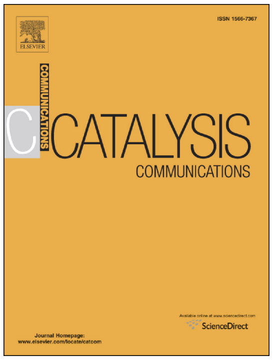

[MoO3(2,2′–bipy)]n catalyzed oxidation of amines and sulfides

Irene Tosi, Carolina Vurchio, Marta Abrantes, Isabel S. Gonçalves, Martyn Pillinger, Fabrizio Cavani, Franca M. Cordero, Alberto Brandi

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$[MoO_3(2,2'–bipy)]_n$ catalyzed oxidation of amines and sulfides

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ABSTRACT

The polymeric catalyst [MoO_3(2,2'–bipy)]$_n$ has been employed in the oxidation of secondary amines to nitrones, and sulfides to sulfoxides or sulfones, using *tert*–butylhydroperoxide (TBHP) as the stoichiometric oxidant. Whereas the oxidation of amines occurs with less proficiency with respect to other previously studied polymeric Mo catalysts, the oxidation of sulfides occurs in high yield and selectivity. The catalyst is flexible in terms of substrate scope (aromatic, aliphatic and cyclic sulfides, thioheterocycles such as dimethyldibenzothiophene, the oxidation of which forms the basis of oxidation/separation processes for the desulfurization of fuels) and the ability to switch sulfoxide/sulfone product selectivities by adjusting the reaction conditions.

Keywords: oxidation; molybdenum; hybrid materials; oxidative desulfurization; sulfides; amines

1. Introduction

The chemistry of Mo(VI) assumes a key role in organic synthesis and in industrial processes, where Mo(VI) catalysts find valuable applications in a large variety of different reactions like oxidation, hydrocarbon dehydrogenation, ammoxidation, and metathesis [1-2].

Complexes containing the *cis*-dioxomolybdenum(VI) structural unit represent the vast majority of the complexes studied as catalysts or catalyst precursors [3-5]. Among the potential applications, catalytic oxidative desulfurization (ODS) of liquid fuels is one of the most important, since it is seen as a viable alternative to conventional hydrodesulfurization (HDS) for the near-complete removal of sulfur-containing compounds from oils [6,7]. ODS is based on the oxidation of the organosulfur compounds to the corresponding sulfoxides and/or sulfones which can then be removed by adsorption, distillation, or solvent extraction. The oxidation and removal of benzothiophene derivatives from a model oil by using the complex [MoO_2Cl_2(4,4'-di-tert-butyl-2,2'-bipyridine)] as a (pre)catalyst was recently reported [8].

One of the main goals in catalytic sulfide oxidation is to obtain both sulfoxide and sulfone with high selectivity by using the same system. Although many methods are known for the selective oxidation of sulfides [7,9-12] only a few studies are available for obtaining sulfoxides and sulfones with the same system, under adjusted reaction conditions [13-18]. Selectivity is very high, mainly for sulfoxides that are usually obtained in high yields [14]. Reaction conditions are mild for the formation of both sulfoxides and sulfones, in contrast to other methods that need a higher amount of oxidant to obtain high yields of sulfones [16]. Molybdenum complexes have already been studied as catalysts for the oxidation of sulfides. Molybdenum oxo–peroxo complexes have shown good results for the formation of sulfoxides [19]. Molybdenum carbonyls [18] and oxides [15] have been able to catalyze both selective oxidations, to sulfoxides and to sulfones, by changing the reaction conditions.

In the course of the exploration of metal oxide-based hybrid materials for their potential properties in the fields of catalysis, sorption, electrical conductivity, magnetism, and optics, some of us have been employing soft inorganic chemistry processes to obtain molybdenum(VI) oxide/organic hybrid materials [20,21]. One of these compounds, a molybdenum oxide/2,2'-bipyridine hybrid material with the formula $\{[MoO_3(2,2'\text{-bipy})][MoO_3(H_2O)]\}_n$, was tested in the oxidation of secondary amines to nitrones using either urea hydrogen peroxide (UHP) adduct or TBHP as the oxidant, and proved to be a good water-tolerant catalyst for the oxidation of secondary amines under mild conditions [22].

