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The condensation/polymerisation of dimethyl siloxane fluids in a three-phase trickle flow monolith reactor

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Abstract

For the production of siloxane fluids, the viability of using a multi-channel monolith as a catalyst support system in a three-phase reactor has been studied. The catalyst was tripotassium phosphate (K_3PO_4). Experiments were performed in a single-channel flow reactor (15 mm i.d. and 500 mm catalyst coated length). The rate of reaction was followed by monitoring the disappearance of the hydroxyl group (–OH). Reaction experiments were performed at a hydroxyl group concentration range from 150 to 170 mol m^{-3}, $T = 373$–413 K and $P = 7.9$ kPa with a nitrogen purge. The maximum temperature of operation was restricted to 413 K to avoid the formation of undesirable by-products. In the regime controlled by chemical kinetics, reaction was of an apparent first order with respect to –OH concentration, and in the apparent rate constant, the pre-exponential factor was 4.19×10^{-4} m s^{-1}, and the apparent activation energy was 16.1 kJ mol^{-1}. These are only valid for the operating pressure and purge gas flowrate used, as both of these are shown to affect water removal from the liquid phase and, hence, reaction rates. Mass transfer coefficients from the liquid to the catalyst surface were estimated and these increased rapidly with flowrate and were higher than expected for a falling liquid film. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic monolith; Trickle flow; Siloxane fluids; Condensation and polymerisation reactions

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1. Introduction

Silicone polymers are a generic class of materials, which form a diverse range of products, e.g. oils, resins, rubbers, greases and emulsions. In the manufacture of silicone polymers, materials known as polydimethyl siloxane fluids are important intermediates. These fluids, in the presence of a catalyst, can undergo polymerisation and condensation reactions to form the desired high molecular weight polymers. In this paper, the development of a monolith catalyst support system is studied for the polymerisation–condensation reaction of a linear silicon fluid

$$HO[Si(CH_3)]_2O[Si(CH_3)_2O]_{96}Si(CH_3)_2\,OSi(CH_3)_2OH \qquad (1)$$

to form the polymer

$$Si(CH_3)_3O[Si(CH_3)_2O]_ySi(CH_3)_2OSi(CH_3)_3 \qquad (2)$$

where y represents the chain length of the polymer. For this process, tripotassium phosphate was selected as a catalyst as it is active and relatively insoluble in the reactants/products. Also, it is readily available in pellet form. A more detailed explanation of the use of catalysts for this reaction is available in [1]. Preliminary experimental trials in a trickle-bed reactor at

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Nomenclature

A_s	geometric surface area of the catalyst ($\mathrm{m^2}$)
C_OH	concentration of hydroxyl groups ($\mathrm{mol\,m^{-3}}$)
d	inside diameter of the uncoated ceramic channel (m)
$F_{\mathrm{OH_0}}$	inlet molar flowrate of hydroxyl groups ($\mathrm{mol\,s^{-1}}$)
$F_{\mathrm{OH_L}}$	outlet molar flowrate of hydroxyl groups ($\mathrm{mol\,s^{-1}}$)
k	apparent chemical reaction rate constant ($\mathrm{m\,s^{-1}}$)
k_m	mass transfer coefficient ($\mathrm{m\,s^{-1}}$)
k_o	apparent overall rate constant ($\mathrm{m\,s^{-1}}$)
L	length of catalytic monolith (m)
r_OH	rate of disappearance of hydroxyl groups ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
R	universal gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
T	temperature (K)
v	volumetric flowrate ($\mathrm{m^3\,s^{-1}}$)
X_OH	fractional conversion of hydroxyl groups
z	axial direction (m)

Dow Corning confirmed the activity of the catalyst. However, as it was suspected that the external surface area of the pellet promoted the reaction, it was apparent that a small particle size would be required.

At present, similar reactions of this type are performed in three-phase trickle-bed reactors using the catalyst in pellet form. Some of these processes suffer from undesirable side reactions, which can adversely affect the quality of the polymers produced. This is suspected to occur as a result of variations in the residence time of the fluid in the reactor. The ability to process and produce high viscosity products is also often throughput-limited by pressure drop. The use of ceramic monolith supports, instead of pellets in packed beds, is already known, e.g. [2–6], to offer many advantages, e.g. low pressure drop, high surface area-to-volume ratio and more uniform residence time distribution; many of these could also be exploited in this application to improve the process and quality of the product.

