Journal of Molecular Catalysis A: Chemical 392 (2014) 188–193

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Polyoxometalate $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$ on MCM-41 as catalysts for sulfide oxygenation with hydrogen peroxide

Dylan J. Thompson, Yang Zhang, Tong Ren *

Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States

ARTICLE INFO

Article history:
Received 29 March 2014
Received in revised form 17 May 2014
Accepted 20 May 2014
Available online 2 June 2014

Keywords:
Polyoxometalate
Sulfide oxygenation
Hydrogen peroxide
MCM-41
Heterogeneous catalysis

ABSTRACT

The polyoxometalate (POM) catalyst, $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$, was introduced into the pores of both as-synthesized (**I**) and amine functionalized MCM-41 (**II**). The resultant catalysts were characterized with powder X-ray diffraction, nitrogen sorption, and diffuse-reflectance UV–vis spectroscopy. Both catalysts were tested for reusability through repeated catalytic conversions of methyl phenyl sulfide to methyl phenyl sulfone with hydrogen peroxide. While the physisorbed catalyst (**I**) exhibits steadily decreasing turnover frequency (TOF), the POM catalyst supported on MCM-41 functionalized with a protonated amine (**II**) exhibits markedly improved reusability. This chemisorbed catalyst effectively showed no change in TOF between the second (21) and the sixth reactions (22). Additionally, sulfoxidations with catalyst **II** were investigated with a small set of substrates focusing on compounds including dibenzothiophene, which serves as a model refractory sulfide.

1. Introduction

Catalytic oxygenation of sulfide to the corresponding sulfoxide and sulfone is of interest for a variety of reasons. Firstly, due to regulations mandating a decreased permissible threshold concentration of sulfur in fuels [1], alternative methods for deep desulfurization such as oxidative desulfurization [2,3] are desirable [4]. Secondly, the detoxification of chemical warfare agents like mustard agent is achieved through its conversion to the corresponding sulfoxide [5]. Lastly, the conversion of sulfides to chiral sulfoxides produces key intermediates in medicinal chemistry [6,7]. Polyoxometalates (POMs) constitute a broad and interesting field with abundant catalytic opportunities, and are specifically attractive in redox reactions due to their high stability under these conditions [8,9]. The current work focuses on the di-vacant Keggin based lacunary polyoxometalate shown in Fig. 1, $[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]^{4-}$ (**1**), which has been reported to activate hydrogen peroxide for the epoxidation of olefins [10,11] and step-wise oxygenation of organic sulfides [12]. In homogenous reactions, **1** is selective with nearly quantitative efficiency in the use of hydrogen peroxide [10,12,13].

As with all homogeneous reactions, recovery and reuse of catalyst can be quite difficult, making the investigation of heterogeneous catalysts worthwhile [14,15]. While there are challenges with heterogenized materials including slower reactions, more expensive and tedious synthesis, as well as a liability of deactivation and leaching, there is a great potential in achieving an easily recyclable and stable catalyst [16]. One of the simplest methods to immobilize POM catalysts involves passive diffusion of polyoxometalate anions into the pores of mesoporous silica, the latter of which have been widely used as the catalyst support since the discovery of MCM-41 [17–20]. Such physisorbed catalysts are generally reported to be reusable up to 3–5 cycles. The most common problem for polyoxometalates physisorbed onto MCM-41 is the loss of catalyst via leaching [21–23]. This is especially the case when the catalyst is soluble in the reaction medium. One way to alleviate this matter is to functionalize the surface of silica with an alkyl amine or other functional groups bearing positive charges on the surface for supporting a chemisorbed catalyst [24–26]. It is worth mentioning that the synthesis of macroporous silica with lacunary γ-decatungstosilicate covalently attached to the wall through siloxy tether has been reported, and the silica supported decatungstosilicate is active in olefin epoxidation by hydrogen peroxide [27]. In order to avoid crowding the pores, it is important to keep the loading of the amine linker to a minimum [28] and not overload the POM catalyst [26]. These modifications can result in an increase in pore congestion [29] and loss of structural integrity of the mesoporous support [30,31]. Both the physisorb and chemisorb approaches were employed in this study, and the reusability and versatility of the resulting heterogeneous catalysts were investigated with a focus on H_2O_2 oxygenation of organic sulfides.

---

* Corresponding author. Tel.: +1 765 494 5466.
E-mail address: tren@purdue.edu (T. Ren).

http://dx.doi.org/10.1016/j.molcata.2014.05.015
1381-1169/

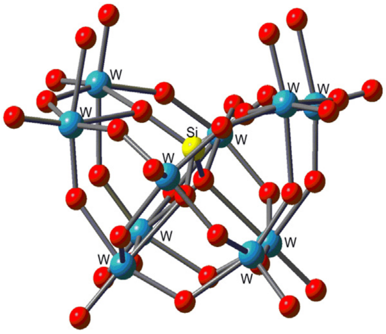


Fig. 1. Structure of [γ-$SiW_{10}(H_2O)_2O_{34}$]$^{4-}$ taken from Ref. [10].