Continuing the study of molybdenum(VI) oxide inorganic-organic hybrid materials in oxidation reactions we now focus on a new catalyst, polymeric $[MoO_3(2,2'\text{-bipy})]_n$ (**1**) (Fig. 1) [20,23-25], for its stability, synthetic availability, and recycling possibilities. Structurally, **1** can be considered as a polymeric version of $[MoO_2X_2(L)]$ complexes such as the dichloro complex mentioned above.

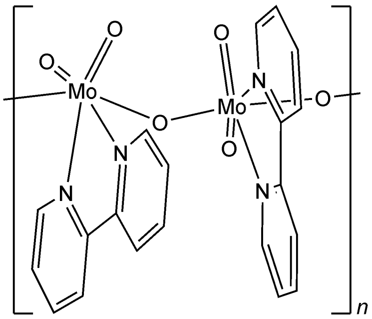

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Fig. 1. Schematic representation of the structure of **1**.

The catalytic potential of **1** for oxidation reactions was apparent after obtaining interesting results for the epoxidation of olefins using TBHP as oxidant [20,24]. In the present work, the oxidation power of this catalyst was tested for the oxidation of secondary amines to nitrones to compare its reactivity with that of other catalysts [22]. The study was then extended to the oxidation of sulfides to sulfoxides and sulfones. All these oxidation products, by-the-way, are versatile synthons in organic chemistry [26,27].

Mo(VI) catalysts have only rarely been examined in parallel as catalysts for the oxidation of sulfides and amines [28]. Although much less studied, the performance of ODS catalysts in the oxidation of nitrogen-containing compounds (or in sulfoxidation in the presence of nitrogen-containing compounds) is important since the removal of such compounds from oils is highly desirable, and there is interest in the development of processes for simultaneous desulfurization and denitrogenation [29].

2. Experimental

2.1. Catalyst synthesis

$[MoO_3(2,2'\text{-bipy})]_n$ (**1**) was prepared as described previously by the oxidative decarbonylation of the tetracarbonyl complex *cis*-$[Mo(CO)_4(2,2'\text{-bipy})]$ with TBHP under mild conditions [20].

2.2. General procedure for amine oxidation

To a 0.5 M solution of amine in anhydrous CH_2Cl_2 (1 mL) was added the catalyst (5 mol%) and TBHP (5.5 M solution in decane, 3 mol equiv.). The reaction mixture was stirred at 40 °C for 63–118 h and then dried over anhydrous Na_2SO_4, and filtered. The solution was concentrated under reduced pressure and the crude residue purified by flash column chromatography (silica gel).

2.3. General procedure for sulfide oxidation

To a 0.5 M solution of sulfide in CH_2Cl_2 was added TBHP (5.5 M solution in decane, 1.5 or 3 mol equiv.) and the catalyst (3 mol%). The suspension was stirred at 20 °C or 40 °C for 1–20 h and then filtered through a short pad of Celite®. The solution was concentrated under reduced pressure and the crude residue purified by flash column chromatography (silica gel). Spectroscopic data of isolated compounds are provided in the Supplementary Data.

3. Results and discussion

3.1. Oxidation of amines

Dibenzylamine **2** was used as a model substrate for preliminary screening and optimization of the reaction conditions for the oxidation of secondary amines to nitrones catalyzed by polymeric $[MoO_3(2,2'\text{–bipy})]_n$ (**1**) (Table 1). Reactions were initially run with dibenzylamine (0.5 mmol), TBHP (1.5 equiv.), and catalyst **1** in $CDCl_3$ at 40 ºC to check the reactivity of the catalyst by NMR in forming nitrone **3** (Fig. 2).

