Vallés-García, C.; Santiago-Portillo, A.; Alvaro Rodríguez, MM.; Navalón Oltra, S.; García Gómez, H. (2020). MIL-101(Cr)-NO2 as efficient catalyst for the aerobic oxidation of thiophenols and the oxidative desulfurization of dibenzothiophenes. Applied Catalysis A General. 590:1-8. https://doi.org/10.1016/j.apcata.2019.117340

MIL-101(Cr)-NO_2 as efficient catalyst for the aerobic oxidation of thiophenols and the oxidative desulfurization of dibenzothiophenes

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Abstract

A series of MIL-101(Cr)-X functionalized materials with electron withdrawing (X: NO_2, SO_3H or Cl) or electron donor (X: NH_2 or CH_3) groups has been tested for the solvent-free oxidative coupling of thiophenol to disulfides. A good relationship between the catalytic activity of these MOFs with the meta Hammet constant of the substituents in the terephthalate organic ligand and with the redox potential of the solids has been found, MIL-101(Cr)-NO_2 being the most active catalyst. This NO_2-substituted MIL-101 is also more efficient than the parent MIL-101(Cr) to promote the aerobic desulfurization of dibenzothiophenes in *n*-dodecane or commercial Diesel as solvent. Importantly, MIL-101(Cr)-NO_2 exhibits higher activity than homogeneous Cr(III) acetate for the aerobic oxidation of thiophenol and aerobic desulfurization. Mechanistic

studies reveal that MIL-101(Cr)-NO_2 is acting as truly heterogeneous catalyst in the case of thiophenol oxidation, while for the aerobic desulfurization is acting as a radical initiator. For both reactions, the catalyst can be reused several times without significant loss of catalytic activity, maintaining its crystallinity and with negligible metal leaching.

Keywords: heterogeneous catalysis; MIL-101(Cr)-NO_2 as catalyst; aerobic oxidations; thiophenol coupling; fuel desulfurization

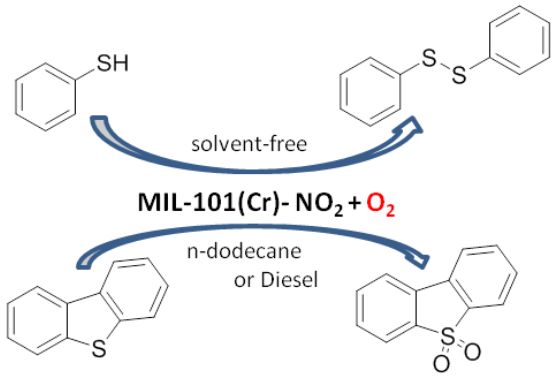
Highlights

- MIL-101(Cr)-NO_2 shows superior activity for the oxidation of thiophenols to disulfides with O_2

- MIL-101(Cr)-NO_2 exhibits high catalytic activity for the aerobic desulfurization of dibenzothiophenes

- MIL-101(Cr)-NO_2 is a stable and reusable catalyst

Graphical abstract



1. Introduction

Metal-organic frameworks (MOFs) are a class of crystalline porous materials constituted by metal ions or metal clusters coordinated to multipodal organic ligands.[1-5] Since the first reports about the preparation and characterization of MOFs at the end of 90s, a vast number of these materials combining many types of organic linkers and inorganic units have been reported.[6, 7] MOFs have found applications in different areas[8] including adsorption and separation,[9, 10] catalysis,[11, 12] photocatalysis,[13] sensing[14, 15] or biological applications,[16] among others.

In particular, the interest of MOFs as heterogeneous catalysts is continuously increasing due to their fascinating possibilities to tune their composition and structure to each specific reaction.[17-26] Among them, MIL-101(Cr) (MIL: Materiaux de l'institut Lavoisier) prepared by Férey and co-workers has attracted a large interest due to its remarkable porosity, surface area and structural stability.[1] MIL-101(Cr) is constituted by terephthalate ligands and Cr_3-μ_3O-carboxylate nodes where octahedrally coordinated metal ions are bond to carboxylate groups and to water molecule or one fluoride ion.[1, 27, 28] Assembly of the nodes and linkers results in supertetrahedral units forming two mesoporous cavities of 1.6 and 1.2 nm diameter accessible through hexagonal (8.6 Å) and pentagonal (5.5 Å) windows, respectively. The wide MIL-101(Cr) windows allow the diffusion of substrates through the large surface area (2700 $m^2\ g^{-1}$) and pore volume (2.1 $cm^3\ g^{-1}$) of the solid. Of special interest in catalysis is the possibility to remove adsorbed molecules present in the MOF by thermal treatment (150 ºC) under vacuum resulting in the formation of coordinatively unsaturated sites (CUS) that can act as Lewis acid or redox centers.[29, 30] More recently it has been reported that the presence of electron donor and electron acceptor functional groups at the terephthalate linker can tune the Lewis acidity[31] and the redox properties[32] of MIL-101(Cr) metallic nodes.

In particular, the NO_2 substitution on the therephthalate linker enhances the catalytic activity with respect to the parent terephthalate for three common Lewis-catalyzed reactions as well as for the oxidative coupling of benzylamine using molecular oxygen as oxidant.[31, 32]

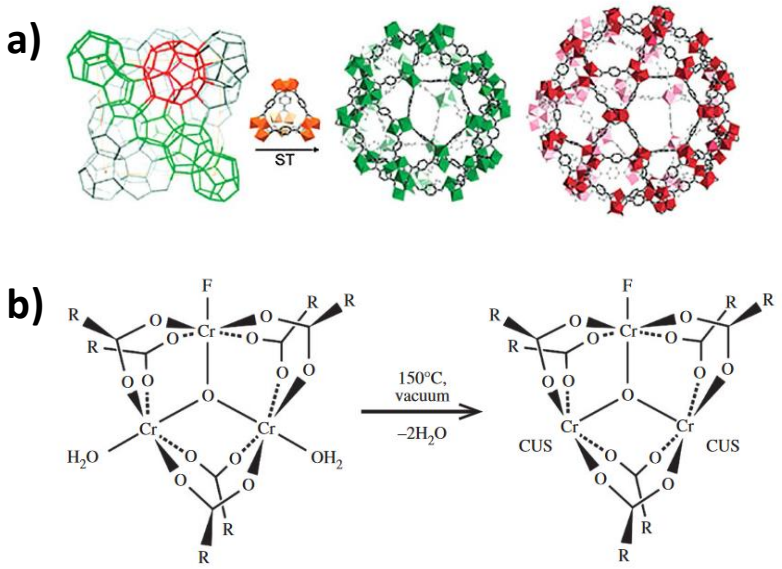


Figure 1. a) Schematic 3D representation of the MIL-101 structure made of smaller (green) and larger (red) cages connected through supertetrahedra (ST). Left: the ensemble of the two types of cages. Right: isolated cages of each type of cavity. b) Formation of CUS in the MIL-101(Cr) metal node by thermal treatment under vacuum.

