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# On-chip catalysis using a lithographically fabricated glass microreactor—the dehydration of alcohols using sulfated zirconia

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**A heated microreactor has been fabricated for heterogeneous catalysis, employing channels microfabricated in glass using photolithography and wet chemical etching; the demonstration reaction is the dehydration of alcohols.**

There remains growing interest in miniaturised systems for chemical analysis and synthesis. These chemical analysis devices are commonly referred to as micro total analytical systems (μTAS), and have been reported for a diverse range of applications. Hadd *et al.*[1] employed laser induced fluorescence detection to determine a number of acetycholinesterase inhibitors after electrophoretic separation on a glass chip. A polymeric microchip was employed for the analysis of PCR products of the hepatitis C virus,[2] again laser induced fluorescence detection was employed. Fibre optically linked spectrophotometric detection of analytes on chip provides a convenient detection method for on-chip measurements, including the determination of nitrite *via* the formation of an azo dye,[3] and orthophosphate *via* the molybdenum blue reaction.[4] The integration of microfabricated devices with mass spectrometry offers a potentially powerful analytical tool, for example in the rapid analysis of proteolytic digests.[5] While electrophoretic processes prove vital for separations on chip, electroosmotic flow offers a very convenient pumping mechanism for fluidic manipulation, such as for moving solutions through micromachined filters.[6]

However, while great interest exists in μTAS, the application of similar devices to synthetic applications is deriving much interest. One only has to look through the proceedings of recent conferences (such as IMRET 3, Frankfurt, April 1999) to see the potential applications of such devices. These include highly exothermic reactions, *e.g.* the direct fluorination of aromatic compounds, the *in situ* generation of hazardous compounds, *e.g.* phosgene, and rapid energy transfer systems, *e.g.* fuel pumps. However, one area of interest to us is on chip heterogeneous catalysis. This represents an important area in organic synthesis, and there are many potential applications for miniaturised synthetic reactors able to utilise small amounts of catalysts in conjunction with very limited reaction volumes. This latter feature permits very rapid mass transfer and control of reaction conditions. In addition, the potential to employ electroosmotic pumping with such devices represents a very attractive feature, permitting reagents to be pumped by a device with no moving parts. Within the Hull group, much extensive work is on-going in the area of microreactors employing catalyst mediation, but the work reported here is the first in a heated system. Miniaturised catalytic devices can be used to conveniently gain kinetic and thermodynamic data for reactions. They are also convenient for screening new reactions and catalysts. The screening can either be with respect to the catalyst, *i.e.* to determine which catalysts show activity, or with respect to the reaction, *i.e.* which reaction shows promise on a certain catalyst.

Here, we report the dehydration of hexanol to hexene, and ethanol to ethene (with some degree of cracking). The catalyst used was sulfated zirconia (zirconia treated with sulfuric acid). This catalyst is known as a super acid catalyst with well documented reactions including the conversion of methanol to hydrocarbons,[7] isobutane/but-1-ene alkylation,[8] and the methoxymethylation of alcohols.[9] It has also been reported for the dehydration of alcohols to the associated alkene, with the added advantage that the reaction conditions are significantly milder than those required for other acid catalysts, such as silica-alumina. In a previous paper,[10] a 1 mm diameter reactor was reported to offer conversion efficiencies of only 3% for the conversion of hexanol to hexene, however in this paper, conversion efficiencies approaching 100% are reported (compared to the industrial process that only gives *ca.* 30% conversion).

