur containing compounds present in fuels.^{30, 31} It should be noted that DBTs, in particular 4-methyl DBT and 4,6-dimethyl DBT, are among the most reluctant sulfur compounds to undergo hydrodesulfuration.^{18, 30, 31} One possibility to remove DBT and its alkyl derivatives from oil distillates is their oxidation to the corresponding sulfoxides and/or sulfones that have an increased hydrophilicity and higher boiling point, thus, making easier their removal from fuels.³⁰ Typically, in these oxidative treatments organic hydroperoxides are used as oxidation reagents in combination with transition metal containing catalysts.^{18, 30, 32-37} It would be advantageous considering the large volumes of fuels to be treated if

^a Departamento de Química, Universidad Politécnica de Valencia, C/Camino de Vera, s/n, 46022 Valencia, Spain.

^b Instituto de Tecnología Química CSIC-UPV, Universidad Politécnica de Valencia, Av. de los Naranjos s/n, 46022 Valencia, Spain.

^c Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah, Saudi Arabia

† Footnotes relating to the title and/or authors should appear here.

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hydroperoxides are replaced by molecular oxygen. Some attempts to use molecular oxygen have been reported using polyoxometalates. For example, a composite of nanocrystalline MOF (NENU-9N) impregnated with a phosphovanadomolybdate has been employed to promote a ultradeep oxidative desulfuration at 80 °C for 1.5 h. The role of the MOF is to facilitate the dispersion of the hydrophilic polyoxometalate in the model or real diesel environment. It is important to note, however, that the catalytic oxidation was carried out in the presence of a large excess of isobutyraldehyde respect to DBT (10:1 molar ratio). It was proposed that isobutyraldehyde becomes oxidized to the corresponding peracid by molecular O₂ and then, in a second step, the peracid promotes the oxidation of DBT to DBT-sulfone. Under the studied conditions a TOF of 80 h⁻¹ was obtained. In other work, an Anderson-type polyoxometalate modified with quaternary ammonium salts was employed for the aerobic oxidation of DBT-derivatives using molecular O₂ as oxidant. The role of the quaternary ammonium salt is to facilitate the dispersion of the polyoxometalate in decalin as reaction medium, otherwise, the catalytic activity of the polyoxometalate is negligible. Good catalytic activity of the system were achieved, while the turnover frequency achieved only achieves 12.8 h⁻¹. However, details of how the quaternary ammonium salt is recovered from the reaction mixture and reusability tests and catalyst stability were not reported and, therefore, the applicability of the materials still needs further research.

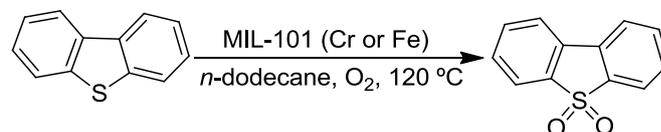
Besides hydrodesulfuration or oxidative desulfuration removal of DBT derivatives from oils can be carried out by adsorption methods.³⁸ Carbonaceous materials (activated carbon, carbon aerogels or carbon nanotubes),^{39, 40} metal or metal oxides,⁴⁰ zeolites,⁴⁰ clays,⁴¹⁻⁴³ silicas,⁴⁴ organic polymers⁴⁰ or metal coordination polymers^{31, 45} have been used among others as adsorbents. In addition, molecular imprinting technology has also been applied for the selective desulfurization of oils.³

In the present paper we report that MIL-101(Cr) (Cr₃F(H₂O)₂O[(O₂C)-C₆H₄-(CO₂)]₃.nH₂O) (n≤25) promotes the transformation of DBT and methyl-substituted derivatives into the corresponding sulfones by just by molecular oxygen without the need of aldehyde or ammonium salts. MIL-101(Cr) can be recovered and reused without decrease of the catalytic activity. The present finding may be advantageous respect to those oxidative desulfurations requiring hydroperoxides as oxidants or the addition of excess amounts of additives.

