NJC Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/njc

Cite this: DOI: 10.1039/coxx00000x

www.rsc.org/xxxxx

Paper

Environmentally friendly route for grafting of molybdenum carbonyl on a diaminosilane-modified SBA-15 molecular sieve and its catalytic behaviour in olefin epoxidation

⁵ Thangaraj Baskaran,^a Raju Kumaravel,^a Jayaraj Christopher,^b Thalasseril. G. Ajithkumar,^c Ayyamperumal Sakthivel^{a*}

Received (in XXX, XXX) XthXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX DOI: 10.1039/b000000x

A simple route has been established for grafting molybdenum carbonyl on the surface of a diaminosilane-modified SBA-15 molecular

¹⁰ sieve. The successful grafting of the molybdenum carbonyl species on diamine-functionalized SBA-15 was evident from FT-IR studies. The resultant molybdenum-carbonyl-complex-grafted SBA-15 (SBA-DA-Mo) materials show promising activity for the epoxidation of various olefins with good conversion (90-95 %) and the formation of epoxide as the major product. The catalytic activity remains constant over several runs.

15 Introduction

The epoxidation of olefin is an important organic transformation, which is of great interest in academic and industrial research.¹ In general, epoxidation is carried out using transition metal complexes.¹ In particular, molybdenum-based compounds are ²⁰ extensively studied for various olefin oxidations.¹⁻⁸ The

- development of the Arco-Lyondell process for the epoxidation of propene using molybdenum carbonyl Mo(CO)₆ precursor in the presence of *tert*-butylhydroperoxide (TBHP) as the oxidant led to increased interest in the oxidative synthesis of dioxo
- ²⁵ molybdenum (VI) complexes of the type CpMoO₂L, MoO₂X₂L, etc. from their carbonyl precursors.²⁻⁸ For example, molybdenum complexes with a cyclopentadienyl(Cp)-based precursor are considered very promising catalysts.^{2-4,6} Heterogenization of such homogeneous catalysts on various supports shown as promising
- ³⁰ recyclable catalysts.⁸ It is important to mention here that supports based on mesoporous molecular sieves have greater advantages over the homogeneous catalysts, such as the uniformity of channels, high surface area, easiness in handling, and recyclability.⁷⁻¹⁰ Although a few reports show the importance of
- ³⁵ Cp-Mo-complexes on mesoporous supports, the synthesis of the homogeneous counterpart involves multiple steps and results in the formation of air sensitive and carcinogenic products.^{3,4} Thus, it is vital to develop molybdenum-based heterogenized catalysts from stable homogeneous counterparts that can be synthesized ⁴⁰ using simple methods and can be handled easily.
- In this regard, we report herein a simple environment friendly method (Scheme 1) for grafting of molybdenum carbonyl on SBA-15 molecular sieves via a diaminosilane moiety (SBA-DA-Mo). The resultant molybdenum-carbonyl-grafted SBA-15
- ⁴⁵ materials were studied for their catalytic activity in the epoxidation of various olefins. For comparison, homogeneous

complex 1 was prepared as per the modified procedure described ⁵⁰ earlier and studied for the oxidation of olefin.¹¹



Scheme 1.Schematic representation of the grafting of molybdenum carbonyl on an SBA-15 molecular sieve.

Experimental Section

All the catalyst preparation and grafting procedure were carried out using standard Schlenk techniques under nitrogen atmosphere. Solvents were dried by standard procedures (THF, toluene with Na/benzophenone ketyl; CH₂Cl₂ with CaH₂), 60 distilled under nitrogen and kept over 4 A° molecular sieves.

Synthesis of Mesoporous SBA-15 Molecular Sieve: Mesoporous SBA-15 molecular sieve was synthesized as per the procedure described in elsewhere.^{9a} Mesoporous silica were synthesized using Pluronic 123 triblock copolymers (poly(ethylene oxide)-⁶⁵ poly(propylene oxide)-poly(ethylene oxide); (Aldrich)) EO_nPO₇₀EO_nas templates. In a typical synthesis, 4.0 g of the $EO_{20}PO_{70}EO_{20}$ copolymer was dissolved in 150 g of 1.6 M HCl. To this solution 8.50 g of TEOS (tetraethyl orthosilicate), was added and the resulting mixture was stirred until TEOS was dissolved. The final molar gel composition of the synthesis σ mixture was 6.89 × 10–4 P123 triblock copolymers: 0.24 HCl : 0.041 TEOS : 7.88 H₂O.The mixture was placed in an oven for 24 h at 308 K and then additional 24 h at 373 under static conditions. The products were filtered, dried, and calcined at 823 K. The calcined SBA-15 was used as support material.

