Novel Mesoporous Titania–Silica Aerogels Highly Active for the Selective Epoxidation of Cyclic Olefins

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Amorphous, mesoporous titania–silica aerogels with high Ti dispersion, synthesised using a sol–gel process followed by semicontinuous extraction with supercritical CO_2, are shown to be excellent catalysts for the epoxidation of bulky cyclic olefins.

The discovery of a Ti-containing silicalite TS-1 represents a major breakthrough in the field of solid-catalysed oxidation of a wide range of organic molecules under mild conditions. It has been shown that TS-1 is effective in the selective epoxidation of lower alkenes with H_2O_2 as oxidant.[1] However, the steric restriction in the microporous zeolite (pore size *ca.* 0.55 nm) prevents its application in the field of fine chemistry. There is an increasing interest in the preparation of 'large' and 'ultralarge' pore zeolites with isomorphous substitution of a part of the Si^{IV} with Ti^{IV}. The recently synthesised Ti-Beta[2,3] and especially Ti-MCM-41[4,5] have larger pore diameters (*ca.* 0.65 nm and 2–3 nm, respectively) and they are more active than TS-1 in the epoxidation of bulky olefins.

Ti- and Si-containing catalysts can also be prepared by the sol–gel technique. Despite the interactions between the two components at the atomic level, the activity of these catalysts in epoxidation reactions with H_2O_2 is considerably lower than that of TS-1.[6,7]

Here we demonstrate that highly active mesoporous epoxidation catalysts with high dispersion of Ti in the silica matrix can be prepared by appropriate selection of the sol–gel synthesis parameters. The catalysts epoxidise bulky cyclic olefins with alkylhydroperoxides under mild conditions with high rate and selectivity.

The titania–silica gels were synthesised by a sol–gel process based on an earlier report.[8] A solution of acetylacetone-modified tetraisopropoxytitanium(IV) and tetramethoxysilicon(IV) in propan-2-ol was hydrolysed with aqueous hydrochloric acid diluted in propan-2-ol. The molar ratio H_2O : alkoxide : acid was 5 : 1 : 0.09. After gelation the sample was dried by semicontinuous extraction with supercritical CO_2 at 40 °C and 240 bar. Calcination was performed in an air flow at temperatures up to 800 °C. For comparison, the corresponding xerogel containing 10 mass% TiO_2 was dried conventionally at 100 °C. The synthesis of a titania-on-silica catalyst (2 mass% TiO_2) was based on a patent to Shell.[9]

All samples were X-ray amorphous up to calcination temperatures of 800 °C. The specific surface areas (S_{BET}) and specific desorption pore volumes (V_p) were determined by nitrogen physisorption at −196 °C. For the aerogels, BET surface areas varied in the range of 410–683 $m^2\ g^{-1}$ and pore volumes in the range of 0.28–2.0 $cm^3\ g^{-1}$, both increasing with increasing TiO_2 content. The mean pore diameter ($d_p = 4\ V_p/S_{BET}$) was calculated assuming a regular cylindrical pore shape. The pore diameters of aerogels calcined at 400 °C are 8–10 nm (Fig. 1), depending on the TiO_2 content. The only exception is the 2 mass% TiO_2 aerogel (2 nm). For comparison, the xerogel exhibits only a mean pore diameter of 0.3 nm, which is considerably smaller than that of TS-1.

The FTIR spectra of titania–silica mixed oxides (Fig. 2) are characterized by a typical band at *ca.* 950 cm^{-1} assigned to framework titanium[10,11] which is usually quoted for the semiquantitative estimate of the Si–O–Ti connectivity.[12] For the evaluation of the FTIR results the bands were deconvoluted into Gaussian curves. $S_{Si–O–Ti}$ and $S_{Si–O–Si}$ are the peak areas of the ν(Si–O–Ti) band and the ν(Si–O–Si) band at *ca.* 950 and 1210 cm^{-1}, respectively. As an estimate of the relative proportions of Si–O–Ti entities in the mixed oxides, the ratios of the deconvoluted peak areas $R = (S_{Si–O–Ti}/S_{Si–O–Si})$ was used. The contribution of Si–O–Ti species expressed as R increases monotonously with increasing TiO_2 content, as illustrated in Fig. 1. The characteristic values of R for the xerogel and TS-1 are 0.57 and 0.39, respectively.

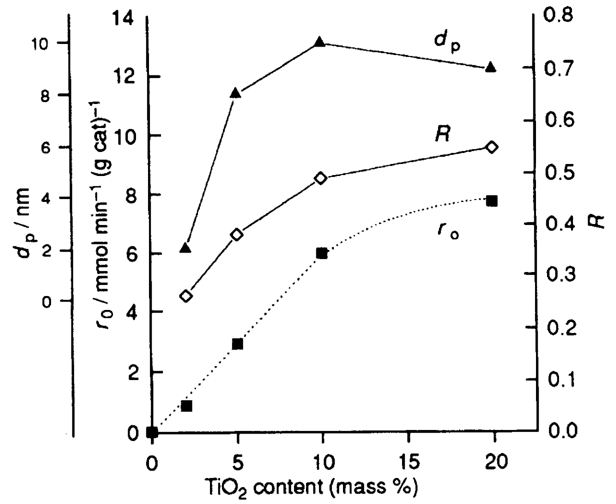

Fig. 1 Influence of TiO_2 content of aerogels (calcined at 400 °C) on: initial rate (r_0) of cyclohexene epoxidation (77 mmol) at 60 °C, mean pore diameter (d_p) and characteristic factor R representing relative proportion of Si–O–Ti connectivities (see text)