2. Experimental

Recognising that polymerisation mechanisms are complex, the rate may be followed (e.g. [7]) by monitoring the disappearance of one of the functional groups, e.g. hydroxyl (–OH). One of the steps in this complex reaction scheme may be represented by

$$2\mathrm{A}_{96} \rightarrow \mathrm{B}_{192} + 2\mathrm{H_2O} \tag{3}$$

where A_{96} represents the linear silicon fluid of chain length 96, and B_{192} represents the polymer formed with a chain length, $y = 192$. In this reaction, water is formed as a by-product.

In order to explore the viability of using a monolith as a catalyst support, preliminary experiments were performed in a spinning basket reactor with the catalyst in the form of pellets and also coated on a monolith support structure. The vessel was filled with the reactant and a nitrogen purge gas stream was fed into the base of the reactor to facilitate the removal of water and any volatile by-products formed during the reaction. These substances were subsequently trapped in two condensers. This, therefore, operated as a semi-batch reactor. The pressure in the system was reduced with the aid of a vacuum pump in order to aid the removal of water from the system. From these experiments, it was shown that the reaction occurred on the external surface area of the catalyst and foaming occurred at the start of the reaction, which was of an apparent first order with respect to –OH concentration.

$$r_\mathrm{OH} = k\,C_\mathrm{OH} \tag{4}$$

More detailed experiments were then performed in a single-channel trickle flow reactor, where the length of the catalyst coated section was 500 mm. The inside diameter of this channel was sufficiently large (15 mm) to ensure that during the course of the experiments, the liquid film around the inside perimeter of the channel would not be bridged as a result of foaming. Had this occurred, the trickle flow would not have been maintained. A purge gas stream of nitrogen was fed co-current with the fluid in order to remove water and any low molecular weight volatile species formed as by-products. The operating pressure in the reactor affects removal rates and, hence, reaction rates.

2.1. Apparatus

Reaction experiments were performed in the apparatus illustrated in Fig. 1. The liquid was fed into the distributor from a heated reservoir. The fluid entered the reactor through small 1 mm diameter holes drilled 2 mm apart in the sides of the ceramic tube. The section of the ceramic tube acting as a liquid distributor was not coated with catalyst. Preliminary trials were performed in a distributor that was partly constructed of glass in which it was ascertained, by visual inspection, that a uniform liquid distribution was obtained on the surface of the ceramic tube. The inlet gas and liquid temperatures were measured with thermocouples. The catalyst coated ceramic tube was housed inside a stainless steel tube that was maintained by a heated fluid at the desired operating temperature. The heat transfer fluid was electrically heated and a nitrogen purge in the base of the heated section ensured good mixing and that a uniform temperature was maintained in the reactor. From preliminary experiments, it was evident that the liquid and gas temperatures approached each other at the reactor outlet, so the exit temperature of the liquid and the gas could be deduced from a single measurement at the end of the tube. The fluid from the reactor could be directed to one of the two reservoirs, one of these was used during start-up and shut-down, whilst the other was dedicated to collecting the products for a controlled experiment once steady-state had been achieved. The reservoirs were graduated so that the quantity of liquid could be determined over a period of time and, hence, the flowrate could be calculated.