10

PreparationofTetracarbonylmolybdenumN-[3-(Trimethoxysilyl)propyl]ethylenediamine:Complex (1)

Tetracarbonylmolybdenum N-[3-(Trimethoxysilyl) propyl] ethylenediamine was prepared (Scheme 1) with the modified presedure⁴ hypersetting of 1 + 2 (A 1(presedure⁴) of Ma(CO) in A0rel

- ¹⁵ procedure⁴ by reaction of 1.1 g (4.16 mmol) of $Mo(CO)_6$ in 40ml dry toluene with addition of 1.08 g (4.16 mmol) N-[3-(Trimethoxysilyl) propyl] ethylenediamine. The resultant solution was reflux at 80 °C for 20 minutes. The solvent was removed under reduced pressure to get brown oily liquid. IR of complex
- ²⁰ 1(CH₂Cl₂): 1825 (m), 1865 (s, sh), 1885 (vs), 2005 (w) cm⁻¹ corresponds to 4(CO), Ligand L1¹H NMR (ô, 400MHz, CDCl₃) 0.62-0.66 (q, 2H, CH₂-Si), 1.23 (s, -NH & H₂N-), 1.6 (m, 2H, -CH₂-), 2.59-2.65 (m, 4H, -CH₂-NH-CH₂), 2.75-2.77 (t, 2H, CH₂-NH₂), 3.55(s, 9H, O-CH₃) and Complex 1, ¹H NMR (ô, 400MHz, CDCH₃)
- ²⁵ CDCl₃) 0.62-0.66 (q, 2H, CH₂-Si), 1.45 (s, -NH & H₂N-), 1.5-1.6 (m, 2H, -CH₂-), 2.59-2.65 (m, 4H, -CH₂-NH-CH₂), 2.75-2.77 (t, 2H, CH₂-NH₂), 3.55(s, 9H, O-CH₃). The shift in broad peak corresponds to amine proton signal from 1.23 to 1.45 supports the formation of complex **1**. Ligand L1 ¹³C NMR (δ, 400MHz,
- ³⁰ CDCl₃); 6-7 (CH₂-Si), 23 (-CH₂-CH₂-Si), 42 (-CH₂-NH₂), 50 (O-CH₃), 52 (-CH₂-NH-CH₂), 80 (CDCl₃); Complex 1,¹³C NMR (δ, 400MHz, CDCl₃); 6-7 (CH₂-Si), 23 (-CH₂-CH₂-Si), 40 (-CH₂-NH₂), 50 (O-CH₃), 52 (-CH₂-NH-CH₂), 200 (-CO), 80 (CDCl₃), 130 (Toluene-peak);
- ³⁵ *Grafting of Mo(CO)*₆: The molybdenum carbonyl grafting was carried out by two-step process. First, SBA-15 support (1 g) was pre-activated at 200 °C for overnight in an air oven followed by under vacuum in a Schlenk round bottom flask for 1 hour. The calculated amount (3 mmol) of N-[3-(Trimethoxysilyl)
- ⁴⁰ propyl]ethylenediamine was introduced into the activated SBA-15 support materials after it was cooled down to room temperature. The mixture was refluxed with dry toluene (30 ml/g support) for 24 h in N₂ atmosphere. After completion, the reaction mixture was cooled to room temperature, toluene and
- ⁴⁵ excess diamine was removed by vacuum filtration. Subsequently it was washed with dichloromethane several times and dried at 40 °C under vacuum. The resultant material is represented as SBA-DA. In second step, about 3 mmol of Mo(CO)₆ was introduced into the SBA-DA material in presence of toluene and refluxed for
- ⁵⁰ 24h in N₂ atmosphere. After the completion of reaction, the final product was filtered and washed with dichloromethane several times and dried under vacuum to get SBA-DA-Mo.

Characterization of materials

⁵⁵ Pure SBA-15 and molybdenum carbonyl complex grafted SBA-15 was systematically characterized using various analytical and spectroscopic techniques.Powder XRD was performed to determine the bulk crystalline phases of the materials using a 18 KW XRD Rigaku (2500V), Japan with Cu-K α radiation (λ = ⁶⁰ 1.54184 Å). The diffraction patterns were recorded in the 20 range 0.5–10°, with a scan speed and step size of 1°/min and 0.02°, respectively. FT-IR spectra were obtained in the range 400–4000 cm⁻¹ using KBr pellets (Perkin-Elmer 2000, FT-IR