In previous studies, some of us have reported the aerobic oxidation of organosulfur compounds using MIL-101(Cr or Fe) and MIL-100(Fe).[34] MIL-100(Fe) (BET 1800 $m^2\ g^{-1}$ and 0.9 $cm^3\ g^{-1}$ pore volume) is a MOF constituted by benzene-1,3,5-tricarboxylate as ligand and Fe_3-μ_3O as metal nodes. In particular, MIL-101(Cr) solid has been reported as a stable catalyst to promote the aerobic oxidative desulfurization of dibenzothiophenes in *n*-dodecane or diesel.[35] The applicability of the system is, however, somehow limited due to the need of long reaction times, especially in diesel solution (~ 48 h). In other study, the aerobic oxidation of thiols to disulfides was

promoted by MIL-100(Fe) as catalyst in acetonitrile as solvent and molecular oxygen as oxidant.[36] Regardless the good results obtained in that study, it is always of interest to develop alternative system to perform the reaction under solvent-free conditions, while still presenting a high catalytic activity.

With these precedents, in the present work it is reported that MIL-101(Cr)-NO_2 solid while still stable is more efficient catalyst than the parent MIL-101(Cr) to promote both the solvent-free oxidative coupling of thiophenols to disulfides and the aerobic oxidative desulfurization of fuels using dibenzothiophenes as model substrates in n-dodecane or commercial diesel as solvent. Importantly, the catalytic activity of MIL-101(Cr)-NO_2 is higher than that of isoreticular MIL-101(Cr)-X (X: SO_3H, Cl, CH_3, H), MIL-100(Fe) solid, or the corresponding Cr_2O_3 oxide. Importantly, the activity of MIL-101(Cr)-NO_2 is higher or comparable to that obtained using the homogeneous chromium acetate salt. In addition, MIL-101(Cr)-NO_2 can be reused several times for both reactions without observing decrease of the resulting catalytic activity or metal leaching from the solid to the solution and maintaining the initial crystallinity of the solid.

2. Materials and methods

2.1. Materials

The reagents such as Cr_2O_3 powder (ref. 393703) and solvents employed in the present study were of analytical or HPLC grade and supplied by Sigma-Aldrich. Commercial diesel was provided by Repsol. The MIL-101(Cr)-X (X: NO_2, SO_3H, Cl, CH_3, NH_2) materials employed in this work are the same batch as those previously prepared and characterized by us.[31, 32]

2.2. Catalyst characterization

Powder XRD measurements were recorded with a Philips XPert diffractometer equipped with a graphite monochromator (40 kV and 45 mA) employing Ni-filtered CuKα radiation.

2.3. Catalytic experiments

The corresponding amount of catalyst (i.e. 20 mg) was previously dried in an oven at 100 ºC for 24 h and, then immediately introduced in a dried two neck round-bottom flask (25 mL). The catalyst was further activated by heating at 150 ºC under vacuum for 12 h. Subsequently, the flask was heated at the reaction temperature (120, 130, 140 or 150 ºC). The required reaction atmosphere was obtained by purging the system with a balloon containing molecular O_2 or Ar. In the case of the aerobic oxidation of thiophenol the reaction started by the addition of the substrate (20 mmol). In the case of the aerobic oxidation of dibenzothiophenes (DBTs) the reaction started by the addition of a solution of DBT (200 mg L^{-1}; 20 mL) prepared in *n*-dodecane or commercial diesel. During the catalytic experiments the reactions were magnetically stirred at 500 rpm with a magnetic bar.

To study the catalyst reusability, the catalyst was recovered at the end of the reaction by filtration, washed with acetonitrile (thiophenol oxidation) or with thioanisole+acetonitrile (DBT oxidation) and, then, dried before use in a new catalytic cycle.

2.4. Product analysis

Aliquots of the reaction mixture (100 μL) at different times were diluted in 2 mL of a solution of acetonitrile (for thiophenol oxidation) or anisole (for the oxidative desulfurization of DBT) containing a known amount of nitrobenzene as external standard. Subsequently, the samples were filtered to remove the catalyst (Nylon filter 0.2 μm adapted to a syringe) and analyzed by gas chromatography (GC) using a flame ionization detector and a methyl-phenyl silicone column (TRB-5MS; 30 m x 0.32 mm x 0.25 μm). Quantification was carried out by using calibration curves of commercial samples and nitrobenzene as the standard. Identity of the products was confirmed by injecting the mixture in a GC-MS (Agilent 5973) with quadrupole and comparing the retention time with authentic samples.

Analyses of the possible metal leaching were carried out at the end of the reaction by quantitative ICP-OES determination. Briefly, at the end of the reaction the catalyst was removed by filtration using a 0.2 μm Nylon filter. Then, a nitric acid aqueous solution (30 mL, 3 M) was added to the organic phase and the system heated under magnetic stirring at 80 ºC for 24 h. Finally, the aqueous phase was analyzed by IPC-OES.

3. Results and discussion

3.1. Catalyst properties

As commented before, the catalysts employed for this study are from the same batch that those previously reported by some of us.[31, 32] Table 1 summarizes the composition and porosity of these solids employed in the present study. Commercially available Cr_2O_3 powder was also employed as catalyst for comparison.