Results and discussion

For the present study two MIL-101 materials, namely MIL-101(Cr) and MIL-101(Fe), were used. These two materials are isostructural differing in the nature of the transition metal and the presence of -F or -Cl as ligand in the case of MIL-101(Cr) and MIL-101(Fe), respectively.^{9, 46} BET surface areas and pore

volumes obtained after synthesis were around 1,850 m² g⁻¹ and 1.12 cm³, respectively.²³ These differences can influence the interaction of the MOF with molecular oxygen and can also modify the polarity of the internal voids of the material.^{12, 23, 47} It has been shown that differences in polarity of the starting compound and the resulting oxidized products determine



significant variations in the affinity for the internal surface, this resulting in changes in product selectivity.²³ In addition, MIL-101 solids exhibit large pores (free diameters of 29 and 34 Å) with microporous windows of 12 and 16 Å, respectively, allowing the adsorption of DBT derivatives into their cavities.⁴⁸ In the initial stage of our work we performed treatment of DBT (200 mg L⁻¹) dissolved in *n*-dodecane at 120 °C (flash point and auto-ignition temperatures ~71 °C and ~203 °C, respectively) with O₂ in the presence of MIL-101(Cr or Fe) without or with pre-activation treatment (Scheme 1). The conditions used are outside the explosion range.

Scheme 1 Aerobic oxidation of DBT to DBT-sulfone using MIL-101(Cr or Fe) as catalyst.

It has been frequently observed that, in order to be used as catalyst, MOFs have to be submitted to an activation process to remove co-adsorbed water and solvent molecules and to generate coordinatively unsaturated sites around the metal centers.^{13, 22, 49, 50} In the present case, MIL-101 solids were activated at 150 °C under vacuum for 6 h and the performance of the materials submitted to activation compared with that of untreated materials. In all cases it was observed that the only reaction product was the corresponding DBT sulfone (DBT-sulfone) and the process is accompanied by some oxidation of the solvent (~ 1 %). In the absence of catalyst, autooxidation occurs in a negligible extent, even if the temperature is increased up to 180 °C (Figure S1). It was observed that this activation treatment does not influence the performance of MIL-101(Cr), while the activity for MIL-101(Fe) increases upon activation. It has been reported that under these activation conditions Fe³⁺ becomes reduced to Fe²⁺ in MIL-101(Fe),⁵¹⁻⁵³ while this reduction process has not been observed for the case of MIL-101(Cr).¹² Also, coordinated water is easier desorbed from MIL-101(Fe) than in MIL-101(Cr).^{12, 47} Comparison between the two MOFs shows that MIL-101(Fe) is less active than MIL-101(Cr), although the performance of the two samples is similar (Figure 1). In one of these experiments, *n*-dodecane containing DBT (200 mg L⁻¹ as S, ~ 267 ppmw S) was submitted to oxidation by MIL-101(Cr) at 120 °C and after the reaction the catalyst was filtered and the resulting clear *n*-dodecane solution extracted with water leading to the complete removal from *n*-dodecane of sulfur below to the detection limit (4 mg L⁻¹, ~5.3 ppmw), indicating that upon transformation of DBT into DBT-sulfone the latter compound can be completely extracted by water.

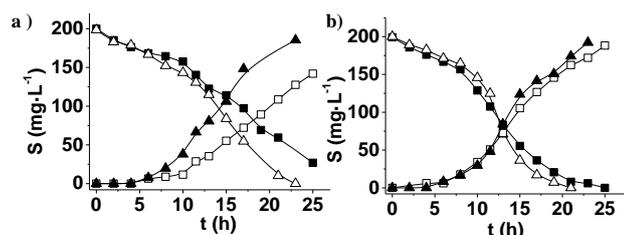


Figure 1 Aerobic oxidation of DBT to DBT-Sulfone using (a) MIL-101(Fe) or (b) MIL-101(Cr) with or without activation. Reaction conditions: Catalyst (500 mg L^{-1}), DBT ($1,150 \text{ mg L}^{-1}$, $1,534 \text{ ppmw}$), *n*-dodecane (10 mL), O_2 (1 atm), $120 \text{ }^\circ\text{C}$. Legend using non-activated catalyst, DBT (\blacksquare) and DBT-sulfone (\square), or using activated catalyst DBT (\blacktriangle), DBT-sulfone (\blacktriangle).