spectrometer). The textural properties (BET surface area, BJH 65 pore volume) of the synthesized materials were derived from N₂ sorption measurements carried out at -196 °C using an automatic micropore physisorption analyser (Micromeritics ASAP 2020, USA) after the samples were degassed at 250 °C for at least 8 h under 10⁻³ Torr pressure prior to each run. The ²⁹Si MAS and ¹³C 70 CPMAS experiments were carried out on a JEOL ECX 400 MHz spectrometer using a 4mm MAS probe which was tuned to 79.4 MHz for ²⁹Si and 100.5 MHz for ¹³C at a spinning speed of 10 KHz. The ²⁹SiMAS experimentswere recorded was using a one pulse sequence with high power ¹H decoupling with a ¹H power 75 of 70 KHz, and a ²⁹Si a 90° pulse of 2.6 µs.11,000 scans wererecorded with a recycle delay of3 s between the scans. The ¹³C CP-MAS experiments were acquired using, a ramped amplitude cross polarization contact time of 3.5 ms with high power TPPM ¹H decoupling during the acquisition time.7900

⁸⁰ scans were collected with a recycle delay of 5 second between them.

Thermogravimetry-analysis (TGA) was carried out in a Thermal Analyzer (Model-2950, TA Instruments, and USA). About5–10 mg of the sample was taken in the platinum pan andheated in air st at the heating rate of 10 °C min ⁻¹ up to 800 °C. Proton NMR spectra was recorded on a JEOL AL-400 FT NMR instrument using CDCl₃ as solvent. The molybdenum content in the sample (SBA-DA-Mo) was determined by inductively coupled plasma – atomic emission spectroscopy (ICP–AES;Model: Optima

90 8300, Make: Perkin Elmer). The sample was first digested with mixture containing equal volume (6 ml) of H₂O₂, ammonium hydroxide and ethanol. The resultant mixture was filtered and the filtrate was aspirated into plasma of ICP-AES equipment. The concentration of Mo in the samples was obtained with respect to 95 standard solution of Mo (Emerck, Germany) for (ICP-AES) analysis.

Epoxidation of olefin using grafted materials

¹⁰⁰ The catalytic activity of SBA-DA-Mo was studied for epoxidation of olefins using *t*-butyl hydroperoxide (5.5M TBHP in decane; used without further purification) as oxidant. The reaction was carried out with constant molar ratio of substrate: oxidant, at 70 °C temperature in presence of mesitylene as ¹⁰⁵ internal standard. The products were analyzed using gas chromatography equipped with FID (Agilent 7890A Series) connected to a HP-5 capillary column (30 m; HP-5). For comparison parent SBA-15 and complex (1) were studied under identical conditions.

Results and discussion

110

Powder XRD patterns of pure SBA-15 and SBA-DA-Mo are shown in Fig. 1. Both the samples exhibit very well-resolved ¹¹⁵ reflections corresponding to the (100), (110), and (200) planes in

the 2 θ range 0.5–2.0°, characteristic of the mesoporous hexagonal structure.^{9,12} Compared to the parent SBA-15 sample, SBA-DA and SBA-DA-Mo showed a clear shift in 20 values towards higher angles, and there is a slight decrease in the *s* relative intensities of the XRD reflections. The above results support the grafting of molybdenum carbonyl on an N-[3-(trimethoxysily1)propy1]ethylenediamine-modified SBA-15

surface.^{8,9}



²⁰ Fig. 1 Powder XRD pattern of (a) SBA-15, (b) SBA-DA and (c) SBA-DA-Mo.



Fig. 2FT-IR spectra of (a) SBA-15, (b) SBA-DA, (c) SBA-DA-Mo, and (d) SBA-DA-Mo-after reaction.

- ⁴⁰ Fig. 2 shows the FT-IR spectra of the parent mesoporous SBA-15, SBA-DA, SBA-DA-Mo, and used SBA-DA-Mo samples. All the samples exhibit bands at 1082, 953, and 807 cm⁻¹, attributed to stretching vibrations of the mesoporous framework (Si–O– Si).^{8-10,14} The band around 960 cm⁻¹ is assigned to a vibration
- ⁴⁵ mode of the silanol (Si–OH) groups⁸ present in the mesoporous channels. Two additional vibrational bands were present around 2927 and 2854 cm⁻¹ for the SBA-DA sample; these result from the C-H stretching of the alky diamine group present on the ligand. SBA-DA-Mo showed a new broad band around 2005 and
- ⁵⁰ 1891 cm⁻¹, which can be assigned to terminal carbonyl group vibrations^{8b} of the in-situ grafted complex 1; the observed signal was due to the loading of molybdenum carbonyl species on the surface of SBA-DA. When SBA-DA-Mo is treated with TBHP, two new bands are observed around 900 and 955 cm⁻¹ (Fig. 4d),

