A METHOD FOR EXTREMELY RAPID REACTION OPTIMISATION USING A CONTINUOUS FLOW MICROREACTOR WITH ON-LINE RAMAN SPECTROMETRY

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Abstract
A microfluidic system is described which can be used to perform reaction optimisation in real time.

Keywords: ***Optimisation, Raman, Oxidation, Catalyst.***

1. Introduction

The optimisation of a chemical process is an extremely expensive procedure, requiring a large investment of time. Performing optimisation using batch reactions, even performed in parallel, is a long process, which must then be followed by scale-up studies for reaction viability on the large scale. With this in mind we chose to study the use of microreaction technology to perform reaction optimisation in real time.

2. Experimental

We present a method for the extremely rapid gathering of optimisation data using a continuous flow microreactor and online Raman spectrometry. This system allows variations in reaction conditions to be performed in real time. The use of microreactors also allows for any reaction to be scaled-out without changing the reaction parameters.[1]

Previous work at Imperial[2] has shown the utility of monitoring reactions using Raman spectrometry, a method complementary to IR spectrometry but which can operate in a glass device. We present herein the first use of on-line Raman spectrometry to gather optimisation data in real time from a synthetically useful system.

The system studied was the catalytic oxidation of a secondary alcohol using the tetra-N-propylammonium perruthenate (TPAP)/N-methylmorpholine-N-oxide (NMO) oxidant system.[3] The oxidation of isopropanol to acetone was chosen as a model reaction illustrating a typical secondary alcohol substrate.

Reactants were motivated through the chip under hydrodynamic flow and studies undertaken to assess the optimum mixture of oxidant to substrate and catalyst to oxidant. Schematics of these experimental setups are shown. Reagents were mixed using high flow multilaminar micromixers , then the catalyst was extracted by in-line silica filtration and the Raman spectrum measured using an on-line confocal Raman microscope. In the initial configuration a set mixture of TPAP and NMO was titrated against isopropanol at various diferential flow rates. The schematic of this setup is shown in Figure 1a. In a subsequent configuration, catalyst and co-oxidant in vaiable ratio were mixed with a fixed ratio of isopropanol. A schematic of this setup is shown in Figure 2a.

3. Results and discussion

Data for the optimal oxidant dosage could be generated very rapidly. Indeed the data shown could be generated within the space of 5 minutes. The data was collected and output as a surface plot of Raman intensity vs. flow rate of oxidant and Raman shift, (Figure 1b). This valley plot allows the rapid interpretation of the experimental data.

Similarly data for the estimation of catalyst turnover and the investigation of catalyst exhaustion could be generated using a slightly reconfigured system. This data (Figure 2b) allows the

calculation of catalyst turnover rates and the estimation of optimal catalyst loading.

4. Conclusions

A microfluidic system for the rapid optimisation of catalytic systems has been described. The system can be used to perform real-time reaction optimisation and catalyst loa determination.

Acknowledgements

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References

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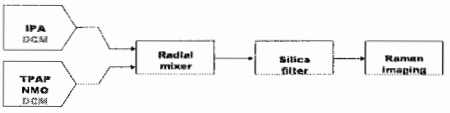

Figure 1a. A schematic of the initial experimental setup. Oxidant mix and substrate are combined and the transformation monitored online by Raman spectroscopy

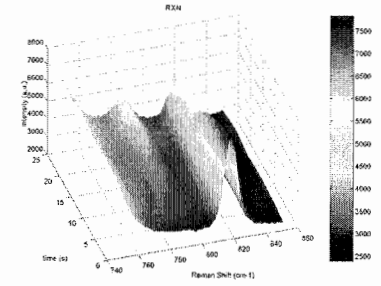

Figure 1b. Valley plot showing the transformation of isopropanol to acetone using a fixed oxidant to catalyst ratio.

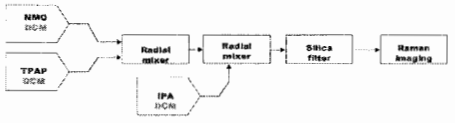

Figure 2a. A schematic of the subsequent experimental setup. Catalyst and co-oxidant are combined in variable ratio and mixed with a fixed ratio of substrate. The transformation was monitored online by Raman spectroscopy

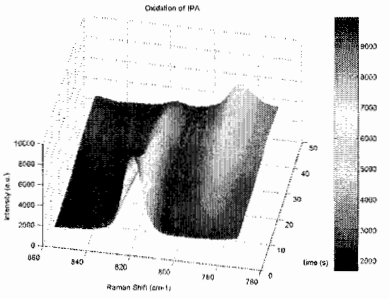

Figure 2b. Valley plot showing the transformation of isopropanol to acetone using a variable oxidant to catalyst ratio.