A notable observation of the temporal evolution of the reaction was the presence of an induction period (Figure 1). To understand the origin of this induction period, several tests were performed including (Figure 2): 1) heating a solution of DBT in *n*-dodecane in the presence of MIL-101(Cr) under Ar for 20 h and then admitting O_2 , 2) heating MIL-101(Cr) in *n*-dodecane under O_2 atmosphere for 12 h and then adding DBT, and 3) heating MIL-101(Cr) in *n*-dodecane under Ar atmosphere for 12 h and then sudden addition of DBT under O_2 atmosphere. In all cases the initial induction period taking about 6 h was not longer observed. This indicates that the diffusion of DBT or oxygen activation are not responsible for the induction period, but most probably the diffusion of *n*-dodecane inside the MIL-101 pores. Overall the above control reactions indicating that the induction period can be avoided by melting MIL-101 and *n*-dodecane at the required temperature before starting the oxidation. In a related adsorption study of linear alkanes, a change in the adsorption regime along the chain length was observed for *n*-nonane, whose adsorption takes a significantly longer equilibration time.⁵⁴ This slow down in the adsorption time from *n*-nonane was attributed as reflecting the large conformational freedom for this linear alkane and their relative dimensions with respect to the size of MIL-101 pores.⁵⁴ Similarly here, diffusion of *n*-dodecane inside MIL-101 will be a slow process influencing the reaction kinetics.

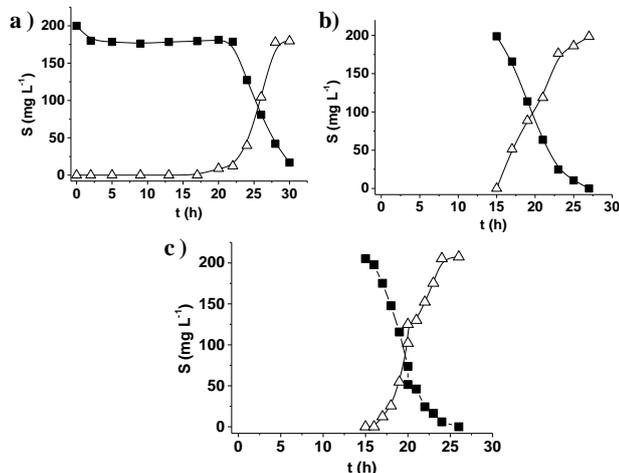


Figure 2 Influence on the aerobic oxidation of DBT (\blacksquare) to DBT-sulfone (Δ) using MIL-101(Cr) as catalyst at various pretreatments. Reaction conditions: Catalyst (500 mg L^{-1}), DBT ($1,150 \text{ mg L}^{-1}$), *n*-dodecane (10 mL), $120 \text{ }^\circ\text{C}$, atmosphere contacting as a function of the experiment (a, b or c). Legend: (a) DBT in *n*-dodecane with MIL-101(Cr) under Ar at $120 \text{ }^\circ\text{C}$ for 15 h and then sudden admission O_2 ; (b) suspending MIL-101(Cr) in *n*-dodecane under O_2 at $120 \text{ }^\circ\text{C}$ for 15 h and then addition of DBT; (c) contacting MIL-101(Cr) in *n*-dodecane under Ar for 15 h at $120 \text{ }^\circ\text{C}$ and then sudden addition of DBT under O_2 atmosphere.

Considering the above explanation for the induction period in the aerobic oxidation of DBT and the convenience of prior suspension in of MIL-101(Cr) in the solvent, we envisioned the possibility that the chain length of the solvent could play a role on the reaction kinetics. As it can be seen in Figure S2 the temporal profile of the DBT oxidation clearly depends on the solvent, following the expected trend that shorter *n*-alkane length decreases the induction period.