- ⁵⁵ indicating the oxidative conversion of the molybdenum carbonyl species into the active Mo(VI) oxo-species (Mo=O).^{3-5,8,15} In addition, there are few weak stretching vibrational bands appeared between 700-850 cm⁻¹ is due to the Mo-O-Mo bridging bond, which comes from the Mo present on the surface which is ⁶⁰ in close proximity react in presence of TBHP (please change).^{5c-}
- ^eHowever, the observed low intensity of these vibrational bands corresponds to SBA-DA-Mocatalyst indicates the presence of molybdenum-oxo species and it is present as monomeric species. The parent SBA-15, SBA-DA, and SBA-DA-Mo samples were ⁶⁵ analysed using solid-state ²⁹Si MAS NMR spectroscopy. The parent SBA-15 sample exhibits (Fig. 3) three broad resonances in the ²⁹Si MAS NMR spectrum at chemical shift (δ) values of -110, -101, and -97 ppm, which can be assigned to the Q₄, Q₃, and Q₂ species of the silica framework, respectively [Q_n = ⁷⁰ Si(OSi)_n(OH)_{4-n}].^{8,13}



Fig. 3 29 Si CP-MAS NMR spectra of (a) SBA-15 and (b) SBA-DA (c) SBA-DA-Mo.



Fig. 4 13 CCP-MAS NMR spectra of (a) SBA-DA and (b) SBA-DA-Mo.

The ²⁹Si MAS NMR spectrum of the molybdenum-carbonylgrafted sample shows a major peak centred around -110.0 ppm, attributed to the Q₄ species, and also exhibits additional broad signals between -55 and -70 ppm, which can be assigned to the ⁸⁰ T₂ and T₃ organosilica species, respectively [T_m = RSi(OSi)_m(OR)_{3-m}],^{8,13} supporting the anchoring of the N-[3-(trimethoxysilyl)propyl]ethylenediamine functionality and molybdenum carbonyl on the surface of SBA-15 molecular sieves. The ²⁹Si MAS NMR of SBA-DA displays an identical spectrum (Fig. 3b) of SBA-DA-Mo since the chemical environment of the Si atoms is not changed during the grafting process.

- ⁵ Further, the ¹³C CP-MAS spectra (Fig. 4) of SBA-DA and SBA-DA-Mo showed peaks around 10, 25, 45, and 52 ppm, which correspond to different aliphatic functionalities arising from the siloxane functional group.^{14,b} The additional unexpected peak seen around 165 ppm for SBA-DA corresponds to carbamic acid
- ¹⁰ type carbonyl functionality.^{14c} The observed carbamic acid type carbonyl may be due to interaction of atmospheric CO₂ with diammine functionality present on the surface of SBA-15.^{14c} The weak signal appeared around 186 ppm may be due to the presence of terminal carbonyl group which is associated with ¹⁵ molybdenum species.¹⁸

Table.1	Textural	properties	of various	SBA-15	molecular	sieves
---------	----------	------------	------------	--------	-----------	--------

Sample code	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)		Mo (wt %) [#]
	BET	Total	Micro pore	
SBA-15	769.0	1.10	0.018	
SBA-DA	347.6	0.56	0.000	
SBA-DA-Mo	276.6	0.44	0.000	28

calculated based (ICP-AES) analysis



Fig. 5 N_2 sorption isotherms of (a) SBA-15, (b) SBA-DA and (c) ²⁰ SBA-DA-Mo.

 N_2 adsorption isotherm studies on SBA-15 and grafted SBA-15 samples and the corresponding pore size distribution (inset) are depicted in Fig 5. All the samples show typical type IV ²⁵ isotherms, as per the IUPAC classification,¹⁴ characteristic of mesoporous materials. A well-defined sharp inflection is observed between relative pressures (p/p_0) of 0.6 and 0.8 due to capillary condensation of nitrogen inside the primary mesoporous.^{8,12,16} Compared to the parent mesoporous sample, ³⁰ the samples modified with ligand and molybdenum carbonyl

display a drastic decrease in nitrogen uptake and a shift in the isotherm towards low relative pressures owing to the presence of an organometallic Mo-complex grafted on the surface of mesoporous channels. 8,9

