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Molybdenum based metallomicellar catalyst for controlled and selective sulfoxidation reactions in aqueous medium

Green Chemistry

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A surfactant based molybdenum system that exhibits catalytic activity for sulfoxidation reaction of various organic sulfides in aqueous medium has been developed and comprehensively characterized with IR, XRD, NMR, ESI-MS, DLS and TEM. The catalyst showcases remarkable selectivity for the preparation of both sulfoxides and sulfones in the range of good to excellent yields. Furthermore the catalyst showed high degree of tolerance towards various sensitive functional groups such as hydroxyl, acetal, aldehyde, amine, imine, oxime, cyano and alkene.

Introduction

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Sulfoxidation is one of the most fundamental reactions in organic synthesis. Many sulfoxides and sulfones are used as versatile intermediates for various organic transformations.¹ Additionally, these compounds are proved as active pharmaceutical ingredients for several therapeutic drug molecules.²Sulfoxidation of organic sulfides is a straight forward method for the selective preparation of sulfoxides or sulfones. Traditional approaches of sulfoxidation reactions involve the usage of peracids³ or halogen derivatives⁴ however they yield stoichiometric amounts of environmentally unfriendly byproducts. Alternative approaches involve the usage of transition-metal based catalysts along with ecofriendly hydrogen peroxide as an oxidant, predominantly in common organic solvents.^{5,6}

Water is undoubtedly a unique solvent that receives phenomenal attention in the field of "green" or sustainable chemistry.⁷ There are a few reports of self-catalyzed⁸ and metalcatalyzed sulfoxidation reactions in aqueous medium.9

Disadvantages of such methods could be the requirement of high temperature and/or long reaction time, poor catalyst recyclability, limited scope of substrates, poor functional group tolerance, and prerequisite to use promoters or involves complicated experimental procedures. This necessitates the development of efficient sulfoxidation processes in aqueous medium.

Molybdenum element is rich in the field of organic, inorganic and biological chemistry.¹⁰ Oxomolybdenum compounds have been reported for their catalytic function in several organic reactions.^{11,12,13,14} In the recent past, our research has focused on studying oxidation reactions catalyzed molybdenum based systems.¹⁵ Notably, we have by successfully developed MoO2Cl2 as a mild and selective catalyst for sulfoxidation reactions featuring high functional compatibilities in organic solvents¹⁶ and its application to selectively oxidize sulfides has been reported by other prominent research groups.¹⁷ And in order to deliver more viable "green" protocols for sulfoxidation reactions, our target has been to design catalysts that can be used in aqueous medium over the conventional organic solvents. As metal based surfactant systems are known to have the desirable attributes of solubilizing the reactants in the aqueous medium and at the same time catalyze the reactions,¹⁸ in the present study we have designed and characterized a surfactant based molybdenum system to catalyze sulfoxidation reactions in water. Its catalytic activity was analyzed in terms of selectivity and yield for controlled oxidation of various organic sulfides with hydrogen peroxide oxidant.

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[†] Electronic Supplementary Information (ESI) available: Experimental procedures, IR, NMR, ESI-MS for all new compounds i.e. 14a, 14b, 14c, 16b including the catalyst 1 as well as powder and single crystal XRD data of 1. CCDC reference number 918215. see DOI: 10.1039/b00000x/

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Results and discussion

An oxodiperoxo molybdenum catalyst $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)] \cdot H_2O$, **1** (Scheme 1) with surfactant containing Cetyl Trimethyl Ammonium cation (CTA) as an integral part of the catalyst was prepared for studying sulfoxidation reactions in pure water. The catalyst **1** could be conveniently synthesized from affordable and readily available starting materials such as sodium molybdate, oxalic acid, hydrogen peroxide and CTA bromide (CTAB).



