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Silica-supported molybdenum complex: A novel, selective and reusable organic-inorganic hybrid catalyst for eco-friendly oxidation of sulfides and olefins

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ABSTRACT

A novel, highly efficient and reusable molybdenum based catalyst has been synthesized by covalent grafting of 2,6-diacetylpyridine-monosalicyloylhydrazone onto functionalized silica followed by complexation with MoO₂(acac)₂, and the resulting organic–inorganic hybrid material was found to be highly effective catalyst for oxidation of various sulfides and olefins to their corresponding sulfoxides/sulfones and epoxides, respectively. The catalyst was characterized by elemental analysis (CHN), diffuse reflectance UV–Vis, ¹³C CPMAS NMR spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET surface area analysis, energy dispersive X-ray fluorescence (ED-XRF), Fourier-transform infrared (FT-IR) and atomic absorption spectroscopy (AAS). Mild reaction conditions, high turnover frequency, high selectivity, easy recovery and reusability of the catalyst render the present protocol very useful to address the industrial needs and environmental concerns.

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1. Introduction

Molybdenum complexes have been known as versatile and useful catalysts for oxidative transformations [1]. A wide range of soluble molybdenum complexes with diverse ligands have been synthesized and employed as homogeneous catalysts for epoxidation and sulfoxidation of various olefins due to their high selectivity [2-8]. However, these homogeneous catalytic systems suffer from problems associated with the separation and recovery of the active catalyst as well as instability at high temperatures. These drawbacks have so far precluded their industrial utilization. Moreover, metal contamination of the products is inevitable when using homogeneous catalysts. Therefore, there is a need to develop improved strategies for recycling of catalysts for economical and environmental concerns. In this scaffold, covalent immobilization of homogeneous catalyst onto inorganic solid support constitutes a potential strategy to combine the advantages of both homogeneous (high activity and selectivity) and heterogeneous (easy separation from the reaction mixture) catalysts [9]. In recent years, silica has been receiving much attention as inorganic solid support material for anchoring of metal complexes due to its numerous advantages such as excellent thermal and mechanical stability, economic viability, high surface area and large pore volume [10,11].

Due to the generation of huge amount of toxic wastes and byproducts arising from chemical processes, chemists have been enforced to develop environmentally friendly catalytic routes that

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minimize waste. In this context, the development of novel, economical and energy efficient routes for the selective and green oxidative transformation of sulfides and olefins represents a challenge to diverse areas of contemporary chemistry since sulfoxides/sulfones are biologically important compounds, and epoxides are versatile precursors in the synthesis of a variety compounds such as resins, cosmetics, surface coatings, sweeteners, perfumes, drugs, etc. [12-15]. The most recent studies have therefore focused on the catalytic oxidations with environmentally benign oxidants, such as oxygen, hydrogen peroxide (H₂O₂) and *tert*-butyl hydroperoxide (TBHP) which are safer and economical for industrial applications [16–18]. Recently, we have reported the synthesis and application of Silica-supported palladium complex for the synthesis of E-stilbenes [19]. In continuation of our research work on the designing and synthesis of organic-inorganic hybrid materials, and their applications as metal scavengers, sensors, and catalysts for various organic transformations [20-27], herein, we report the synthesis, characterization and application of silica supported molybdenum catalyst in the oxidation of various sulfides and olefins to their corresponding sulfoxides/sulfones and epoxides, respectively.

2. Experimental

2.1. Materials and physical measurements

APTES (98%), silica gel, SiO₂ (60–100 mesh), 2,6-diacetylpyridine and sulfides were purchased from Sigma–Aldrich. Olefins and Ammonium heptamolybdate were obtained from Alfa Aesar. Salicyloyl hydrazide, H_2O_2 (30% in water), urea- H_2O_2 (UHP) & TBHP



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Scheme 1. Preparation of Silica-supported molybdenum catalyst (Mo-DAPSH@APTES@SiO2).



Fig. 1. ¹³C CPMAS NMR spectrum of APTES@SiO₂.