The influence of oxygen pressure and reaction temperature on the aerobic DBT oxidation promoted by MIL-101(Cr) was also studied (Figures S3 and S4). It was found that oxygen concentration influences the induction period, but not the reaction rate after initiation. Thus, the reaction can be suitably carried out under air. This can be interpreted considering that besides *n*-dodecane diffusion, oxygen diffusion also contributes to the induction period that is resulting from the faster of these two process. When oxygen pressure increases, oxygen can access faster to the metal centers and form the superoxide that will react with DBT outside MIL-101 crystallites. Whatever is faster, either filling of the micropores by *n*-dodecane or diffusing of the reactive oxygen species outside the MIL-101 crystalline will initiate DBT oxidation. As expected the induction period decreases and the reaction rate increases along with the reaction temperature in the range from 110 to $140 \text{ }^\circ\text{C}$. The Arrhenius plot of the natural logarithm of the rate after the induction period follows a linear relationship with the inverse of the absolute temperature, that allows estimation of an apparent activation energy (E_a) of 137 kJ mol^{-1} . This E_a value is higher than those reported in the literature for analogous DBT oxidation by TBHP using MIL-47(V) or MIL-125(Ti) that were estimated as 51 and 75 kJ mol^{-1} , respectively.³² Considering that organic peroxides are more reactive than molecular oxygen, the higher E_a value is not unexpected for the present aerobic oxidation. One additional experiment in where the amount of catalyst is increased resulted in a further decrease of the induction period as well as the final reaction time. Complete DBT conversions could be achieved in 4 h reaction time (compare Figure S4d and Figure S5).

MIL-101(Cr) was found to be stable as catalyst with respect to its activity. Figure 3 shows the temporal profile of DBT disappearance and DBT-sulfone formation in five consecutive runs using the same MIL-101(Cr) sample that was recovered from the reaction mixture by filtration washed with water and recycled. As it can be seen in Figure 3, exactly the same

temporal profile was reproduced in these five consecutive runs, indicating that no catalyst deactivation is taking place. This result was also confirmed by ICP-OES analysis of the liquid phase after the reaction that shows that the chromium content was below 0.5 % of the total initial Cr present in the fresh catalyst. Blank control experiments using similar amounts of leached Cr^{3+} in the absence of MIL-101(Cr) reveals that the reaction is promoted by MIL-101(Cr) with negligible activity measured for the small amount of leached chromium (Figure S6). In addition, XRD and ATR-FT-IR of the MIL-101(Cr) fresh, three and five times used were coincident indicating that the crystal structure remains unaltered during the process (Figure S7). These findings on MIL-101(Cr) stability agrees with previous results that also employed this material as catalyst and noticed its remarkable stability.^{16, 22, 23}

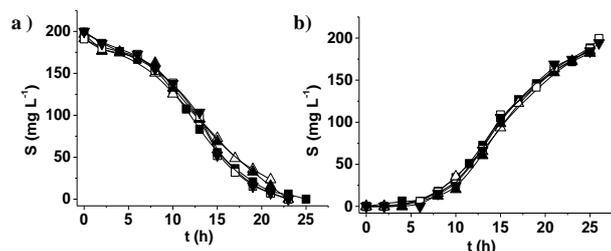


Figure 3 Reusability of MIL-101(Cr) as catalyst in the aerobic oxidation of DBT (a) to DBT-sulfone (b). Reaction conditions: catalyst (500 mg L^{-1}), DBT ($1,150 \text{ mg L}^{-1}$, $\sim 1,534 \text{ ppmw}$), *n*-dodecane (10 mL), O_2 (1 atm), 120°C . Legend: 1st use (■), 2nd use (Δ), 3th use (▲), 4th use (□), 5th use (▼).

The catalyst stability was further supported by performing an additional catalytic test in which five times higher DBT amount was submitted to oxidation using 50 times lower catalyst amount and observing almost complete disappearance of DBT at sufficiently long periods of time (Figure S8). It was noticed, however, in this experiment that a gradual precipitation of DBT-sulfone as solid develops as the reaction progresses as consequence of the low solubility of DBT-sulfone in *n*-dodecane.

Heterogeneity of the process was studied by carrying out two twin experiments and removing the catalyst in one of them once the induction period was overcome (10 h) (Figure 4). Exactly the same temporal profiles for DBT disappearance and DBT-sulfone formation were observed in these two experiments indicating that once the reaction has started the presence of MIL-101(Cr) is not longer necessary. This type of behavior is common for radical chain autooxidation reactions in where the role of the initiator is to generate the first radicals that subsequently undergo a propagation cycle by reaction with molecular oxygen that does not requires any catalyst.^{23, 55, 56}

To provide some support to this autooxidation mechanism, TEMPO was added as radical trap, observing that in the presence of this radical inhibitor, no DBT oxidation takes place for periods longer than 30 h. On the other hand, if the reaction is started by MIL-101(Cr) in the absence of TEMPO and then, once the reaction progresses, TEMPO is added, a significant decrease in the reaction rate is observed (Figure 4).