The complex was characterised by IR, NMR, ESI-MS and XRD techniques. The sharp and strong peaks at 948 and 859 cm⁻¹ in the IR spectrum correspond to the characteristic (Mo=O) and (O-O) stretching frequencies, respectively and the peaks at 648 and 583 cm⁻¹ are characteristic to the stretching of (Mo-(O₂)) moieties (Fig. 1). These frequencies are in well agreement with literature values of similar bonds.¹⁹ The structure of the complex was unambiguously confirmed by single crystal X-ray diffraction technique. Single crystals suitable for XRD analysis were obtained by slow evaporation of a solution of 1 in chloroform:ethanol (1:1). The compound was crystallized as monohydrate complex 1 where the asymmetric unit is composed of one dianionic molybdenum component, two CTA cations and one water molecule (Fig.2). The axial positions in the coordination sphere are occupied by the oxo group and one of the oxygen atoms of the oxalate ligand, whereas the equatorial positions by four oxygen atoms of the peroxo groups and the remaining oxygen of the oxalate ligand. The excellent agreement between the simulated and the experimental powder XRD data certifies the purity and





Fig. 2 Crystal structure of $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)] \cdot H_2O$, 1.

homogeneity of the bulk complex (Fig. 3). The ¹H-NMR spectrum of the complex 1 was recorded in CDCl₃ that displays signature peaks required to establish the presence of CTA moiety whereas the ¹³C-NMR spectrum confirms the existence of bound oxalate group as well. The observation of the 164.9 and 167.8 ppm peaks indicates the asymmetric environment of the oxalate ligand upon coordination. ESI-MS study (negative ion mode) substantiated the composition of the anionic molybdenum entity of the compound 1 with correct isotopic pattern. The peaks at m/z = 550.21 corresponds to the anion of [1-(CTA+H₂O)] fragment. Surfactant compounds are known to form self-assembled aggregates called micelle. The critical micelle concentration (CMC) of 1 was determined by conductivity method and was found to be 2.24 mM (see ESI). The size and shape of the aggregates in water were determined using TEM and DLS analysis. TEM micrograph (Fig. 4) clearly demonstrated that the surfactant complex 1 was aggregated as







Fig.4 TEM image of complex 1

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spherical micelle with the average size of 46 ± 7 nm. DLS analysis showed that the micelles are of narrow size distribution with the average diameter of about 56 nm (see ESI).

Next, we explored the abilities of 1 as a catalyst for sulfoxidation reactions in aqueous conditions. Due to the mild nature of molybdenum catalysts, functional group anticipated. To begin compatibilities were also with, thioanisole, 1a was chosen as a model substrate for catalytic sulfoxidation reactions. To a solution of thioanisole (1.5 mmol) in 2.5 mL water, 1 equiv. of aqueous H₂O₂ and 2.5 mol% catalyst, 1 were added at 25 °C and the concentration of the

addition to probing the functional group tolerance (Table 1). Typical sulfides like methyl p-tolylsulfide, methyl 4methoxyphenylsulfide and 2-chlorophenyl, methylsulfide zgave corresponding sulfoxides in 90-94% yields. However, 4chlorophenyl methyl sulfoxide was obtained at moderate yield of 78%. Octyl phenyl sulfide (17a) and tetrahydrothiophene (18a) also afforded the corresponding sulfoxides under this catalytic condition. Organic sulfides having various other functional groups like alkene, oxime, aldehyde, imine and further analyzed for their tolerance. acetal were





catalyst was maintained well above the CMC (ca.15 mM in water). To our delight, the sulfoxide **1b** was obtained at 95% yield with reaction time of 30 min. This result prompted us to investigate the generality and versatility of our catalytic system. Having the optimized reaction condition for the model substrate, we explored the substrate scope of the catalyst in



Reaction conditions: ^aCatalyst:sulfide: $H_2O_2 = 0.025$:1:3 in 0.5 mL water. ^bIsolated yields. ^cCatalyst:sulfide: $H_2O_2 = 0.025$:1:2.2 no additional solvent. ^dCatalyst:sulfide: $H_2O_2 = 0.15$:1:1 in 1 mL water. ^cCatalyst:sulfide: $H_2O_2 = 0.025$:1:3 in 4 mL water.

Sulfides having oxime, acetals and imines groups are known to undergo deprotection in presence of acid or acidic impurities under aqueous medium. Interestingly, the metallomicellar catalyst selectively oxidized such sulfides to the corresponding sulfoxides with high selectivity. Sulfide containing aldehydes did not show any functional group Published on 07 January 2014. Downloaded by Heinrich Heine University of Duesseldorf on 08/01/2014 19:23:50.

