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ORIGINAL PAPER

Immobilization of MoO_2Cl_2 on polystyrene via different linkers and oxidation of sulfides in the presence of hydrogen peroxide

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Abstract Chloromethylated polystyrene was oxidized to aldehydic polystyrene and by reaction of this aldehydic polystyrene resin with furfuryl amine and 2-(amino methyl) pyridine, imine-bounded polystyrene resins **1a** and **1b** were obtained. Amine-bounded polystyrene resins **1c**–**1f** were also prepared by direct reaction of chloromethylated polystyrene and amines. These functionalized polystyrene resins were used to immobilize MoO_2Cl_2 on polystyrene. These functionalized polystyrene resins were characterized with elemental analysis (CHN) and FT-IR spectrum. Polymer-supported catalysts were characterized with FT-IR and neutron activation analysis (NAA). These catalysts were used in oxidation of methyl phenyl sulfide in the presence of H_2O_2 as oxidant and the results showed that these catalysts were highly active and selective. The reusability of these heterogeneous catalysts was also investigated and the results showed that the supported MoO_2Cl_2 catalyst on polystyrene via imidazole liker was highly reusable as it was used 15 times in oxidation of methyl phenyl sulfide in the presence of environmental benign oxidant (H_2O_2) and solvent (H_2O) without any decrease in its activity. Then the catalytic activity of these supported catalysts was investigated in oxidation of some aliphatic and aromatic sulfides. Almost all of these supported molybdenum-based catalysts were highly active and selective in the conversion of these sulfides to their corresponding sulfoxides.

Keywords Polymer-support · Supported catalyst · MoO_2Cl_2 · Oxidation · Sulfoxide

Introduction

Sulfoxides are very important reagents in synthetic organic chemistry; particularly, they are very useful synthetic intermediates for the construction of various chemically and biologically significant molecules [1–3]. Thus, increasing interests have stimulated investigations on new methodologies of sulfoxide synthesis. Among those methods, oxidation of sulfides to sulfoxides or sulfones is an attractive and important method in organic synthesis. Catalytic oxidation of sulfides with environmentally benign oxidant has become increasingly important. Hydrogen peroxide is an ideal oxidant because of high-efficient oxygen content, low cost, safety in storage and operation, readily available, environmentally benign and production of water as a byproduct [3]. In the recent years, many procedures have been developed for hydrogen peroxide oxidation of sulfides catalyzed by several transition metal complexes such as W(VI) [3], Mo(VI) [4], V(V) [5], Ti(IV) [6], Mn(III) [7], Cu(II) [8]. Homogeneous catalysts often provide the best results but use of these catalysts has some disadvantages such as contamination of products with catalyst and difficult separation of catalyst from reaction medium to reuse. In order to overcome to these problems, much effort has been devoted to attachment of homogeneous transition metal complexes to insoluble organic or inorganic solid supports and used as sulfoxidation catalysts [9–15]. These heterogenized catalysts may combine the ease of product separation with reactivity and selectivity founded with homogeneous catalysts.

Recently Chand et al. [16] used MoO_2Cl_2 as effective homogeneous catalyst in oxidation of sulfides. In this article, we report the immobilization of MoO_2Cl_2 on polystyrene via different linkers, and the catalytic activity and reusability of supported catalyst in oxidation of sulfides.

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Experimental

Material

Chloromethylated polystyrene purchased from Aldrich and all other materials were used purchased from Merck. $MoO_2Cl_2(DMF)_2$ was prepared according to the literature [20].