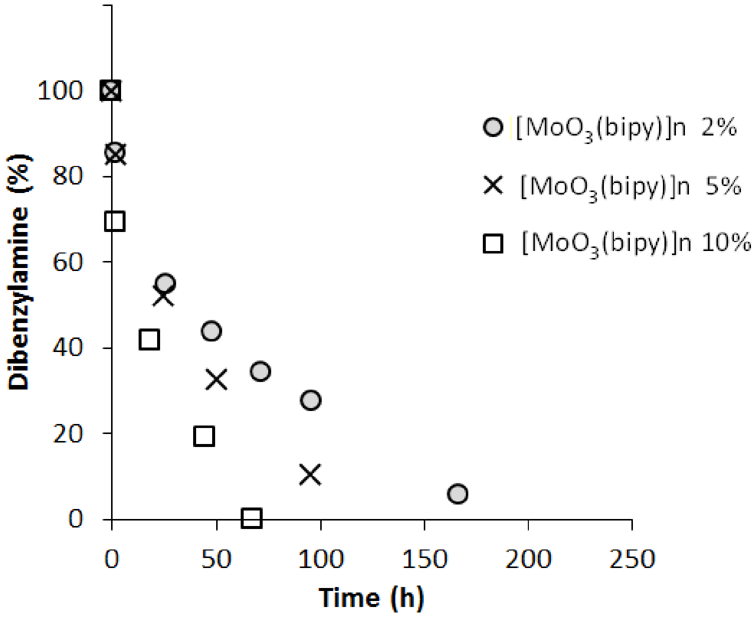
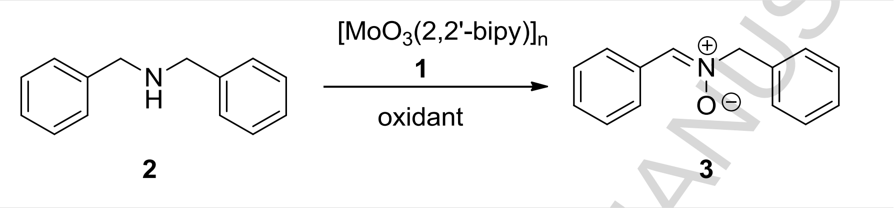


Fig. 2. Oxidation of dibenzylamine with different amounts of catalyst **1**.

The catalyst amount affects intensely the reaction rate and the best choice (5 mol%) was a compromise between the very long reaction times required when using 2 mol% of catalyst and the somewhat shorter times, but less practical in terms of costs, required when 10 mol% of catalyst was employed.

Reactions were then repeated at different temperatures with a view to testing the stability of nitrones under the reaction conditions. Conversions and yields were calculated from the ^1H NMR spectra with 1,4–dioxane as internal standard, and measured by recovery of the amine and the nitrone after purification (Table 1). A slight increase of the temperature from 40 to 55 °C provides a higher conversion and much shorter reaction time (25 vs 95 h); however, as expected, the yield of the nitrone, which is temperature sensitive, is reduced. As already observed, the change of the reaction solvent from $CDCl_3$ to CH_2Cl_2 does not affect the results [22]. UHP was also tested as oxidant under the same reaction conditions except for the solvent because UHP requires polar solvents, such as MeOH. UHP is able to increase the reaction rate (23 hours), but the nitrone is less stable in a protic solvent and a higher amount of benzaldehyde and other decomposition products, such as benzyloxime, were present in the final reaction mixture. Accordingly, the use of TBHP in CH_2Cl_2 was preferred because the reaction can be more readily carried out under anhydrous conditions.

Table 1 Oxidation of dibenzylamine **2** to *C*-phenyl,*N*-benzyl nitrone **3**[a]



T (°C)	Oxidant	Solvent	Time (h)	Conv. (%)	Yield **3** (%)
40	TBHP	$CDCl_3$	95	90[b]	89[b]
40	TBHP	CH_2Cl_2	94	93[c]	75[c]
55	TBHP	$CDCl_3$	25	>99[b]	67[b]
55	TBHP	$CDCl_3$	24	>99[c]	54[c]
40	UHP	MeOH	23	96	26[c]

[a] Reaction conditions: dibenzylamine (0.5 mmol), TBHP (3 mol equiv.), catalyst **1** (5 mol %).
[b] Conversions and yields calculated by using internal standard method (1,4-dioxane as internal standard).