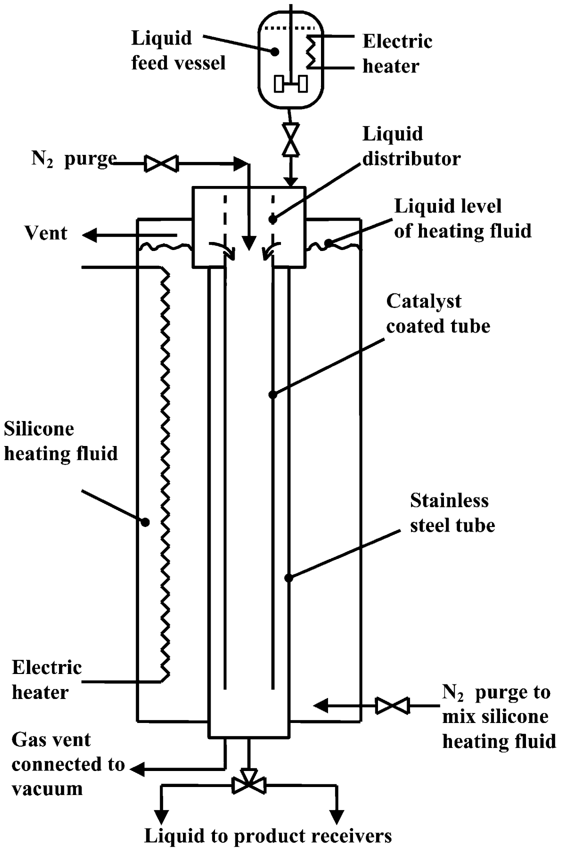

Fig. 1. Simplified schematic diagram of the single-channel trickle flow apparatus.

2.2. Catalyst system

Commercially available pellet form of tripotassium phosphate (K_3PO_4) was ground to a fine powder and mixed with ethanol (87% pure) until a smooth slurry was formed. The slurry was poured into the ceramic tube and then allowed to drain, thereby coating the surface of the tube with catalyst. The section of the tube acting as the distributor was not coated. The tube was slowly dried in a nitrogen atmosphere at room temperature, and then at 100°C. The nitrogen atmosphere was maintained to prevent the catalyst from reacting with carbon dioxide in the atmosphere. The description of the catalytic reactor is provided in Table 1.

2.3. Operation

The feedstock reservoir was initially charged with the siloxane fluid (see Table 2) and the temperature of the fluid and reactor tube were gradually raised up to the desired operating temperature. The vacuum pump was started and a nitrogen purge was initiated into the system. The liquid was then fed into the distributor and adjusted with the in-line needle valve. Liquid flowrate was calculated by timing a known volume of liquid in one of the graduated product reservoirs. Once steady-state conditions had been achieved, the liquid product was directed to the second product reservoir for a controlled run. At the end of the run, the product was re-directed to the first reservoir.

Table 1
Details of the catalytic reactor

Ceramic support	
Trade name	Pormulit
Material	Alumina silicalite (porous)
Inside channel diameter	15 mm
Channel wall thickness	2.5 mm
Total length	740 mm
Coated length	500 mm
Catalyst section	
Loading	15 g
Catalyst	K_3PO_4
Coated surface area	0.0235 m^2
Distributor	
Length of uncoated ceramic tube	240 mm
Stainless steel reactor housing	
Tube i.d.	20 mm
Length	780 mm
Heat transfer fluid	Silicone

Table 2
Physical and chemical properties of the polydimethyl siloxane feedstock (data supplied by Dow Corning Ltd.)

Boiling point (°C)	>230
Vapour pressure (kPa, 20°C)	<0.7
Solubility in water (%, w/w, 10°C)	<0.1
Specific gravity	0.97
Unreacted content (%, v/v) (water and cyclic siloxane)	15.0
Viscosity at 25°C (cst)	150.0
Viscosity temperature coefficient	0.6
Coefficient of volume expansion ($J\,K^{-1}$)	0.00096
Refractive index at 25°C	1.403
Surface tension at 25°C ($N\,m^{-1}$)	21.0
Thermal conductivity at 50°C ($W\,m^{-1}\,K^{-1}$)	0.155

2.4. Analysis

The progress of the reaction was monitored by measuring the –OH concentration. This was determined by titration with lithium aluminium dibutylamide, using 4-phenylazodiphenylamine as an indicator. Kinematic viscosity was also measured using a U-tube, reverse flow viscometer.

3. Results

Reaction experiments were performed at: a hydroxyl group (–OH) concentration range from 150 to 170 mol m^{-3}, $T = 373$–413 K and $P = 7.9$ kPa. The maximum temperature of operation was restricted to 413 K to avoid the formation of undesirable by-products.