2. Experimental

2.1. General

Reagents for the syntheses of the catalyst and the synthesis and functionalization of the MCM-41 were purchased from Sigma-Aldrich. Acetonitrile solvent was also purchased from Sigma-Aldrich. Sulfide substrates for the reaction, and the internal standard, 1,2 dichlorobenzene, were purchased from ACROS Organics.

The syntheses of MCM-41 [17,32,33] and the tetrabutylammonium (TBA) salt of [γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$ catalyst [10] were completed according to literature procedures. The infrared spectra of the [γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$ catalyst and its precursors were taken with ATR-IR on a JASCO FT/IR 6300 to authenticate the products from each synthetic step. The diffuse reflectance UV–vis spectra of the MCM-41 material as well as the impregnated MCM-41 catalysts **I** and **II** were taken with a JASCO V-670 spectrophotometer fitted with a JASCO ILN-725 integrating sphere. The powder X-ray diffraction (XRD) measurements of both catalysts and parent MCM-41 materials were taken in PANalytical MRD X'Pert Pro High Resolution XRD at 45 kV and 40 mA, with Cu Kα radiation. Nitrogen sorption measurements of the same materials were taken on a Micromeritics ASAP 2010 at 77 K after degassing at 200 °C for 15 h.

Reaction samples were analyzed by Agilent 7890A GC system equipped with a flame ionization detector. Separation of sulfide, sulfoxide and sulfone was achieved using an Agilent HP-5 column with dimensions of 30 m × 0.320 mm with 25 μm film thickness.

2.2. Functionalization of MCM-41

Starting with 3.5 g calcined MCM-41, the first step was to maximize the surface silanol population by refluxing in 20 mL of 6 M HCl [21]. The material was then filtered and rinsed with de-ionized water until the pH of the rinse water became neutral (4 mL × 15 mL). The material was then dried overnight at 110 °C to remove as much water as possible. In order to ensure complete removal of the water, the material was refluxed in toluene (30 mL) with a Dean-Stark trap for 4 h to azeotropically remove any remaining water. Afterwards, the Dean-Stark trap is removed, and APTES (115 μL, 0.48 mmol) was added to the toluene suspension of MCM-41 and refluxed for 24 h. The resulting material was filtered, air dried, and then protonated by suspending in dichloromethane (10 mL) with 2 equiv. of concentrated nitric acid with respect to the amount of APTES originally added (74 μL). [34] The product of this synthesis is designated MCM-41-NH_3^+.

2.3. Impregnation of MCM-41

As synthesized MCM-41 (0.6 g) was heated to 100 °C for an hour and then suspended in 10 mL of acetonitrile containing 0.12 g of [γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$ [22]. This was stirred for 24 h and then filtered and rinsed with acetonitrile to yield 0.6 g [γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$@MCM-41 (**I**). The amount of **1** affixed inside the pores of MCM-41 was estimated by the change in absorbance at about 270 nm of the solution from before and after impregnation implying a 6% loading.

2.4. Impregnation MCM-41-NH_3^+

The [γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$ catalyst was heterogenized onto MCM-41-NH_3^+ based on modified procedures from literature [34]. Briefly the catalyst was affixed through ion-exchange by stirring 3.0 g of MCM-41-NH_3^+ in a 20 mL acetonitrile containing 0.6 g **1** for 24 h. At the end of this time, the [γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$@MCM-41-NH_4^+ (**II**) was filtered off, and rinsed with acetonitrile: recovered 3.1 g. The amount of **1** affixed inside the pores of MCM-41-NH_3^+ was estimated in the same fashion as **I**, and corresponds to an 8% loading.

2.5. Oxygenation reactions

Oxygenation reactions of organic sulfides were carried out similarly to similar homogeneous reactions described in literature [12]. The heterogeneous catalyst **II** was used in quantities that were calculated to give approximately 1 mol% loading of **1** with respect to 0.5 mmol organic sulfide substrate. All reactions were carried out in duplicate.

Specific reaction conditions were: 0.20 g catalyst **I** or **II**, 0.50 mmol organic sulfide substrate, and 0.40 mmol 1,2-dichlorobenzene for internal standard. The reactions were run in 5 mL of acetonitrile at room temperature, and the heterogeneous catalyst was kept in suspension with vigorous stirring. Each reaction was initiated by the rapid addition of 2.0 equiv. of hydrogen peroxide. Samples were taken by removing 20 μL of the reaction mixture, followed by diluting to 60 μL with acetonitrile, shaking and centrifuging. After centrifugation, the samples were decanted into fresh centrifuge tubes to keep the sulfoxide/sulfone species from adsorbing to the silica.