- ³⁵ Table 1 summarizes the textural properties of the SBA-15, SBA-DA, and SBA-DA-Mo samples. The parent SBA-15 shows a surface area and total pore volume of around 769 m²/g and 1.10 cm³/g respectively, which reduces drastically in diaminefunctionalized materials owing to the grafting of diammine silane
- ⁴⁰ in the mesoporous channel. SBA-DA-Mo samples exhibit a further decrease in the surface area and total pore volume to 276 m²/g and 0.44 cm³/g, respectively. The observed decrease in surface area and total pore volume support the grafting organometallic complex 1 on the surface of mesoporous SBA-15; 45 this is also in agreement with the FT-IR data.^{8,9}
- Thermal stability of the SBA-DA-Mo sample was studied using TGA (Fig. 6). A weight loss of around 17 % was observed in the grafted materials due to the loss of the carbonyl group and the methyl and methylene group from the complex and amino silane ⁵⁰ moiety, respectively.



Fig. 6 TGA profile of SBA-DA-Mo.

Thermal stability of the SBA-DA-Mo sample was studied using TGA (Fig. 6). A weight loss of around 17 % was observed in the grafted materials due to the loss of the carbonyl group and the ⁵⁵ methyl and methylene group from the complex and amino silane moiety, respectively.

Further, in order to confirm the formation of the molybdenum carbonyl diammine complex, an unsupported homogenous complex 1 (DA-Mo) was prepared by the treatment of N-[3-60 (trimethoxysilyl) propyl]ethylenediamine with Mo(CO)₆ using dry toluene as the solvent under nitrogen atmosphere. The ¹H NMR spectra of complex 1 showed a shift in the chemical shift values (see, Fig. S1, ESI⁺) of the amine proton, clearly supporting the formation of adduct complex 1. 13 C NMR (δ , 65 400MHz, CDCl₃) of the complex **1** is shown in Fig. S2 and it is compared with diaminosilane ligand. ¹³C NMR spectra (a) and (b) shows peaks around 10-65 ppm which corresponds to aliphatic region of amine-functional group and it is in good agreement with the literature.¹⁷ Further, an additional peak 70 observed around 200 ppm indicates the presence of carbonyl group (CO) in the complex $1^{.18}$ The estimated molybdenum percentage in SBA-DA-Mo sample is shown in Table 1. The sample shows about 28 wt % Mo content and is similar to theoretically calculated value. The above fact indicates that all the

molybdenum species is effectively anchored on the surface of diamine.

Thorough characterization of SBA-DA-Mo was carried out for epoxidation of cyclooctene at different temperatures, catalyst 5 loadingand solvent etc., in the presence of 5 M TBHP in decane



Fig. 7.Effect of temperature on epoxidation using SBA-DA-Mo catalyst.



Fig. 8 Effect of solvent on epoxidation using SBA-DA-Mo catalyst.

10

Table 2.Effect of catalyst loading on epoxidation using SBA-DA-Mo catalyst.

S. No	Catalyst amount (mg)	Conversion (%)	Selectivity (%)
1	12.5	39	97
2	25	72	96
3	50	89	97
4	100	97	96

[#]Reaction details; catalyst: Oxidant: substrate: 2:1, Temperature: 70 °C, Time: 24 h; Solvent: Mesitylene (4 ml).

¹⁵ as the oxidant. Figure 7 shows the effect of reaction temperature on epoxidation of cyclooctene. It can be seen from the figure that as the reaction temperature increases, the olefin conversion is increases linearly. The maximum conversion of about 90-95 % has been observed at 60-70 °C with exclusive formation of ²⁰ epoxide as major product. Subsequently, by keeping reaction temperature at 70 °C, the reaction was studied to understand the role of various solvents, such as methanol, acetonitrile, hexane and mesitylene. The results are displayed in Fig 8. It is evident from the figure that, irrespective of the solvent the olefin ²⁵ conversion was found to be more than 90 % in all cases. Since the

solvent is not coordinating with active molybdenum species, irrespective of the solvent chosen for the present studies, similar conversion has been observed. The effect of catalyst amount on epoxidation of olefin was further studied by varying the catalyst

³⁰ amount ranging from 12.5 to 100 mg per 50 mmol of octene and the results are summarized in table 2. From the table it can be evident that upon increase in catalyst amount, increase in the olefin conversion linearly has been observed. Maximum olefin conversion was obtained for the reaction which is carried out ³⁵ using 100 mg of catalyst. Based on the above kinetic studies, the optimum reaction conditions viz., temperature of 70 °C, catalyst loading of 100 mg and mesitylene as solvent were chosen for further studies.