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transformation other than the targeted sulfoxidation. Similarly sulfides bearing amino, hydroxyl and cyano functional groups were also selectively oxidized in excellent yields. The highest yield of 96% obtained thus far for this catalyst was observed in the case of 4-(methylsulfinyl)aniline.²⁰

To further highlight the synthetic utility of our protocol, the selective oxidation of sulfides to sulfones were also carried out by varying the amount of oxidant. Under similar conditions, thioanisole was tested with 3 equiv. of aqueous H_2O_2 for the preparation of the corresponding sulfone 1c. The reaction gave only 80% conversion over a period of 3 hours. Subsequent optimizations lead in reduction of the amount of water from 2.5 mL to 0.5 mL, with the final concentration of the catalyst being 75 mM in water, resulting in significantly improving yield of (methylsulfonyl)benzene 1c increased to 97% within just 10 min of reaction time. This illustrates the effect of the catalyst concentration on oxidation reactions. To explore the scope of substrates several organic substrates were analyzed for the preparation of sulfones (Table 2). The reaction proceeded with high chemo-selectivity and we obtained the highest yield of 98% in the case of 2-(phenylsulfonyl)acetonitrile 13c. It is noteworthy that even in presence of excess oxidant, a high degree of functional group tolerance was observed for most of the sensitive groups like cyano, acetal, imine, aldehyde, alcohol, amine, oxime and alkene (Table 2) proving the catalyst to be mild yet effective.

Lastly, recyclability of the catalyst being an attractive feature, we studied the recyclability for the oxidation of thioanisole to the corresponding sulfoxide **1b**. The reaction mixture was centrifuged after the first run and the obtained solid residue was washed with ethyl acetate, dried under vacuum and reused for at least another three more catalytic runs without any significant loss of activity. The high yields between the range of 91-94% (Fig. 5) from such runs indicated the modest recyclability of this newly developed catalyst.



Fig. 5 (a) Recyclability of the catalyst (b) figure shows the catalyst recovery after centrifugation.

Conclusion

In conclusion, we have developed, characterized and demonstrated the first example of surfactant based molybdenum system for selective and controlled oxidation of sulfides in aqueous medium. The catalyst shows high functional group compatibility in producing both sulfoxides and sulfones in good to excellent yields. The reasonable recyclability and the usability of this catalyst in aqueous medium cater of the cateron of the solution towards sulfoxidations.

Experimental

Materials and Methods

Thioanisole, 4-(methylthio)benzaldehyde, 4-nitrothioanisole, methyl p-tolylsulfide, 4-methoxythioanisole, 2-chlorothio anisole, 4-chlorothioanisole, allyl sulfide, 4-(methyl thio)aniline 4-(methylmercapto)phenol, tetrahydrothiophene and p-toluene sulfonic acid monohydrate were purchased from sigma-aldrich company.(Phenylthio)acetonitrile and 1,3-propanediol were purchased from Alfa-Aesar 4-(methylthio)phenyl methanol, 1-(4-(methylthio)phenyl)ethanol, 4-(methylthio) benzaldehyde oxime and octyl phenyl sulfide were prepared following literature protocol.²¹ Sodium molybdate dihydrate, oxalic acid dihydrate, CTAB, aniline, sodium hydroxide, ethanol, diethyl ether and toluene were purchased from SISCO research laboratories Pvt. Ltd., India and used without purification. The oxidant hydrogen peroxide was purchased from Merck specialities Pvt. Ltd., and the concentration was determined by permanganate titration method. The deuterated solvents were obtained from Cambridge Isotope Laboratories. ¹H and ¹³C NMR spectra were recorded on Bruker Avance-400 instrument. IR spectra of the complexes were recorded on Jasco FT/IR 4100 instrument by KBr pellet method. Single crystal X-ray analyses were carried out using Bruker X8 Kappa XRD instrument. Powder XRD was recorded in BrukerD8 advance instrument. ESI-Mass spectrumwas recorded on Micromass Q-Tof mass spectrometer in a negative ion mode. A SYSTRONICS digital bench top conductivity meter (Model 306) was used for the measurements of critical micellar concentration. Dynamic light scattering (DLS) experiments were done on a Malvern Zetasizer nano-series 25 °C. The wavelength of the laser used was 632.8 nm and the scattering angle was kept at 90. TEM images were obtained on PHILIPS CM12 transmission electron microscope, using an accelerating voltage of 120 kV.