Table 1. List of catalysts employed in the present study[a]		
Catalyst / Formula[b]	BET surface area ($m^2\ g^{-1}$)	Pore volumen ($cm^3\ g^{-1}$)
MIL-101(Cr)-H {$Cr_3F(H_2O)_2O(bdc)_3$)}	2,750	2.2
MIL-101(Cr)-NO_2 {$Cr_3Cl(H_2O)_2O(bdc\text{-}NO_2)_3$)}	1,850	1.3
MIL-101(Cr)-SO_3H {$Cr_3Cl(H_2O)_2O(bdc\text{-}SO_3H)_3$)}	1,900	1.4
MIL-101(Cr)-Cl {$Cr_3Cl(H_2O)_2O(bdc\text{-}Cl)_3$)}	1,300	1.1
MIL-101(Cr)-CH_3 {$Cr_3Cl(H_2O)_2O(bdc\text{-}CH_3)_3$)}	1,800	1.8
MIL-101(Cr)-NH_2 {$Cr_3Cl(H_2O)_2O(bdc\text{-}NH_2)_3$)}	1,950	2.0
MIL-100(Fe) {$Fe_3Cl(H_2O)_2O(btc)_3$)}	1,700	0.8
[a] For preparation and additional characterization data see refs. [31, 32] [b] bdc: benzenedicarboxylate; btc: 1,3,5-benzenetricarboxylate		

3.2. Aerobic oxidation of thiophenols to disulfides

As commented in the introduction, the MIL-101(Cr) and MIL-100(Fe) materials are characterized by their excellent chemical and thermal stability and the possibility to be employed for the molecular oxygen activation.[31, 34, 35] With these precedents, in the first stage of this work, the influence of substituents at the bdc linkers on the catalytic activity of MIL-101(Cr)-X (X: NO_2, SO_3H, Cl, CH_3, NH_2) for the solvent-free aerobic oxidative coupling of thiophenol to diphenyl disulphide was explored. Previous studies have established that the functionalization of the terephthalate organic ligand of the MIL-101(Cr) with electron donor or electron withdrawing groups influences the redox properties of the metal nodes and, therefore, their catalytic activity for oxidation reactions.[32] A blank control in the absence of catalyst reveals that thiophenol conversion is lesser than 12 % under the reaction conditions employed in the study. This observation can be attributed to the occurrence of same degree of spontaneous autoxidation.[34] The presence of several substituents in the organic ligand of the MIL-101(Cr)-X (X: NO_2, SO_3H, Cl, H, CH_3, NH_2) influences both the initial reaction rate

and the substrate conversion at a given reaction time (Figure 1). In all cases the only observed product was diphenyl disulphide with complete selectivity. MIL-101(Cr)-NO_2 resulted the most active catalyst to promote the solvent-free aerobic oxidation of thiophenol with an initial reaction rate 4 times higher than that of the parent MIL-101(Cr)-H and a final yield at 24 h of 90 %, about 3 times higher than that of the parent MIL-101(Cr)-H.

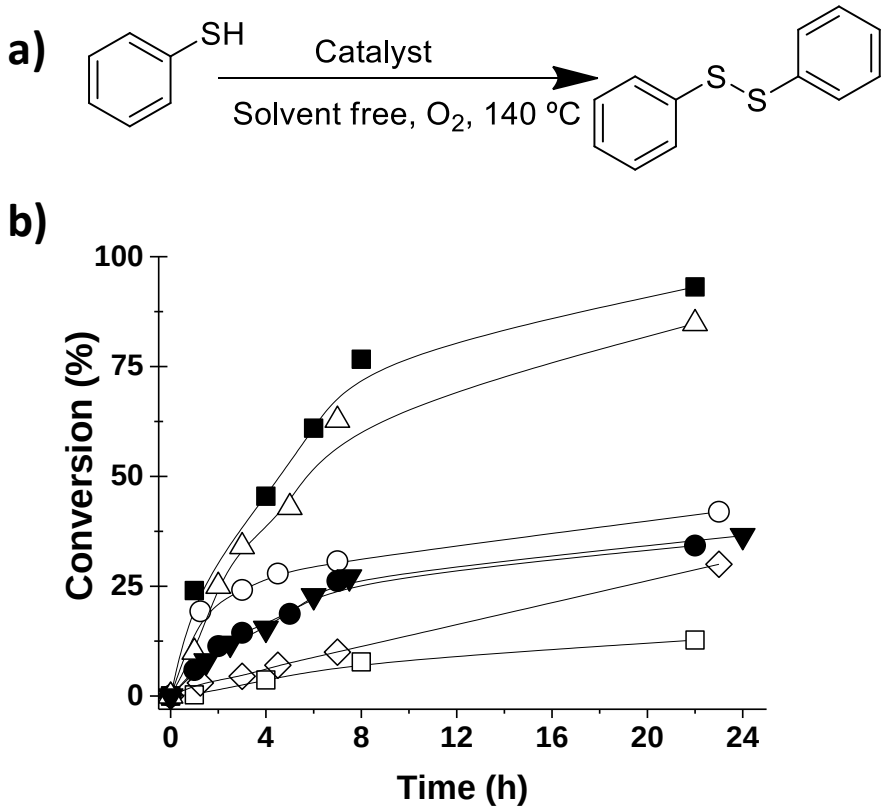


Figure 1.

In order to understand the observed catalytic activity using the series of MIL-101(Cr)-X (X: NO_2, SO_3H, Cl, H, CH_3, NH_2) solids, the logarithm of the relative first order rate constant (k_x/k_0) as a function of the different meta Hammett constant for each substituent in MIL-101(Cr)-X catalysts was plotted. A good linear relationship between log k_x/k_H vs σ_m was observed for the MIL-101(Cr)-X catalysts having both electron donor or electron withdrawing groups in the organic ligand. This observation is

compatible with previous reports showing that the presence of electron donor or electron withdrawing groups at the organic ligand of the MIL-101(Cr) solids decreases or increases, respectively, the Lewis acidity of the metal center, due to inductive effects of the terephthalate linker on the metal ions of the nodes.[31, 32, 37] In connection with the previous finding, a good relationship between the initial reaction rate and the reported oxidation potential of the MIL-101(Cr)-X (X: H, NO_2, SO_3H, Cl) was also found here, the higher the redox potential the higher the catalytic activity (Figure 2).

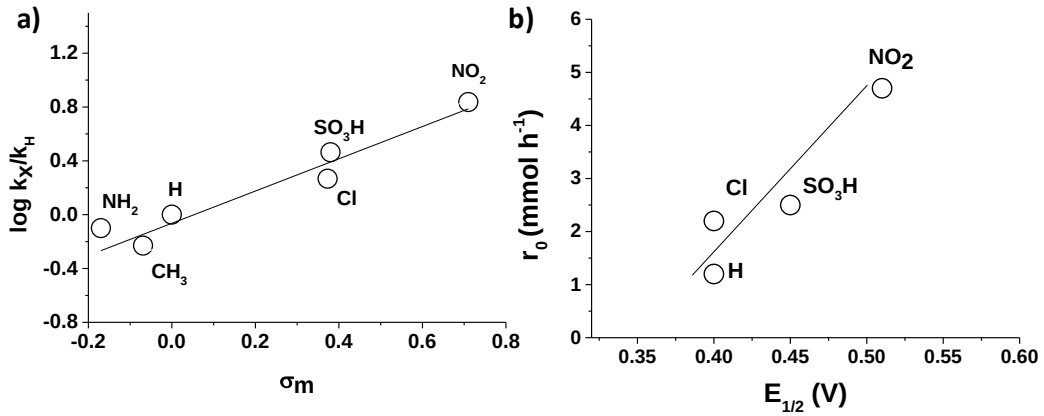


Figure 2.