⁴⁰ **Table 3.**Oxygenation of olefin using various materials.[#]

S. No	Catalyst	Time (h)	Con. (%)	Epoxide Sel. (%)
1		4	18	15
I	without catalyst	24	23	12
2	CD & 15	4	22	17
2	SBA-15	24	30	14
	Commiss 1	4	10	43
3	Complex 1	$\begin{array}{c} 24 \\ 20 \\ \text{Complex 1} \\ 24 \\ 4 \\ 24 \\ 4 \\ 4 \end{array}$	50	94
4		4	93	86
	SBA-DA-Mo	24	97	96
5 ^a	1 st recycled	4	96	87
6 ^b	2 nd recycled	4	97	92
$7^{\rm c}$	3 rd recycled	4	94	90

[#]Reaction details; catalyst: Oxidant: substrate: 0.0063: 2:1, Temperature: 70 °C, Solvent: Mesitylene; a, b, c are 1st,2nd, 3rd-recycled SBA-DA-Mo catalyst respectively.

The reaction was also studied with different catalyst and results

⁴⁵ are reported in Table 3. The pure complex showed only about 10 % conversion at 4 h, which increases to 50 % after 24 h of reaction. The slow decomposition of complex 1 in solution results in the lower activity observed.

Further, no significant conversion was observed in the absence of ⁵⁰ catalyst and parent SBA-15 materials. The molybdenum carbonyl grafted on diamine-functionalized SBA-15 (SBA-DA-Mo) shows about 93 % conversion at 4 h, reaching almost 97 % after 24 h of reaction. The conversion of molybdenum carbonyl species into active Mo(VI) species was responsible for the observed higher ⁵⁵ catalytic activity.^{3-5,8,9} Importantly, the FT-IR spectrum of SBA-DA-Mo after the reaction (Fig. 2) retains the vibrational band around 910 and 955 cm⁻¹, indicating the stability of the Mo complex on the support. After the reaction, the SBA-DA-Mo samples were filtered and washed with dichloromethane and ⁶⁰ reused; the results are shown in Table 2. It is clear that molybdenum is retained as a dioxo complex on the diaminefunctionalized SBA-15 surface and remains active for several recycle runs.

	5				
S. No	Reactant	product	Time (h)	Con. (%)	Epoxide Sel. (%)
1		\bigcirc	4	93	86
1			24	97	96
2	\frown		4	91	78
		0	24	98	34
3		\sim	4	42	95
			24	96	16
4	PhPh	PhOPh	24	59	70
5	~~~/	$\sim\!$	4	16	82
			24	89	91
6	$\sim\sim\sim\sim$	$\frown \frown \bullet$	4	39	19
			24	17	86
7	$\sim\!\!\!\sim\!\!\!\sim$	$\sim \sim \circ$	4	19	76
			24	60	86

Table 4.Oxygenation of various olefins over SBA-DA-Mo 5 catalyst.#

[#]Reaction details; catalyst: Oxidant: substrate: 0.0063: 2:1, Temperature: 70 °C, Solvent: Mesitylene.

Further, SBA-DA-Mo was studied for series of olefin and the results are summarized in Table 4. The catalyst showed excellent

- 10 conversion for both cyclic and acyclic olefins, forming epoxide as the major product. In the case of cyclohexene, a considerable amount of the ring-opening product was formed after 24 h, as evident from GC-MS. The catalyst also showed about 59 % conversion after 24 h for stilbene. However, in the case of
- 15 styrene, the polymerization of styrene occurred under these reaction conditions. For acyclic olefins, the double bond at the terminal position (1-octene) showed better conversion compared to olefins containing a double bond at the 2- or 4- (2-Octene and 4-Octene) position owing to the orientation effect of olefins on
- 20 active sites. Overall, the catalyst is found to be stable and active for several olefins epoxidation under moderate reaction conditions.

Conclusion

- 25 In summary, the current work established a simple method to graft molybdenum carbonyl on the surface of mesoporous molecular sieves. The presence of active molybdenum oxo species on SBA-DA-Mo, which was formed upon TBHP treatment, resulted in promising catalytic activity for olefin 30 epoxidation. Importantly, the active species remain intact on the
- surface and the catalyst is recyclable.

Acknowledgements

Authors extend his sincere and grateful thanks to CSIR (Project 35 No: 01(2516)/11/EMR-II), New Delhi for the financial supports.