Preparation of 2-(4-(methylthio)phenyl)-1,3-dioxane

To a solution of 4-(methylthio)benzaldehyde (3.8 g, 25 mmol) in toluene (50 ml), was added 1,3-propanediol (4.41 g, 58 mmol) and *p*-toluenesulfonic acid monohydrate (50 mg, 0.26 mmol). The reaction mixture was taken in a round bottom flask fitted with a Dean-stark apparatus and reflux condenser. The solution was refluxed for two days. The solution was then allowed to cool to room temperature. Next, the reaction mixture was washed with 0.1 M aqueous NaOH. The organic layer was separated, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product thus obtained was purified by distillation. Isolated as colorless liquid; Yield 71% (3.73 g); IR (NaCl plates-neat) v(C-O) 1106 cm⁻¹;¹H-NMR (CDCl₃, 400 MHz): δ =1.46-1.42 (m, 1H), 2.15-2.29 (m, 1H), 2.47 (s, 3H), 4.01-3.94 (m, 2H), 4.28-4.23 (m,

2H), 5.46 (s, 1H), 7.24 (BB', 2H), 7.40 (AA', 2H); ¹³C-NMR (CDCl₃, 100 MHz): δ = 15.95, 25.85, 67.48, 101.41, 126.47, 126.60, 135.80, 139.24.

Preparation of N-(4-(methylthio)benzylidene)aniline

Aniline (2.33 g, 25 mmol) was added into the solution of 4-(methylthio)benzaldehyde (3.8 g, 25 mmol) in ethanol(25 ml) and the resulting mixture was stirred at room temperature. After 3 hours the solvent was removed under reduced pressure to obtain the crude product. The N-(4-(methylthio)benzylidene) aniline thus obtained was purified by crystallization from ethanol. Isolated as pale yellow solid; Yield 75 % (4.26 g); mp 92-94°C; IR (KBr pellet) v(C=N) 1620 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz): $\delta = 2.50$ (s, 3H), 7.23-7.18 (m, 3H), 7.28 (d, 2H, J= 8.4), 7.40-7.36 (m, 2H), 7.79 (d, 2H, J= 8.4), 8.38 (s, 1H); ¹³C-NMR (CDCl₃, 100 MHz): δ = 15.18, 120.99, 125.78, 125.94, 129.20, 129.24, 132.97, 143.32, 152.19, 159.70.

Synthesis of (C₁₉H₄₂N)₂[MoO(O₂)₂(C₂O₄)]·H₂O

Catalyst $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)] \cdot H_2O$ was synthesized by a slight modification of literature protocol. Solution A: 5ml of 0.15954 M (0.193 g, 0.8 mmol) sodium molybdate dihydrate was added into a beaker containing 5 ml water and the acidity of the solution was adjusted to pH 2 with 0.1 M sulfuric acid. Then 1 ml of 40% (w/v) hydrogen peroxide (10 mmol) was added and the resulting solution was diluted to 20 mL with water. Solution B: Oxalic acid dihydrate (0.106 g, 0.84 mmol) was added into a beaker containing 2.5 ml of an aqueous solution of cetyltrimethyl ammonium bromide (0.604 g, 1.66 mmol) and the resulting solution was diluted to 5 mL with water. In an ice-cold condition with vigorous stirring solution A was added slowly drop wise into the solution B and the acidity of the solution was maintained at pH 2 by adding sulfuric acid. After 5 min the formation of pale yellow precipitate was observed. The reaction mixture was centrifuged and the precipitate was washed 2-3 times with water and dried under vacuum (Yield 82%).mp 264-268 °C (decomposed). Single crystals suitable for X-ray analysis were obtained by slow evaporation of1:1 ethanol-chloroform solution of complex. Anal. Calcd for C₄₀H₈₆MoN₂O₁₀: C, 56.45; H, 10.19; N, 3.29. Found C, 56.40; H, 10.34; N, 3.34.