(70% in water) were obtained commercially from Spectrochem. Pvt. Ltd., India and used without purification. The dioxo molybdenum acetylacetonate complex, $MoO_2(acac)_2$ and 2,6-diacetyl pyridine salicyloyl monohydrazone (DAPSH) were synthesized according to the reported procedures [28,29]. Solid-state ¹³C cross-polarization magic-angle spinning (CPMAS) NMR spectra were recorded on Bruker DSX-300 NMR spectrometer under the following pulse conditions: spectrometer frequency (SF) 300.1312005 MHz, acquisition time (AQ) 0.0249665 s, number of acquisitions (NS) 1351, pulse duration



Fig. 2. Diffuse reflectance UV–Vis spectra of (a) SiO $_2$ and (b) Catalyst, Mo–DAPSH@APTES@SiO $_2$.

(P3) 4.25 μ s, receiver gain (RG) 16384, time of contact(P15) 2000 μ s, interval between pulse (D1) 5 s, rotor size 4 mm.

Elemental analysis (CHN) was performed using Elementar Analysensysteme GmbH VarioEL V3.00 instrument. Powder XRD patterns were recorded on Bruker D8 ADVANCE X-ray diffractometer using graphite monochromatized Cu K α radiation (λ = 1.54183 Å) over 2θ range 5–40° at a scan rate of 2θ min⁻¹. Surface area was calculated using the BET method on Gemini-V2.00 instrument (Micromeritics Instrument Corp.). Samples were outgassed at 100 °C for 3 h to evacuate the physically adsorbed moisture before measurement. Scanning electron microscopy (SEM) images were obtained using a ZEISS EVO 40 instrument. The samples were placed on a carbon tape and then coated with a thin layer of gold using a sputter coater. Qualitative analysis of catalyst for metal was performed using energy dispersive XRF spectrometer (Fischerscope X-ray XAN-FAD BC). The amount of molybdenum content was detected using LABINDIA AA 7000 Atomic Absorption Spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer spectrometer using KBr in the range of 4000–400 cm⁻¹. The products obtained were analyzed and confirmed by GC–MS using Agilent gas chromatography (6850 GC) with a HP-5MS 5% phenyl methyl siloxane capillary column $(30.0 \text{ m} \times 250 \text{ } \mu\text{m} \times 0.25 \text{ } \mu\text{m})$ and a guadrupole mass filter equipped 5975 mass selective detector (MSD). The carrier gas was helium (rate 0.9 ml min⁻¹) and the temperature of the injection port was 250 °C. The temperature program of the column



Fig. 4. SEM image of catalyst (Mo-DAPSH@APTES@SiO2).



Fig. 5. XRD patterns of (a) SiO₂ (b) APTES@SiO₂ and (c) Mo-DAPSH@APTES@SiO₂.

was set to an initial oven temperature of 60 °C and was increased at a rate of 10 °C/min to 250 °C, and the oven was held at 250 °C for 10 min.

2.2. Preparation of Silica-supported 2,6-diacetylpyridine salicyloylhydrazone molybdenum complex (Mo-DAPSH@APTES@SiO₂)

Aminopropylated silica gel (APTES@SiO₂) was prepared according to the reported method [30]. The grafting of DAPSH on APTES@SiO₂ was performed by refluxing DAPSH (5 mmol) with APTES@SiO₂ (2 g) in DMF (20 mL) for 2 h. The obtained



Fig. 3. ED-XRF spectrum of catalyst (Mo-DAPSH@APTES@SiO2).

Table 1

Oxidation of sulfides using Mo-DAPSH@APTES@SiO2 catalyst.

Entry	Substrate	Sulfoxide ^a		Sulfone ^b			
		Conv. ^c (%)	Selectivity (%)	TOF (h^{-1})	Conv. ^c (%)	Selectivity (%)	$TOF^{d}(h^{-1})$
1		98	95	111	100	98	113
2	S CH ₃	100	98	113	100	100	113
3	S S	92	98	104	99	96	112
4		97	99	110	99	98	112
5	NO ₂	96	95	109	98	99	111
	S S						
6	S CH3	82	90	93	86	94	98
7	CI SCH3	97	95	110	98	98	111
	H ₃ C C						
8	s_	98	97	111	100	100	113
9	CH ₃ (H ₂ C) ₁₀ H ₂ C CH ₂ (CH2) ₁₀ CH ₃	94	94	106	97	98	110
	H ₂ C						
10	ОН _S_	97	98	110	100	98	113
11	$H_3C(H_2C)_2H_2C$ $CH_2(CH2)_2CH_3$	94	98	106	95	100	107
	H ₃ C CH ₃	דע	50	100	55	100	107
12	s S	96	97	109	100	98	113
	*						

^a Reaction conditions: sulfide (1 mmol), 30% H₂O₂ (1.2 equiv), catalyst (30 mg), 0.5 h., rt.

