

Catalytic epoxidation of alkenes with hydrogen peroxide over first mesoporous titanium-containing zeolite

Iver Schmidt,^{a,b} Anne Krogh,^{a,c} Katrine Wienberg,^{a,c} Anna Carlsson,^a Michael Brorson^a and Claus J. H. Jacobsen^{*a}

^a Haldor Topsøe Research Laboratories, Nymøllevej 55, DK-2800 Lyngby, Denmark. E-mail: chj@topsoe.dk

^b Leverhulme Centre for Innovative Catalysis, University of Liverpool, Liverpool, UK L69 3BX

^c Inter-Disciplinary Research Center for Catalysis (ICAT), Technical University of Denmark, DK-2800 Lyngby, Denmark

Received (in Cambridge, UK) 7th August 2000, Accepted 2nd October 2000

First published as an Advance Article on the web

Novel mesoporous TS-1 catalyst is shown to be active in epoxidation of oct-1-ene and significantly more active in epoxidation of cyclohexene than conventional TS-1.

Since the first report by Taramasso *et al.*¹ there have been numerous demonstrations of the outstanding catalytic properties of titanium silicalite 1 (TS-1) for selective oxidation and epoxidation of various organic compounds with aqueous hydrogen peroxide. However, TS-1 suffers from intracrystalline diffusion limitations owing to the small size of the zeolite micropores; this limitation is most pronounced for low-temperature liquid phase reactions with bulky reactants and products. This has stimulated research into zeolites with larger pores (*e.g.* BEA, UTD-1) and amorphous mesoporous titanium-containing materials. Mesoporous materials only exhibit high selectivities towards epoxides if organic peroxides are used as oxidants.² This reduces the environmental and economic advantages, since management of by-products due to reduced selectivities and decomposition of the organic oxidant becomes an important issue. Comparative studies of TS-1 and Ti-BEA have shown that different catalytic behaviour and lifetime are to be expected,³ *i.e.* the excellent catalytic properties of TS-1 might not be observed for Ti-BEA. The diffusional properties of TS-1 catalysts can be altered by preparation of nanosized TS-1 (*e.g.* by the recently developed Confined Space Synthesis method^{4,5}), but separation of the finely crystalline catalyst from the product mixture might involve costly high-speed centrifugation or flash distillation.

Recently we reported the preparation of mesoporous zeolite single crystals that compared with conventional zeolite crystals, exhibiting significantly improved diffusional properties.⁶ Typical mesoporous zeolite single crystals of $1.0 \times 0.5 \times 0.5 \text{ mm}^3$ incorporate an interconnected network built from more than 1500 primary carbon particles during growth. Contrary to nanosized TS-1, separation of mesoporous TS-1 from the product mixture can be performed by simple filtration. Here, the catalytic performance of mesoporous TS-1 in the epoxidation of linear and cyclic alkenes is compared with that of conventional TS-1.

Carbon Black Pearls 700[®] (supplied by Carbot Corp.) with an average particle diameter of 18 nm (ASTM D-3249) were impregnated to incipient wetness with a clear solution of tetrapropylammonium hydroxide, water and ethanol. After evaporation of the ethanol, the carbon particles were impregnated with 20% excess (relative to incipient wetness) of a mixture of tetraethylorthotitanate and tetraethylorthosilicate. The composition of the resulting synthesis gel was 20 TPA₂O:TiO₂:100 SiO₂:200 H₂O, and the resulting zeolite concentration *ca.* 20 wt%. After ageing for a minimum of 3 h at room temperature, the impregnated carbon black was introduced into a stainless steel autoclave containing sufficient water to produce saturated steam. The autoclave was heated slowly (0.5 °C min⁻¹) to 170 °C and maintained at this temperature for 72 h. After cooling the autoclave to room

temperature, the product was suspended in water and isolated by suction filtration. The product was washed four times as a suspension with water and then dried at 110 °C for 10 h. The carbon black was removed in a muffle furnace by controlled combustion in air at 550 °C for 8 h. In this manner a white material was obtained which according to chemical analysis was shown to contain <0.5 wt% C.