General procedure for the catalytic oxidation of sulfides to sulfoxides

A mixture of molybdenum complex (2.5 mol%) and sulfide (1.5 mmol) in 2.5 ml of water was stirred at room temperature. Then 40% (w/v) hydrogen peroxide (1.5 mmol) was added slowly into the reaction mixture. Stirring was continued for 10 min to 6 hours as per requirement. Reaction progress was monitored by TLC. After completion, ethyl acetate was added to it. The reaction mixture was then centrifuged and decanted to separate molybdenum compound. The aqueous phase is extracted with ethyl acetate 3-4 times. Then the combined organic extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude

product thus obtained was purified by column chromatography with hexane: ethyl acetate as an eluent.

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General procedure for the catalytic oxidation of sulfides to sulfones

A mixture of molybdenum complex (2.5 mol%) and sulfide (1.5 mmol) in 0.5 ml of water was stirred at room temperature. Then 40% (w/v)hydrogen peroxide (4.5 mmol) was added slowly into the reaction mixture. Stirring was continued for 10 min to 8 hours as per requirement. Reaction progress was monitored by TLC. After completion, the aqueous phase is extracted with ethyl acetate 3-4 times. Then the organic extracts were dried over anhydrous sodium sulfate. Molybdenum catalyst slowly precipitated out on standing. Centrifuged and decanted the ethyl acetate layer to remove the catalyst. The solvent was removed under reduced pressure. Most of the cases, pure sulfone was obtained. Further purification was done by column chromatography with hexane:ethyl acetate as an eluent.

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References

- E. N. Prelizhaeva, Russ. Chem. Rev., 2000, 69, 367.
- S. Caron, R. W. Dugger, S. G. Ruggeri, J. A. Ragan and D. H. B. 2 Ripin, Chem. Rev., 2006, 106, 2943.
- (a) B. M. Trost, T. N. Salzmann and K. Hiroi, J. Am. Chem. Soc., 3 1976, 98, 4887; (b) C. G. Venier, T. G. Squires, Y.-Y. Chen, G. P. Hussmann, J. C. Shei and B. F. Smith, J. Org. Chem., 1982, 47, 3774.
- 4 Review: P. Kowalski, K. Mitka, K. Ossowska and Z. Kolarska, Tetrahedron, 2005, 61, 1933.
- Review: K. Kaczorowska, Z. Kolarska, K. Mitka and P. Kowalski, 5 Tetrahedron, 2005, 61, 8315.
- Selected publications: (a) M. K. Panda, M. M. Shaikh and P. Ghosh 6 Dalton Trans., 2010, 39, 2428; (b) K. Kamata, T. Hirano and N. Mizuno, Chem. Commun., 2009, 3958; (c) C. Yang, Q. Jin, H. Zhang, J. Liao, J. Zhu, B. Yu and J. Deng, Green Chem., 2009, 11, 1401; (d) M. Kirihara, J. Yamamoto, T. Noguchi and Y. Hirai, Tetrahedron Lett., 2009, 50, 1180; (e) K. Bahrami, Tetrahedron Lett., 2006, 47, 2009; (f) K. Bahrami, M. M. Khodaei, and M. S. Arabi, J. Org. Chem., 2010, 75, 6208.
- 7 (a) C.-J. Li and L. Chen, Chem. Soc. Rev., 2006, 35, 68; (b) M.-O. Simon and C.-J. Li, Chem. Soc. Rev., 2012, 41, 1415.
- 8 (a) H. S. Schultz, H. B. Freyermuth and S. R. Buc, J. Org. Chem., 1963, 28, 1140; (b) F. Shi, M. K. Tse, H. M. Kaiser and M. Beller, Adv. Synth. Catal., 2007, 349, 2425; (c) T. Noguchi, Y. Hirai and M. Kirihara, Chem. Commun., 2008, 3040; (d) M. Jereb, Green Chem., 2012, 14, 3047. (e) B. Zhang, M.-D. Zhou, M. Cokoja, J. Mink, S.-L. Zang and F. E. Kühn, RSC Adv., 2012, 2, 8416.
- 9 (a) H. Egami and T. Katsuki, J. Am. Chem. Soc., 2007, 129, 8940; (b) K. Sato, M. Hyodo, M. Aoki, X.-Q. Zheng and R. Noyori, Tetrahedron, 2001, 57, 2469; (c) A. Shaabani and A. H. Rezayan, Catal. Commun., 2007, 8, 1112; (d) A. Scarso and G. Strukul, Adv. Synth. Catal., 2005, 347, 1227.
- 10 A. Holder, Molybdenum: Its Biological and Coordination Chemistry and Industrial Applications, Nova Science Publishers, Inc., New York, 2013.