Importantly, the initial reaction rate for thiophenol conversion using MIL-101(Cr)-NO_2 is five times higher than that of the homogeneous chromium acetate and six-times higher than that of the heterogeneous Cr_2O_3. This comparison highlights the benefits of using functionalized MIL-101(Cr)-X solid with nitro groups as heterogeneous catalysts respect to the use of analogous soluble metal salts or heterogeneous metal oxides. Even though MIL-100(Fe) solid possesses higher Lewis acidity and, therefore, catalytic activity (r_0 1.21 mM h^{-1}) than MIL-101(Cr)-H (r_0 1.13 mM h^{-1}), the presence of the nitro group in the MIL-101(Cr)-NO_2 increases its catalytic activity in a large extent (r_0 4.8 mM h^{-1}). The superior catalytic activity observed for MIL-101(Cr)-NO_2 should be a reflection of the higher Lewis acid strength of the Cr^{3+}

ions with CUS, resulting in a decrease of the apparent activation energy (Ea) for the solvent-free aerobic oxidation of thiophenol. From the Arrhenius plot of the influence of the temperature on the reaction rate for MIL-101(Cr)-NO_2 a value of 32 kJ mol^{-1} was estimated (Figure 3).

The influence of the reaction atmosphere on the resulting catalytic activity using MIL-101(Cr)-NO_2 was evaluated. Figure 3 shows a good linear relationship between the atmospheric oxygen pressure and the initial reaction rate, indicating that that relation is first order respect to oxygen pressure.

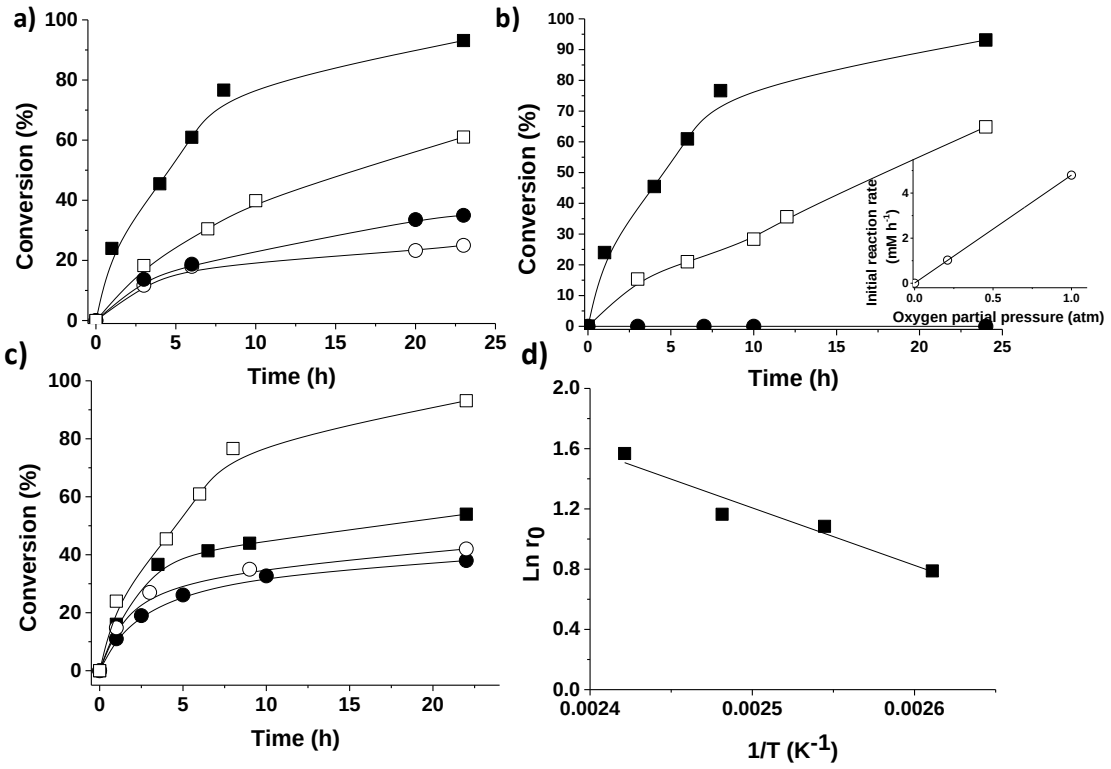


Figure 3.

The heterogeneity of the reaction using MIL-101(Cr)-NO_2 as catalyst was confirmed by performing the so-called hot filtration test. In this experiment the reaction was started under typical conditions and once conversion has reached about 25 %, a portion of the reaction medium is filtered to remove the solid catalyst and placed in a

parallel reaction setup and the reaction allowed to proceed further on the absence of any solid. Figure 4 shows that once the catalyst is removed the reaction stops, confirming that the reaction is truly heterogeneous. Furthermore, the stability of the MIL-101(Cr)-NO_2 catalyst was evidenced by performing ten consecutive catalytic reactions without observing any decrease of the catalytic activity. Powder XRD measurements of the fresh and used catalysts confirm that the solid retains its initial crystallinity upon reuse. The absence of chromium leaching from the solid to the solution at the end of the reaction reinforces the stability of the heterogeneous MIL-101(Cr)-NO_2 catalyst. To put the stability of MIL-101(Cr)-NO_2 into context, it should be commented that $Cu_3(btc)_2$, also frequently reported as catalyst, undergoes a complete decomposition in a single run under similar conditions.[38]

