1-PENTENE EPOXIDATION IN TITANIUM SILICALITE-1
MICROCHANNEL REACTOR: EXPERIMENTS AND MODELLING

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INTRODUCTION

Advances in silicon micromachining, microfluidic architecture and microelectromechanical systems (MEMS) design contribute towards the success in miniaturization of several chemical engineering processes and the birth of a new paradigm for on-site, on-demand and on-time distributed network for chemical production. Several design and fabrication procedures for micromixers, microreactors and microseparators have been reported (Ehrfeld et al., 2000). The reactor, being the heart of chemical production process, has received a lot of attention. Miniaturization can improve mass and heat transfer by decreasing diffusion distances within the microreactor and increasing interfacial area per unit reactor volume (Gobby et al., 2001; Jensen, 2001).

Microreactors can suppress formation of hot spots and prevent reaction runaway, enabling safe operation under otherwise aggressive conditions (Srinivasan et al., 1997; Ajmera et al., 2001).

Microreactors are becoming a crucial component in lab-on-a-chip microdevices, where the combination of miniaturized reaction systems and chip-based microanalytical devices is responsible for the development of DNA-chips, bio-MEMS, smart sensors and a wide range of novel devices designed for high-throughput screening and testing of pharmaceuticals, materials, catalysts and synthesis pathways (Jakeway et al., 2000; Greenway et al., 2000; Haswell et al., 2001; Jensen, 2001; Mitchell et al., 2001). Well-defined flow characteristics, rapid transport properties, spatial and temporal control over temperature, mixing and residence time provide ideal conditions for studying reaction mechanisms and kinetics (Gavrilidis et al., 2002). These features enable microreactors to operate under conditions that cannot be easily attained in a conventional reactor system, providing much-needed kinetic information (Wörz et al., 2001).

There are a number of literature reports on zeolite incorporation in microsystems. Zeolite coatings and films can be grown on both bare and seeded silicon substrates (Chau et al., 2002). The structural characteristics and chemical properties of the deposited zeolite are dictated by the synthesis composition and conditions (Karge and Weitkamp, 1998). The growth environment has been shown to affect the zeolite’s crystal habit and film orientation (Lai et al., 2002a), which could significantly affect transport properties across the zeolite layer. Rebrov et al. (2001) deposited ZSM-5 zeolite on stainless steel microchannels and evaluated their performance in selective catalytic reduction of NO with ammonia while den Exter et al. (1997) fabricated free-standing zeolite films in silicon microchannels. Wan et al. (2001, 2003) and Lai et al. (2002b) described several strategies for incorporating zeolites in silicon and metal-based microchemical systems.

Computational modelling and simulation are important tools for the design of microreactor systems (Quiram et al., 2002). Microfluidic calculations provide valuable information on fluid flow, component mixing and mechanical friction that are important in designing the architecture of microreactors (Commenge et al., 2002). Detailed simulation and modelling studies conducted by various researchers (Hsing et al., 2000; Rebrov et al., 2002) have provided important insights to reaction behaviour in a microsystem environment.

Olefin epoxidation is a highly exothermic process (Deubel et al., 2000) and as such it can benefit from the
use of microreactor due to its good heat transfer properties. By confining hazardous chemicals within small units, the risk of dealing with strong oxidizing agents like hydrogen peroxide can be minimized. 1-Pentene epoxidation with hydrogen peroxide in titanium silicalite-1 (TS-1) is chosen as the model reaction because in addition to the above safety concerns, it has the fastest reaction rate among TS-1-catalysed epoxidations (Clerici and Ingallina, 1993). A simple reactor model for predicting the behaviour of a TS-1 coated microreactor is presented. The kinetic data for the model are obtained from separate batch experiments, while transport data are taken from literature. The influence of reactor geometry, catalyst properties and reaction conditions are evaluated and the results are compared with experimental data.