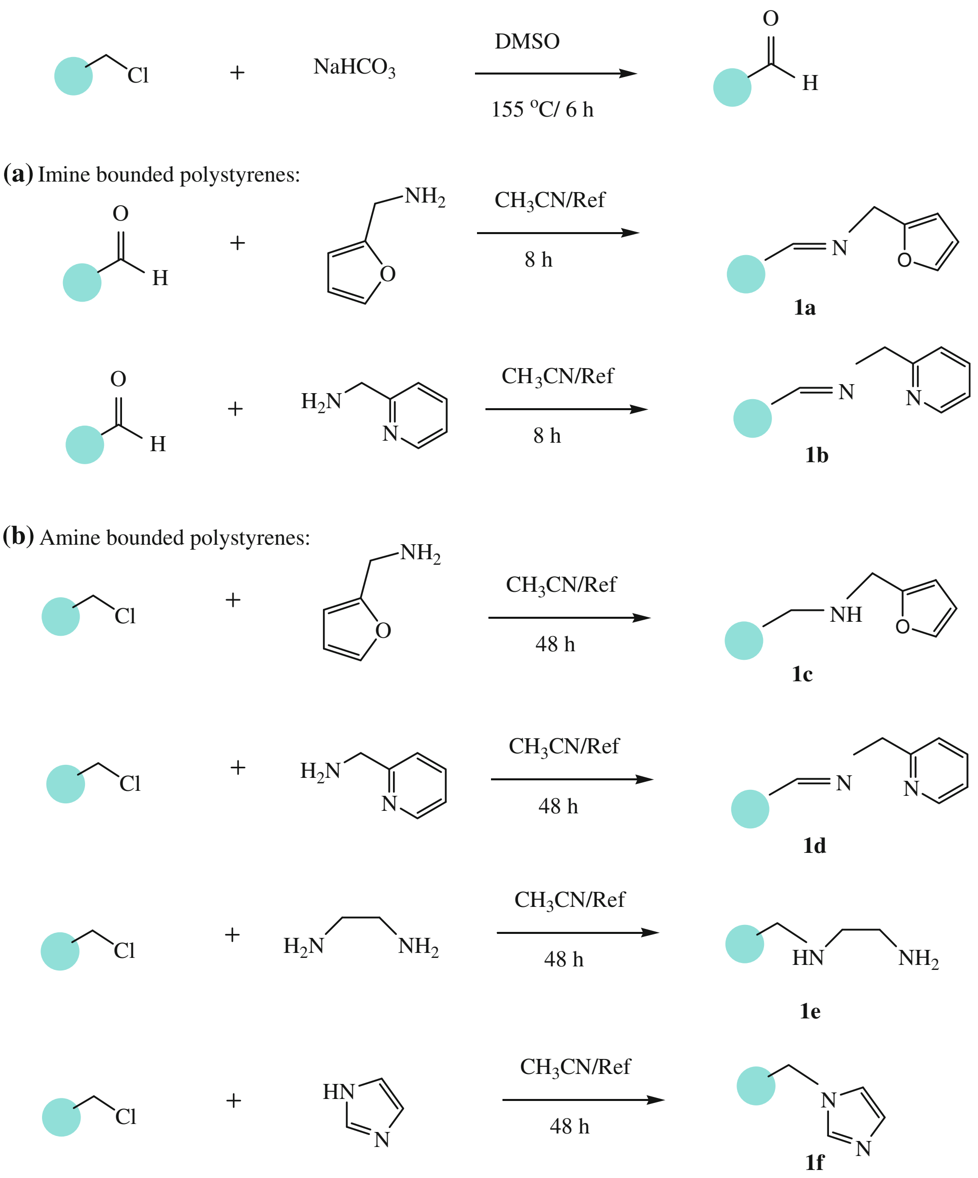
Apparatus and techniques

Infrared spectra were recorded using KBr disks on a FT-IR Perkin–Elmer spectrophotometer. All yields for aliphatic sulfides and methyl phenyl sulfide based on starting materials were obtained by using Varian CP-3800 instrument with silicon-DC 200 column.

Functionalization of polystyrene

*Preparation of imine-bounded polystyrenes (**1a**, **1b**)*

Polystyrene resin (2% DVB) was oxidized to aldehydic polystyrene as described in Ref. [17]. In two separated round-bottom flasks the aldehyde-bearing beads were allowed to swell in methanol and a solution(0.5 M in 25 ml methanol) of amine (furfuryl amine and 2-(amino methyl) pyridine) was added drop-wise to this mixture over a period of 1 h and then refluxed for 7 h. The content was cooled to



Scheme 1 Preparation procedures of functionalized polstyrenes (**1a–1f**)

Table 1 Elemental analysis data of the functionalized polystyrenes **1a**–**1f** and $\nu_{C=N}$ (cm^{-1}) of imine-bounded polystyrenes **1a** and **1b**

Functionalize polystyrene	%C	%H	%N	$\nu_{C=N}$
1a	89.40	8.58	2.02	1,640
1b	87.95	8.70	3.35	1,645
1c	89.17	8.72	2.11	–
1d	88.3	8.41	2.42	–
1e	89.1	8.61	2.29	–
1f	87.09	7.43	3.01	–

room temperature, filtered off, washed thoroughly with methanol and petroleum ether, and dried in vacuum.