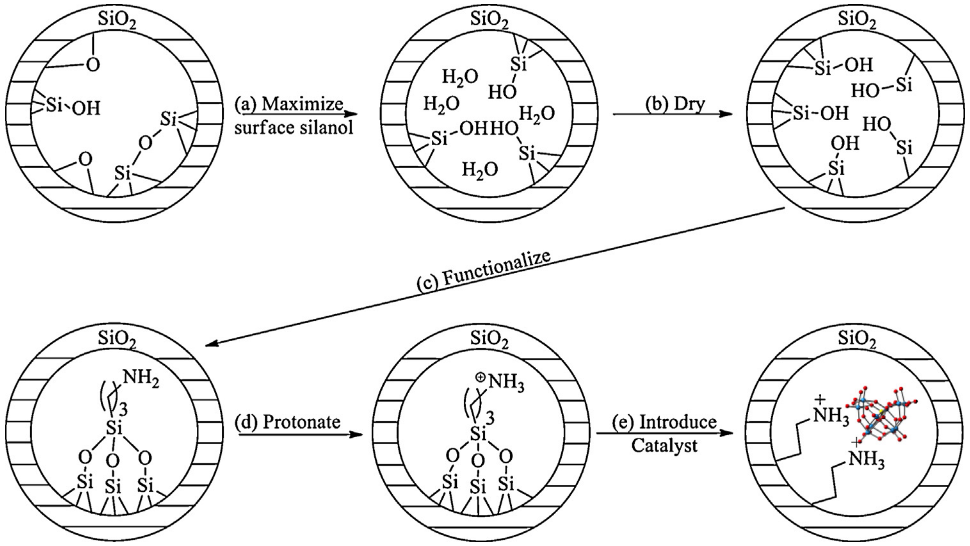
Six recycling reactions were completed with both catalysts **I** and **II**. These reactions used methyl phenyl sulfide for the model substrate. The recycling procedure involved filtering off the heterogeneous catalyst from the MeCN solutions of both the parallel reactions, and then after rinsing and drying, separating the material into halves for the next parallel reaction [35].

Finally a few other substrates: methyl *p*-tolyl sulfide, phenyl sulfide, benzothiophene, and dibenzothiophene were used to test the versatility of catalyst **II**. The reactions of the last three substrates were completed at 40 °C to accelerate the otherwise slow reactions.

3. Results and discussion

3.1. Synthesis of catalyst [γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$@MCM-41 (I)

The catalyst [γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$ was immobilized upon MCM-41 by suspending MCM-41 in a acetonitrile solution of catalyst **1** for 24 h followed by filtration and rinsing with MeCN. The catalyst loading was estimated by monitoring the change in absorbance at 270 nm in the acetonitrile solution after uptake, and the decrease in absorbance (32%) corresponds to an estimated loading of 6% (0.019 mmol/g).



Scheme 1. Functionalization and impregnation of MCM-41 silica. Conditions: (a) 6 M HCl reflux; (b) dried in oven at 100 C and refluxed in tolune with attached Dean-Stark trap; (c) reflux in toluene with APTES; (d) suspend in DCM with 2 equiv. HNO_3; (e) suspend in acetonitrile solution of **1**.

3.2. Synthesis of catalyst $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$@MCM-41-$NH_4^+$ (*II*)

The catalyst **II** was prepared by first functionalizing the MCM-41 with aminopropyl triethoxy silane (APTES) in toluene reflux as shown in Scheme 1. The functionalized product was then protonated with nitric acid in dichloromethane. Catalyst **1** was introduced into the pores of the functionalized MCM-41 and the loading was estimated in the same manner as that for **I** [30]. The absorbance of the impregnation solution showed a 40% decrease in absorbance, which corresponds to an approximate 8% uptake (0.025 mmol/g).

3.3. Characterizations of catalysts *I* and *II*

Both catalysts **I** and **II**, as well as pristine MCM-41 were characterized with nitrogen sorption (Fig. 2a) and powder X-ray diffraction (XRD) (Fig. 2b). From the nitrogen sorption, the BET surface area of MCM-41, **I**, and **II** were 962 m^2/g, 540 m^2/g, and 418 m^2/g, and the pore volumes were 0.85 cm^3/g, 0.46 cm^3/g and 0.50 cm^3/g, respectively, indicating the decreases in surface area and pore volume upon the loading of catalysts (Table 1). The pore diameters of MCM-41 and **I** are ca. 27 Å, but is reduced to 22 Å for **II**. The nitrogen sorption isotherms of **I** and MCM-41 are quite similar in shape, indicating that physical loading of catalyst induced minimal change of the mesoporous structure. On the other hand, the nitrogen sorption isotherm of **II** is significantly different from that of MCM-41 or **I**, especially in the deviation of the shape of the hysteresis loop from the typical H_1-type in MCM-41 and **I**. These changes imply a partial loss of structural integrity and an overall pore shrinking, likely occurred during the functionalization process. This supposition is confirmed by the powder XRD study. Compared with the diffraction pattern of MCM-41, the characteristic (1 0 0) peak around 2θ of 2.1° is diminished in intensity and severely broadened for catalyst **II**, and the (1 1 0) and (2 0 0) peaks at 3.6° and 4.3° disappeared, evident of the deterioration of the mesoporous ordering. In contrast, the diffraction pattern of catalyst **I** is almost identical to that of MCM-41.