EXPERIMENTAL
Fabrication of Catalytic TS-1 Microreactor

Microreactors were fabricated onto Si(100) wafer using standard lithography and etching procedures (Madou, 1997). Anisotropic etching with KOH (30 wt%, 80 °C) results in a trapezoidal channel cross-section (Figure 1). The crystal orientation of the channel walls is (111), while the silicon at the channel floor has (100) orientation. Catalyst incorporation is an important issue in catalytic microreactors. For metal and metal oxide catalysts, a thin layer of active material can be deposited using thermal deposition, chemical vapour deposition or sputter coating (Thomas and Thomas, 1997). Alternatively, a porous oxide layer can be formed by anodization and impregnated with a metal precursor solution to give the desired catalyst (Wießmeier and Hönicke, 1996). However, incorporation of zeolite catalysts requires a different strategy. Zeolites are usually prepared by hydrothermal crystallization from a synthesis solution containing metal precursors and growth-directing reagent.

A selective seeding and regrowth synthesis procedure (Wan et al., 2001) was used for the localized incorporation of TS-1 zeolite in the microreactor. The titanium silicalite-1 seeds (100 nm) were prepared from a synthesis solution with mole ratios of 20 tetraethyl orthosilicate (TEOS):0.75 tetraethyl orthotitanate (TEOT):9 tetrapropylammonium hydroxide (TPAOH):404 H2O. The synthesis was conducted in a 125 ml Teflon autoclave (Parr Scientific Inc.) at an oven temperature of 398 K for 8 h. The colloidal zeolites were recovered and purified using a series of centrifugation and rinsing steps. X-ray diffraction (XRD, Philips PW 1030) analysis showed that the colloidal zeolite seeds were crystalline and had an MFI-type structure, while chemical analyses using energy dispersive X-ray spectroscopy (EDXS, Oxford Instruments), X-ray photoelectron spectroscopy (XPS, Physical Electronics) and Raman microscopy (Renishaw RM 3000) indicated that the colloidal TS-1 had a spatially uniform Si/Ti content of 20, with most of the titanium being incorporated within the zeolite framework. The seeds had a BET surface area of 425 m² g⁻¹, as measured by N2 physisorption (Coulter, SA3100) after removing the organic template by calcination.

In order to confine the zeolite growth only within the microchannel, the etched silicon channel was first functionalized with mercapto-3-propyltrimethoxysilane to provide a better adhesion of colloidal zeolite. The channel was then seeded with colloidal zeolite seeds to locally promote the growth of the zeolite layer. The seeding was repeated more than once to obtain a uniform seed coverage. The seeded sample was calcined in air at 823 K for 6 h. A S-1 zeolite film was grown from a synthesis solution containing 40 TEOS:0–1.6 TEOH:0–0.4 triethoxymethylsilane (TEMS):10–14 TPAOH:10,000 H2O under hydrothermal conditions at 448 K for 12–24 h. The growth inhibitor, TEMS was added to better control the zeolite crystal size. Zeolite coatings were characterized by scanning electron microscopy (SEM, JEOL JSM 6300), XPS and EDX after the reaction experiment in order to determine their microstructure and composition. The final microreactor was obtained by bonding the micromachined silicon wafer to a clean glass cover that contained pre-drilled inlet holes. A thin layer of SU-8 photosresist was spun-coated onto the glass cover and placed on top of the wafer. The drilled holes on the glass cover were aligned over the fluid ports. A leak-free sealing between silicon and glass was formed after exposure to UV-light. The sealing was able to withstand hydrocarbons (i.e. methanol, MTBE and 1-pentene) and reaction temperatures up to 373 K. Table 1 summarizes the range of values for reactor geometry and zeolite coating properties investigated in this work.