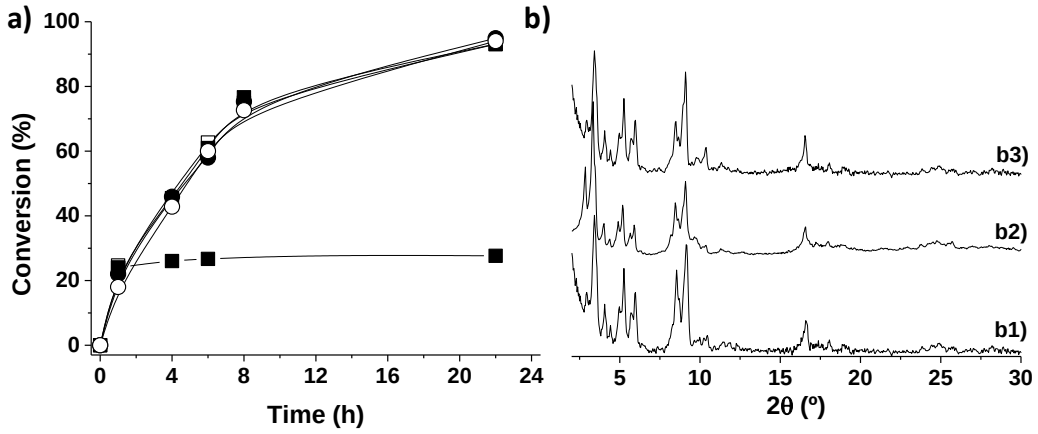


Figure 4.

Based on the present experimental data and previous results using MIL-101(Cr)-X materials, Scheme 1 summarizes a plausible reaction pathway for the aerobic oxidation of thiophenol to diphenyl disulphide using MIL-101(Cr)-NO_2. The observation that the higher the electron withdrawing character of the terephthalate substituent in the MIL-101(Cr)-X, the higher the redox potential of the metal center and consequently the higher the catalyst activity is rationalized with the proposed electron

transfer process from the electron rich SH functional group to the catalyst.[32] The catalytic cycle is restored by the presence of O_2 that becomes reduced to $O_2^{\cdot-}$. Then, the $O_2^{\cdot-}$ can lead to the formation of $HOO^{\cdot}$ radicals that eventually will form H_2O_2 and/or H_2O by a series of consecutive electron and proton transfer steps through the intermediacy of the corresponding reactive oxygen species.[31, 32] It should be noted that any of these reactive oxygen species would react with thiophenol forming the phenylsulphide radical due to the relative strength of O-H bonds respect to S-H bonds

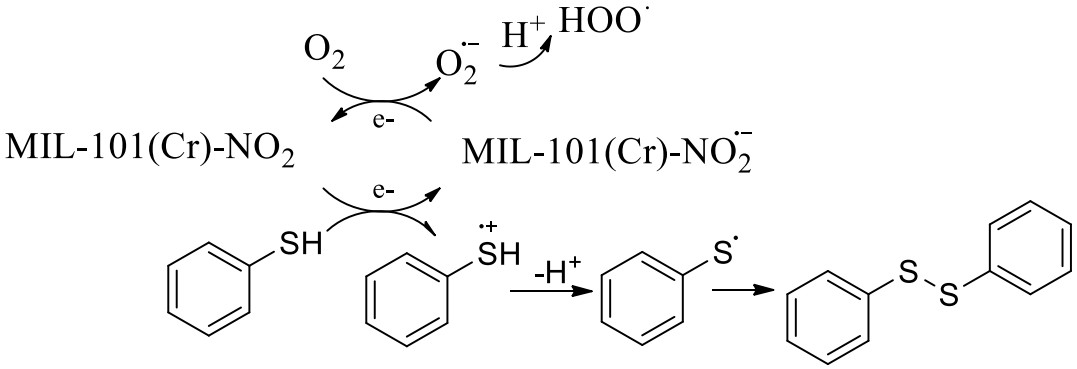


Figure 5.

The MIL-101(Cr)-NO_2 can be also employed as catalyst for the solvent-free oxidative coupling of a series substituted thiophenols having electron donor (CH_3) or electron withdrawing groups (Figure S2) .

3.3. Aerobic oxidative desulfurization of diesel fractions. Use of DBTs.

The second part of the work is focused on the study the applicability of MIL-101(Cr)-NO_2 solid to promote the aerobic oxidation of DBTs in both *n*-dodecane or commercial diesel, a process that has been proposed for the deep oxidative desulfurization of gasoil.[35, 39]

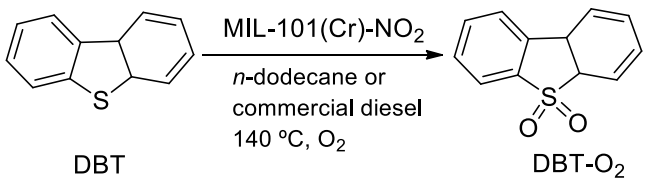


Figure 6.

Initially, a blank control in the absence of catalyst using *n*-dodecane as solvent shows that DBT conversion is less than 10 % under the reaction conditions employed in the present study. Analogously to the results obtained for the aerobic oxidation of thiophenol, it was also observed that the catalytic activity of MIL-101(Cr)-NO_2 is about 3 times higher than that of MIL-101(Cr) to promote the aerobic oxidation of DBT to DBT-O_2 in *n*-dodecane as solvent. In good agreement with this observation, the estimated Ea value for the aerobic oxidation of DBT in n-dodecane using MIL-101(Cr)-NO_2 catalyst is lower (117 kJ mol^{-1}; Figure S2) than that previously reported for MIL-101(Cr)-H under the same conditions (137 kJ mol^{-1}).[35] Notably, the catalytic activity of MIL-101(Cr)-NO_2 was also higher than that of the MIL-100(Fe) or Cr_2O_3 solids as heterogeneous catalysts or the soluble Cr(III) acetate salt (Figure 7).