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Page 6 of 7

- Reviews on oxomolybdenum catalysis: (a) K. Jeyakumar and D. K. Chand, J. Chem. Sci., 2009, **121**, 111; (b) R. Sanz, and M. Pedrosa, *Curr. Org. Synth.*, 2009, **6**, 239; (c) S. C. A. Sousa, I. Cabrita and A. C. Fernandes Chem. Soc. Rev., 2012, **41**, 5641; (d) M. R. Maddani and K. P. Prabhu, J. Indian Inst. Sci. **2010**, *90*, 287.
- 12 Selected publications: (a) C. Stock and R. Brueckner, Adv. Synth. Catal., 2012, 354, 2309; (b) N. Garcia, P. Garcia-Garcia, M. A. Fernandez-Rodriguez, R. Rubio, M. R. Pedrosa, F. J. Arnaiz and R. Sanz, Adv. Synth. Catal., 2012, 354, 321; (c) C.-Y. Liu, H.-L. Chen, C.-M. Ko and C.-T. Chen, Tetrahedron, 2011, 67, 872; (d) C.-Y. Liu, V. D. Pawar, J.-Q. Kao, and C.-T. Chen, Adv. Synth. Catal., 2010, 352, 188.
- 13 Review on oxoperoxomolybdenum catalysis: M. Amini, M. M. Haghdoost and M. Bagherzadeh, *Coord. Chem. Rev.*, 2013, 257, 1093.
- 14 Selected examples on molybdenum catalyzed sulfoxidation: (a) J. J. Boruah, S. P. Das, S. R. Ankireddy, S. R. Gogoi and N. S. Islam, *Green Chem.*, 2013, 15, 2944; (b) C. Yang, Q. Jin, H. Zhang, J. Liao, J. Zhu, B. Yu and J. Deng, *Green Chem.*, 2009, 11, 1401; (c) M. M. Khodaei, K. Bahrami and M. Khedri, *Can. J. Chem.*, 2007, 85, 7; (d) I. Sheikhshoaie, A. Rezaeifard, N. Monadi and S. Kaafi, *Polyhedron* 2009, 28, 733.

- 15 D. K. Chand and R. D. Chakravarthy, *The Handbook of Reagents for Organic Synthesis: Catalytic Oxidation Reagents*, P. L. Fuchs, John Wiley & Sons, Ltd, England, 1st edn., 2013, pp 407-410_{kew Article Online}
- 16 K. Jeyakumar and D. K. Chand, Tetrahedron Detto, 2006, 47, 457345C
- (a) P. W. Davies and S. J.-C. Albrecht, Angew. Chem. Int. Ed., 2009, 48, 8372; (b) T. Cavattoni, T. D. Giacco, O. Lanzalunga, M. Mazzonna and P. Mencarelli, J. Org. Chem., 2013, 78, 4886; (c) E. Baciocchi, T. D. Giacco, O. Lanzalunga, P. Mencarelli and B. Procacci J. Org. Chem., 2008, 73, 5675.
- 18 Review on metallomicellar catalysis: (a) S. Kobayashi and K. Manabe, Acc. Chem. Res., 2002, 35, 209; (b) B. H. Lipshutz and S. Ghorai Aldrichimica Acta, 2008, 41, 59; (c) J. Zhang, X.–G. Meng, X.–C. Zeng and X.–Q. Yu, Coord. Chem. Rev., 2009, 253, 2166.
- 19 T. T. Bhengu and D. K. Sanyal Thermochim. Acta, 2003, 397, 181.
- 20 D. K. Chand and R. D. Chakravarthy, Indian Patent Application No: 4639/CHE/2013.
- (a) K. Jeyakumar, *PhD Thesis*, Indian Institute of Technology Madras, 2008; (b) V. G. Shukla, P. D. Salgaonkar and K. G. Akamanchi, *J. Org. Chem.*, 2003, 68, 5422.

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Highlights

Surfactant based molybdenum catalyst for eco-friendly sulfoxidation reactions in aqueous medium.

Graphical Abstract