Notes and references

^{a*}Department of Chemistry, Inorganic Materials and Catalysis Laboratory, University of Delhi, New Delhi-110007, India, ^bIndian Oil 40 Corporation Ltd, R&D Centre, Faridabad-12100, India, Central NMR Facility, CSIR-National Chemical Laboratory, Pune-411008, India. E-mail: asakthivel@chemistry.du.ac.in

- 1. (a) R. A. Sheldon, and J. K. Kochi, Metal-catalyzed oxidation of 45 organic compounds, Academic Press, New York (1981); (b) C. L. Hill, in Advances in Oxygenated Processes, A.L. Baumstark, Ed. (JAI, London, 1988), vol. 1, pp. 1; (c) N. Mizuno, K. Yamaguchi, and K. Kamata, Coord. Chem. Rev. 2005, 249, 1944; (d) S. A. Hauser, M. Cokoja, and F. E. Kuhn, Catal. Sci. Technol. 2013, 3, 552.
- (a) A. Sakthivel, and M. Sathiyendiran in Molybdenum and its 50 2. compounds, V. S. Saji and S. I Lopatin (Eds.), Nova Science Publishers (2014)ISBN:978-1-63321-210-7 at press and the reference therein; (b) N. Grover, and F. E. Kuhn, Current Org. Chem., 2012, 16, 16; (c) K. R Jain, W. A. Hermann, and F. E. Kuhn, Coord. Chem. Rev., 2008, 252, 556; (d) F. E. Kuhn, A. M. Santos, and M. Abrantes, 55 Chem. Rev., 2006, 106, 2455.
- (a) J. Zhao, K. R. Jain, E. Herdtweck and F. E. Kuhn, Dalton Trans., 3. 2007, 5567; (b) J. Zhao, A. M. Santos, E. Herdtweck, and F.E. Kuhn, J. Mol. Catal. A: Chemical., 2004, 222, 265; (c) F. E. Kuhn, A. D.
- Lopes, A. M. Santos, E. Herdtweck. J. J. Haider, C. C. Romão, and 60 A. Gil Santos, J. Mol. Catal. A: Chemical. 2000, 151, 147; (d) F. E. Kühn, A. M. Santos, A. D. Lopes, I. S. Gonçalves, E. Herdtweck, and C. C. Romão, J. Mol. Catal. A: Chemical., 2000, 164, 25.
- (a) M. Abrantes, A. Sakthivel, C. C. Romao, and F. E. Kuhn, J 4 Organomet. Chem., 2006, 691, 3137; (b) R. Poli, Coord. Chem. Rev., 2008, 252, 1592; (c)A. Sakthivel, M. Abrantes, A. S.T. Chiang, and F. E. Kuhn, J. Organomet. Chem., 2006, 691, 1007;(d) M. Jia, A. Seifert, and W. R. Thiel, Chem. Mater. 2003, 15, 2174; (e)M. Jia and W. R. Thiel, Chem. Commun., 2002, 2392.
- (a) A. C. Gomes, S. M. Bruno, S. Gago, R. P. Lopes, D. A. Machado, 70 5. A. P. Carminatti, A. A. Valente, M. Pillinger, and I. S. Gonçalves, J. Organomet. Chem., 2011, 696, 3543; (b) P. Neves, T. R. Amarante, A. C. Gomes, A. C. Coelho, S. Gago, M. Pillinger, I. S. Goncalves, C. M. Silva, and A. A. Valente, Appl. Catal. A: General., 2011, 395, 71; (c) S. Figueiredo, A. C. Gomes, J. A. Fernandes, F. A. Almeida Paz, A. D. Lopes, J. P. Lourenço, M. Pillinger, and I. S. Gonçalves, J. Organomet. Chem., 2013, 723, 56; (d) T. R. Amarante, P. Neves, A. C. Coelho, S. Gago, A. A. Valente, F. A. Almeida Paz, M. Pillinger, and I. S. Goncalves, Organometallics 2010, 29, 883; (e) C. Bhaumik, E. Manoury, J-C Daran, P. Sözen-Aktas, F. Demirhan, R. Poli, J. 80 Organomet. Chem, 2014, 760, 115.
- (a) C. A. Gamelas, A. C. Gomes, S. M. Bruno, F. A. Almeida Paz, A. 6. A. Valente, M. Pillinger, C. C. Romão and I. S. Gonçalves, Dalton Trans., 2012, 41, 3474; (b) M. Abrantes, F. A. Almeida Paz, A. A. Valente, C. C. L. Pereira, S. Gago, A. E. Rodrigues, J. Klinowski, M. 85 Pillinger, and I. S. Gonçalves, J. Organomet. Chem., 2009, 694,
 - 1826;(c) S. A. Hauser, M. Cokoja, M. Drees, and F. E. Kuhn, J. Mol. Catal. A: Chemical., 2012, 363-364, 237; (d)F. E. Kuhn, J. Zhao and W. A. Herrmann, Tetrahedron: Asymmetry., 2005, 16, 3469.
- (a) R. Bakhtchadjian, S. Tsarukyan, J. Barrault, F. O. Martinez, L. 90 7. Tavadyan, and N. J. Castellanos, Transition Met. Chem. 2011, 36, 897; (b) N. J. Castellanos, F. Martínez, F. Lynen, S. Biswas, P. V. Der Voort, and H. Arzoumanian, Transition Met. Chem. 2013, 38, 119; (c) H. Arzoumanian, N. J. Castellanos, F. O. Martínez, E. A. Páez-Mozo, and F. Ziarelli, Eur. J. Inorg. Chem., 2010, 1633; (d) F. 95