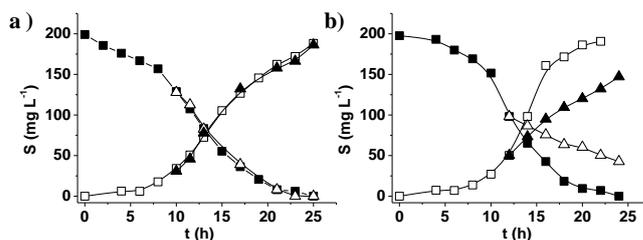
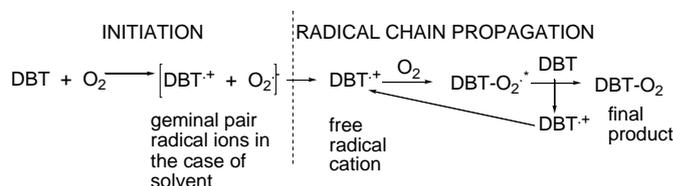


Figure 4 (a) Hot filtration test at 38 % conversion for the aerobic oxidation of DBT to DBT-sulfone using MIL-101(Cr) as catalyst. Reaction conditions: Catalyst (500 mg L^{-1}), DBT ($1,150 \text{ mg L}^{-1}$), *n*-dodecane (10 mL), O_2 (1 atm), 120°C . Legend: In the presence of catalyst DBT (■), DBT-sulfone (□); after catalyst filtration of the catalyst DBT (Δ), DBT-sulfone (▲). b) Hot filtration test at 38 % conversion in the presence of TEMPO (20 mol % respect DBT). Legend: in the presence of catalyst DBT (■), DBT-sulfone (□); after catalyst filtration in the presence of TEMPO DBT (Δ), DBT-sulfone (▲).

According to these data, the following autooxidation mechanism shown in Scheme 2 is proposed. In this mechanism after initiation by generation of the first DBT^+ , a propagation chain occurs by reaction with molecular oxygen, formation of DBT-O_2^+ and electron abstraction from neutral DBT. The first DBT^+ radical would be generated by some reactive oxygen species formed by interaction of the Cr^{3+} with O_2 , the most probable one being superoxide (O_2^-).^{34, 57, 58}



Scheme 2 Proposed reaction mechanism for the aerobic oxidation of DBT with molecular O_2 in the presence of MIL-101(Cr) as catalyst.

To provide experimental evidence to the generation of reactive oxygen species, EPR spectra using phenyl α -*tert*-butyl nitron (PBN) as radical trap were carried out. As Figure 5 shows while MIL-101(Cr) and O_2 exhibits only a weak EPR signal when PBN is added the EPR signal attributed to the adduct of PBN-OOH was recorded. This HOO· radical will be formed from O_2^- by protonation by moisture present in the medium and constitutes experimental evidence of the involvement of the generated reactive oxygen species by acting MIL-101(Cr) solid as initiator.²³ Selective radical quenching experiments using *p*-benzoquinone⁵⁹ or DMSO^{60, 61} as $\text{O}_2^-/\text{HOO}^\cdot$ or HO^\cdot quenchers, respectively, support the generation of $\text{O}_2^-/\text{HOO}^\cdot$ species from molecular O_2 . The presence of *p*-benzoquinone completely inhibits the reaction (Figure S9), supporting the generation of $\text{O}_2^-/\text{HOO}^\cdot$ radicals,

while the presence of DMSO (a HO \cdot radical quencher) does not affect the reaction profile of DBT oxidation to form DBT-sulfone. The oxidation of DBT to DBT-sulfone by O $_2$ $^{\cdot-}$ /HOO \cdot was further supported by performing additional experiments employing TBHP as oxidant and observing the conversion of DBT to its corresponding DBT-sulfone (Figure S10). In contrast, the use of benzoyl peroxide as oxidant does not promote the oxidation of DBT to DBT-sulfone (Figure S10).