Preparation of amine-bounded polystyrenes (**1c**–**1f**)

The functionalized polystyrene resin (2% DVB) with imidazole and ethylene diamine linkers was prepared as we have described previously [18, 19]. Functionalization of polystyrene with furfuryl amine and 2-(amino methyl) pyridine was carried out in similar route except in that furfuryl amine and 2-(amino methyl) pyridine was used instead of imidazole.

Immobilization of $MoO_2Cl_2(DMF)_2$ on polystyrene

To a solution of $MoO_2Cl_2(DMF)_2$ (2.5 g) in DMF (100 ml) was added functionalized polystyrene (1 g). The mixture was vigorously stirred at 100 °C for 24 h. After cooling, the obtained resin was collected by filtration, washed thoroughly with CH_2Cl_2 and dried in vacuum at room temperature for several hours.

General procedure for catalytic oxidation of sulfides in different solvents

All of the reactions were carried out at room temperature under air in a 25 ml flask equipped with a magnetic stirrer bar. In 10 ml of solvent, were added 1 mmol of sulfide, 5 mmol of H_2O_2 and 0.017 mmol/Mo of catalyst, and the reaction mixture was stirred. The progress of reactions was monitored by GLC or TLC.

Scheme 2 Immobilization of MoO_2Cl_2 on polystyrene via different imine and amine linkers (**2a**–**2f**)

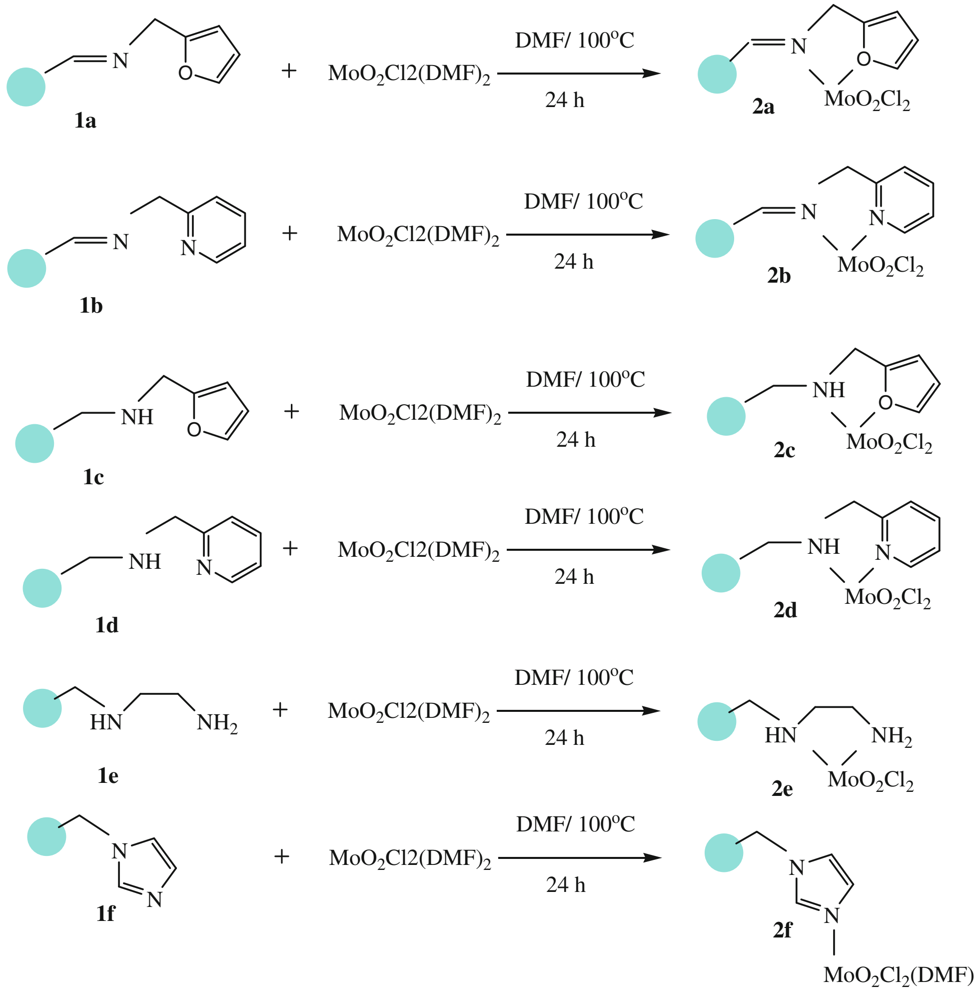


Table 2 The results of neutron activation analysis and $\nu_{Mo=O}$ (cm^{-1}) of polymer-supported catalysts **2a**–**2f**

Polymer-supported catalyst	% Mo	$\nu_{Mo=O}$
2a	5.3	903, 965
2b	7.6	903, 970
2c	1.5	903, 954
2d	3.9	903, 971
2e	9.3	903, 960, 926
2f	6.2	903, 948

General procedure for reusability of catalysts

All reactions were carried out as described above. The progress of reactions was monitored by GLC. At the end of each reaction the mixture was filtered off and the obtained resin beads washed with 4 × 10 ml of CH_2Cl_2 and then were used in the next cycle.