^b Reaction conditions: sulfide (1 mmol), 30% H_2O_2 (3.6 equiv), catalyst (30 mg), 0.5 h., rt.

^c Conversion and selectivity were determined by GC, Conversion = [(initial moles of substrate – final moles of substrate)/initial moles of substrate] \times 100, Selectivity to sulfoxide = [sulfoxide%/(sulfoxide% + sulfone%)] \times 100.

^d TOF = number of moles of substrate converted per mole of catalyst per hour.

solid (DAPSH@APTES@SiO₂) was filtered, washed with ethanol and dried under vacuum at 110 °C for 4 h. Then, the complexation of DAPSH@APTES@SiO₂ (1 g) was done by refluxing it with

alcoholic solution of $MoO_2(acac)_2$ (0.4 mmol) for 4 h. The resulting organic–inorganic hybrid catalyst (Mo-DAPSH@APTES@SiO₂) was washed with ethanol and dried in vacuum oven (Scheme 1).



Fig. 6. Optimization of amount of catalyst.

2.3. General procedure for the oxidation of sulfides to sulfoxides/ sulfones

A mixture of sulfide (1 mmol), catalyst (30 mg) and solution of 30% H₂O₂ (1.2 & 3.6 equiv. for sulfoxides & sulfones, respectively) was stirred at room temperature. The progress of reaction was monitored by GC. After completion of the reaction, the product was extracted with ethyl acetate and the combined organics was washed with brine, dried over anhydrous Na₂SO₄, and analyzed by GC–MS.

2.4. General procedure for the oxidation of olefins to epoxides

The catalytic reactions were performed in a 25 mL two-necked round-bottomed flask equipped with a septum, a magnetic stirring bar, and a reflux condenser. The oxidation was carried out as follows: catalyst (25 mg) and olefin (1 mmol) were taken in the reaction flask. The reaction was carried out at 60 °C with continuous stirring. TBHP (1.2 equiv) was progressively added to the reaction mixture using a syringe. After completion of the reaction, the product was extracted with ethyl acetate and the combined organics was washed with brine, dried over anhydrous Na₂SO₄, and analyzed by GC–MS.

3. Results and discussion

3.1. Characterization of silica supported molybdenum complex

The FT-IR spectroscopy was employed to examine the covalent grafting reactions (Supplementary information). The FT-IR spectrum of SiO₂ exhibits the characteristic band at 973 cm⁻¹ assigned to silanol group. The post-grafting of APTES onto SiO₂ is confirmed by the appearance of new band (in the range of 2900–2800 cm⁻¹) in the spectrum of APTES@SiO₂, which is due to the C–H stretching



Scheme 3. Catalytic epoxidation of olefins.

of the functionalized aminopropyl group (which does not appear in the parent SiO₂ spectrum). Also, the band due to silanol groups present in SiO₂ has disappeared in FT-IR spectrum of APTES@SiO₂. The FT-IR spectrum of silica supported molybdenum catalyst (Mo-DAPSH@APTES@SiO₂) shows band around 848–960 cm⁻¹ due to asymmetric and symmetric stretching vibrations of O=Mo=O, confirming the complexation of DAPSH@APTES@SiO₂ with MoO₂ (acac)₂ [31]. The conservation of 3-aminopropyl group after functionalization of SiO₂ with APTES was confirmed by solid state ¹³C CPMAS NMR spectroscopy. The ¹³C CPMAS NMR spectrum of AP-TES@SiO₂ presents three well resolved peaks at 9.44, 20.99 and 42.68 ppm assigned to C1, C2, and C3 carbons of the incorporated aminopropyl group- O₃SiCH₂(1)CH₂(2)CH₂(3)NH₂ respectively (Fig. 1) which authenticate the preparation of APTES@SiO₂ [32,33].