Sulfated zirconia ($ZrO_2/SO_4^{2-}$) catalyst (MEL Chemicals, Swinton, Manchester, UK) was first activated by heating to 600 °C for 1 h in a microwave furnace (CEM). The microreactor used with syringe pumping was constructed from two plates. The base plate was produced by photolithography and wet chemical etching. The mask was produced in house and used to transfer the pattern onto glass coated with chrome and photo resist layers (Alignrite, Bridgend, South Wales). After etching in 1% $HF\cdot NH_3$(aq) for 1 h at 70 °C, the remaining photo-resist and chrome was removed. The channel dimensions were 200 μm wide by 80 μm deep and 30 mm long (in a 'Z' shaped configuration). The top plate was prepared from Sylgard 184 (ISL, West Midlands, UK), a polydimethylsiloxane (PDMS) resin and cast in a mould containing inserts to form the reservoirs. After baking for 1 h at 100 °C, the resin was released from the mould and the inserts removed. The mating face was then coated with a thin layer of PDMS and activated catalyst dusted over the surface; it was then baked at 100 °C for 1 h. The effect of this step was to give a high surface area for the catalyst reactor, but with the catalyst firmly immobilised. When these two surfaces were clamped together, the effect was to produce a reactor with one wall of the channel being catalytically active. The *in situ* heater was fabricated from Nichrome wire (Ni90/Cr10) 0.25 mm o.d. (Goodfellows, Cambridge, UK) immobilised in the PDMS top plate. The heating wire was inserted into the mould near to the mating face before the liquid PDMS was poured into the mould. The PDMS was stable to heating up to 175 °C (this temperature was not exceeded so no data exists beyond this point). Heating was achieved by a potentiostat (0–270 V) and monitored *via* a digital thermometer (Jencons model 2003) with the temperature probe (RS components) located close to the reaction channel. Where electroosmotic flow was used as a pumping method, a 2 cm long tube (0.5 mm i.d.) was inserted into the base plate, butting up to the start of the reaction channel. On-chip electroosmotic pumping is at present unreliable owing to vapourisation of the ethanol on the heated chip, however, this limitation is being overcome with the aid of a heat sink.

The hexan-1-ol was obtained from Avocado Research Chemicals (Heysham, UK), while other alcohols were obtained from supplies bottled in-house. Alcohols were purged with nitrogen for 10 min prior to use in order to minimise coking in the reactor; a frequent problem at high temperatures when trace oxygen is present. Pumping was achieved using a syringe pump (Baby Bee, BAS) or an electroosmotic pump fabricated as previously reported.[10]

The effect of temperature on the dehydration of hexan-1-ol to hexene has been studied in prior work, and an optimum conversion occurred at a temperature of 155–160 °C. This was

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used in this work. Currently, no optimisation of the ethanol temperature has been undertaken.

Hexan-1-ol was pumped through the reactor chip at a flow rate of 3 μL min$^{-1}$ and a reaction temperature of 155 °C. The products were collected and analysed by gas chromatography using a Porapak Q column at 220 °C. From the gas chromatogram, a hexan-1-ol to hexene conversion on average between 85 and 95% could be determined. No additional products were detected, and the reaction was specific to hexene. The conversion efficiency is favourable compared to that observed with large-scale reactors, where 30% is common. The reactor was used constantly over three working days, and no degradation of the performance was observed.

Ethanol has been pumped by both electroosmotic flow and by means of a syringe pump. Initially, ethanol was pumped through the chip at a flow rate of 3 μL min$^{-1}$ using a syringe pump and a reaction temperature of 155 °C. The products were collected and analysed by gas chromatography using a Porapak Q column at 50 °C. Only trace amounts of ethanol were detected, with most of the feedstock converted to ethene (68%), ethane (16%), and methane (15%). The electroosmotic pump produced repeatable flow rates of 0.9–1.1 μL min$^{-1}$ at a field strength of 200 V cm$^{-1}$, giving a significantly greater residence time for ethanol in the reactor. The effect of this could clearly be seen in the GC results obtained where the only detectable product was methane. This indicates that the reaction has gone beyond dehydration to complete cracking of the feedstock. Trace amounts of methanol were also detected.

In conclusion, open channel on-chip microreactors have been demonstrated for the dehydration of alcohols to the associated alkene. While excellent results have been obtained with mechanical pumping, electroosmotic pumping appears to offer a significant advantage over other types of pumping, namely a very slow flow rate resulting in long residence times in the reactor. This can lead to a significant decrease in the required path length for reaction. Electroosmotic flow has a disadvantage since many liquids, *e.g.* hexanol exhibit no flow under applied potential, indeed the volume flow rate is inversely proportional to carbon chain length. The obvious outcome of this will be the further miniaturisation of reactors, and the potential for *in situ* production of chemicals.

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