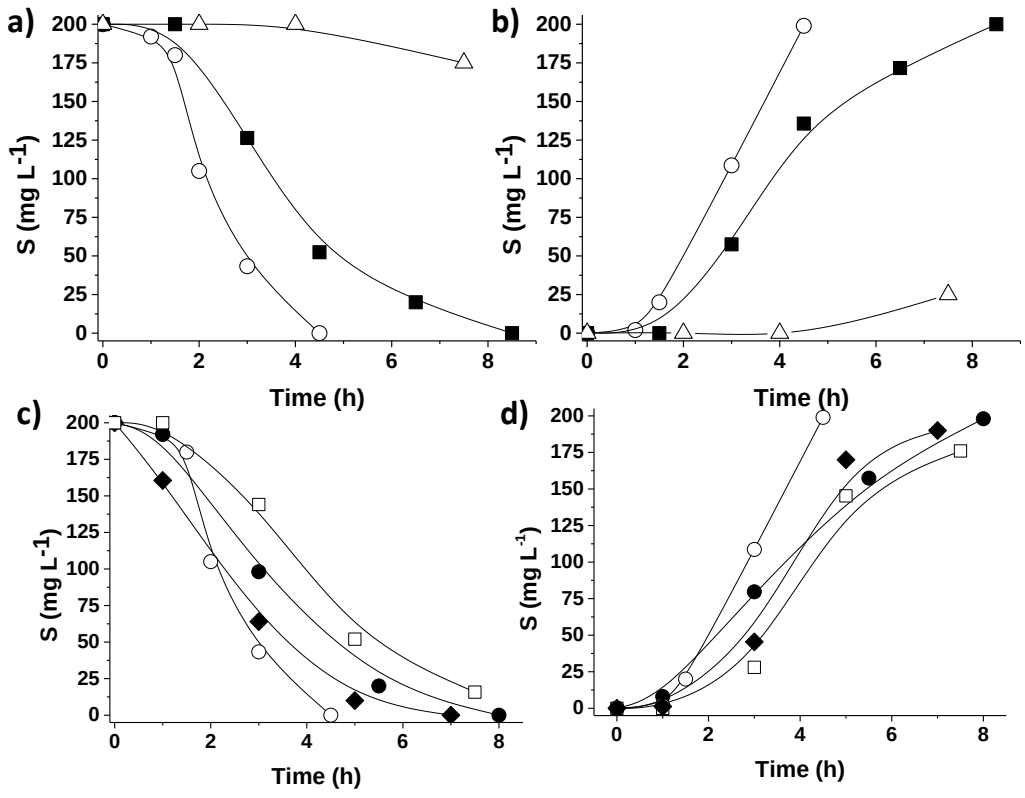


Figure 7.

The stability of the MIL-101(Cr)-NO_2 was assessed by performing five consecutive reaction cycles without observing any decrease of catalytic activity for DBT disappearance or DBT-O_2 formation, while the solid crystallinity is maintained as revealed by powder XRD. Non-detectable chromium leaching from the solid to the solution was observed under the present reaction conditions. In this case, however, the hot filtration test reveals that the reaction still progresses once the solid catalyst is removed from the reaction. If TEMPO is added to the filtered reaction, however, the reaction stops. In addition, the presence of organic hydroperoxides was confirmed indirectly by their quenching with PPh_3 resulting in the formation of $(Ph_3)P=O$.[34] Thus, it can be proposed that the MIL-101(Cr)-NO_2 solid is acting in the aerobic oxidation of DBT to DTB-O_2 in *n*-dodecane as a radical initiator rather than a real catalyst.

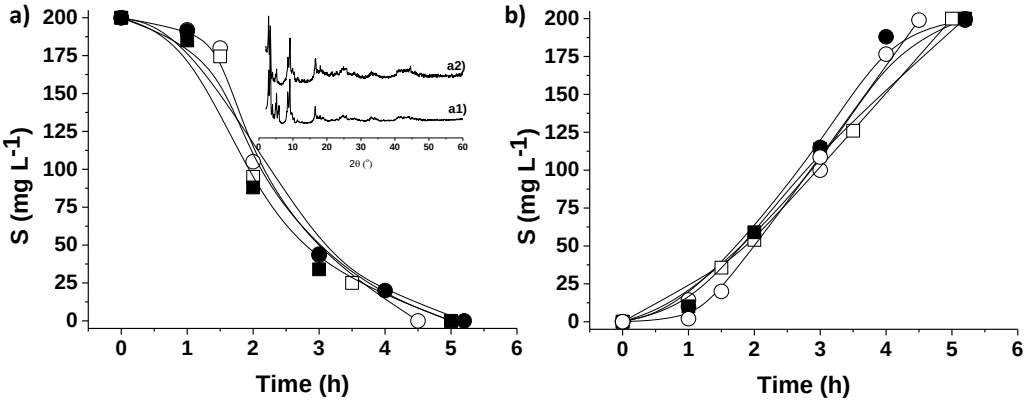


Figure 8.

Previous studies have reported that MIL-101(Cr)-NO_2 activates molecular O_2 leading to the formation of $O_2^{\cdot-}$/$HOO^{\cdot}$ species.[31] In this work, a control experiment using an inert N_2 atmosphere instead O_2 reveals that the catalytic oxidation does not occur in the absence of O_2. With these data Figure 9c summarizes a plausible reaction

mechanism for the aerobic oxidation of DBT to DBT-O_2 by MIL-101(Cr)-NO_2 as radical initiator that is in accordance with previous proposals.[35]