Results and discussion

Chloromethylated polystyrene resin was oxidized to the aldehydic polystyrene by the reaction with DMSO in the presence of $NaHCO_3$. Imine-bounded polystyrenes (**1a** and **1b**) were prepared by the reaction of this aldehydic polystyrene with amines (furfuryl amine and 2-(amino methyl) pyridine) in acetonitrile in two separated reactions (Scheme 1a). These functionalized polystyrenes were finely characterized by disappearing of $\nu_{C=O}$ of aldehydic polystyrene at 1,699 cm^{-1} and producing of new bands at 1,640 and 1,645 cm^{-1} that related to $\nu_{C=N}$ of new imine-bounded formation of **1a** and **1b**, respectively (Table 1). Other functionalized polystyrenes (**1c**–**1f**) were prepared by direct reaction of chloromethylated polystyrene with amines in acetonitrile (Scheme 1b). By reaction of amines with chloromethylated polystyrene, the peak at 1,266 cm^{-1} corresponded to wagging mode of HCCl of $-CH_2Cl$ group on polystyrene in FT-IR spectrum of original chloromethylated polystyrene resin, was diminished or very decreased in its intensity. Further evidence for producing of amines and imines on polystyrene obtained from elemental analysis of amine- and imine-bounded polystyrenes. The results of CHN analysis for functionalized polystyrenes (**1a**–**1f**) and $\nu_{C=N}$ for imine-bounded polystyrenes (**1a**, **1b**) are given in Table 1. Reaction of these functionalized polystyrene resins (**1a**–**1b**) with a solution of $MoO_2Cl_2(DMF)_2$ in DMF led to attachment of MoO_2Cl_2 onto the functionalized polystyrene via covalent bond (Scheme 2). The supported MoO_2Cl_2 catalysts were characterized by FT-IR spectra and neutron activation analysis (NAA). In FT-IR spectrums of supported catalysts, new peaks were appeared in the 900–1,000 cm^{-1} region that attributed to $\nu_{Mo=O}$. In addition, the metal loading on polystyrene was determined with NAA. The Mo (%) and $\nu_{Mo=O}$ of supported catalysts (**2a**–**2f**) are given in Table 2. These data confirm the immobilization of MoO_2Cl_2 on polystyrene. Then we investigated the catalytic activities of supported catalysts in oxidation of methyl phenyl sulfide. We studied the oxidation of methyl phenyl sulfide with each catalyst in different solvents in the presence of H_2O_2 (Table 3). Among the H_2O, CH_3OH, C_2H_5OH, THF, CH_2Cl_2, CH_3CN, and $(CH_3)_2CO$, protic solvents gave better results, but water was the best solvent for almost all supported catalysts **2a**–**2f**. All catalysts showed high activity and selectivity in oxidation of methyl phenyl sulfide to the methyl phenyl sulfoxide in the presence of H_2O_2 as oxygen donor in protic solvents (H_2O, CH_3OH, C_2H_5OH). Catalyst **2f** showed the highest activity in oxidation of methyl phenyl sulfide in the presence of H_2O_2.

Table 3 Oxidation of methyl phenyl sulfide by polymer-supported catalysts **2a**–**2f** in different solvents in the presence of H_2O_2 30%, at room temperature

Solv	%Conversion[a] (%sulfoxide)											
	Catal **2a**	*t*[b]	Catal **2b**	*t*[b]	Catal **2c**	*t*[b]	Catal **2d**	*t*[b]	Catal **2e**	*t*[b]	Catal **2f**	*t*[b]
H_2O	97 (100)	25	98 (100)	20	100 (100)	25	98 (100)	25	100 (92)	15	100 (100)	15
CH_3OH	100 (100)	25	96 (100)	20	100 (100)	65	95 (100)	40	100 (100)	15	100 (100)	30
C_2H_5OH	92 (100)	25	93 (100)	20	93 (100)	65	80 (100)	40	95 (100)	15	84 (100)	30
THF	43 (100)	25	41 (100)	20	40 (100)	65	44 (100)	40	54 (100)	15	42 (100)	30
CH_2Cl_2	65 (100)	25	56 (100)	20	30 (81)	65	9 (100)	40	13 (64)	15	10 (100)	30
CH_3CN	48 (100)	25	54 (100)	20	57 (100)	65	45 (100)	40	55 (100)	15	45 (100)	30
Acetone	32 (100)	25	35 (100)	20	42 (100)	65	8 (100)	40	38 (100)	15	13 (100)	30