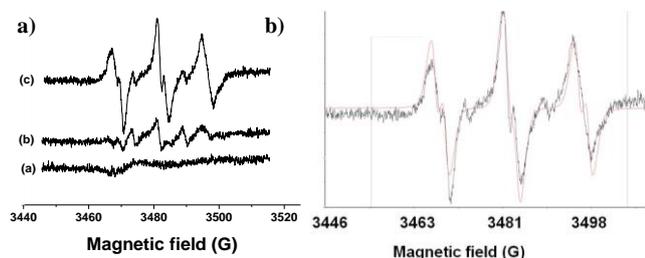


Figure 5 (A) Experimental EPR spectra in *n*-dodecane as solvent at 120 °C for 5 h and using (a) MIL-101(Cr) + O $_2$, (b) PBN + O $_2$ y (c) MIL-101(Cr) + PBN + O $_2$. (B) Experimental and simulated EPR spectra of PBN-OOH under (c) conditions. Hyperfine coupling constants of PBN-OOH (~90 % area) AG $_N$ = 14.0 and AG $_H$ = 2.05 and tert-butyl aminoxyl from degraded PBN AG $_N$ = 14.0 and AG $_H$ = 14.0.

Besides EPR spectroscopy, Raman also provided valuable information in support of the intermediacy of O $_2$ $^{\cdot-}$ as the initial reactive oxygen species promoting DBT autooxidation. Oxygen activation on both MIL-101(Cr) and MIL-101(Fe) samples has been studied by Raman spectroscopy.⁶²⁻⁶⁴ In the MIL-101(Cr) sample (Figure 6A), two Raman bands at 998 cm $^{-1}$ and 1035 cm $^{-1}$ have been detected when the sample was exposed to O $_2$ flow at 120 °C. These bands have been attributed to peroxy and superoxy species, respectively.⁶³ Notice that the stability of these bands is relatively weak, since they are easily removed at room temperature by purging the sample with N $_2$. Similar to the MIL-101(Cr) sample, oxygen activation leading to peroxy (826 cm $^{-1}$), superoxy (1161 cm $^{-1}$) and O $_2$ $^{\delta-}$ (1313 cm $^{-1}$) species have been observed in the MIL-101(Fe) sample (Figure 6B) when exposed to O $_2$ flow at 120 °C.^{63, 64} These species are easily removed by purging with N $_2$ at room temperature. The Raman band at 1502 cm $^{-1}$ has been ascribed to adsorbed molecular oxygen species,^{62, 63} which decrease in intensity by purging with N $_2$. However a different behavior is observed with the 1430 cm $^{-1}$ Raman band which becomes better resolved after 120 °C oxygen treatment. Probably this band could be assigned to some structural modification in the MOF framework, indeed, structural modification in the 1650-1400 cm $^{-1}$ range has already been detected by IR spectroscopy (spectra not shown). According to these results, oxygen peroxy and superoxy species are generated by molecular oxygen and become stabilized on both MIL-101(Cr) and MIL-101(Fe) samples. The peaks corresponding to these reactive oxygen species in

Raman spectroscopy disappear or decrease significantly if a N $_2$ flow is flushed, indicating that O $_2$ $^{\cdot-}$ can diffuse away from MIL-101 once formed. All these observations are in good agreement with EPR spectroscopy detection of HOO \cdot adduct and the mechanistic proposal shown in Scheme 2.

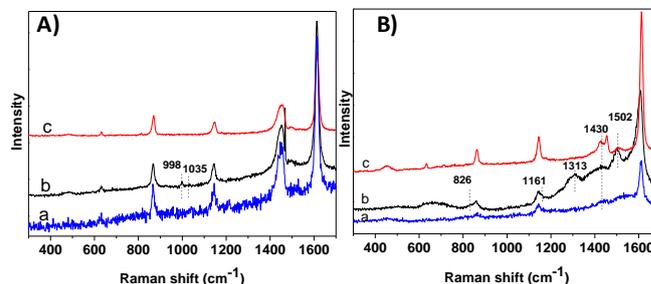


Figure 6 Raman spectra of MIL-101(Cr) (A) and MIL-101(Fe) (B) samples in N $_2$ flow at 120 °C (a), O $_2$ flow at 120 °C (b) and N $_2$ flow at 25 °C (c).