3.1. Effect of flowrate on rate controlling process

For the range of conditions summarised in Table 3, preliminary experiments were initially conducted at a temperature of 413 K in which the effect of flowrate was investigated. The results of these experiments are presented in Fig. 2, where the reaction rate was calculated from:

$$r_{OH} = \frac{F_{OH_O} - F_{OH_L}}{A_s} \tag{5}$$

where A_s is the geometric surface area of the inside of the coated channel. From Fig. 2, at flowrates less than $7 \times 10^{-7}\ m^3\ s^{-1}$, it is evident that flowrate and, hence, mass transfer affects reaction rate. However, since fractional conversion can range from $0.1 < X_{OH} < 0.35$ (see Fig. 3), then in accordance with Eq. (4) the depletion of –OH in the bulk fluid would also affect reaction rates. It is, however, interesting to note that above a flowrate of $7 \times 10^{-7}\ m^3\ s^{-1}$, a change in liquid flowrate has a very small effect on reaction rate. It

Table 3
Experimental conditions for reaction experiments

	Effect of flowrate on rate controlling process	Chemical kinetics
Initial C_{OH} ($mol\,m^{-3}$)	172	172
Initial viscosity ($m^2\,s^{-1}$) × 10^4	1.5	1.5
Purge gas flow at STP ($m^3\,s^{-1}$) × 10^5	3.33	3.33
Pressure (kPa)	7.9	7.9
Liquid flowrate ($m^3\,s^{-1}$) × 10^7	0.13–13	>7.7
Temperature range (K)	413	373–418
Catalyst coated length (m)	0.5	0.5

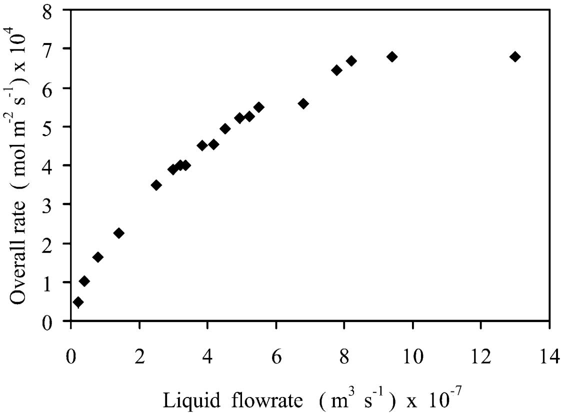

Fig. 2. Reaction rate as a function of liquid flowrate for $T = 413$ K.

was, therefore, considered that at these flowrates the reaction rate was predominantly controlled by chemical kinetics, and reaction experiments could be performed to determine the rate constant.

3.2. Chemical kinetics

In the regime controlled by chemical kinetics, i.e. $v > 7 \times 10^{-7}\,\mathrm{m^3\,s^{-1}}$, experiments were performed for the range of conditions summarised in Table 3. For the single-channel represented in Fig. 4, assuming a constant temperature and volumetric flowrate, the differential mole balance may be integrated and

$$\ln(1 - X_{\mathrm{OH}}) = \frac{\pi d L k}{v} \qquad (6)$$

where k is the apparent reaction rate constant, L the length of the catalyst coated section, d the internal diameter and X_{OH} the fractional conversion of –OH.

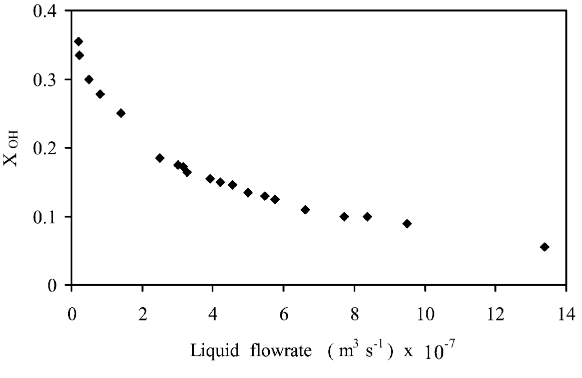

Fig. 3. Fractional conversion as a function of liquid flowrate for $T = 413$ K.