Reaction conditions: Methyl phenyl sulfide 1 mmol, catalyst: 0.017 mmol/Mo, H_2O_2 5 mmol, solvent 10 ml

[a] Based on starting materials

[b] *t* = min

Table 4 Reusability of polymer-supported catalysts **2a–2f** in oxidation of methyl phenyl sulfide in H_2O in the presence of H_2O_2 30%, at room temperature

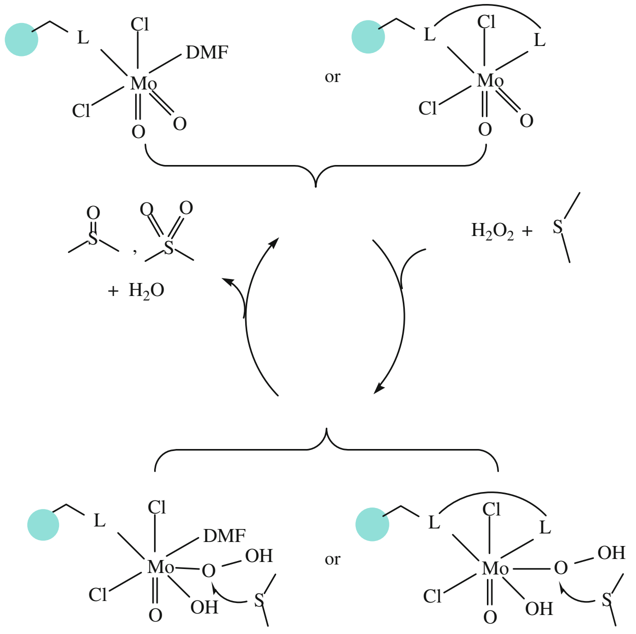
Run	%Conversion (%sulfoxide)											
	Catal 2a	t^a	Catal 2b	t^a	Catal 2c	t^a	Catal 2d	t^a	Catal 2e	t^a	Catal 2f	t^a
1	97 (100)	25	98 (100)	20	100 (100)	25	98 (100)	25	100 (92)	15	100 (100)	15
2	53 (100)	25	33 (100)	20	100 (100)	25	98 (100)	25	100 (92)	15	100 (100)	15
3	8 (100)	25	12 (100)	20	100 (100)	25	98 (100)	25	92 (94)	15	100 (100)	15
4	–	–	–	–	100 (100)	25	98 (100)	25	71 (95)	15	100 (100)	15
5	–	–	–	–	100 (100)	25	98 (100)	25	33 (95)	15	100 (100)	15
6	–	–	–	–	97 (100)	25	98 (100)	25	–	–	100 (100)	15
7	–	–	–	–	92 (100)	25	93 (100)	25	–	–	100 (100)	15
8	–	–	–	–	65 (100)	25	90 (100)	25	–	–	100 (100)	15
9	–	–	–	–	21 (100)	25	56 (100)	25	–	–	100 (100)	15
10	–	–	–	–	–	–	18 (100)	25	–	–	100 (100)	15
11	–	–	–	–	–	–	–	–	–	–	100 (100)	15
12	–	–	–	–	–	–	–	–	–	–	100 (100)	15
13	–	–	–	–	–	–	–	–	–	–	100 (100)	15
14	–	–	–	–	–	–	–	–	–	–	100 (100)	15
15	–	–	–	–	–	–	–	–	–	–	100 (100)	15

Reaction conditions: Methyl phenyl sulfide 1 mmol, catalyst: 0.017 mmol/Mo, H_2O_2 5 mmol, solvent 10 ml

[a] t = min

Blank experiments in the absence of catalysts (in the solvents of Table 3) showed that only 3–11% of methyl phenyl sulfoxide was produced.