3.4. Sulfide oxygenation reactions with catalyst *I*

In order to test the physisorbed catalyst, **I** was subjected to repeated catalytic cycles of the conversion of methyl phenyl sulfide

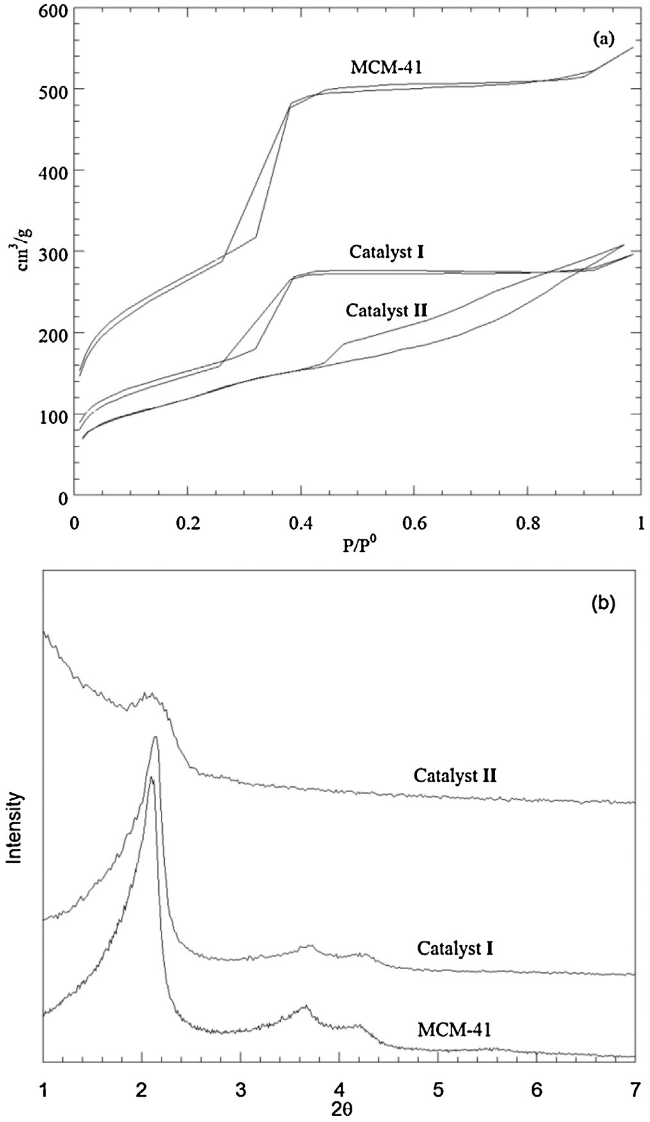


Fig. 2. (a) Nitrogen sorption isotherms and (b) powder XRD patterns of catalysts **I**, **II** and pristine MCM-41.

Table 1
Summary of the physicochemical properties and the loading ratio of MCM-41, catalyst **I** and **II**.

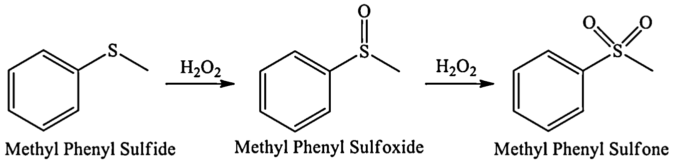
Material	Surface area (m^2/g)	Pore volume (cm^3/g)	Diameter (Å)	Loading (wt%)
MCM-41	962	0.85	27	N/A
Catalyst **I**	540	0.46	27	6
Catalyst **II**	418	0.50	22	8

Table 2
Catalytic oxygenation of methyl phenyl sulfide with **I**.[a]

Reaction number	3 h			5 h			
	% MPS	% MPSO	% $MPSO_2$	% MPS	% MPSO	% $MPSO_2$	TOF[b]
1	47	45	7	10	77	11	20
2	21	64	14	7	72	18	22
3	21	64	12	6	77	15	21
4	27	60	11	7	77	15	21
5	32	55	9	11	76	13	20
6	47	43	8	19	69	10	18

[a] Each of the duplicate catalytic reactions were completed with 0.2 g of catalyst **I** (1 mol% of the catalyst $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ with respect to 0.50 mmol MPS) in 5 mL of acetonitrile. The reaction slurry was stirred for 15 min before initiation with 2.0 equiv. of hydrogen peroxide. After the reaction was completed, the powder catalyst **I** from both reactions was collected via filtration, rinsed well with acetonitrile, and air dried. For the subsequent reactions, the material was split in half and the next recycle was repeated the same way as the first.

[b] Turn over frequency (h^{-1}) = {[RR'SO] + 2[RR'SO_2]}/{[cat] × time (h)}.



Scheme 2. Oxygenation of methyl phenyl sulfide (MPS) to methyl phenyl sulfoxide and sulfone (MPSO and $MPSO_2$).