1-Pentene Epoxidation Reaction
Titanium silicalite-1 is known to catalyse a variety of partial oxidation reactions including the conversion of alcohols to aldehydes, alkanes to secondary alcohols and

![Figure 1. Mole of hydrogen peroxide and 1,2-epoxypentane in the batch reactor as a function of reaction time during TS-1 epoxidation.](image-url)
ketones, phenol to hydroquinone and catechol, and amines to hydroxylamines (Clerici, 1993; Clerici, et al., 1993; Maspero and Romano, 1994; Hutchings et al., 1995; Adam et al., 1997; Sheldon et al., 1998). The TS-1 catalysed reaction between 1-pentene and hydrogen peroxide gives 1,2-epoxypentane as the main product with glycols and glycol monoethylethers as byproducts.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}_2
\rightarrow \text{CH}_3\text{CH} (=\text{CH})\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}
\]

**Batch reactor**

The reaction kinetics was determined using a batch reactor. The catalysts were TS-1 zeolite grown onto seeded silicon wafer prepared following the synthesis procedure described previously. The 5 μm-thick TS-1 film contained 2.5 at% titanium and consisted of intergrown 2 μm zeolite crystals. The wafer was crushed into 5 μm powder and added to the reaction mixture containing 3 g of 1-pentene and 1 ml of hydrogen peroxide dissolved in 50 ml of methanol. This gives an initial 1-pentene and hydrogen peroxide concentration of 1.49 and 0.33 M, respectively. One gram of methyl tert-butyl ether (MTBE) was added as internal standard. The reaction was conducted under well-mixed and iso thermal conditions using a mechanical stirrer and a constant temperature water bath (298 K). Samples were taken using a syringe at fixed time intervals for analysis. One millilitre of sample was used for iodometric titration to determine hydrogen peroxide concentration and the rest was analysed by gas chromatography (HP 6890) to obtain the concentration of the hydrocarbons in the sample. The gas chromatograph was equipped with a 30 m PoraPLOT Q column (Chrompack) and flame ionization detector.

**TS-1 Coated Microreactor**

A mixture containing 0.9 M 1-pentene and 0.18 M hydrogen peroxide reactants, MTBE internal standard and methanol solvent was fed to the microreactor using a syringe pump (KDSScientific). The reactor was immersed in a water bath thermostated at 298 K to maintain a constant reaction temperature. Samples were collected from the reactor outlet using a vial cooled by an acetone ice bath. Three samples were obtained each time for analysis by gas chromatography.

**Materials**

The materials and chemicals used in the fabrication of TS-1 microreactor included the Si(100) wafer (MEMC-CSMS Electronic Materials Ltd), glass cover (Corning) SU-8 photoresist (MicroChem Corp.), tetraethyl orthosilicate (98%, Aldrich Chemicals), tetraethyl orthotitanate (95%, Merck-Schuchardt), triethoxymethylsilane (99%, Aldrich Chemicals) and tetrapropylammonium hydroxide (1 M, Aldrich Chemicals). The 1-pentene (99%), MTBE (99.8%) and methanol (99.8%) used in the reaction were from Fluka, while the hydrogen peroxide (30%) was from BDH.

**MICROREACTOR MODEL**

A simple two-dimensional axisymmetric reactor model was employed to predict the reactant and product concentration profiles within the TS-1 coated microreactor. The model assumes isothermal, steady-state operation. Equations (1) and (2) are the hydrogen peroxide mass balance equations for the bulk fluid in the channel and across the catalyst layer, respectively.

\[
\frac{U}{r} \frac{\partial C}{\partial y} = \frac{1}{x} \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right)
\]

(1)

\[
\frac{1}{x} \frac{\partial}{\partial x} \left( D_{\text{eff}} \frac{\partial C}{\partial x} \right) + r \rho S_a = 0
\]

(2)

The total external surface area of the zeolite crystals in the coating, \( S_a \) was calculated based on the measured external surface area of 0.1 μm zeolite crystals (60 m² g⁻¹) and accounting for the effect of crystal size. The reaction was assumed to take place only at the external surface of the zeolite crystals according to a second order reaction rate law

\[
r = -k_2[\text{H}_2\text{O}_2][\text{C}_{18/C19}]
\]

(3)

The inter-particle diffusion coefficient, \( D_{\text{eff}} \) was calculated based on the bulk diffusivity of water in methanol \( 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) (Welty et al., 1984) a film porosity of 0.4 and tortuosity of 10 (Fogler, 1992). The fluid enters the microreactor from channels of similar width. It has uniform concentration and fully developed flow where the velocity profile is invariant along the flow axis. The parabolic flow is described by the Hagen–Poiseuille equation

\[
U_r = 2U_m (1 - x^2)
\]

(4)

In the model, the experimental trapezoidal channel was approximated by a cylindrical channel having the same surface to volume ratio. It was also assumed that the fluid is incompressible and that its properties remain unchanged during the reaction. The mass balances were integrated along the reactor to calculate the hydrogen peroxide concentration profiles using Femlab™. For the computation, the microchannel was partitioned into finite element cells using an adaptive mesh. The mesh is denser at the proximity of the catalyst layer where the reaction takes place in order to ensure a more accurate calculation of the concentration profiles.