Kerdi, V. Caps, A. Tuel, *Microporous Mesoporous Mater*. 2011, **140**, 89

- (a) A. Sakthivel, J. Zhao, and F. E. Kuhn, *Microporous and Mesoporous Mater.*, 2005, 86, 341; (b)A. Sakthivel, J. Zhao, M.
- ⁵ Hanzlik, A. S. T. Chiang, W. A. Herrmann and F. E. Kuhn, Adv. Synth. Catal., 2005, **347**, 473; (c) A. Sakthivel, J. Zhao, G. Raudaschl-Sieber, M. Hanzlik, A.S.T. Chiang and F. E. Kuhn, Appl. Catal. A: General., 2005, **281**, 267; (d) A. Sakthivel, J. Zhao, and F. E. Kuhn, Catal. Lett., 2005, **102**, 115; (e) J. Zhao, A. Sakthivel, A.
- 10 M. Santos, and F. E. Kuhn, Inorg. Chim.Acta., 2005, 358, 4201.
- (a) A. Sakthivel, F. M. Pedro, A. S. T. Chiang, and F. E. Kuhn, *Dalton Trans.*, 2007, 320; (b) S. Syukri, A. Sakthivel, W. Sun, and F. E. Kuhn, *Catal.Lett.*, 2009, **128**, 18; (c) A. Sakthivel, W. Sun, G. Raudaschl-Sieber, A. S.T. Chiang, M. Hanzlik and F. E. Kuhn, *Catal Comm.*, 2006, **7**, 302.
- (a) A. Sakthivel, and P. Selvam, *J. Catal.*, 2002, 211,134-143; (b) A. Sakthivel, S.J. Huang, W.H. Chen, Z.H. Lan, K.H. Chen, H.P. Lin, C.Y. Mou, and S.B.Liu, *Adv. Funct. Mater.*, 2005, 15, 253; (c) A. K. Singh, R. Yadav, V. Sudarsan, K. Kishore, S. Upadhyayula and A. Sakthivel, *BCC* 44, 2014, 4, 9727
- ²⁰ Sakthivel, *RSC Adv.*, 2014, **4**, 8727.
 - A. Hervè, J-J. Yaouanc, J-C. Clèment, H des Abbayes, L. Toupet, J. Organometallic Chem., 2002, 664, 214.
 - D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, and G. D. Stucky, *Science*. 1998, 279
- 25 13. P. Plueddemann Edwin, and A. Revis, US Patent 4,866,192 (1989).
- (a) S. Shylesh, A. Wagner, A. Seifert, S. Ernst and W. R. Thiel, *Chem. Eur. J.*, 2009, **15**, 7052; (b) T. M. Suzuki, T. Nakamura, K. Fukumoto, M. Yamamoto, Y. Akimoto, K. Yano, *J. Mol. Catal. A: Chemical.*, 2008, **280** 224; (c) J. C. Vartuli, G. J. Kennedy, B. A.
- 30 Yoon, and A. Malek, *Microporous Mesoporous Mater.*, 2000, **38**, 247.
 - 15. Y. Iwasawa, and S. Ogasowara, J. Chem. Soc. Faraday Trans. I, 1979, **75**, 1465.
 - 16. K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscow, R.A. Pierotti,
- T. Rouquerol, and T. Siemienewska, *Pure Appl. Chem.* 1985, **57**, 603.
 - 17. I. Warad, Molecules, 2010, 15, 4652.
 - (a) J. Gimenez, C. D. Nunes, P. D. Vaz, A. A. Valente, P. Ferreira, M. José Calhorda, *J. Mol. Catal. A: Chemical*, 2006, **256**, 90; (b) M.
- 40 S. Saraiva, C. D. Nunes, T. G. Nunes, M. José Calhorda, J. Mol. Catal. A: Chemical, 2010, 321, 92.