Metal silicates by a molecular route as catalysts for epoxidation of alkenes with *tert*-butyl hydroperoxide
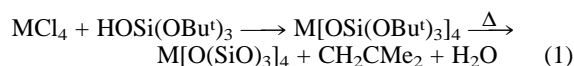
David Juwiler,[a] **Jochanan Blum**[b] **and Ronny Neumann***[a]†

[a] *Casali Institute of Applied Chemistry, Graduate School of Applied Science, The Hebrew University of Jerusalem, Jerusalem, Israel 91904*

[b] *Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel 91904*

Macroporous, site isolated metal silicates are synthesized by a molecular route; the molybdenum silicate is especially active for the selective epoxidation of alkenes with *tert*-butyl hydroperoxide.

The epoxidation of alkenes with 'redox molecular sieves' has been studied intensively during the last decade.[1] The titanium-substituted silicalite of the MFI structure, TS-1, has been the flagship of this effort. The small pored TS-1 is remarkably effective for epoxidation of small linear olefins due to the isomorphous distribution of titanium in the silicalite framework leading to isolated Ti–(OSi)$_4$ active centers held responsible for its unique activity. In the quest to develop similar catalysts viable for larger substrates, most attention has been directed towards mesoporous catalysts such as Ti–MCM-41.[2] A much less studied approach has been to use amorphous metallosilicate aerogels[3] and xerogels[4] prepared by sol–gel synthesis. The use of the sol–gel technique has limited the possibility of obtaining only M–O–Si connectivities (M = Ti, V, Mo and W) because the rate of reaction of the metal alkoxides in the sol–gel method is much faster than that of the silicon alkoxide.[5] Reduced metal site isolation considerably reduces the catalytic effectiveness of amorphous metallosilicates. Recently, a non-aqueous molecular route has been described for the preparation of metal silicates[6] [eqn. (1)] (M = Ti, Zr, Hf, Cu) which by design leads to metal site isolation within the silicate.

$$\text{MCl}_4 + \text{HOSi(OBu}^{\text{t}})_3 \longrightarrow \text{M[OSi(OBu}^{\text{t}})_3]_4 \xrightarrow{\Delta}$$
$$\text{M[O(SiO)}_3]_4 + \text{CH}_2\text{CMe}_2 + \text{H}_2\text{O} \qquad (1)$$

The molecular route procedure is based on the synthesis of an alkoxy intermediate which forms a metal silicate polymer by thermal elimination of isobutene and water rather than by hydrolysis and condensation as in the sol–gel technique. We have now utilized this technique to prepare macroporous titanium, vanadium, molybdenum and tungsten silicate. The molybdenum analog was especially active towards the selective epoxidation of bulky alkenes with *tert*-butyl hydroperoxide (TBHP).

The metal silicates described in this paper were prepared by adapting the method reported for the titanium silicate.[7] Thus, 40 mmol tri-*tert*-butoxysilanol[7,8] in 100 ml toluene was reacted with 10 mmol of metal chloride, TiCl$_4$, V(O)Cl$_3$, Mo(O)Cl$_4$ and W(O)Cl$_4$, respectively, in the presence of 40 mmol Et$_3$N at room temperature for 2 h. The precipitates were filtered and then calcined for 12 h at ~250 °C to yield TiO$_2$–4SiO$_2$, VO$_{2.5}$–3SiO$_2$, MoO$_3$–4SiO$_2$ and WO$_3$–4SiO$_2$, respectively. The calcination temperature was chosen after thermogravimetric measurements showed clean peaks for isobutene and water elimination at this temperature.‡ N$_2$—physisorption measurements using the BET method showed that the metal silicates were macroporous with large pore sizes of 130 ± 20 Å and relatively low surface areas of 25 ± 5 m^2 g^{-1}. The IR spectra showed the expected peak[9] at 950–960 cm^{-1} attributable to the Si–O stretching vibration polarized by the metal atom.§

The catalytic activity of the four metallosilicates was first compared using the reactive but bulky cyclooctene as the model

Table 1 Epoxidation of cyclooctene catalysed by metal silicates[a]

Metal silicate	Conversion (mol%) (Oxidant 30% H$_2$O$_2$)	Conversion (mol%) (Oxidant 6 M TBHP)
TiO$_2$–4SiO$_2$	0	5
VO$_{2.5}$–3SiO$_2$	0	40
MoO$_3$–4SiO$_2$	5	90
WO$_3$–4SiO$_2$	15	7