Micron-sized TS-1 with a similar titanium content, prepared according to ref. 7, was used as a reference.

XRPD showed that both samples consisted of highly crystalline MFI-structured material. Characterisation by diffuse UV-VIS reflectance spectroscopy and Raman spectroscopy verified the presence of titanium in the zeolite framework while no extra-framework anatase was detected. Chemical analysis of the two TS-1 samples gave Si/Ti ratios of 110 in both cases. Electron microscopy of the conventional TS-1 revealed a highly crystalline material consisting of twinned coffin-shaped crystals with a narrow size distribution of *ca.* 1.5 μm as shown in Fig. 1.

Transmission electron micrographs were recorded with a Philips CM200 FEG, operating at 200 kV. The sample was suspended in ethanol and dispersed on a copper grid coated with lacey carbon film.

Relatively large (*ca.* 0.3–1.2 μm) and well shaped crystals are obtained by hydrothermal crystallisation in carbon black, and a representative crystal is shown in Fig. 2. Inspection of high-resolution transmission electron micrographs revealed lattice fringes extending through the entire crystal. The significant mesoporosity was observed as bright spots, *ca.* 20 nm in diameter, dispersed throughout the entire crystal. This diameter matches that of the carbon primary particles (18 nm) which occupy these positions prior to combustion. It was shown by N₂ adsorption/desorption that the mesoporous TS-1 exhibited a

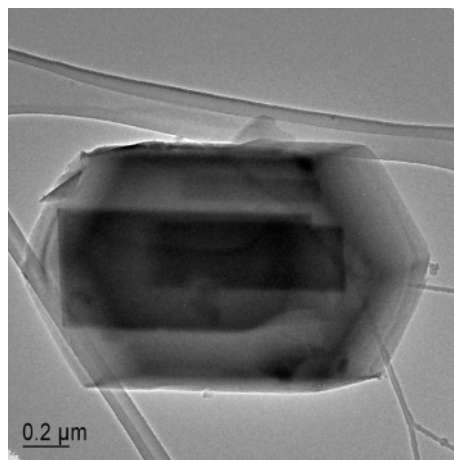


Fig. 1 Transmission electron microscopy image of a conventional TS-1 crystal.

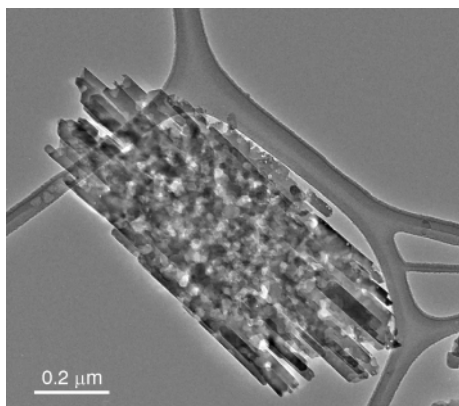


Fig. 2 Transmission electron microscopy image of mesoporous TS-1 single crystal.

porosity similar to that reported previously for ZSM-5 prepared by a similar route.⁶

The two TS-1 samples were tested as catalysts for epoxidation of oct-1-ene and cyclohexene with aqueous hydrogen peroxide using methanol as solvent and *n*-heptane as internal standard. The reaction was performed at ambient pressure in a magnetically stirred round-bottomed flask fitted with a condenser and placed in a thermostated oil bath. Alkene (4.2 ml of oct-1-ene or 2.7 ml of cyclohexene), 20.0 ml methanol, 0.75 ml *n*-heptane (internal standard) and 0.18 g of TS-1 catalyst were added to the flask and preheated to the reaction temperature (40 °C). The kinetic experiment was started when 0.50 ml 35 wt% H₂O₂ was added; samples of the reaction mixture were taken at regular intervals. The samples were cooled, the zeolite catalyst removed by filtration and analysed by GC. The initial hydrogen peroxide/olefin molar ratio was 0.25, and the H₂O₂/titanium molar ratio was *ca.* 230. The selectivities towards the corresponding epoxides were >90% in all cases. The catalytic performance of the two types of TS-1 is compared by plotting the ratio of product concentrations as a function of time. This is illustrated in Fig. 3 for the epoxidation of oct-1-ene and cyclohexene.