[c] Conversions and yields based on the recovered amine and nitrone after purification.

At the end of the reactions, the catalyst can be recovered unchanged by centrifugation of the reaction mixture and subsequent washing. The recovered catalyst shows the same activity in a second run (conversion of substrate 90%, yield to **3** 87%, for the reaction carried out at 40°C and 90 h reaction time, with TBHP oxidant).

The optimized conditions were then applied to different substrates to verify the scope of the reaction (see Supplementary Data, Table S1, Scheme S1 and S2). The study confirmed the moderate reactivity of the catalyst. A test of oxidation of 1,2,3,4–tetrahydroisoquinoline conducted in the presence of the reactive dipolarophile N–Ph maleimide showed the formation of the amine Michael addition product besides minor amounts of the cycloaddition product. Indeed, the Michael addition is preferred over the cycloaddition of 3,4–dihydroisoquinoline *N*–oxide, because of the very slow formation of the nitrone (see Supplementary Data).

A plausible oxidation mechanism could involve the coordination of the stoichiometric oxidant by the metal without changing the metal oxidation number. In analogy with the hypothesized mechanism [30-32] for catalytic alkene epoxidation, the oxygen is transferred only from the hydroperoxide and not from the catalyst that is found unchanged at the end of the reaction. The proposed mechanism involves a rate determining nucleophilic attack of the amine to an oxygen of the coordinated hydroperoxide giving the corresponding hydroxylamine. A further faster oxidation followed by water elimination results in the nitrone.

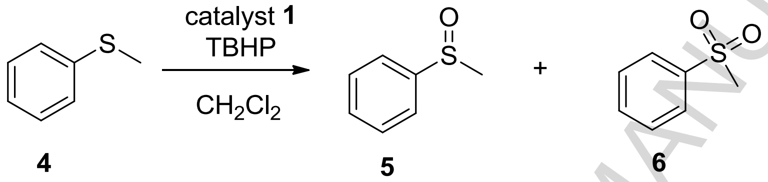
3.2. Oxidation of sulfides

The catalyst $[MoO_3(2,2'\text{–bipy})]_n$ showed a higher selectivity in the oxidation of sulfides than other molybdenum compounds previously studied. It seems to have a similar reactivity to MoO_2Cl_2: this compound, previously studied for the oxidation of sulfides to sulfoxides or sulfones [15], showed high efficacy and selectivity without affecting other functional groups present in the molecule. The extension of the study to $[MoO_3(2,2'\text{–bipy})]_n$ can bring several advantages because of its stability, availability and possibilities of recycling.

Thioanisole **4** was chosen as a model substrate to check the best reaction conditions. At the beginning the same conditions as used for the oxidation of amines were used. The $[MoO_3(2,2'\text{–bipy})]_n$ catalyst showed much higher efficiency in the oxidation of sulfides than amines. The sulfoxide **5** was recovered after an easy filtration of the reaction mixture in good yield (Table 2).

Using 5 mol% of catalyst **1** and 3 mol equiv. of TBHP at room temperature, the thioanisole consumption was complete after just two hours (Table 2, entry 1). The catalyst in these conditions showed high selectivity: although an excess of oxidant (3 mol equiv. of TBHP) was used, the ratio between sulfoxide **5** and sulfone **6**, the product of over–oxidation, was 22:1 in the final crude mixture, calculated from ^{1}H–NMR spectra (see spectroscopic data for sulfides and sulfones in the Supplementary Data). Using a stoichiometric amount of oxidant (1 mol equiv. of TBHP) (Table 2, entry 2), the reaction was slower: the thioanisole consumption was complete after 24 hours, the ratio between **5** and **6** was slightly higher (26:1), and the isolated yield of sulfoxide **5** high (88%).

Table 2 Oxidation of thioanisole **4** to sulfoxide **5** and sulfone **6** with TBHP and $[MoO_3(2,2'\text{-bipy})]_n$ catalyst.