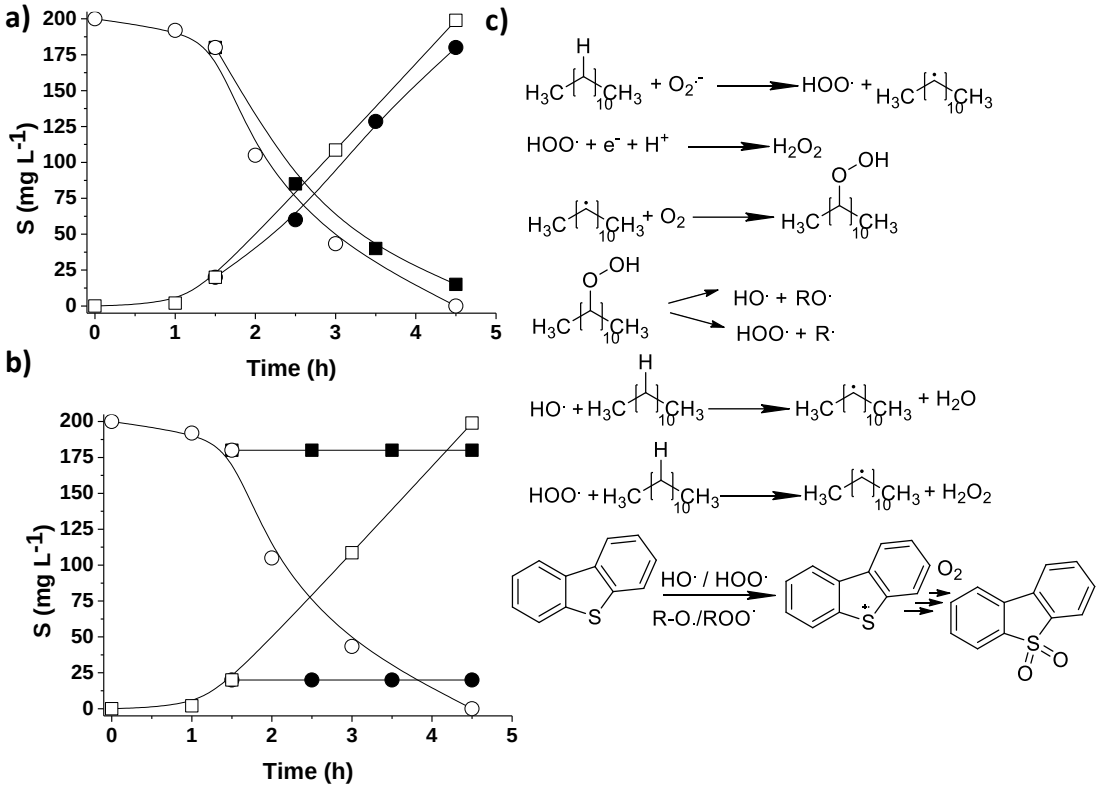


Figure 9.

Figure 10 shows that MIL-101(Cr)-NO_2 is catalytically more active than MIL-101(Cr)-H to promote also the 4-MeDBT and 4,6-diMeDBT oxidation to their corresponding sulfones. The observed order of reactivity 4,6-diMeDBT>4-MeDBT>DBT can be rationalized considering the increase of the electron density on the sulfur atom due to the presence of electron donor methyl groups in positions 4 and/or 6.[35] This relative reactivity order compares favourable respect to the conventional hydrodesulfurization process in which the methyl substituted DBTs are increasing by more difficult to be removed due to steric encumbrance around the S atom, this requiring high hydrogen pressures (200 atm) combined with high temperatures (>300 ºC) to make 4-MeDBT and 4,6-diMeDBT reactive.[40, 41]

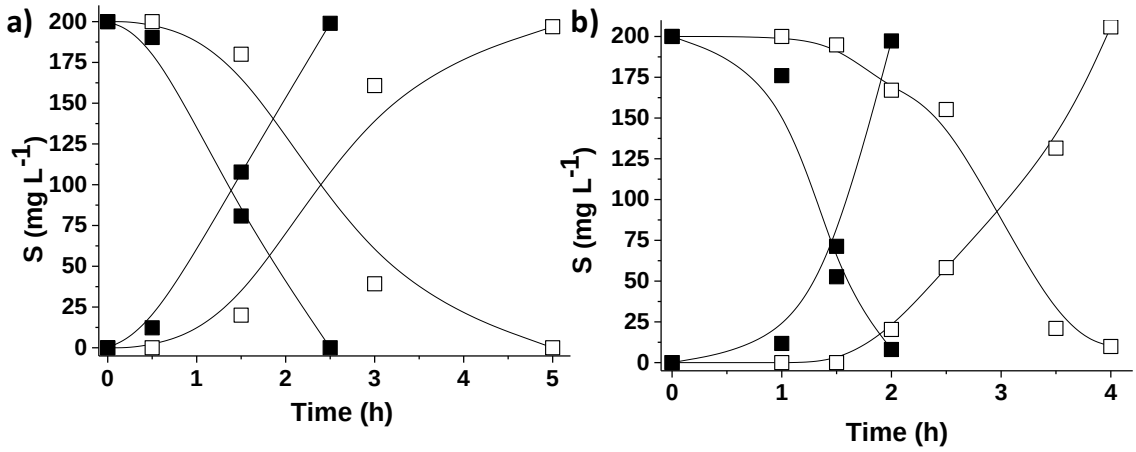


Figure 10.

Importantly, the oxidative desulfurization of DBT using MIL-101(Cr)-NO_2 as catalyst can be carried out efficiently in commercial diesel exhibiting higher activity respect to MIL-101(Cr)-H. The increase of reaction time required for the conversion of DBT and formation of DBT-O_2 in commercial diesel respect to the *n*-dodecane is easily rationalised considering the chain length in diesel that is constituted by a complex mixture of alkanes and/or the presence antioxidant additives. In any case, oxidative desulfurization process is about two times higher using MIL-101(Cr)-NO_2 as catalyst respect to its parent MIL-101(Cr)-H.[35]

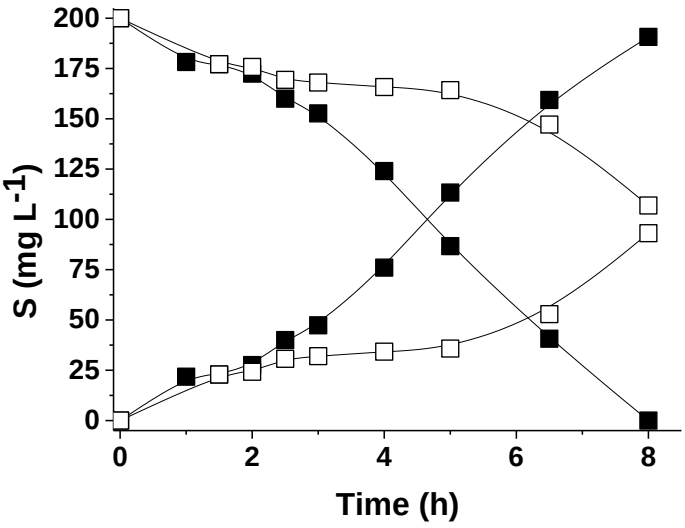


Figure 11.

4. Conclusions

The present work has shown that the catalytic activity of the benchmark MIL-101(Cr)-H MOF can be tuned by the presence of electron donor (CH_3 or NH_2) or withdrawing (NO_2, Cl or SO_3H) substituents on the terephthalate organic ligand. MIL-101(Cr)-NO_2 is the most active catalyst of the series by a factor of 4 and 3 respect to MIL-101(Cr)-H, promoting the solvent-free aerobic oxidation of benzenethiol to diphenylsulfide and the aerobic oxidation of dibenzothiophenes in *n*-dodecane or commercial diesel, respectively. The activity of MIL-101(Cr)-NO_2 is also higher than MIL-101(Fe), Cr_2O_3 or soluble Cr(III) salts for the aerobic oxidation of thiophenol and the aerobic desulfurization of dibenzothiophenes. Catalytic experiments reveal that MIL-101(Cr)-NO_2 is acting as a truly heterogeneous catalyst in the case of aerobic oxidation of thiophenol, while for the oxidation of dibenzothiophenes it is acting as a radical initiator. For both processes, the catalyst can be reused several times without any decrease in activity, maintaining its initial crystallinity with negligible metal leaching. In summary, this work exemplifies how the activity of the benchmark MIL-101(Cr) solid to promote oxidations using exclusively molecular oxygen can be enhanced by introducing NO_2 groups on the organic ligand.