Furthermore, we investigate the possibility that the sulfur atom of DBT coordinates somehow with the Cr $^{3+}$ ions of MIL-101(Cr), therefore, intervening in the oxidation mechanism. For this purpose, the absorption of DBT in the MIL-101(Cr) was carried out at room temperature and, then, the diffuse reflectance UV-Vis absorption or ATR-FT-IR spectrum of the resulting sample recorded. Figure S11 does not show any change that could be attributable to the interaction between Cr $^{3+}$ ions of MIL-101(Cr) with DBT. Therefore, the observed adsorption of DBT in MIL-101(Cr) should occur probably by simply π - π interaction of DBT with MIL-101 organic linkers. The scope of MIL-101(Cr) as promoter of the aerobic oxidation of aromatic sulfur compounds with DBT structure was checked by carrying out under analogous conditions the oxidation of 4-methyl and 4,6-dimethyl substituted DBT (Figure S12). It was observed that these methyl substituted DBT undergo oxidation to the corresponding sulfones exhibiting the same features as parent DBT, but reacting even faster (Figure S12). This reactivity pattern follows the expected order according to the expected influence of electron donor substituents on the electronic density of the S atoms as reported in the literature.⁶⁵ A similar behaviour respect to the oxidation of individual components was observed when working in a multicomponent model solution (Figure S13). Importantly, the aerobic oxidation of DBT, 4-methyl and 4,6-dimethyl DBT to their corresponding sulfones was also efficiently achieved using commercial diesel (Repsol) as medium although we notice that in this case the reaction time is higher respect to the use of *n*-dodecane (Figure S14). This may be explained considering the large number additives that for different purposes are present in commercial diesel and the negative influence that these additives can play for DBT adsorption and reaction. Finally, the aerobic oxidative process of DBT and its derivatives using MIL-101(Cr) as solid promoter was coupled with a liquid-liquid extraction process for the removal of the sulfur

compounds. The process consists in the simply removal of the catalyst by filtration and, then, the extraction of the sulfone compounds present in the organic phase with water. Interestingly, this process allowed the complete extraction of the DBT-sulfone derivatives to the water phase leading to an organic phase with a sulfur content below the detection limit of our analytical system ($< 4 \text{ mg L}^{-1}$ of S, $\sim 5.3 \text{ ppmw S}$). It is worthy to mention that the maximum sulfur content according to the legislation should be lower than 10 ppmw .^{30,31}

Experimental section

Materials: DBT ($\geq 99\%$), DBT-sulfone (97 %), 4-methylDBT (96 %) and 4,6-dimethylDBT (97 %), tert-butylhydroperoxide (TBHP) solution in decane ($\sim 5.5 \text{ M}$), *n*-decane, *n*-dodecane and *n*-tetradecane were of analytical grade and supplied by Sigma-Aldrich. The other reagents and solvents used in this work were analytical or HPLC grade.

Catalyst preparation: MIL-101(Cr) and MIL-101(Fe) were prepared and characterized as previously reported by our group²³ following well-established procedures by Ferey⁹ and others.^{17, 46} Briefly, a mixture of terephthalic acid (0.25 g, 1.5 mmol), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.4 g, 1 mmol) and HF (10 μl) in water (8 mL) was placed in a Teflon-lined autoclave and heated at 200°C for 8 h. The resulting precipitate was purified by several washings with DMF and, then, with ethanol at 70°C for 2 h.

MIL-101(Fe) was prepared by dissolving terephthalic acid (0.206 g, 1.25 mmol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.675 g, 2.5 mmol) in DMF (15 mL) in a Teflon-lined autoclave and, then, heating the system at 135°C for 8 h. The resulting precipitate was purified by double extraction with ethanol by stirring the powder in this alcohol (10 times in weight) at 60°C for 2 h.

