Engineering an atomically well defined active site for the catalytic epoxidation of alkenes

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The improvement effected by replacing one of the three O–Si≡ groups to which a Ti^{IV} ion is anchored (to a mesoporous silica support) by a O–Ge≡ group is described, as is the detailed structure retrieved by *in situ* X-ray absorption spectroscopy of the created active site.

The immediate atomic environment of a catalytically active metallic ion may be determined by X-ray absorption spectroscopy.[1–3] Using this technique we find that, in the case of Ti^{IV} ions anchored onto the walls of a high-area, crystalline mesoporous silica[4] (Ti ↑ MCM41) by condensing titanocene dichloride and pendant ≡Si–OH groups in a manner previously described,[5,6] the coordination numbers and spatially averaged bond distances for the epoxidation catalyst (see Fig. 1) are as shown in Table 1. It has hitherto been established[6,7] that this epoxidation catalyst functions in a radical-free fashion, and that it epoxidises cyclohexene with a selectivity as high as 95% and turnover numbers of *ca.* 35 h^{-1} (under the conditions used in the cited study) with alkyl hydroperoxide oxidants. This performance is a good deal superior to that of the catalyst produced by incorporation of Ti^{IV} ions into the interior of the walls during the synthesis of the MCM41 mesoporous silica from the parent gel (Ti→MCM41).[8–10]

Titanium and germanium K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy, supplemented by FTIR spectroscopy and spatially resolved elemental analysis (using scanning transmission electron microscopy), show that the exposed active sties in the Ti ↑ MCM41 catalyst (Si : Ti = 44.7 : 1) are Ti^{IV} centres tripodally attached to the support *via* three Ti–O–Si≡ linkages (Fig. 1). We have grafted Ge^{IV} centres onto the MCM41 surface using a procedure similar to that of Nédez *et al.*[11] to which the catalytically active Ti^{IV} centres have been subsequently attached. The synthesis entails exposing the dehydrated mesoporous silica (surface area = 1020 ± 10 m^2 g^{-1}) to tetrabutylgermanium at 180 °C and then, after washing, calcining and dehydrating the resulting sample, introducing the $TiCp_2Cl_2$ in an analogous fashion to the procedure used for unmodified MCM41. The resulting atomic ratios are Si : Ge : Ti = 44.9 : 0.07 : 1 and 44.7 : 0 : 1 for the germanium-modified and Ti ↑ MCM41 catalysts, respectively. Full preparative and analytical details are to be given elsewhere.[12]

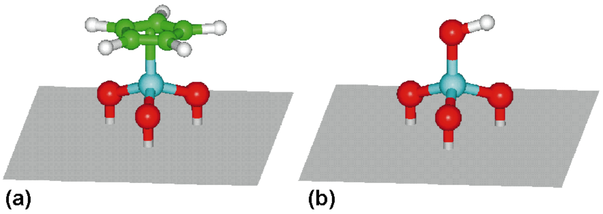

Fig. 1 Illustration of the Ti environment in Ti ↑ MCM41 before (*a*) and after (*b*) removal of the Cp moiety by calcination. (Ti = cyan, C = green, O = red, H = white). For clarity, the SiO_2 background of the mesoporous support is not shown in atomic detail.

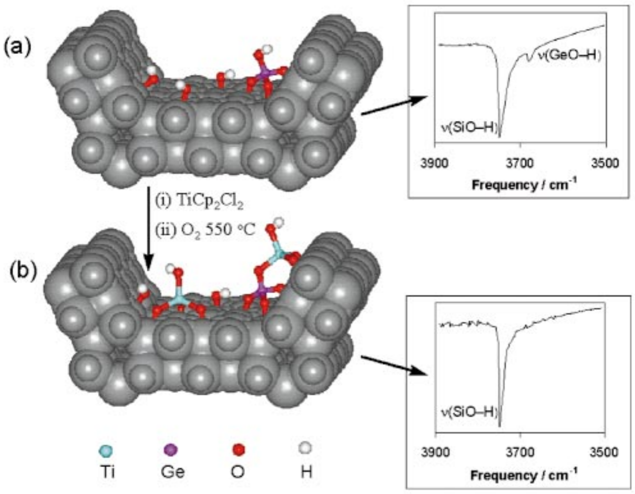

Fig. 2 Representation of the derived structures of calcined Ge ↑ MCM41 (*a*) and Ti ↑ Ge ↑ MCM41 (*b*). The insets show the respective FTIR spectra. Most of the surface silanol groups have been omitted for clarity. (Note that the ratio of the different active sites shown here are not the same as in the real catalyst, but are purely illustrative.)

Table 1 Bond distances and angles derived from analysis of Ti and Ge K-edge EXAFS data

Material	Edge	Atom type	Occupancy	Distance/Å	$2\sigma^2$/Å^2	Angle/°
Ti ↑ MCM41 (calcined)	Ti	O	4.1	1.82	0.005	Ti–O–Si(A) : 138
		Si(A)[a]	2.3	3.19	0.006	Ti–O–Si(B) : 160
		Si(B)	0.8	3.37	0.006	
Ge ↑ MCM41 (calcined)	Ge	O	3.9	1.73	0.004	Ge–O–Si : 132
		Si	2.7	3.04	0.005	
Ti ↑ Ge ↑ MCM41(calcined)	Ti	O	3.8	1.81	0.002	Ti–O–Si(A) : 139
		Si(A)[a]	1.7	3.19	0.004	Ti–O–Si(B) : 158
		Si(B)	1.1	3.34	0.004	
	Ge	O	4.1	1.72	0.004	Ge–O–Si : 136
		Ti	0.8	2.80	0.003	Ge–O–Ti : 106
		Si	3.3	3.10	0.003	

[a] Self-consistent results pertaining to coordination numbers and bond lengths are best achieved by recognising two distinct Si shells.

The resulting so-called Ti↑Ge↑MCM41 catalyst was investigated by scanning transmission electron microscopy, X-ray absorption spectroscopy and also by IR spectroscopy. The salient results are given in Table 1, from which the representation of the created active sites (Fig. 2) is derived. It is evident that titanium attaches to the germanium centres (as well as unmodified regions of the MCM41 surface) from the disappearance of the ν(GeO–H)[13] band at 3680 cm^{-1} in the IR spectrum and the appearance of a Ge···Ti shell from the Ge K-edge EXAFS spectrum.

The difference in catalytic activity between the two catalysts is quite dramatic. Although the germanium loading on the MCM41 surface is low (only *ca.* 0.15 mass%) there is a substantial improvement in catalytic activity of as much as 18%. It can be calculated that for those titanium centres that are surrounded tripodally by two O–Si≡ and one O–Ge≡ there is a 140% increase in turnover frequency with *tert*-butyl hydroperoxide (TBHP) and some 80% increase with cumene hydroperoxide (CuHP) as oxidants at 30 °C compared to titanium centres bound to three O–Si≡ moieties. Turnover frequencies towards the epoxide were 33.8 and 39.8 h^{-1} for Ti↑MCM41 and Ti↑Ge↑MCM41 respectively in the presence of TBHP, and 31.2 and 34.9 h^{-1} using CuHP. In each case the selectivity towards cyclohexene oxide was $>75\%$, the remaining products being cyclohexenol and cyclohexan-1,2-diol.

Attempts to modify the active site with Sn (using SnBu$_4$ in place of GeBu$_4$)[14] prior to anchoring the titanium were not successful since there was a strong tendency for Sn–O–Sn linkages to form, and hence crystallites of extraframework SnO$_2$, which significantly inhibited catalysis. A detailed account of this work will be submitted elsewhere.[12]

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Footnote and References

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