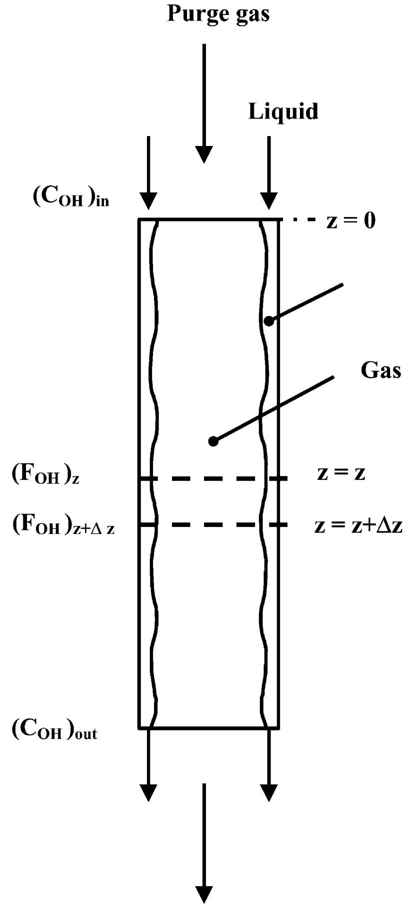

Fig. 4. Liquid and gas flow in the single-channel reactor.

At each temperature, a concentration *versus* flowrate plot was obtained to which a non-linear regression was applied. Making use of the regressed fit and considering only data where $v > 7 \times 10^{-7}\,\mathrm{m^3\,s^{-1}}$, the results are plotted in Fig. 5. In accordance with Eq. (6), a straight line is expected and indeed obtained, and the apparent rate constant, k, was determined from the gradient. The results of these experiments at different temperatures are presented in Fig. 6 as a plot of $\ln k$ *versus* $1/T$. Applying linear regression, the following rate constant was determined:

$$k = 4.19 \times 10^{-4} \exp\left\{-\frac{1.61 \times 10^{4}}{R T}\right\} \qquad (7)$$

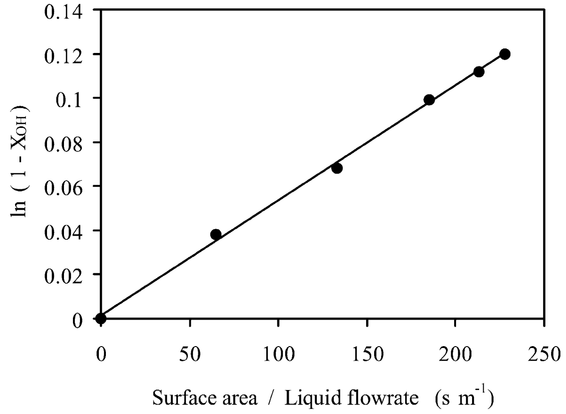

Fig. 5. Determination of the chemical reaction rate constant for $T = 413\,\mathrm{K}$.

The reaction kinetics are only valid for the fixed value of operating pressure and purge gas flowrate used, as both of these affect water removal from the liquid phase and, hence, reaction rates. Although the rate expression was shown to be well represented by a first order rate expression, the effect of purge gas flowrate on reaction rates confirms that the polymerisation reaction is very complicated.

3.3. Mass transfer

From the results of reaction experiments at a range of temperatures and at low flowrate, $v > 7 \times 10^{-7}\,\mathrm{m^3\,s^{-1}}$, the apparent overall rate constant, k_o, at various values of v and T was determined from a rearranged form of Eq. (6) where:

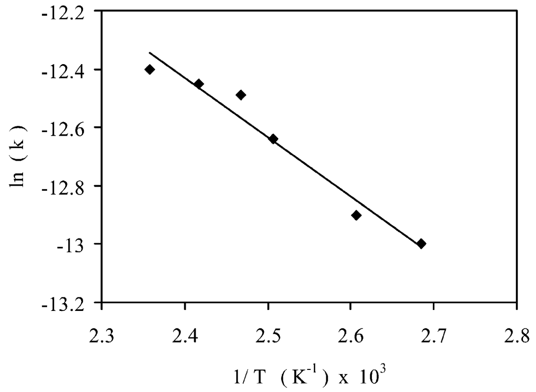

Fig. 6. Results of kinetic experiments.