(MPS) to methyl phenyl sulfone ($MPSO_2$) by hydrogen peroxide (Scheme 2). In general, methyl phenyl sulfide was treated with 2 equiv. of hydrogen peroxide and 1 mol% of supported catalyst, and the actual conditions and results are summarized in Table 2. At the end of each reaction cycle, catalyst was recovered by filtration and washed with copious amount of acetonitrile.

For reaction 1 (the initial cycle), productions of MPSO and $MPSO_2$ are 45% and 7% at 3 h, and 77% and 11% at 5 h, respectively. Upon the first recycling (reaction 2), the product distribution reveals an increased activity with 64% sulfoxide and 14% sulfone at 3 h, and 72% sulfoxide 18% sulfone at 5 h. Subsequent recycles (reactions 3–6) showed a slight decrease in formation of both MPSO and $MPSO_2$, which corresponds to a drop in the TOF over 5 h from 22 to 18 h^{-1}.

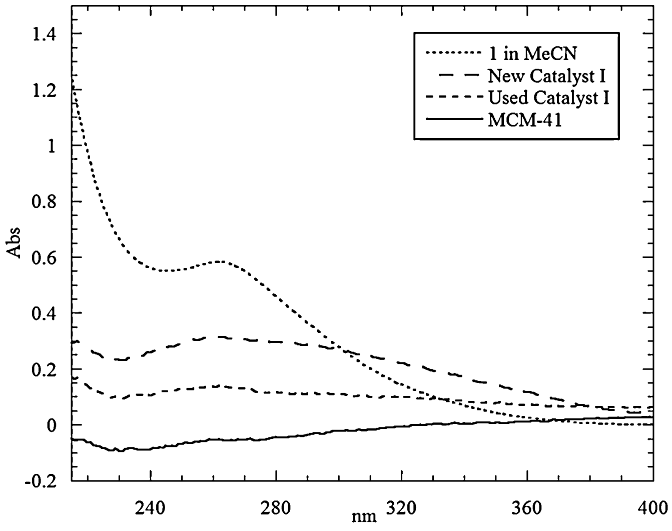


Fig. 3. Diffuse reflectance spectra of catalyst **I** before and after six reactions, along with that of pristine MCM-41 and solution spectrum of $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ in acetonitrile.

While the catalyst **I** certainly is reusable, its effectiveness began to decrease noticeably after the fourth reaction. The only exception is that the second reaction was faster than the first, which is likely attributed to the opening of the pores [21]. All subsequent reactions show apparent loss of reactivity at the sample time of 3 h. This may be due to the loss of **1** through leaching from the silica pores. The diffuse reflectance UV–vis spectra of catalyst before and after the recycles were recorded (Fig. 3), which showed a clear decrease in the absorbance at 270 nm. This lends credence to the postulation that the catalyst has been washed out of the MCM-41 support.

3.5. *Recycling reactions of **II***

To assess the efficacy of **II**, catalytic runs with **II** were performed in the same fashion as that of catalyst **I**. For reaction 1 (the initial cycle), as shown in Table 3, productions of MPSO and $MPSO_2$ are 55% and 3% at 3 h, and 78% and 9% at 5 h, respectively. Similar to **I**, a slight increase in conversion was observed between reactions 1 and 2. It is noteworthy that there is no loss of catalytic activity from the second to the last (sixth) reactions.

Overall, the TOFs at 5 h, ranging from 18 to 22 h^{-1}, reveal no sign of catalyst deactivation. The diffuse reflectance spectral measurements (Fig. 4) showed that the characteristic absorption at about 270 nm was less drastically affected than catalyst **I** over the course of the recycling reactions, further indicating a much improved retention of the POM catalyst.

3.6. *Stability of **I** versus **II***

Shown in Fig. 5a and b are the reaction profiles of four recycles for each catalyst, where the percentage reaction yield is defined as [SO]% + 2[SO_2]%, namely the oxygenation yield. For catalyst **I**, the reaction yield dropped 39% at 3 h and 23% at 5 h between the second and the sixth reactions. On the other hand, while there is some variability among the reactions, the percent yield increases 9% at 3 h and 5% at 5 h from the second to the sixth reaction.

In order to investigate the stability of the heterogeneous catalyst, it is most productive to investigate reaction progress before

Table 3
Recycling summary of **II** with methyl phenyl sulfide for model substrate.[a]

Reaction number	3 h			5 h			
	% MPS	% MPSO	% $MPSO_2$	% MPS	% MPSO	% $MPSO_2$	TOF[b]
1	40	55	3	9	78	9	19
2	39	55	5	5	78	13	21
3	36	56	7	8	77	12	20
4	58	39	0	11	77	7	18
5	32	59	2	5	77	14	21
6	27	62	6	4	81	14	22

[a] All entries are averages of two reactions. Reactions were completed in an analogous fashion as those described in Table 2.
[b] Turn over frequency (h^{-1}) = {[RR'SO] + 2[RR'SO_2]}/{[cat] × time (h)}.