Entry	TBHP (mol eq.)	Cat. **1** (mol%)	T (°C)	Time (h)	^{1}H-NMR Ratio **5/6**	Isolated Yield (%) **5**	**6**
1	3	5	20	2	22:1	-	-
2	1	5	20	24	26:1	88	-
3	3	3	20	2	81:1	97	traces
4	3	1	20	4	39:1	94	traces
5	1.5	3	20	3	70:1	93	traces
6	3	5	40	16	-	-	97

The impact of catalyst amount was also evaluated. Use of 3 mol% of **1** with 3 equiv. of oxidant affords **5** in excellent yield and selectivity after 2 hours (Table 2, entry 3). When the catalyst amount was reduced to 1 mol% a lower selectivity is observed and a longer reaction is required for the complete conversion of the reagent (Table 2, entry 4). Finally the best conditions from a practical point of view turned out to be the use of 3 mol% of **1** with 1.5 mol equiv. of TBHP at 20

°C since this combines lower amounts of catalyst and oxidant with efficiency and short reaction times (Table 2, entry 5). It should be stressed here the role of the catalyst. The same reaction of Table 2, entry 5 run without the presence of catalyst **1** leads after 16 h to only a 37% conversion of sulphide **4** to sulfoxide **5**.

Interestingly, by heating **4** in the presence of 3 mol equiv. of TBHP and 5 mol% of catalyst at 40 °C for 16 hours only sulfone **6** was obtained and isolated in excellent yield with opposite selectivity of that observed at room temperature (Table 2, entries 6 and 1).

The fast sulfide oxidation to sulfoxide and the slower oxidation to sulfone, which is the key for the observed selectivity, can be appreciated from Fig. 3. These results open new interesting paths for selective oxidation of sulfides, because catalyst **1** shows high efficiency and selectivity, and prompted us to study the scope of the oxidation by polymeric catalyst **1**.

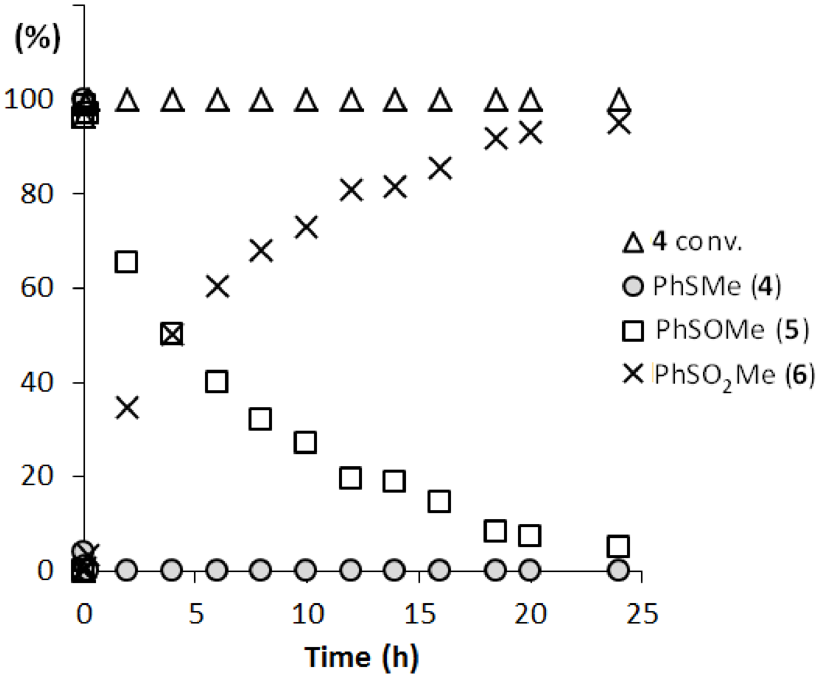
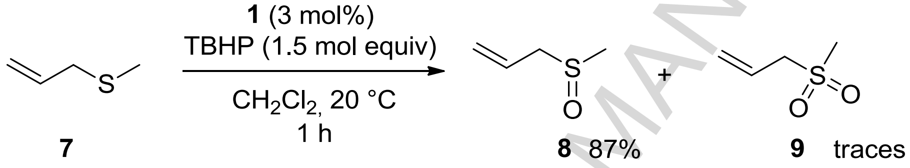


Fig. 3. Kinetics of thioanisole (**4**) oxidation. Reaction conditions: **1** (3 mol%), TBHP (3 mol equiv.), CH_2Cl_2 or $CDCl_3$, 40 °C.