Acknowledgements

Financial support by the Spanish Ministry of Science and Innovation (Severo Ochoa and RTI2018-098237-CO21) and Generalitat Valenciana (Prometeo 2017/083) is gratefully acknowledged. S.N. thanks financial support by the Fundación Ramón Areces (XVIII Concurso Nacional para la Adjudicación de Ayudas a la Investigación en Ciencias de la Vida y de la Materia, 2016) and Ministerio de Ciencia, Innovación y Universidades CTQ-2018 RTI2018-099482-A-I00 project.

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Figure captions

Figure 1. a) Oxidative coupling of the aerobic oxidation of thiophenol to diphenyl disulphide by oxygen. b) Time-conversion plot for the aerobic oxidation of thiophenol to diphenyl disulphide using MIL-101(Cr)-H (●), MIL-101(Cr)-SO_3H (Δ), MIL-101(Cr)-Cl (○), MIL-101(Cr)-NO_2 (■), MIL-101(Cr)-NH_2 (▼), MIL-101(Cr)-CH_3 (◊) and without catalyst (□). Reaction conditions: Catalyst (0.04 mmol Cr), thiophenol (2 mL, 20 mmol), O_2 atmosphere (balloon), reaction temperature (140 ºC).

Figure 2. a) Plot of the logarithm of the relative first order rate constant measured at initial reaction time for thiophenol oxidation versus the meta Hammett constant of each substituent on the terephthalate linker of MIL-101(Cr)-X solids; b) Plot of the half-wave potential ($E_{1/2}$) versus the initial reaction rate for the aerobic oxidation of thiophenol promoted by MIL-101(Cr)-X solids with different substituent at the bdc ligand.

Figure 3. a) Comparison of the catalytic activity for the aerobic oxidation of thiophenol to disulphide using MIL-101(Cr)-NO_2 (■), MIL-100(Fe) (□), commercial Cr_2O_3 (●) or Cr(III) acetate (○). b) Time profile of thiophenol conversion in the presence of O_2 (■), Air (□) or Ar (●). The inset show a plot of the initial reaction rate vs the O_2 pressure showing a first order relationship. c) Time conversion plots for the aerobic oxidation of thiophenol in the presence of MIL-101(Cr)-NO_2 at different reaction temperatures: 140 ºC (□), 130 ºC (■), 120 ºC (○), 110 ºC (●). d) Arrhenius plot of the natural logarithm of the initial reaction rate obtained from panel c versus vs 1/T (K^{-1}). Reaction conditions: catalyst (0.04 mmol Cr), thiophenol (2 mL, 20 mmol), O_2 atmosphere (balloon) and reaction temperature (140 º C for panels a, b).

Figure 4. a) Hot filtration test and reusability experiments for the aerobic oxidation of thiophenol to disulphide using MIL-101(Cr)-NO_2 as catalyst. b) PXRD of the fresh (b1), six-times (b2) and ten-times (b3) used MIL-101(Cr)-NO_2 catalyst.

Figure 5. Proposed pathway for the aerobic oxidation of thiophenol to benzene disulphide using MIL-101(Cr)-NO_2 as catalyst.

Figure 6. Aerobic oxidation of DBT to DBT-O_2 using MIL-101(Cr)-NO_2 as catalyst.

Figure 7. DBT oxidation (a, c) to DBT-O_2 (b, d) using MIL-101(Cr)-NO_2 (○), MIL-101(Cr)-H (■), MIL-100(Fe) (□), Cr_2O_3 (●) or Cr(III) acetate (♦). A control experiment in the absence of catalyst (Δ) is also shown. Reaction conditions: Catalyst (0.04 mmol Cr), DBT (11.5 mg), *n*-dodecane (10 mL), O_2 atmosphere (balloon), reaction temperature (140 ºC).

Figure 8. Reusability experiments of MIL-101(Cr)-NO_2 for the aerobic oxidation of DBT (a) to DBT-O_2 (b) in *n*-dodecane as solvent. Legend: 1st use (○), 3th use (□), 4th use (■) and 5th use (●). The inset in panel a shows from bottom to top the PXRD of the fresh (a1) and three-times used catalyst (a2). Reaction conditions: Catalyst (0.04 mmol Cr), DBT (11,5 mg), *n*-dodecane (10 mL), O_2 atmosphere (balloon), reaction temperature (140 ºC).

Figure 9. a) Hot filtration experiment showing DBT oxidation (○, ●) to DBT-O_2 (□, ■) in the presence of catalyst (open symbols) or once the catalyst is removed by filtration (close symbols). b) Hot filtration experiment showing DBT oxidation (○) to DBT-O_2 (□) in the presence of catalyst (open symbols) or once the catalyst is removed by filtration and TEMPO as radical quencher is added (close symbols). Reaction conditions: Catalyst (0.04 mmol Cr), DBT (11,5 mg), *n*-dodecane (10 mL), O_2 atmosphere (balloon), reaction temperature (140 ºC), when the catalyst is filtered and TEMPO added (20 mol%. c) Proposed pathway for the aerobic oxidative of DBT to DBT-O_2 in the presence of MIL-101(Cr) solid and *n*-dodecane as solvent.

Figure 10. Oxidation of 4-DBT (a) and 4,6-DBT (b) to their corresponding sulfones (a, b) using MIL-101(Cr)-NO_2 (■) or MIL-101(Cr)-H (□). Reaction conditions: Catalyst (0.04 mmol Cr), 4-DBT (200 ppm S) or 4,6-DBT (200 ppm S), *n*-dodecane (10 mL), O_2 atmosphere (balloon), reaction temperature (140 ºC).

Figure 11. Aerobic oxidation of DBT to DBT-O_2 using MIL-101(Cr)-NO_2 (■) or MIL-101(Cr) (□) using commercial Diesel as solvent. Reaction conditions: Catalyst (0.04 mmol Cr), DBT (200 ppm S), Diesel (10 mL), O_2 atmosphere (balloon), reaction temperature (140 ºC).