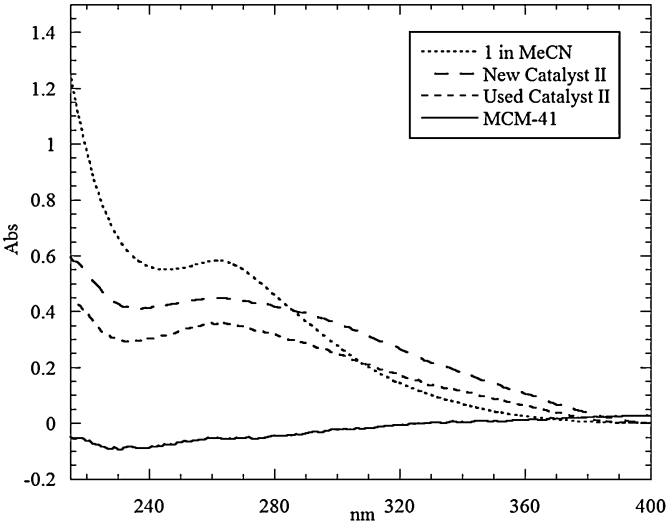


Fig. 4. Diffuse reflectance of catalyst **II** before and after six reactions.

completion of the reaction [16]. Since the S → SO reaction is significantly faster than the SO → SO_2 reaction, earlier times are dominated by the S → SO reaction, after which the reaction is dominated by the much slower SO → SO_2. Thus, any deactivation of the heterogeneous catalyst will be more obvious at an earlier time. As shown in Fig. 5, comparing the recyclability of **I** to **II**, the deactivation of Catalyst **I** is most noticeable at 3 h. At this time the TOF for catalyst **I** decreases from 31 to 20 h^{-1} while the for catalyst **II** actually the TOF increases slightly from 22 to 25 h^{-1}.

The decrease in activity for **I** is likely caused by the loss of catalyst back into acetonitrile solution, while the slight increase in activity for **II** is possibly due to the reduction of pore blockage during the course of catalytic runs [21]. This demonstrates that the additional effort to functionalize the MCM-41 silica is likely to be worthwhile.

3.7. *Catalytic oxygenation of other substrates*

The reactivity of catalyst **II** was examined with several other substrates shown in Scheme 3 under conditions similar to those of MPS. These substrates were chosen for their diverse electronic and steric characteristics. For methyl p-tolyl sulfide (MpTS), the *para*-methyl substituent enhances the electron richness of the sulfur center. The other substrates are models of refractory sulfides, and their oxygenation is relevant to sulfur removal from petroleum via oxidative desulfurization (ODS) [4].

The oxygenation of MpTS was performed at room temperature and the reaction was terminated at 4 h. The oxygenation reactions of the model refractory sulfides were carried out at a mildly elevated temperature (40 °C) and terminated at 24 h. As shown in Fig. 6, the smaller sulfides, MpTS and BT, were converted to the corresponding sulfones exclusively. Among the larger substrates, the reaction of PPS yielded 58% sulfoxide and 40% sulfone, while the reaction of DBT produced 90% sulfone with 9% unreacted DBT. The outcome of these reactions highlights the potential utility of **II** in the removal of refractory sulfides via ODS.

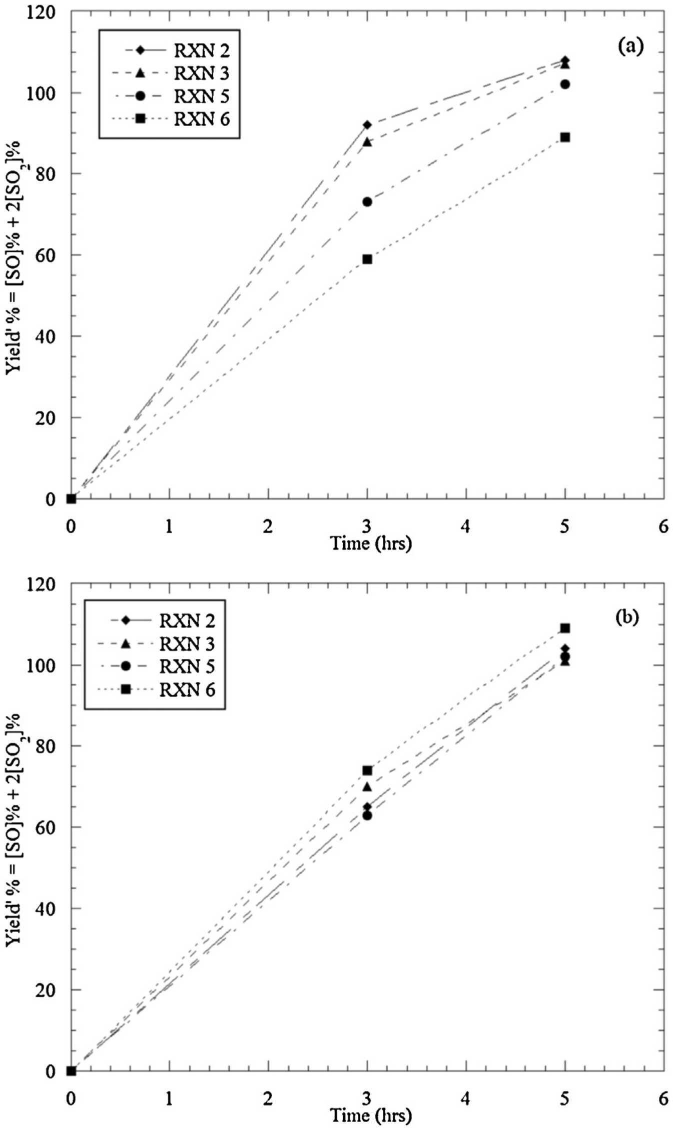
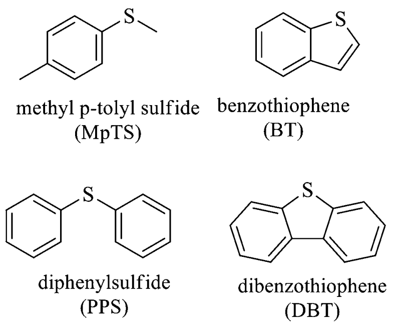