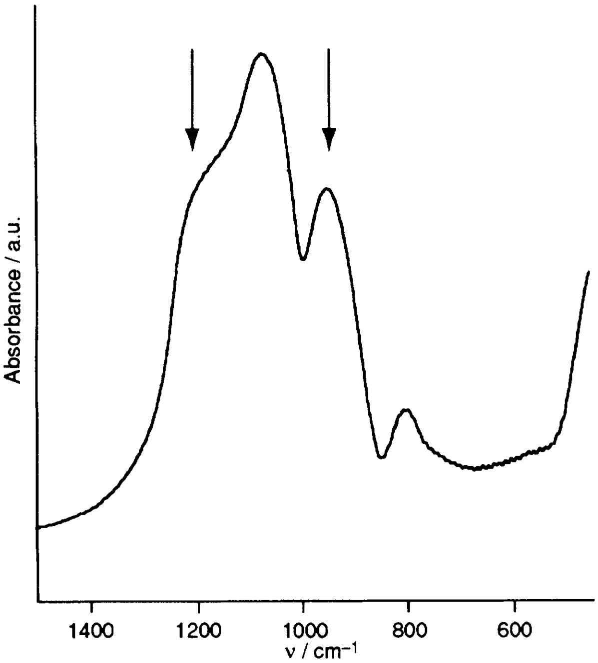

Fig. 2 FTIR spectrum of the aerogel containing 20 mass% TiO_2 (calcined at 600 °C)

The epoxidation of olefins was carried out under argon with 16.7 cm^3 (13.4 mmol) of 12 mass% cumene hydroperoxide in cumene over 100 mg catalyst. Conversion and selectivity were determined by GC analysis and iodometric titration. The initial rate was defined as the epoxide formation in 5 min (60 min for low activity).

Fig. 1 demonstrates that the activity of sol–gel titania–silica catalysts increases monotonously with increasing TiO_2 content. This curve runs parallel with that representing the relative proportions of Si–O–Ti and Si–O–Si structural units. This is an indication that the increasing activity is—at least partly—due to the increasing proportion of Si–O–Ti connectivities. Another factor is the mean pore size of the aerogel samples which is increased by using 5 mass% or more TiO_2 (Fig. 1).

Table 1 Epoxidation of olefins using 20 mass% TiO_2 aerogel[a]

Olefin	Initial rate/ mmol min^{-1} (g cat)$^{-1}$	Peroxide conversion after 1 h (%)	Selectivity[b] (%)	
			Peroxide	Olefin
Cyclohexene	17.1	100	90[c]	*ca.* 100
Cyclododecene[c]	6.7	76	89	97
Norbornene[d]	10.3	95	94	99
Limonene	9.5	100	78[e]	87[e]

[a] 60 mmol olefin, 90 °C. [b] Selectivity with respect to peroxide and olefin at 50% peroxide conversion. [c] Mixture of *cis* and *trans* isomers. [d] *exo*- and *endo*-epoxides. [e] Selectivity to 4-isopropenyl-1-methyl-1-cyclohexene-oxide.

No steric restrictions are expected in these catalysts even for reactants which are bulkier than cyclohexene or cumene hydroperoxide. Some examples on the epoxidation of cyclic olefins are shown in Table 1. 76–100% peroxide conversion was obtained in 1 h with only 1–2 mass% catalyst/olefin ratio. For comparison, Ti-MCM-41, which has been found to be more active than Ti-β and TS-1, provided only 30% peroxide conversion after 5 h in the epoxidation of cyclododecene despite the extreme catalyst/olefin ratio (> 100 mass%).[4]

A direct comparison of the activity of various Ti- and Si-containing catalysts in the epoxidation of cyclohexene is shown in Fig. 3. The titania–silica aerogel has outstanding activity and selectivity. The low activity of the conventionally dried xerogel is attributed to its microporous structure (d_p = 0.3 nm).

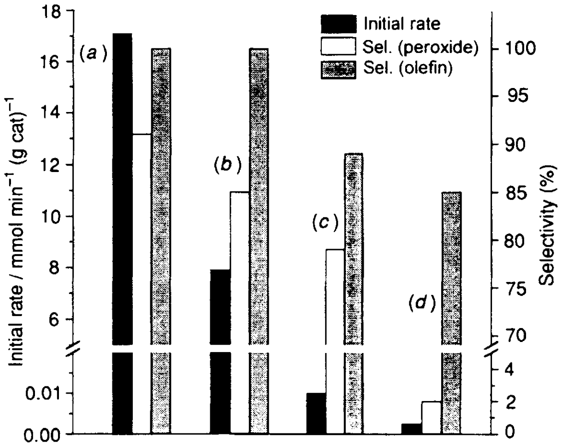

Fig. 3 Comparison of initial rates and selectivities (related to olefin and peroxide) observed for the epoxidation of cyclohexene over (*a*) the uncalcined aerogel (20 mass% TiO_2), (*b*) titania-on-silica, (*c*) TS-1 and (*d*) xerogel; (77 mmol olefin, 90 °C)

Our study demonstrates that amorphous titania–silica aerogels possessing high Ti-dispersion in the silica matrix and a mesoporous structure with 8–10 nm mean pore diameter can be prepared by the sol–gel–aerogel technique. Supercritical drying at low temperature is a prerequisite for circumventing titania agglomeration and producing aerogels highly active for epoxidation of bulky olefins.

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