# One-step synthesis of SBA-15 containing tungsten oxide nanoclusters: a chemoselective catalyst for oxidation of sulfides to sulfoxides under ambient conditions†

**Ankur Bordoloi,[a] Ajayan Vinu[b] and S. B. Halligudi*[ab]**

*Received (in Cambridge, UK) 21st June 2007, Accepted 4th September 2007*
*First published as an Advance Article on the web 12th September 2007*
**DOI: 10.1039/b709459k**

**Tungsten oxide nanoclusters supported highly ordered mesoporous SBA-15 material has been successfully synthesized in a single step using a non-ionic surfactant as a template and used for the selective oxidation of sulfur compounds, giving excellent yields at room temperature with exceptional catalyst recyclability.**

The design and development of heterogeneous catalysts having a high surface area is one of the major objectives in a current area of research interest. There are very few reports describing the use of mesoporous silica as a support for tungsten oxide species.[1] Zhang *et al.* described the synthesis of tungsten containing MCM-41 with good dispersion, but segregated crystalline $WO_x$ was detected after mild thermal treatments.[2] Briot *et al.* attempted to avoid crystalline phases by using oxoperoxometalate precursors that form at low pH in presence of $H_2O_2$. The poor stability of these materials was evident from the extensive leaching of the tungsten species.[3] Recently an atomic layer deposition (ALD) method has been applied for grafting of tungsten oxide species onto mesoporous silica (SBA-15).[4]

Oxidation of sulfur compounds is an attractive method in organic chemistry.[5] Sulfoxide is one of the useful building blocks especially useful as chiral auxiliaries in organic synthesis[6] and plays a key role in enzyme activation.[7] Organic transformations using conventional catalysts are possible, but there are several disadvantages such as over-oxidation and toxic wastes.[8] In the present study, an alternative approach has been taken for the first time for the encapsulation of tungsten oxide species during *in-situ* synthesis of SBA-15. Polymers are effective mediators for organizing tungsten oxide species into higher order composite structures.[9] Tungsten oxide nanoclusters in SBA-15 (hereafter $WO_x$/SBA-15) with large pore diameters have been synthesized and employed as a catalyst for the oxidation of sulfur compounds under ambient reaction conditions.

Hexagonally ordered mesoporous $WO_x$/SBA-15 was synthesized by using tetraethyl orthosilicate (TEOS) as a silica source and poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer (Aldrich, *MW* avg. 5800, $EO_{20}PO_{70}EO_{20}$, P123) as a structure-directing agent. In a typical synthesis, 4.0 g of P123 block copolymer were dissolved with stirring in a solution of 30.0 g of water and the required amounts (20 mL, 10 mL, 5 mL, 2.5 mL) of aqueous sodium tungstate solution ($NaWO_4 \cdot 2H_2O$, 0.5 M) were simultaneously and quickly added into the mixture under vigorous stirring. After one hour 120.0 g of HCl (2 M), and then 9.1 g of TEOS were added with stirring at 40 °C. After being stirred for 24 h at 40 °C, the gel composition was kept at 100 °C for 48 h without stirring. After being cooled to room temperature, the solid product was recovered by filtering, washing, drying and calcining at 550 °C.[9] The samples are denoted as $WO_x$/SBA-15($x$) where $x$ denotes the volume of sodium tungstate solution.