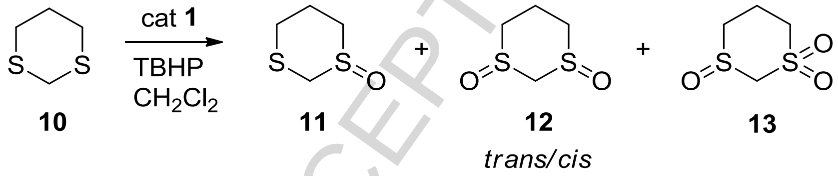
Allylmethylsulfide **7** was selectively oxidized to the sulfoxide **8** under the common reaction conditions (Scheme 1). Only traces of sulfone **9** were observed in the crude mixture. The lack of reactivity of the allylic double bond with this reagent is noteworthy.

Oxidation of dithiane **10** turned out to be strongly affected by the amount of the oxidant TBHP used (Table 3). Using an almost stoichiometric amount of TBHP and 3 mol% of the catalyst, monosulfoxide **11** was selectively obtained in good yield (86%) after 4 hours (Table 3, entry 1). When pure **11** was treated with 1.5 mol equiv. of TBHP in the presence of the catalyst, 1,3–dioxides **12** and 1,1,3–trioxide **13** were obtained in a 1.6:1 ratio and quantitative overall yield (Table 3, entry 2). Oxidation of **10** with 3 mol equiv. of TBHP afforded a higher **12**/**13** ratio (3.3:1) (Table 3, entry 3). The thermodynamically more stable disulfoxide *trans*–**12** [33] was obtained as the major product (45–46% yield) in both the last two experiments. The combined yields of *cis*–**12** and **13** were 52–54% in entries 2–3 (Table 3) suggesting that trioxide **13** derives almost exclusively from *cis*–12 under the reported reaction conditions.



Scheme 1. Oxidation of allylmethylsulfide.

Table 3 Oxidation of dithiane **10**[a]



				Yield (%)[b]			
Entry	SM[c]	TBHP (mol equiv)	Time (h)	**11**	*trans*-**12**	*cis*-**12**	**13**
1	**10**	1.1	4	86	traces	traces	-
2	**11**	1.5	14	-	46	16	38
3	**10**	3	17	-	45	30	22

[a] reaction conditions: $[MoO_3(2,2'\text{-bipy})]_n$ (3 mol%), TBHP (5.5 M in decane), CH_2Cl_2, 20 °C.
[b] Yield of isolated compounds
[c] SM = starting material.

A competition experiment on the ability of catalyst **1** to oxidize sulfides in the presence of amines was carried out. A 1:1 mixture of thioanisole **4** and 2–methylpiperidine was treated with 3 mol% of the catalyst **1** and 1.5 mol equiv. of TBHP at 20 °C in CH_2Cl_2. After 3 hours reaction, a mixture of thioanisole, its sulfoxide, and piperidine in a 1:0.7:0.8 ratio (calculated by ^{1}H NMR) was obtained along with traces of the nitrone. Accordingly, complex **1** is able to catalyze a selective oxidation of the sulfide in the presence of the amine. However, the oxidation rate of sulfide was significantly slowed down (see Table 2, entry 5). During the reaction a solubilization of the catalyst was observed [34], suggesting a coordinative interaction of the amine with Mo that causes a reduction of the oxidative power of the Mo complex. This result might also explain the sluggishness of the catalyzed oxidation of secondary amines (see Table S1, Supplementary Data).

2–Methylbenzothiazole, which contains nitrogen and sulfur in an aromatic ring, was inert to oxidation under the standard reaction conditions.