[a] Reaction conditions: 1.5 mmol cyclooctene, 1.5 μmol metal silicate (according to formula in table above), 0.1 ml 30% H$_2$O$_2$ + 1 ml acetone or 0.25 ml 6 M TBHP in *n*-decane, 60 °C, 12 h. Analysis was carried out by GLC (HP-5890) using a dimethyl polysiloxane column (RTX-1, 30 m, 0.32 mm id, 0.25 μm coating).

substrate (Table 1). Using 30% hydrogen peroxide as oxidant, reactivity was very low and the metal silicate was dissolved into the homogeneous phase, presumably by aqueous hydrolysis. On the other hand, using 6 M *tert*-butyl hydroperoxide in *n*-decane as oxidant, a high yield of cyclooctene oxide was observed for the molybdenum silicate, MoO$_3$–4SiO$_2$. The vanadium silicate showed intermediate activity, whereas TiO$_2$–4SiO$_2$ and WO$_3$–4SiO$_2$ were only slightly active. With both oxidants there was no cyclooctene conversion without metal silicate. The stability of MoO$_3$–4SiO$_2$ was tested by filtering the reaction mixture at reaction temperature. There was no discernible loss in activity when the heterogeneous silicate was recycled in three consecutive runs. No metal leaching into the organic phase was measurable.¶

A more complete examination of the activity of MoO$_3$–4SiO$_2$ was carried out using different alkene substrates. First, the effect of the TBHP:alkene ratio was studied in the epoxidation of linear alkenes (Fig. 1). In general, doubling the amount of
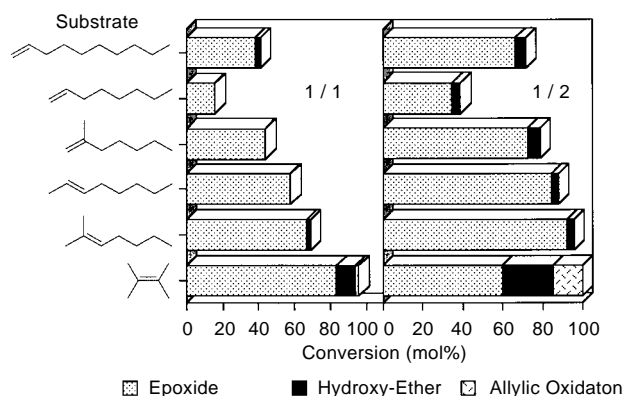

Fig. 1 Epoxidation of linear alkenes catalysed by MoO$_3$–4SiO$_2$ as a function of the oxidant : substrate ratio. Reaction conditions: 1.5 mmol substrate, 7.5 μmol (0.5 mol%) metal silicate, 1.5 mmol 6 M TBHP in *n*-decane (left panel), 3.0 mmol 6 M TBHP in *n*-decane (right panel), 50 °C, for dec-1-ene 80 °C, 12 h. Analysis was carried out by GLC (HP-5890) using a dimethyl polysiloxane column (RTX-1, 30 m, 0.32 mm id, 0.25 μm coating). Unknown products were identified by GC–MSD (HP-GCD) under similar conditions.
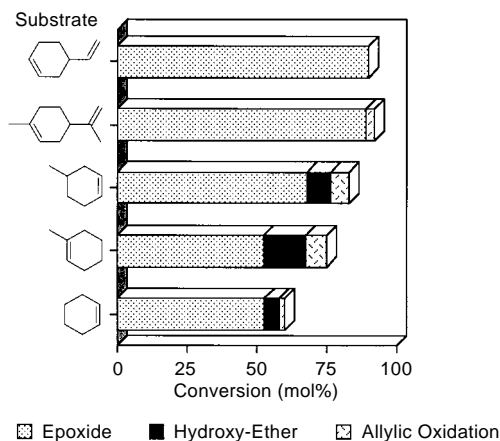
Fig. 2 Epoxidation of cyclic alkenes catalysed by MoO_3–$4SiO_2$. Reaction conditions: 1.5 mmol substrate 7.5 μmol (0.5 mol%) metal silicate, 1.5 mmol 6 M TBHP in n-decane, 50 °C, 12 h. For limonene and 4-vinylcyclo-hexene 0.15 μmol (0.1 mol%) metal silicate was used. Analysis was as described for Fig. 1.