The wide and lower angle XRD patterns of the $WO_x$/SBA-15 with different loadings of $WO_x$ are shown in Figs. 1A and 1B, respectively. All diffraction peaks in the pattern except for the sample (a) that contains the lowest amount of $WO_x$ can be indexed to monoclinic $WO_3$, and are in good agreement with those of bulk monoclinic crystal (JCPDS Card No. 83-0951). Small angle XRD measurements show that $WO_x$/SBA-15 materials exhibit three peaks at a $2\theta$ in the range 0.5–5°, which can be indexed to (100), (110), and (200) reflections of the hexagonal *p6mm* space group. The observation is in agreement with the XRD pattern of pure hexagonally ordered SBA-15 material reported by Zhao *et al.*,[9] indicating that the $WO_x$/SBA-15 materials possess a well-ordered two-dimensional mesoporous structure with a hexagonal porous network. Fig. 1B clearly displays the peaks at higher angle and the intensity of the peaks increases on increasing the loading of $WO_x$. The size of the $WO_x$ crystallites in the SBA-15 porous matrix is calculated using the Scherrer equation to be in the range 2–5 nm. HRTEM images of $WO_x$/SBA-15 (Fig. 2) show that the materials retain the hexagonally ordered porous structure even after the formation of $WO_x$ nanoclusters in the mesochannels. However, the $WO_x$ nanoclusters are not seen in the HRTEM images. This confirms that the $WO_x$ nanoclusters are not deposited on the external surface but are indeed present inside the mesochannels of SBA-15.[10] The nitrogen sorption isotherms (Fig. 1S†) of SBA-15 and $WO_x$/SBA-15 are found to be type IV isotherms and a sharp increase in the adsorbed amount of nitrogen at a relative pressure ($P/P^o$) of 0.6–0.9, features typical curves of mesoporous structures which are still maintained in $WO_x$/SBA-15 (Fig. 2S).[9]† The amount of nitrogen adsorbed is found to decrease on increasing the loading of $WO_x$ nanoclusters. Interestingly, the pore diameter of the SBA-15 materials is much larger than that of the pure SBA-15. On the other hand, the BET surface area and pore volume are lower for the $WO_x$/SBA-15 samples compared to SBA-15 (Table 1S). XPS, elemental mapping, and EDAX experiments show the composition and the high purity of the product (Figs. 2S-1, 2S-2, 3S

---

[a] *Inorganic Chemistry & Catalysis Division, National Chemical Laboratory, Pune 411 008, India. E-mail: sb.halligudi@ncl.res.in*
[b] *Nano-ionics Materials Group, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305 0044, Japan*

† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/b709459k

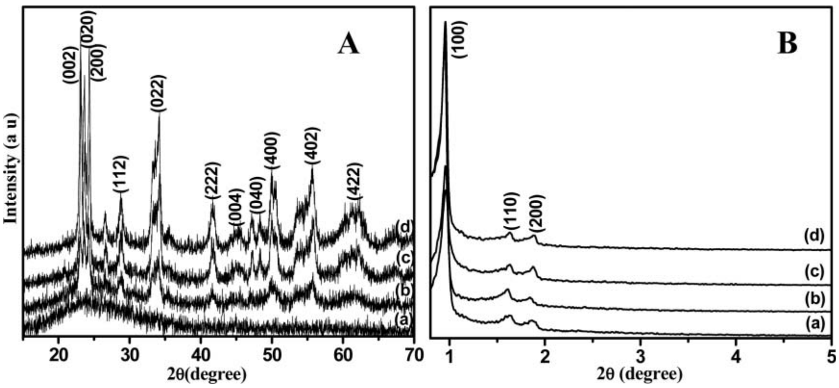


**Fig. 1** (A) Wide and (B) low angle XRD patterns of $WO_x$/SBA-15 with different concentrations of $WO_x$: (a) $WO_x$/SBA-15(2.5), (b) $WO_x$/SBA-15(5), (c) $WO_x$/SBA-15(10), and (d) $WO_x$/SBA-15(20).

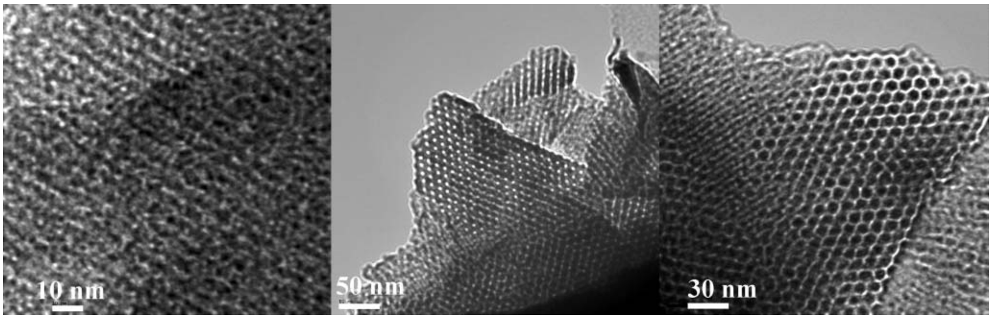
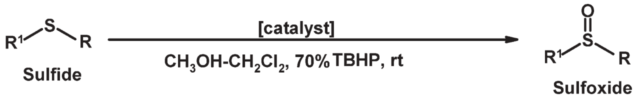