BET surface area measurements were also carried out to analyze the grafting reactions. The surface area of the un-functionalized SiO₂ was approximately 235 m²g⁻¹. The surface area of aminopropylated silica gel (APTES@SiO₂) and immobilized complex (Mo-DAPSH@APTES@SiO₂) was found to be 132 m²g⁻¹ and 125 m²g⁻¹ respectively. Generally, anchoring of organic and organometallic moieties on SiO₂ surface blocks the access of nitrogen molecules, thus reducing the surface area [34,35]. Therefore, the reduction in surface area according to the sequence SiO₂ > APTES@SiO₂ > -Mo-DAPSH@APTES@SiO₂ confirmed the functionalization of SiO₂ with APTES to give APTES@SiO₂, and its further modification to yield the catalyst, Mo-DAPSH@APTES@SiO₂.

The diffuse reflectance UV–Vis spectrum of SiO₂ does not have any absorption band in the region of 200–650 nm. The spectrum of Mo-DAPSH@APTES@SiO₂ (Fig. 2) shows weak bands around 200–300 nm due to intra-ligand transitions, and a strong broad absorption band around 300–400 nm due to ligand to metal charge transfer transition ($O^{2-} \rightarrow Mo^{6+}$) [36]. The elemental analysis data of APTES@SiO₂ shows the appearance of nitrogen (2.05%) as well as the carbon surface content (6.14%), providing an evidence for the APTES immobilization onto SiO₂. The ED-XRF spectrum of catalyst (Fig. 3) confirms the presence of molybdenum in the catalyst, and its molybdenum content (5.6 wt.% of silica) was further confirmed and estimated by AAS.

The morphology of Mo-DAPSH@APTES@SiO₂ was examined by SEM. During the preparation of APTES@SiO₂ as well as Mo-DAP-SH@APTES@SiO₂, SiO₂ beads were subjected to vigorous stirring but it is evident from SEM image of catalyst (Fig. 4) that no clog between particles occurred during the grafting reactions, and particles maintained regular lumpy shape. It signifies that the particles of silica had good mechanical stability, and they had not been damaged during surface modification reactions. The structural features of SiO₂ before and after functionalization were checked by XRD measurements (Fig. 5). The broad peak centered around $2\theta = 23^{\circ}$ in the XRD patterns of SiO₂, APTES@SiO₂ and



Table 2		
Recycling of catalyst in the	oxidation	of sulfides

Cycle	Sulfoxide ^a			Sulfone ^b		
	Conv. ^c (%)	Selectivity (%)	Recovery efficiency ^d (wt.%)	Conv. ^c (%)	Selectivity (%)	Recovery efficiency (wt.%)
1	98	95	99	100	98	98
2	98	95	97	100	98	99
3	98	95	99	100	98	95
4	97	95	98	99	98	97
5	97	95	98	99	97	98
6	96	94	96	98	97	99

^a Reaction conditions: diphenyl sulfide (1 mmol), 30% H₂O₂ (1.2 equiv), catalyst (30 mg), 0.5 h., rt.

^b Reaction conditions: diphenyl sulfide (1 mmol), 30% H₂O₂ (3.6 equiv), catalyst (30 mg), 0.5 h., rt.

^c Conversion and selectivity were determined by GC.

^d When the amount of recovered catalyst was not equal to the amount added in the first run, fresh catalyst was added to keep the same amount of catalyst in the reaction system in each run.

Table 3

Oxidation of olefins using Mo-DAPSH@APTES@SiO2 catalyst.^a

Entry	Substrate	Epoxide		$TOF^{c}(h^{-1})$	
		Conv. ^b (%)	Selectivity (%)		
1		100	100	28	
2		95	100	27	
3	\sim	92	100	26	
4		84	100	23	
5	(CH ₂) ₅	80	100	22	

^a Reaction conditions: olefin (1 mmol), TBHP (2 equiv), catalyst (25 mg), 2 h, 60 °C.

^b Conversion and selectivity were determined by GC, Conversion = [(initial moles of substrate – final moles of substrate)/initial moles of substrate] × 100 and Selectivity to epoxide = [epoxide%/(epoxide% + other product%)] × 100.

^c TOF = number of moles of olefin converted per mole of catalyst per hour.

Mo-DAPSH@APTES@SiO₂ is assigned to the diffraction peak of amorphous silica, which clearly depicts that topological structure of SiO₂ is retained after grafting reactions. Apparently, by functionalizing SiO₂ and eventually anchoring molybdenum complex, the intensities of reflections have decreased significantly confirming the immobilization [37].

