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TS-1 zeolite microengineered reactors for 1-pentene epoxidation

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A zeolite-based microengineered reactor was fabricated and tested for 1-pentene epoxidation over titanium silicalite-1 (TS-1) catalyst, which has been selectively incorporated within the microreactor channel using a new synthesis procedure.

Smart, integrated microchemical systems are expected to bring into realization a distributed, on site and on demand production network for high value added products employing advanced green technology to ensure minimal environmental impact under safe and automated conditions. Recently, zeolites have been considered as catalysts and membranes in microchemical devices. Free-standing silicalite-1 film has been fabricated on a silicon wafer[1] and ZSM-5 zeolite has been coated onto 500 μm stainless steel channels.[2] Zeolites are important catalysts in petrochemical and fine chemicals production, as well as in environmental applications for pollution abatement.[3] Titanium silicalite-1 (TS-1) zeolite is known to be an efficient catalyst for selective oxidation of alcohols, epoxidation of alkenes and hydroxylation of aromatics[4,5] which are important reactions in fine chemicals production.

There are various methods for incorporating catalysts in microreactors such as sol–gel coatings, nanoparticle-based coatings, chemical vapour deposition, microengineered catalysts *etc*.[6–9] In this work, the zeolite microreactors were prepared through selective incorporation of TS-1 zeolites within microchannels (see also ref. 10). The microreactor channel was etched onto a silicon wafer using traditional microfabrication methods.[11] The TS-1 zeolite was grown directly within the confines of the microchannel through selective seeding. This was accomplished by functionalization of the channel with mercapto-3-propyltrimethoxysilane for better adhesion of the colloidal TS-1 zeolites. This method is fairly simple and does not require a clean room. The surfactant and TS-1 seeding solution were introduced consecutively into the microchannel using a micropipette. The wafer was then calcined in air at 873 K for 6 h to ensure good adhesion of the seed layer on the microchannel. A layer of TS-1 catalyst was grown onto the seeded channel from a hydrothermal synthesis solution containing the precursors, tetraethyl orthosilicate (TEOS, 98% Aldrich) and tetraethyl orthotitanate (TEOT, 95% Merck) and the organic templating agent, tetrapropylammonium hydroxide (TPAOH, 1 M Aldrich) to give a final composition of 40 TEOS : 1.6 TEOT : 10 TPAOH : 10 000 H_2O. The incorporated TS-1 catalyst was activated by thermal treatment in air to remove the occluded template from the zeolite pores. The microreactor was then bonded to a clean glass cover. The glass was spin coated with a thin layer of SU-8 (positive resist) which acted as glue between the two layers after UV exposure. The glass cover was pre-drilled with holes for reactant feedthrough and outlet. The reaction mixture was collected in sampling vial and analysed by gas chromatography.

Because of its fast reaction rate over TS-1 catalyst, 1-pentene epoxidation was chosen as a convenient test reaction to demonstrate the feasibility of zeolite microreactors in fine chemicals production. The reactant mixture contained 0.9 M 1-pentene (97% Fluka), 0.18 M hydrogen peroxide (30 wt.%, BDH) as the oxidiser, 0.2 M *tert*-butyl methyl ether, (MTBE, 99.8% Fluka) as the internal standard and methanol as the solvent (99.8%, Fluka). The mixture was fed to the microreactor using a syringe pump (Cole Parmer) at a rate of 30–120 μl h^{-1}, and allowed to react at 298 K. The products were collected in an ice bath for analysis with gas chromatography (HP 6890) equipped with a 30 m × 0.53 mm PoraPLOT Q column (Chrompack) and flame ionisation detector. Iodometric titration was also carried out to confirm the results.

A cross-section of a zeolite microreactor channel is shown in Fig. 1. The TS-1 zeolite deposits as a uniform film along the length of the microchannel. The zeolite crystals are well intergrown, and are oriented with their < 101 > crystallographic axis perpendicular to the silicon surface. The zeolite growth during the hydrothermal synthesis is confined within the microchannel. The film has a thickness of 6 μm and a surface roughness of < 1 μm. The isomorphous substitution of titanium during the synthesis gave a Si/Ti ratio of about 50. Grown directly onto the silicon, the zeolite film exhibits better adhesion and stability capable of withstanding high temperature (~ 850 K) treatments without cracks or delamination. Using this new synthesis procedure, the zeolite microstructure and chemistry were successfully engineered and incorporated within the architecture of a microchemical device. TS-1 catalytic layers with different titanium content (Si/Ti ratio = 10 to ∞), different orientations (*e.g.*, (101), (200/020), (002) and random), different surface roughness and intergrowth, as well as different film thickness and grain sizes have been prepared.