**Fig. 2** HRTEM pictures of $WO_x$/SBA-15.

and Table 2S). In FTIR spectroscopy, a typical band at 960 $cm^{-1}$ is observed along with all characteristic bands due to the siliceous content in the material (Fig. 4S).[11] A band at 960 $cm^{-1}$ has been widely assigned to the stretching Si–O vibration mode perturbed by the neighbouring transition metal ions.†

To test the catalytic activity, we selected the oxidation of methyl phenyl sulfide using 70% *tert*-butyl hydroperoxide (TBHP) as a model reaction at room temperature (Scheme 1).‡ The catalyst gave an excellent yield of the corresponding sulfoxide within 10 h (Table 1, entry 1). In the absence of the catalyst, no marked oxidation was observed under similar reaction conditions.

In a similar way, various types of structurally divergent aryl alkyl sulfides underwent smooth oxidation to selectively afford the corresponding sulfoxides in excellent yields (Table 1, entries 2–6). Another useful feature of the present protocol can be seen in the selective oxidation of allyl phenyl sulfide to the corresponding sulfoxide; neither over-oxidation to the sulfone nor epoxidation of the double bond occurred and the corresponding sulfoxide was obtained in good yields (Table 1, entry 7). Interestingly, under the described reaction conditions, even hindered diaryl sulfides furnished the corresponding sulfoxides in excellent yields (Table 1, entry 8). The compounds which have an electron-withdrawing ring substituent, such as bromo and chloro, are less reactive (Table 1, entries 9–11). It is also worth mentioning that the strongly electron-withdrawing $NO_2$ group on the phenyl ring does not much affect the synthetic efficiency (Table 1, entry 12). On the other hand, interestingly when using the protocol for the oxidation of dialkyl sulfides, the formation of the corresponding sulfoxides



**Scheme 1** Oxidation of sulfide.

**Table 1** $WO_x$/SBA-15(20) catalysed oxidation of sulfide to sulfoxide with 70% TBHP

| Entry | R | $R^1$ | Yield (%)[a,b] |
|---|---|---|---|
| 1 | Me | Ph | 99 |
| | 1st | | 97[c] |
| | 2nd | | 95[c] |
| | 3rd | | 91[c] |
| | 4th | | 90[c] |
| 2 | Et | Ph | 99 |
| 3 | *i*-Pr | Ph | 99 |
| 4 | $–CH_2–C_6H_5$ | Ph | 95 |
| 5 | $–CH_2$–*p*-Tol | $4-Me–C_6H_4$ | 99 |
| 6 | Me | $4-MeO–C_6H_4$ | 99 |
| 7 | $–CH_2–CHCH_2$ | Ph | 92[d] |
| 8 | Ph | Ph | 95 |
| 9 | Me | $2-Cl–C_6H_4$ | 68 |
| 10 | Me | $4-Cl–C_6H_4$ | 65 |
| 11 | Me | $4-Br–C_6H_4$ | 68 |
| 12 | Me | $4-NO_2–C_6H_4$ | 49 |
| 13 | Et | Et | 99 |
| 14 | $–CH_2–C_6H_5$ | $–CH_2–C_6H_5$ | 92 |

[a] Isolated yields. [b] GC conversion unless otherwise stated. [c] Recycling experiment. [d] No epoxidation product was detected. [e] Reaction conditions: substrate (2 mmol) using 70% TBHP (3 equiv.) and catalyst (0.05 g) in $CH_3OH–CH_2Cl_2$ (1 : 1) (10 mL) at room temperature.

was observed. We found that under similar reaction conditions, diethyl sulfide converted into diethyl sulfoxide in excellent yield (Table 1, entry 13). In the same way, dibenzyl sulfide furnished the corresponding sulfoxide in high yields (Table 1, entry 14). Catalyst stability and recyclability were studied using standard procedures. The results clearly show the practical reusability of the reported catalyst system.†

In conclusion, we have successfully demonstrated that highly dispersed $WO_x$ nanoclusters in the mesochannels of SBA-15 could be prepared by an *in-situ* hydrothermal method in a highly acidic medium. The catalyst exhibits high catalytic activities for oxidation of sulfur compounds due to highly dispersed tungsten oxide species being present in the SBA-15 mesochannels. The enhanced chemoselectivities at higher substrate conversions achieved over this catalyst are attributed to the unique large pore diameters and low surface acidity of $WO_x$/SBA-15, which allow the facile discharge of the desired products from the channels of the catalyst at room temperature and atmospheric pressure. In addition to this the catalyst is recyclable without much loss of activity. This strategy could be used for similar chemical transformations to use in an eco-friendly manner.