Another thio–heterocycle, 4,6–dimethyldibenzo[*b*,*d*]thiophene (DMDBT, **14**), was then considered due to its importance in the petrochemical industry and diesel fuel production. In fact, the removal of this compound from diesel fuel is a practice to improve the quality of the fuel, mainly regarding pollution by exhaust fumes, and oxidative desulfurization is one of the foremost possibilities of removing such compounds from liquid fuels by oxidation/extraction [6,35].

Under treatment of DMDBT with 1.5 mol equiv. of TBHP in the presence of 3 mol% of **1** at room temperature, the conversion after 24 h is only moderate (40%), but only the sulfoxide **15** can be observed. Increasing the temperature to 40 °C boosts the conversion to over 80%, but a mixture of sulfoxide **15** and sulfone **16** is formed in a 2.8:1 ratio. More practically, 3 mol equiv. of TBHP in the presence of 3 mol% of **1** at 40 °C affords a complete conversion after 20 h into a 1.8:1 mixture of sulfoxide **15** and sulfone **16**, that can be isolated in 56% and 30% yield, respectively, after chromatography.

These last results show that the species $[MoO_3(bipy)]_n$ is an active catalyst for the selective oxidation of different types of sulfides, extending the existing technologies [6,7] using a heterogeneous, recyclable and easy to prepare system.

3. Conclusion

The one–dimensional inorganic/organic hybrid polymer $[MoO_3(2,2'–bipy)]_n$ (**1**) is one member of a very large family of molybdenum oxide/organonitrogen hybrid materials that has only recently started to be explored as a source of useful catalysts for oxidation reactions. Some advantages of these materials are that they can be prepared through convenient soft chemistry routes and are crystalline, stable, storable forms of $[MoO_2X_2(L)]$ complexes, for eventual use as either heterogeneous catalysts or sources of soluble organonitrogen-coordinated Mo^{VI} active species.

In the present work, the scope of reactions catalyzed by **1** has been extended to include the oxidation of amines and sulfides using TBHP as oxidant under mild conditions. Mo-based catalysts have very rarely been concurrently examined for these two reactions. However, both transformations are important in the context of developing new oxidative processes for the synthesis of valuable synthons such as nitrones, sulfoxides and sulfones as well as the production of clean transportation fuel oils. The findings obtained in the present work suggest that the catalyst **1** may have potential in this regard and furthermore can be used in procedures for the switchable synthesis of sulfoxide or sulfone via the oxidation of sulfides with the same oxidant by changing a reaction parameter.

Although the results are in line with other literature results for oxidation of this substrate [9, 10], only few studies are available for the obtainment of sulfoxides and sulfones with the same system [13-18]. We point out the remarkable selectivity observed with our polymeric catalyst and the mild reaction conditions.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2017.xx.xxx.

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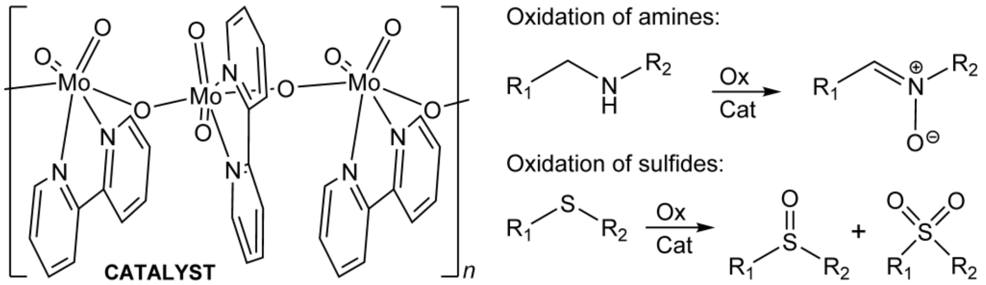
Graphical abstract



Highlights

- $[MoO_3(2,2'–bipy)]_n$ is active in oxidation of amines and sulfides with *t*-BuOOH.
- The oxidation of sulfides occurs in high yield and selectivity.
- Selectivity to sulfones and sulfoxide can be tuned by changing reaction conditions.