3.2. Catalytic studies

3.2.1. Catalytic activity of Mo-DAPSH@APTES@SiO₂ in oxidation of sulfides

In order to obtain best catalytic activity, reaction conditions were optimized for the oxidation of sulfides. The oxidation of diphenyl sulfide was carried out as the model reaction with different oxidants (H₂O₂, UHP & TBHP) at room temperature under solventfree conditions (Supplementary information). The results showed that H_2O_2 is the best oxidizing agent for oxidation of sulfides as higher conversion was obtained. The effect of different solvents was also investigated and results are presented in supplementary information. Since, solvent-free reactions are usually quantitative and waste free, reaction was also carried out under solvent-free conditions in the presence of catalyst. Interestingly, under solvent free conditions, maximum conversion of diphenyl sulfide was obtained. Next, we optimized the quantity of the catalyst (Fig. 6) and it was observed that on increasing the amount of catalyst, conversion also increased due to the availability of large number of active sites on the porous surface of catalyst. It is noteworthy that in

Table 4	
Recycling of catalyst in the oxidation of olefins. ^a	

Cycle	Epoxide ^a		
	Conv. ^b (%)	Selectivity (%)	Recovery efficiency ^c (wt.%)
1	100	100	98
2	100	100	98
3	98	100	99
4	98	100	97
5	98	100	98
6	98	100	99

 $^{\rm a}$ Reaction conditions: cyclooctene (1 mmol), TBHP (2 equiv), catalyst (25 mg), 2 h, 60 °C.

^b Conversion and selectivity were determined by GC.

^c When the amount of recovered catalyst was not equal to the amount added in the first run, fresh catalyst was added to keep the same amount of catalyst in the reaction system in each run.

a blank experiment, no significant sulfoxidation was observed under similar reaction conditions in the absence of catalyst, and only a low conversion was observed in the presence of 2 equiv of H_2O_2 after prolonged reaction time. Hence, in all cases, neat reactions were carried out at room temperature using H_2O_2 as oxidant in presence of 30 mg of Mo-DAPSH@APTES@SiO₂ catalyst under solvent-free conditions (Scheme 2). After optimization of the reaction conditions, applicability of catalyst was tested for oxidation of various sulfides (Table 1). A variety of structurally diverse substratesaryl–alkyl, diaryl and dialkyl sulfides undergo effective and

Table 5	
Comparison of the activity of molybdenum catalysts in the oxidation of sulfide	s.

Entry	Catalytic system	Sulfide	Reaction conditions Sulfoxide		Sulfone		Ref.	
				Conv. (%)	Selectivity (%)	Conv. (%)	Selectivity (%)	
1	[MoO ₂ (L)(CH ₃ OH)]	methyl phenylsulfide	urea-hydrogen peroxide Ethanol, r.t, 30 min	92	100	100	98	[38]
2	Oxo-peroxido Mo schiffs base complex	methyl phenylsulfide	urea-hydrogen peroxide, methanol/ dichloromethane r.t. , 35.25 min	100	96	-	-	[39]
3	Mo-oxazoline complex cis- [MoO ₂ (phox) ₂	methyl phenylsulfide	urea-hydrogen peroxide, dichlromethane/ methanol, r.t	95	100	-	-	[40]
4	$[MoO_2(L)(CH_3OH)]$	diphenyl sulfide	urea-hydrogen peroxide ethanol, r.t, 30 min	75	93	95	97	[38]
5	Cp'Mo(CO) ₃ Cl Cp-cvclopentyl	diphenyl sulfide	hydrogen peroxide, dichloromethane, 35 $^{\circ}\mathrm{C}$, 5 h	100	100	-	-	[41]
6	Cp'Mo(CO) ₃ Cl Cp-cyclopentyl	methyl phenylsulfide	hydrogen peroxide, dichloromethane, r.t, 1 h	100	-	96	-	[41]

Table 6

Comparison of the activity of Silica-supported molybdenum catalysts in the oxidation of olefins.