**RESULTS AND DISCUSSION**

**Batch Reactor**

Reaction kinetics and the corresponding rate constant were calculated from the reaction data obtained from the batch reactor experiment using TS-1 zeolite grown on silicon wafer as catalyst. Based on experimental results that demonstrated that reaction rate increases with decreasing crystal size, it was assumed that intra-particle diffusion resistance is large and most of the reaction occurs at the external surface of the zeolite crystal. Therefore the reaction rate is expressed per external surface area of the zeolite crystals. Figure 1 shows the amounts of hydrogen peroxide consumed and 1,2-epoxypentane produced in the batch reactor as a function of reaction time. More than 90% 1,2-epoxypentane selectivity was calculated based on the ratio (epoxypentane produced)/(hydrogen peroxide consumed).
Shea and Kim (1992) and Arasasingham et al. (1993) have indicated that the oxidation of alkene to epoxide is a second-order reaction. Hence, the experimental data were fitted to a second-order reaction rate law [equation (3)] and a rate constant of $7.643 \times 10^{-12} \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1}$ was calculated.

**TS-1 Microreactor**

Figure 2 displays a typical cross-section of the zeolite-coated microchannel. It can be seen from the insets that a uniform 5 μm-thick, intergrown TS-1 film was deposited on the surface of microchannel. The zeolite growth was confined *within* the microchannel leaving bare silicon surface outside the pattern, which is essential for obtaining a leak-free sealing. Several TS-1 microreactors were prepared and tested in this study (Table 2). Among the variables investigated were the channel width, Ti-content of catalyst and zeolite crystal size. Figure 3 displays SEM micrographs of TS-1 coatings in four different microreactors. By adjusting the preparation conditions and adding growth inhibitors, four morphologically similar films of different average crystal sizes (i.e. 2, 2.5, 3 and 4 μm) were obtained. All four films have the same average film thickness of 5 μm and contain 0.9–2.8 at% titanium. They also display comparable porosity, crystal morphology and film orientation.

Reaction tests conducted on bare silicon, TiO$_2$-coated (P25, Degussa), and anatase TiO$_2$-coated (Hombikat UV100, Sachtleben) microreactors showed that these materials are inactive for 1-pentene epoxidation. Five 500 μm microreactors (S1a–S1e) were prepared and coated with TS-1 zeolite film grown from standard synthesis solution and conditions (40 TEOS:1.6 TEOT:0.4 TEMS:14 TPAOH:10,000 H$_2$O, $T = 448 \text{ K}, t = 24 \text{ h}$) to test reproducibility. Analyses show