TBHP increases the conversion and yield to epoxide, but the selectivity is somewhat lowered due to formation of α,β-hydroxy *tert*-butyl ethers by ring opening of the epoxide formed. In very reactive (nucleophilic) compounds such as 2,3-dimethylbut-2-ene excess oxidant also brought on forma-tion of allylic oxidation products. An increase in the reaction temperature was also beneficial for the epoxidation reaction. For example, in the opoxidation of dec-1-ene, the conversions under conditions given in Fig. 2 (TBHP:1-decene = 2:1) were 37, 72 and 96 mol% for 50, 80 and 110 °C, respectively, with some decrease in selectivity to epoxide from 93% (50 and 80 °C) to 85% at 110 °C. The reactivity of bulkier cyclic alkenes has also been investigated (Fig. 2). In contrast to the microporous TS-1, there was no sieving effect and all substrates tested were reactive. For the monofunctional cyclic alkenes moderate selectivity was observed with some epoxide ring opening to the α,β-hydroxy *tert*-butyl ethers and the formation of a mixture of allylic oxidation products. 4-Vinylcyclohexene reacted quite selectively to form epoxide at the ring double bond (10:1 ratio). In addition, a small amount of diepoxide was formed (ratio monoepoxides:diepoxide = 13.3). The reaction of limonene was considerably less selective. Both epoxides were formed in similar amounts. There was a considerable amount of diepoxide formed as well (ratio monoepoxides:diep-oxide = 5.5) as well as a small amount of allylic oxidation products. It is notable that the decrease in the amount of catalyst has a positive effect on reaction selectivity coupled with only a small decrease in conversion. The MoO_3–$4SiO_2$ prepared by the molecular route is a new heterogeneous catalyst for effective epoxidation of alkenes with anhydrous TBHP and compares well with 'redox molecular sieves'[1] and amorphous aerogels.[3]

Notes and References

† E-mail: ronny@vms.huji.ac.il

‡ The thermogravimetric analysis showed weight loss (sharp peaks) at 250, 260 and 270 °C for TiO_2–$4SiO_2$, WO_3–$4SiO_2$ and MoO_3–$4SiO_2$, re-spectively, which was ±2% of the loss expected upon elimination of isobutene and water according to eqn. (1).

§ IR spectra: TiO_2–$4SiO_2$ 1084, 959, 800 (sh), 461 cm^{-1}; $V_2O_{2.5}$–$3SiO_2$ 1169, 1080, 990, 804, 749, 675, 505 cm^{-1}; MoO_3–$4SiO_2$ 1092, 951, 903, 855, 588, 465 cm^{-1}; WO_3–$4SiO_2$ 1078, 961, 924, 803, 586, 465 cm^{-1}.

¶ Leaching for MoO_3–$4SiO_2$ was tested according to the method suggested by Lempers and Sheldon (ref. 10) by heating 39 mg (0.1 mmol) MoO_3–$4SiO_2$ with 20 mmol 6 M TBHP in n-decane for 24 h at 60 °C, and filtering the solution while 'hot'.

1 I. W. C. E. Arends, R. A. Sheldon, M. Wallau and U. Schuchardt, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1143.
2 A. Corma, M. T. Navarro and J. Pérez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1994, 147.
3 R. Hutter, T. Mallat, D. Dutoit and A. Baiker, *Top. Catal.*, 1996, **3**, 421; R. Hutter, T. Mallat and A. Baiker, *J. Catal.*, 1995, **153**, 165 and 177.
4 R. Neumann and M. Levin-Elad, *Appl. Catal. A*, 1995, **122**, 85; R. Neumann and M. Levin–Elad, *J. Catal.*, 1997, **166**, 206.
5 J. Livage, M. Henry and C. Sanchez, *Inorg. Solid State Chem.*, 1988, **18**, 259.
6 K. W. Terry, and T. D. Tilley, *Chem. Mater.*, 1991, **3**, 1001; K. W. Terry, C. G., Lugmair, P. K. Gantzel and T. D. Tilley, *Chem. Mater.*, 1996, **8**, 274.
7 M. G. Voronkov, A. N. Lazarev and A. K. Baigozhin, *J. Gen. Chem. (USSR)*, 1956, **26**, 3421.
8 Y. Abe and I. Kijima, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1118.
9 M. A. Camblor, A. Corma and J. Pérez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1993, 557.
10 H. E. B. Lempers and R. A. Sheldon, *Stud. Surf. Sci. Catal.*, 1996, **105**, 1061.