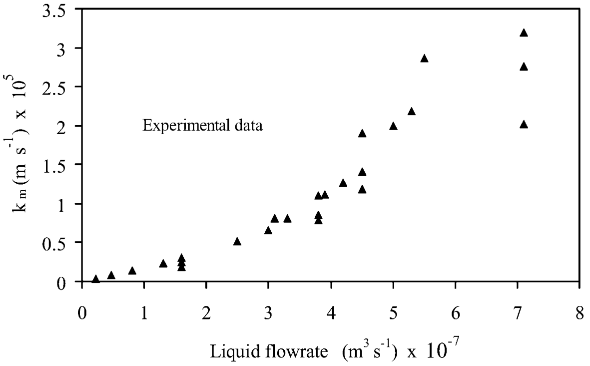

Fig. 7. Estimated values of mass transfer coefficients.

$$k_o = v \frac{\ln(1 - X_{OH})}{\pi d L} \tag{8}$$

For an apparent first order reaction, the reciprocal of the overall rate constant, k_o, may be shown to be:

$$\frac{1}{k_o} = \frac{1}{k_m} + \frac{1}{k} \tag{9}$$

Where the mass transfer coefficient, k_m, describing the rate of transport of hydroxyl groups from the bulk liquid phase to the catalyst surface may be determined from a rearranged form of Eq. (9). Therefore,

$$k_m = \frac{k_o k}{k - k_o} \tag{10}$$

As k_o is evaluated from Eq. (8), and k is known from Eq. (7), values of k_m can be determined and these are plotted as a function of liquid flowrate in Fig. 7. These increase rapidly with flowrate and are higher than would be expected from a falling liquid film. The values are enhanced by the roughness of the catalyst coating and the turbulence in the film as a result of the formation of bubbles of vapour (water and volatiles).

3.4. Effect of purge gas flowrate and system pressure

The results of some of these experiments are illustrated in Fig. 8. Unfortunately, because of limitations in the apparatus, it was not possible to maintain constant system pressure, whilst purge gas flow was changed. However, this provides clear evidence of the

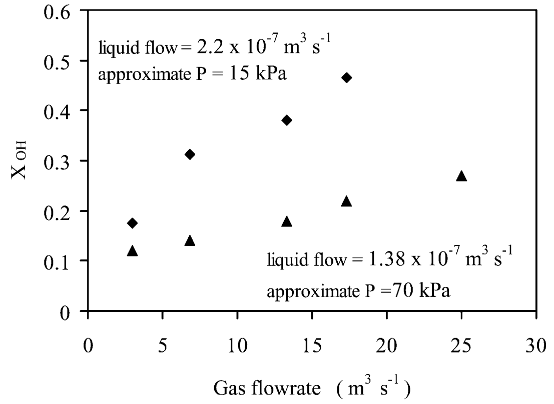

Fig. 8. Investigating the effect of varying purge gas flowrate at $T = 413\,\mathrm{K}$.

effect of gas flow and system pressure on reaction rates.

4. Concluding remarks

The viability of using a monolith catalyst support system for this reaction has been demonstrated. In any development of this scheme, further experimental work would need to proceed in parallel with modelling. The effects of system pressure and purge gas flow on reaction rates confirm that the reaction is complex. However, the approach followed in this paper provides a pragmatic method of progressing with this initiative.

In the application, trickle flow is preferred as it created a void in the channels of the monolith reactor in which the gas can flow freely and a vacuum can be drawn. By operating the reactor at reduced pressure ($<50\,\mathrm{kPa}$), this would help to remove the water and volatiles from the liquid product, thus increasing the rate of reaction and conversion to product. In a packed bed, because of the foaming nature of the reaction, it would be difficult to sustain this reaction in trickle flow. Whereas in a monolith to avoid fluid bridging across the channel, larger diameter channels could be used in the entrance region where high rates of reaction (hence, foaming) are expected. Further down in the bed, where reaction rates are lower, narrower channels could be used taking advantage of a higher catalyst external surface area to bed volume ratio. The use of an inert gas as a purge (e.g. nitrogen) helps to remove the volatile by-products and water. We believe that in the 'foaming zone' it would be preferable to pass the gas in a co-current direction with the liquid. If the gas were to be admitted in a countercurrent direction, then it may increase the risk of liquid bridging in the channels. In the 'non-foaming zone', if this is a second stage in the reactor, to increase the efficiency of this transfer, countercurrent flow could be employed. Further information on the potential application of this technique to the commercial process may be found in [8].

Although in the results presented in this paper, the catalyst was coated onto the surface of the ceramic tube, there is no reason why the catalyst could not be incorporated into the monolith structure and form an integral part of the support. This was done in a project that followed on from this study.

Acknowledgements

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