<table>
<thead>
<tr>
<th>Sample</th>
<th>Channel width (μm)</th>
<th>Titanium content (at%)</th>
<th>Crystal size (μm)</th>
<th>Residence time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1a</td>
<td>500</td>
<td>2.02</td>
<td>2–2.5</td>
<td>40–240</td>
</tr>
<tr>
<td>S1b</td>
<td>500</td>
<td>2.04</td>
<td>2–2.5</td>
<td>40–240</td>
</tr>
<tr>
<td>S1c</td>
<td>500</td>
<td>1.89</td>
<td>2–2.5</td>
<td>40–240</td>
</tr>
<tr>
<td>S1d</td>
<td>500</td>
<td>1.72</td>
<td>2–2.5</td>
<td>40–240</td>
</tr>
<tr>
<td>S1e</td>
<td>500</td>
<td>2.42</td>
<td>2–2.5</td>
<td>40–240</td>
</tr>
<tr>
<td>S2</td>
<td>500</td>
<td>3.48</td>
<td>2–2.5</td>
<td>40–100</td>
</tr>
<tr>
<td>S3a</td>
<td>500</td>
<td>1.52</td>
<td>2–2.5</td>
<td>40–100</td>
</tr>
<tr>
<td>S3b</td>
<td>500</td>
<td>1.39</td>
<td>2–2.5</td>
<td>40–100</td>
</tr>
<tr>
<td>S4</td>
<td>500</td>
<td>0.88</td>
<td>2–2.5</td>
<td>40–100</td>
</tr>
<tr>
<td>S5</td>
<td>500</td>
<td>2.81</td>
<td>2</td>
<td>40–100</td>
</tr>
<tr>
<td>S6</td>
<td>500</td>
<td>2.13</td>
<td>2.5</td>
<td>40–100</td>
</tr>
<tr>
<td>S7</td>
<td>500</td>
<td>1.22</td>
<td>3</td>
<td>40–100</td>
</tr>
<tr>
<td>S8</td>
<td>500</td>
<td>0.95</td>
<td>3.5</td>
<td>40–100</td>
</tr>
<tr>
<td>S9</td>
<td>500</td>
<td>0.86</td>
<td>4</td>
<td>40–100</td>
</tr>
<tr>
<td>S10</td>
<td>500</td>
<td>0.66</td>
<td>4.5</td>
<td>40–100</td>
</tr>
<tr>
<td>S11a</td>
<td>1000</td>
<td>1.74</td>
<td>2–2.5</td>
<td>90–350</td>
</tr>
<tr>
<td>S11b</td>
<td>1000</td>
<td>1.95</td>
<td>2–2.5</td>
<td>90–350</td>
</tr>
<tr>
<td>S11c</td>
<td>1000</td>
<td>2.13</td>
<td>2–2.5</td>
<td>90–350</td>
</tr>
</tbody>
</table>

*Figure 2.* SEM pictures of microchannel cross-section and TS-1 catalyst layer (insets have 5× larger magnification).
that deposited zeolite catalysts have a titanium content of 1.7–2.4 at%. They also display similar film morphology and have an average film thickness of 5 μm and a crystal size in the range 2–2.5 μm. These microreactors were tested for 1-pentene epoxidation at a residence time (t) of 100 s. A 1,2-epoxypentane yield of 10 ± 2% was obtained. The yield was defined as the ratio of the amount of 1,2-epoxypentane produced to the initial amount of hydrogen peroxide, which is the limiting reagent. Prolonged reaction usually led to a decrease in catalyst activity but thermal treatment at 823 K for 24 h was generally sufficient to recover most of the activity. Reproducibility was further ensured, by preparing more than one sample for each test microreactor listed in Table 2, and by repeating some of the reaction experiments more than once. In general, the reproducibility of the reaction results for the same sample is better than ±5% and for different samples of the same test microreactor ±10%.

Influence of reactor geometry

Figure 4 shows modelling results of 1,2-epoxypentane yield as a function of residence time for different channel widths. The experimental data for two channel widths 500 μm (S1a–S1e) and 1000 μm (S11a–S11c) are included for comparison. There is reasonable agreement between the model prediction and experimental data, considering the various simplifications made and experimental error. The experimental yield at higher residence time was lower than predicted, and this is attributed mainly to deactivation by titanium leaching (Wan et al., 2003). The model agreement to experimental results could be improved by a more accurate reaction rate law and accounting for the catalyst deactivation effect on kinetics. The modelling results indicate that 100 μm channels would achieve higher yields.
Symbols, experimental results; lines, model results (Figure 5). Volume is higher for narrower channels, even though the actual amount of catalyst is less due to fixed thickness of zeolite catalyst layer (5 μm). However, a narrower microchannel will experience more severe pressure drop, which increases in inverse proportion to the cube of the channel width (Welty et al., 1984). Pressure drop would be a major problem for channel widths narrower than 100 μm, posing severe limitations on microreactor operation. During this study bubbles of hydrocarbon vapour were formed during the reaction, because of the relatively high volatility of 1-pentene. Problems from bubble formation can become severe at low channel diameters, since bubble dislocation would require the use of excessive pressures. Bubble formation can be suppressed by operation at higher pressure but this would require improvement of the sealing method.