Fig. 5. Comparison of recyclability of **I** and **II** Selected reactions of **I** (a) and **II** (b).

3.8. *Effect on selectivity*

In the corresponding homogeneous reactions, catalyst **1** was reported to convert sulfide to sulfoxide entirely before the



Scheme 3. The four additional substrates.

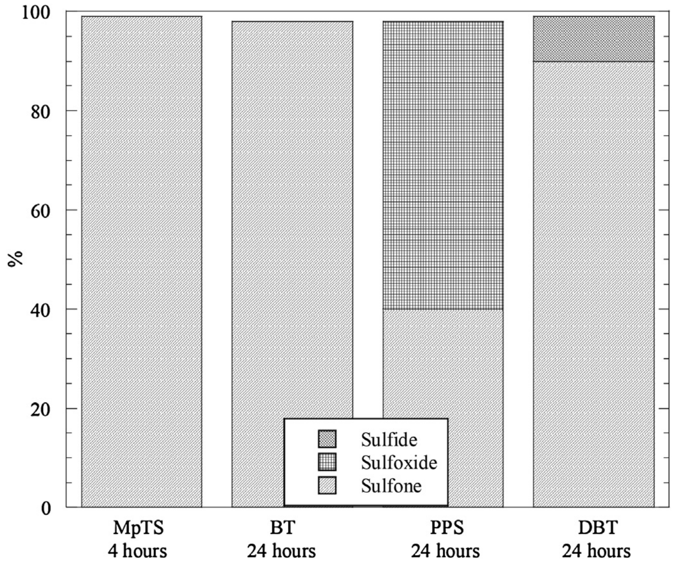


Fig. 6. Oxygenation of other substrates: Reactions were completed with 0.2 g **II** suspended in 5 mL of acetonitrile, followed after 15 min by the addition of 0.5 mmol sulfide and initiated by the addition of 2.0 equiv. of H_2O_2. For sulfides BT, PPS, and DBT, reactions were run at 40 °C, while MpTS was completed at room temperature.

appearance of sulfone [12]. The step-wise nature of the reaction appeared diminishing in the reactions based on supported catalyst. This was evident from the appearance of sulfone prior to the complete consumption of sulfide. To further investigate this phenomenon, reactions with 1.0 equiv. of H_2O_2 were performed with MPS and PPS as substrates and **II** as the catalyst. As shown in Table 4, the selectivity for sulfoxide is 90% with MPS, and 75% with PPS. This is probably explained by the reduced mass-transport efficiency in a supported catalyst, which enhances the successive oxygenation of substrate. The loss of selectivity is significantly greater for PPS since it is bulkier than MPS.

Table 4
Selectivity loss upon impregnation.[a]

Analyte	Homogeneous [12]	Heterogeneous
MPS	0	13
MPSO	100	77
$MPSO_2$	0	8
Selectivity	100%	90%[b]
PPS	1	16
PPSO	99	61
$PPSO_2$	0	20
Selectivity	100%	75%[b]

[a] Reactions completed with 1.0 equiv. H_2O_2 with respect to 0.5 mmol sulfide in 5 mL acetonitrile. Reactions were sampled at 24 h to ensure completion.

[b] Calculated by $(\%\,RSOR/\%\,RSOR + \%\,RSO_2R) \times 100\%$.

4. Conclusion

Two approaches of a heterogenized polyoxoanion catalyst **1** onto MCM-41: physisorbed and chemisorbed, have been developed. While the physisorption of catalyst into the pores of MCM-41 resulted in minimal alteration to the porous structure, ligand-grafting process led to partial loss of crystallinity in the chemisorbed catalyst. The recyclability of both physisorbed and chemisorbed catalysts were tested, and the latter is clearly advantageous in maintaining full reactivity throughout recycling. Further investigation of the chemisorbed catalyst revealed its utility for converting organic sulfides, especially refractory sulfides such as DBT, into corresponding sulfones, and the impact of mass transport limitation on the stepwise nature of sulfide oxygenation. Further investigation will be focused on improving the functionalization procedure to minimize the loss of structural integrity, increasing the rates of these reactions, and limiting the loss of selectivity.