Entry	Olefin	Catalytic system	Reaction conditions	Conv. (%)	Selectivity (%)	Ref.
1	1-octene	silica-supported MoO ₂ Cl ₂ (dmf) ₂	dichloromethane, TBHP, 55 °C, 6 h	36	100	[42]
2	Cyclohexene	silica-supported MoO ₂ (acac) ₂	1,2-dichloroethane, TBHP, reflux, 2 h	90	100	[43]
3	1-octene	silica-supported MoO ₂ histidine(acac)	chloroform, TBHP, reflux, 9 h	17	-	[44]
4	Cyclohexene	silica-supported MoO ₂ ala(acac)	chloroform, TBHP, reflux, 9 h	30	-	[44]
5	1-hexene	silica-supported MoO ₂ furfuryl	chloroform, TBHP, reflux, 7 h	42	98	[45]
6	Dodecene	silica-supported Schiff base-MoO ₂ (acac)	1,2-dichloroethane, TBHP, reflux, 16 h	90	100	[46]
7	1-octene	silica supported imidazole-MoO ₂ (acac) ₂	1,2-dichloroethane, TBHP, reflux, 14 h	88	100	[47]

selective oxidation to produce the corresponding sulfoxides/sulfones. Further to broaden the domain of present protocol, and making it better in comparison to other reported systems a variety of sulfides containing sensitive functional group were also tested under same reaction conditions. The sulfide containing allyl, keto and hydoxy groups (Table 1, entries 3, 7, 9) were selectively oxidized to their corresponding sulfoxides/sulfones without affecting these reactive functional groups. It is also interesting to mention that even the presence of strong electron withdrawing NO₂ group, present in the phenyl ring of diaryl sulfides, does not affect the synthesis of sulfoxide considerably (Table 1, entry 5). The catalytic oxidation of sulfides under given conditions showed good efficiency in terms of conversion, TOF and selectivity.

3.2.2. Catalytic activity in oxidation of olefins

This study was further extended to the epoxidation of several linear and cyclic olefins using Mo-DAPSH@APTES@SiO₂ as catalyst (Scheme 3). Initially, for optimization of reaction conditions for epoxidation, cyclooctene was chosen as the model substrate (Supplementary information). The reaction was carried out using various oxidants (H₂O₂, UHP & TBHP) and in different solvents and solvent-free conditions. The best results were obtained using TBHP as oxidant under solvent-free conditions at 60 °C in presence of Mo-DAPSH@APTES@SiO₂ catalyst. Generally, excellent epoxide selectivity was observed for all aliphatic and aromatic substrates. The results of catalytic studies using Mo-DAPSH@APTES@SiO₂ catalyst reveals that it is highly efficient towards all the substrates with maximum conversion, TON, and selectivity (Table 2). It is suggested that the olefin having higher electron donating ability and less sterically hindered gives higher conversion with high selectivity.

3.3. Catalyst stability and reusability

To confirm the heterogeneous nature of the catalyst, filtration test was applied. During the oxidation of diphenyl sulfide and of cyclooctene, catalyst was separated from the reaction mixture by filtration (after 15 min). The filtrate was allowed to react further, and no increment in conversion was observed. Further, the filtrate was subjected to AAS analysis and absence of molybdenum in the reaction mixture suggested that no leaching of the catalyst was observed during the reaction. The reusability of silica supported molybdenum catalyst was also investigated in the oxidation of diphenyl sulfide and of cyclooctene. Catalyst was separated by filtration after the first catalytic run, washed, dried under vacuum and then subjected to the second run under similar reaction conditions. The catalytic run was repeated with addition of substrates under optimized reaction conditions, and the selectivity of the products was comparable to that of the original one. It was observed that the activity and selectivity of the catalyst does not change significantly after seven consecutive runs (Tables 3 and 4).

3.4. Comparison with reported molybdenum catalyst

The present catalytic system was also compared with some reported molybdenum catalysts (Tables 5 and 6), and found that our organic–inorganic hybrid catalytic system (Mo-DAPSH@APTES@ SiO₂) is superior to some reported catalytic protocols in terms of cost, reaction time, selectivity, conversion, turn-over frequency (TOF) and reusability [38–47].

4. Conclusion

In conclusion, we have prepared a silica supported molybdenum catalyst which was used in the oxidation of sulfides and olefins using environmentally benign oxidants. Mild reaction conditions, high activity and selectivity, economic viability, easy preparation and reusability of the catalyst make the present protocol a greener alternative for the synthesis of commercially important sulfoxides/sulfones and epoxides.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.07.065.

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