For the reaction study, TS-1 zeolites were grown onto 500 and 1000 μm wide microchannel reactors. The channel depth was 250 μm while the channel length was 33 mm. The zeolite catalytic layers were 3 μm thick with (101) orientation and a Si/Ti ratio of 17. Fig. 2(a) compares the performance of the 500 and 1000 μm microchannel reactors for epoxypentane production. The residence time (τ) was calculated from the volume of the microchannel and total liquid flow rate. The amount of epoxypentane formed in the absence of catalyst is negligible (Fig. 2(a)). The figure shows that the epoxypentane production displays a monotonic increase with residence time as one would

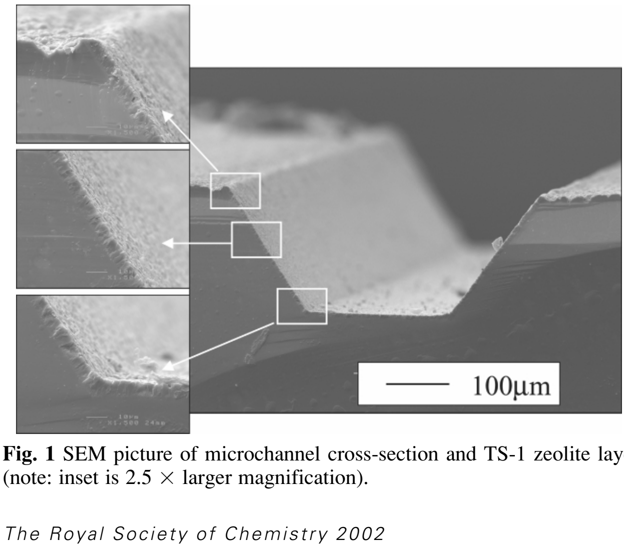

Fig. 1 SEM picture of microchannel cross-section and TS-1 zeolite layer (note: inset is 2.5 × larger magnification).

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have expected. It is also apparent that the microreactor with a 500 μm channel has higher epoxypentane yield than the 1000 μm microreactor. This is due to the fact that a narrow microchannel has a larger surface area to volume ratio and therefore affords a higher catalyst concentration (*i.e.* 47.6 g dm^{-3} for 500 μm and 27.1 g dm^{-3} for 1000 μm). One problem encountered is the deactivation of the TS-1 catalysts during reaction. After an operation period of > 100 h, it was found that the activity of TS-1 decreases by a factor of three and regeneration through air calcination was unable to recover the initial activity. This suggests that the deactivation was not due to fouling. Further study is needed in order to determine the source of this problem.

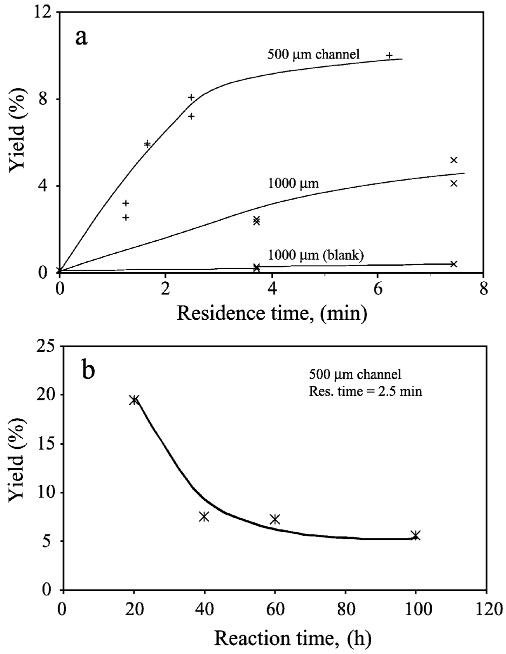

Fig. 2 1,2-Epoxypentane yield as a function of (a) residence time and (b) reaction time (1-pentene = 0.9 mol L^{-1}, H_2O_2 = 0.18 mol L^{-1}, T = 298 K).

In summary, active TS-1 catalytic layers with engineered microstructure and chemistry have been successfully incorporated within microchannel reactors and employed in 1-pentene epoxidation. The structural design of the microreactor affects the reaction performance clearly demonstrating the importance of chemical reaction engineering in microreactor design. The reactivity of 1-pentene epoxidation is enhanced by increasing the surface area to volume ratio of the microchannel.

Notes and references

1 M. J. den Exter,, H. van Bekkum, C. J . M. Rijn, F. Kapteijn, J. A. Moulijn, H. Schellevis and C. I. N. Beenakker, *Zeolites,* 1997, **19**, 13–20.

2 E. V. Rebrov, G. B. F. Seijger, H. P. A. Calis, M. H. J. M. de Croon, C. M. van den Bleek and J. C. Schouten, *Appl. Catal. A.*, 2001, **206**, 125–143.

3 I. E. Maxwell and W. H. J. Stork, *Stud. Surf. Sci. Catal.*, 1991, **58**, 571–630.

4 M. G. Clerici, G. Bellussi and U. Romano, *J. Catal.*, 1991, **129**, 159–167.

5 F. Maspero and U. Romano, *J. Catal.*, 1994, **146**, 476–482.

6 M. Fichtner, W. Benzinger, K. Haas-Santo, R. Wunsch and K. Schubert, *Proc.3rd Int. Conf. Microreaction Technol.*, 1999, pp. 90–101.

7 A. Y. Tonkovich, J. L. Zilka, M. J. LaMont, Y. Yang and R. S. Wegeng, *Chem. Eng. Sci.*, 1999, **54**, 2947–2951.

8 W. Ehrfeld, V. Hessel and H. Löwe, *Microreactors: New Technology for Modern Chemistry*, Wiley-VCH, Weinheim, 2000.

9 A. Gavriilidis, P. Angeli, E. Cao, K. Yeong and Y. S. S. Wan, *Chem. Eng. Res. Des.*, 2002, **80**, 3–30.

10 Y. S. S. Wan, J. L. H. Chau, A. Gavriilidis and K. L. Yeung, *Microporous Mesoporous Mater.*, 2001, **42**, 157–175.

11 M. Madou, *Fundamentals of Microfabrication*, CRC Press, Boca Raton, FL, 1997.