Acknowledgements

We gratefully acknowledge the financial support from Purdue University and the Army Research Office (W911NF-06-1-0305). We also thank Prof. Fabio Ribeiro and Mr. Dhairya Mehta of Purdue School of Chemical Engineering for nitrogen sorption characterization.

References

[1] A. Attar, W.H. Corcoran, Ind. Eng. Chem. Prod. Res. Dev. 17 (1978) 102.
[2] M.R. Maurya, A. Arya, A. Kumar, M.L. Kuznetsov, F. Avecilla, J.C. Pessoa, Inorg. Chem. 49 (2010) 6586.
[3] F.M. Collins, A.R. Lucy, C. Sharp, J. Mol. Catal. A: Chem. 117 (1997) 397.
[4] I.V. Babich, J.A. Moulijn, Fuel 82 (2003) 607.
[5] Y.-C. Yang, Acc. Chem. Res. 32 (1998) 109.
[6] M.C. Carreno, Chem. Rev. 95 (1995) 1717.
[7] K. Sato, M. Hyodo, M. Aoki, X.Q. Zheng, R. Noyori, Tetrahedron 57 (2001) 2469.
[8] M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer-Verlag, Berlin, 1983.
[9] M.T. Pope, A. Muller, Angew. Chem. Int. Ed. 30 (1991) 34.
[10] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, Science 300 (2003) 964.
[11] N. Mizuno, K. Yamaguchi, Chem. Rec. 6 (2006) 12.
[12] T.D. Phan, M.A. Kinch, J.E. Barker, T. Ren, Tetrahedron Lett. 46 (2005) 397.
[13] K. Kamata, M. Kotani, K. Yamaguchi, S. Hikichi, N. Mizuno, Chem. Eur. J. 13 (2007) 639.
[14] M. Heitbaum, F. Glorius, I. Escher, Angew. Chem. Int. Ed. 45 (2006) 4732.
[15] D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, Chem. Rev. 102 (2002) 3615.
[16] C.W. Jones, Top. Catal. 53 (2010) 942.
[17] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[18] W.J. Roth, J.C. Vartuli, in: J. Cejka, H. van Bekkum (Eds.), Zeolites and Ordered Mesoporous Materials: Progress and Prospects, vol. 157, Elsevier, Amsterdam, 2005.
[19] C.T. Kresge, W.J. Roth, Chem. Soc. Rev. 42 (2013) 3663.
[20] H. Tuysuz, F. Schuth, Adv. Catal. 55 (2012) 127.
[21] T. Blasco, A. Corma, A. Martinez, P. Martinez-Escolano, J. Catal. 177 (1998) 306.
[22] A. Maldotti, A. Molinari, G. Varani, M. Lenarda, L. Storaro, F. Bigi, R. Maggi, A. Mazzacani, G. Sartori, J. Catal. 209 (2002) 210.
[23] I.V. Kozhevnikov, K.R. Kloetstra, A. Sinnema, H.W. Zandbergen, H. vanBekkum, J. Mol. Catal. A: Chem. 114 (1996) 287.
[24] J.A.F. Gamelas, D.V. Evtuguin, A.P. Esculcas, Transit. Met. Chem. 32 (2007) 1061.
[25] S.S. Wu, P. Liu, Y. Leng, J. Wang, Catal. Lett. 132 (2009) 500.
[26] D. Kumar, C.C. Landry, Micropor. Mesopor. Mater. 98 (2007) 309.
[27] R.C. Schroden, C.F. Blanford, B.J. Melde, B.J.S. Johnson, A. Stein, Chem. Mater. 13 (2001) 1074.
[28] V.N. Panchenko, I. Borbath, M.N. Timofeeva, S. Gobolos, J. Mol. Catal. A: Chem. 319 (2010) 119.
[29] A. Tarlani, M. Abedini, A. Nemati, M. Khabaz, M.M. Amini, J. Colloid Interface Sci. 303 (2006) 32.
[30] W. Kaleta, K. Nowinska, Chem. Commun. (2001) 535.
[31] A. Bordoloi, E. Lefebvre, S.B. Halligudi, J. Catal. 247 (2007) 166.
[32] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, J. Am. Chem. Soc. 114 (1992) 10834.
[33] Q.S. Huo, D.I. Margolese, G.D. Stucky, Chem. Mater. 8 (1996) 1147.
[34] B. Karimi, M. Ghoreishi-Nezhad, J.H. Clark, Org. Lett. 7 (2005) 625.
[35] O.A. Kholdeeva, M.P. Vanina, M.N. Timofeeva, R.I. Maksimovskaya, T.A. Trubitsina, M.S. Melgunov, E.B. Burgina, J. Mrowiec-Bialon, A.B. Jarzebski, C.L. Hill, J. Catal. 226 (2004) 363.