Similar product concentrations ($C_{\text{mesoporous}}/C_{\text{conventional}} = 1$) are obtained when the epoxidation of oct-1-ene is catalysed by mesoporous and by conventional TS-1. This suggests that the epoxidation of oct-1-ene is not limited by intra-crystalline diffusion and therefore not dependent on whether or not the crystals are mesoporous. The results also suggest that the intrinsic activity of mesoporous TS-1 is similar to conventional TS-1. In contrast, the epoxidation of cyclohexene exhibits a product concentration ratio, which exceeds a value of 10 within the contact times studied. Since the experiments with oct-1-ene suggest similar intrinsic activity of the two types of TS-1, the

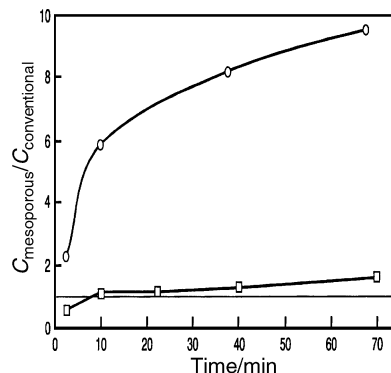


Fig. 3 Ratio of product concentrations [sum of epoxide and secondary products; (■) from oct-1-ene and (●) from cyclohexene] obtained with mesoporous and conventional TS-1 as a function of the contact time. It is seen that mesoporous TS-1 has a similar activity for oct-1-ene epoxidation as conventional TS-1. However, the mesoporous TS-1 is significantly more active for cyclohexene epoxidation.

enhanced catalytic performance of the mesoporous sample must be due to a better accessibility of the active sites. Experiments using cyclooctene have also been performed, showing a similar pattern as observed for cyclohexene. Thus, the improved catalytic activity of the mesoporous TS-1 is attributed to its improved diffusional properties compared with conventional micron-sized TS-1.

Compared with conventional TS-1, mesoporous TS-1 improves the catalytic performance without changing the product distribution, which might be an advantage compared with the alternative of using titanium-containing zeolites with larger pores. Generally, it seems possible to prepare mesoporous crystals of most zeolites with the present technique. This may lead to improved new catalysts for many different zeolite catalysed reactions. Particularly, in bifunctional catalysis it appears attractive to disperse another catalytic functionality 'inside' every individual zeolite crystal.

Notes and references

- 1 M. Taramasso, G. Perego and B. Notari, *US Pat.*, 4 410 501, 1983.
- 2 M. C. Capel-Sanchez, J. M. Campos-Martin, J. L. G. Fierro, M. P. de Frutos and A. Padilla Polo, *Chem. Commun.*, 2000, 855.
- 3 A. Carati, C. Flego, E. Previde Massara, R. Millini, L. Carluccio, W. O. Parker, Jr. and G. Bellussi, *Microporous Mesoporous Mater.*, 1999, **30**, 137.
- 4 C. Madsen and C. J. H. Jacobsen, *Chem. Commun.*, 1999, 673.
- 5 I. Schmidt, C. Madsen and C. J. H. Jacobsen, *Inorg. Chem.*, 2000, **39**, 2279.
- 6 C. J. H. Jacobsen, J. Houzvicka, I. Schmidt, C. Madsen and A. Carlsson, *J. Am. Chem. Soc.*, 2000, **122**, 7116.
- 7 A. J. H. P van der Pol and J. H. C. van Hooff, *Appl. Catal. A.*, 1992, **92**, 93.