Catalytic experiments: In a typical experiment a certain catalyst amount was added to a round-bottom flask (25 mL). When required, activation of MIL-101 catalyst was carried out by heating at 150°C under vacuum for 6 h. Subsequently, the reaction temperature was fixed ($110, 120, 130$ or 140°C) and the required reaction atmosphere was obtained by purging the system with a balloon containing O_2 , air or argon under atmospheric pressure. The reaction time started by addition of a solution of DBT (200 mg L^{-1} of S) to the preheated round-bottom flask. As reaction solvents, *n*-dodecane as model of real hydrocarbons mixtures or commercial diesel (Repsol) were used.

Selective radical quenching experiments using TEMPO, *p*-benzoquinone or DMSO were carried out as described above but in the presence of 20 mol % of these reagents respect to the initial DBT.

Liquid-liquid extraction. At the end of the reaction the catalyst was removed from the organic phase by filtration through a Nylon filter ($0.2 \mu\text{m}$). Then, the organic phase (10 mL) was extracted with distilled water ($3 \times 10 \text{ mL}$) using a separating funnel. This process resulted efficient for the complete DBT-Sulfone extraction from the organic to the aqueous phase.

Product analysis: Aliquots of the reaction mixture at different times were diluted in a solution of anisole containing a known

amount of nitrobenzene as external standard. Then, the samples were filtered to remove the catalyst and, then, analyzed by gas chromatography (GC) using a flame ionization detector. Quantification was carried by using calibration curves of commercial samples and nitrobenzene as standard.

To evaluate the metal leaching at the end of the reaction the solid catalyst was filtered through a $0.2 \mu\text{m}$ nylon filter. Subsequently, an HNO_3 aqueous solution (30 mL, 3 M) was put in contact with the organic phase reaction and the system magnetically stirred and heated at 80°C for 24 h. The presence of Cr in the aqueous phase was finally analyzed using a ICP-OES instrument.

Raman measurements: Raman spectra were recorded with a 514 nm laser excitation on a Renishaw Raman Spectrometer ("Reflex") equipped with a CCD detector. The laser power on the sample was 25 mW and a total of 20 acquisitions were taken for each spectra. A commercial Linkam cell (THMS600) was used for collecting spectra under controlled conditions. Thus, the sample were first subjected to N_2 flow (20 ml min^{-1}) at 120°C for $\sim 3 \text{ h}$. Afterwards the gas was changed to O_2 (20 ml min^{-1}) at the same temperature. Finally, the temperature was lowered to 25°C in O_2 flow and changed to N_2 . Spectra were collected at 25°C in N_2 flow.

EPR measurements: MIL-101(Cr) or MIL-101(Fe) (5 mg) were added to a round-bottom flask (25 mL) containing PBN ($1,150 \text{ mg L}^{-1}$) dissolved in *n*-dodecane (10 mL). After sonication (15 min) the system was purged with a balloon containing O_2 and the system heated at 120°C for 5 h. Then, an aliquot was filtered (Nylon filter, $0.2 \mu\text{m}$) and the sample purged with N_2 before recording the EPR. EPR spectra were recorded using a Bruker EMX instrument with the following parameters: frequency 9.803 GHz, sweep width 3489.9 G, time constant 40.95 ms, modulation frequency 100 kHz, modulation width 1 G, microwave power 19.92 mW.

Conclusions

In the present manuscript it has been shown that MIL-101 is an efficient, stable and reusable promoter for the aerobic oxidation of DBT and its methyl substituted derivatives in alkanes. The reaction exhibits an induction period that is related to the solvent diffusion and formation of the first reactive oxygen species, probably $\text{O}_2^{\cdot -}$ or HOO^{\cdot} that initiate a radical chain autooxidation mechanism. Evidence for the involvement of these species has been obtained by EPR spectroscopy after trapping the PBN-OOH adduct and by Raman spectroscopy of MIL-101(Cr) exposed to O_2 . Considering that in the literature hydroperoxides have been proposed for the desulfuration of fuels, the present results can constitute an advantageous alternative based on the use of molecular oxygen as oxidant and a stable solid material as promoter.

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Table of contents. MIL-101(Cr) promotes the oxidative desulfuration of dibenzothiophenes by air.