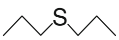
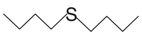
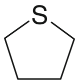
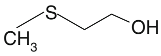
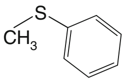
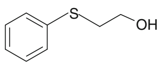
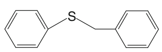
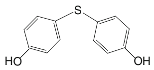
The reusability of a supporting catalyst can be the most important property and if this character was the better for a catalyst, it might make it sufficient for commercial application. Therefore, we investigated the reusability of polymer-supported catalysts (**2a–2f**). The reusability of the catalysts was monitored by using multiple sequential oxidation of methyl phenyl sulfide with H_2O_2 (Table 4). The activity of catalysts **2a** and **2b** was decreased after first run. It was related to hydrolyzing of imine bond in the presence of water as a solvent or byproduct that was produced from catalytic cycle of oxidation(in proposed mechanism (Scheme 3)) and leaching of the catalyst from the support. In the FT-IR spectrums of these supported catalysts (**2a** and **2b)** after the first using, the intensity of peaks for imine and Mo=O bonds was decreased that approved the hydrolyzing of imine bond and leaching of catalyst from support. The catalyst **2e** shows two times reusability and catalysts **2c** and **2d** were highly active about six times reusing in oxidation of methyl phenyl sulfide. The supported catalyst **2f** is highly reusable and it was reused 15 times without a considerable change in its activity. It can be attributed to strong coordination of imidazole to Mo(VI) center.



Scheme 3 Proposed mechanism of oxidation of sulfides by the polymer-supported MoO_2Cl_2 catalysts in the presence of H_2O_2

In order to assess the scope of catalytic activities of these supported molybdenum-based catalysts, we studied the oxidation of some aliphatic and aromatic sulfides in the presence of H_2O_2 (Table 5). We obtained that these catalysts were highly efficient in oxidation of different sulfides. Almost all sulfides were completely converted to their oxidized product in low times. The main product for aliphatic sulfides was sulfoxide and the selectivity of the

Table 5 Oxidation of some aliphatic and aromatic sulfides by polymer-supported catalysts **2a–2f** in the presence of H_2O_2 30%, at room temperature

Run	Sulfide	%Conversion (sulfoxide)[a]											
		Catal[a]2a	*t*[b]	Catal[a] 2b	*t*[b]	Catal[a] 2c	*t*[b]	Catal[a]2d	*t*[b]	Catal[a] 2e	*t*[b]	Catal[a] 2f	*t*[b]
1		100 (100)	10	100 (100)	25	100 (100)	90	100 (100)	45	100 (100)	5	100 (100)	5
2		100 (100)	10	100 (100)	10	100 (100)	165	100 (100)	60	100 (100)	10	100 (100)	10
3		100 (100)	5	100 (100)	5	100 (100)	25	100 (100)	25	100 (100)	10	100 (100)	5
4		100 (100)	5	100 (100)	5	100 (100)	50	100 (100)	50	100 (100)	5	100 (100)	5
5		97 (100)	25	98 (100)	20	100 (100)	25	98 (100)	25	100 (92)	15	100 (100)	15
6		100 (100)	35	100 (100)	35	90 (10)	375	100 (100)	155	100 (100)	55	100 (100)	35
7		100 (100)	35	100 (100)	30	90 (10)	285	100 (10)	120	100 (100)	40	100 (100)	45
8		100 (10)	45	100 (10)	50	80 (20)	250	100 (20)	205	100 (40)	65	100 (40)	70

Reaction conditions: sulfide 1 mmol, catalyst 0.017 mmol/Mo, H_2O_2 5 mmol, solvent 10 ml. The used solvent for catalysts **2a**, **2b**, **2d** and **2e** was MeOH, for catalyst **2c** was EtOH and for catalyst **2f** was H_2O

[a] For runs 1–5 based on GLC and for runs 6–8 based on TLC

[b] t = min

catalysts for these aliphatic sulfides was very high, but some of these catalysts converted some of aromatic sulfides to sulfone as main product.

In conclusion, we immobilized the MoO_2Cl_2 on polystyrene in simple routes via different linkers and found that these catalysts were highly reactive and selective in oxidation of sulfides to their corresponding sulfoxides. Catalyst **2f** in that active complex have been immobilized on polystyrene via imidazole linker was highly reusable for 15 times without any change in its activity in oxidation of methyl phenyl sulfide to the methyl phenyl sulfoxide in the presence of environmental benign oxidant (H_2O_2) and solvent (H_2O) that could be very important in green chemistry.

Conclusions

In summary, MoO_2Cl_2 has been immobilized on polystyrene, via different imine and amine linkers in simple procedures. Some of them have showed high activity, selectivity and reusability in oxidation of different aliphatic and aromatic sulfides in the presence of hydrogen peroxide.

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