Influence of catalyst characteristics

One of the advantages of the selective seeding and regrowth technique is that the microstructure and chemistry of the deposited zeolite coatings could be directly engineered within the confined environment of the microchannel. In this study, two catalyst properties, the framework titanium-content (S1–S4) and crystal size (S5–S10), were investigated. Vayssilov et al. (1997) reported that for TS-1-catalysed oxidation of anisole, catalyst activity is directly proportional to the titanium content of the catalyst. Therefore, a simple linear relationship between titanium content and kinetic constant was assumed in the computational model taking into account that TS-1 catalysts with less than ca. 1 at% titanium content are inactive for epoxidation. Figure 5 shows 1,2-epoxypentane yield as a function of titanium content at fixed residence time of 100 s. The framework titanium content was measured by X-ray photoelectron spectroscopy. The experimental data show a monotonic increase in yield with titanium content of catalyst. Furthermore, there is a good fit between the model and experimental results. Although a higher titanium-content should lead to higher yield, the maximum concentration of titanium that could be inserted reproducibly into the zeolite framework is about 3 at% (Bellussi and Rigutto, 1994). The catalyst coatings of the S5–S10 microreactors have similar thickness and surface morphology. They have titanium content of 0.6–2.8 at%, and differ in the size of zeolite crystals (cf. Figure 3). Figure 6 shows that there is good agreement between the experimental data and simulation results which assume very high intraparticle transport resistances. Small zeolite crystal size is beneficial for this reaction system and different synthesis conditions/techniques are required to reduce crystal size below 2 μm.

CONCLUDING REMARKS

This work employs a selective seeding and regrowth technique to incorporate zeolite catalysts at precise locations within the microreactor. The technique’s ability to engineer the zeolite film microstructure and chemistry can be utilized for improving the catalytic and transport properties of the incorporated catalyst layer. The deposited TS-1 films were active for catalysing 1-pentene epoxidation to produce 1,2-epoxypentane. A computational model showed reasonable agreement with experimental microreactor performance. The model and experimental results demonstrate that a channel coated with a layer of TS-1 catalyst possessing high titanium content and small crystal size results in higher product yields. Zeolite synthesis methodology and microfabrication need to be further improved in order to increase titanium content and decrease zeolite crystal size.

NOMENCLATURE

$C_1$ [H$_2$O$_2$] concentration of hydrogen peroxide, mol m$^{-3}$
$C_3$ concentration of 1-pentene, mol m$^{-3}$
$D$ depth of channel, μm
diffusivity of hydrogen peroxide in bulk fluid, m$^2$ s$^{-1}$
$D_{eff}$ effective diffusivity of hydrogen peroxide in zeolite film, m$^2$ s$^{-1}$
$k_2$ kinetic constant of second order reaction, m$^4$ mol$^{-1}$ s$^{-1}$
$k$ channel length, mm
$e$ hydrogen peroxide consumption rate per unit catalyst surface area, mol m$^{-2}$ s$^{-1}$
$S_b$ external zeolite crystal surface area per unit mass, m$^2$ g$^{-1}$
$T$ reaction temperature, K
$U_m$ mean velocity, m s$^{-1}$
$U_f$ fluid axial velocity, m s$^{-1}$
$w$ channel width, μm
$x$ dimensionless radial coordinate, m
$y$ dimensionless axial coordinate, m

Greek symbols

$\beta$ titanium content, at%$
\delta$ catalyst layer thickness, μm
$\varepsilon$ zeolite crystal size, μm

Figure 5. 1,2-Epoxypentane yield as a function of titanium-content. Symbols, experimental results; lines model results ($t = 100$ s, $w = 500$ μm).

Figure 6. 1,2-Epoxypentane yield as a function of crystal size. Symbols, experimental results; lines, model results ($t = 100$ s, $w = 500$ μm).
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