## Notes and references

‡ The liquid-phase catalytic oxidation of sulfides was conducted in a reaction vessel equipped with a magnetic stirrer at room temperature. In a typical experiment, substrate (2 mmol), 70% TBHP (3 equiv.) and catalyst (0.05 g) were reacted in $CH_3OH–CH_2Cl_2$ (1 : 1) (10 mL) at room temperature. The products were analysed and confirmed by gas chromatography, GC-MS, GC-IR, $^1H$ NMR, and authentic samples. To increase the accessibility of TBHP to the catalyst, we chose the solvent $CH_3OH–CH_2Cl_2$ (1 : 1).

1 (*a*) X.-L. Yang, W.-L. Dai, H. Chen, Y. Cao, H. Li, H. He and K. Fan, *J. Catal.*, 2005, **229**, 259; (*b*) J. Jarupatrakorn, M. P. Coles and T. D. Tilley, *Chem. Mater.*, 2005, **17**, 1818.

2 Z. Zhang, J. Suo, X. Zhang and S. Li, *Appl. Catal., A*, 1999, **179**, 11.

3 E. Briot, J.-Y. Piquemal, M. Vennat, J.-M. Bregeault, G. Chottard and J.-M. Manoli, *J. Mater. Chem.*, 2000, **10**, 953.

4 J. E. Herrera, J. H. Kwak, J. Z. Hua, Y. Wang, C. H. F. Peden, J. Macht and E. Iglesia, *J. Catal.*, 2006, **239**, 200.

5 (*a*) G. Soladie, *Synthesis*, 1981, 185; (*b*) M. C. Carreno, *Chem. Rev.*, 1995, **95**, 1917.

6 (*a*) J. Fuhrhop and G. Penzlin, *Organic Synthesis, Concepts, Methods, Starting Materials*, VCH, Weinheim, 2nd edn, 1994; (*b*) E. Block, *Reaction of Organosulfur Compounds*, Academic Press, New York, 1978.

7 (*a*) C. G. Venier, T. G. Squires, Y. Y. Chen, G. P. Hussmann, J. C. Shei and B. F. Smith, *J. Org. Chem.*, 1982, **47**, 3773; (*b*) R. W. Murray and R. Jeyaraman, *J. Org. Chem.*, 1985, **50**, 2847; (*c*) S. W. Kaldor and M. Hammond, *Tetrahedron Lett.*, 1991, **32**, 5043; (*d*) W. Adam and L. Hadjiarapoglou, *Tetrahedron Lett.*, 1992, **33**, 469; (*e*) G. W. Breton, J. D. Fields and P. J. Kropp, *Tetrahedron Lett.*, 1995, **36**, 3825.

8 (*a*) D. H. R. Barton, W. Li and J. A. Smith, *Tetrahedron Lett.*, 1998, **39**, 7055; (*b*) M. Hirano, S. Yakabe, J. H. Clark and T. Morimoto, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2693.

9 (*a*) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548; (*b*) D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024; (*c*) H. Song, R. M. Rioux, J. D. Hoefelmeyer, R. Komor, K. Niesz, M. Grass, P. Yang and G. A. Somorjai, *J. Am. Chem. Soc.*, 2006, **128**, 3027.

10 Y. J. Han, J. M. Kim and G. D. Stucky, *Chem. Mater.*, 2000, **12**, 2068.

11 (*a*) X. L. Yang, W. L. Dai, H. Chen, J. H. Xu, Y. Cao, H. X. Li and K. N. Fan, *Appl. Catal., A*, 2005, **283**, 1; (*b*) P. Ku'strowski, L. Chmielarz, R. Dziembaj, P. Cool and E. F. Vansant, *J. Phys. Chem. B*, 2005, **109**, 11552.