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Catalytic isomerisation of α-pinene oxide to campholenic aldehyde using silica-supported zinc triflate catalysts
II. Performance of immobilised catalysts in a continuous spinning disc reactor

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Abstract

The performance of silica-supported zinc triflate ($Zn(CF_3SO_3)_2$) catalyst immobilised on the surface of the spinning disc reactor (SDR) has been studied for the isomerisation reaction of α-pinene oxide to campholenic aldehyde. Process selectivity and conversion were assessed to determine the viability of SDR for performing catalytic reactions under a range of SDR operating conditions.

Different catalyst loadings and supports were tested in this study: 0.05 mmol/g Zn-triflate/K60 (Catalyst 1), 0.01 mmol/g Zn-triflate/K100 (Catalyst 2) and 0.05 mmol/g Zn-triflate/HMS_{24} (Catalyst 3). The latter catalyst was found to give the best performance in the SDR, with observed selectivity of 75% towards campholenic aldehyde and α-pinene oxide conversion of 85% at a disc temperature of 45 °C, disc speed of 1500 rpm and reactant feed flow rate of 6 cm^3/s. Empirical models relating conversion and selectivity to disc speed and feed flow rate were developed for each catalyst using multiple linear regression analysis of experimental data collected in the study.

A comparison with corresponding batch reactions indicates that the high shear rates in the thin SDR film flowing over the immobilised catalyst may give rise to intense mixing characteristics which overcome any mass transfer limitations within the immobilised matrix which would otherwise restrict the reaction rate. The short and controllable disc residence time in the SDR (of the order of seconds) promotes the desired reaction and minimises unwanted side reactions for enhanced process selectivity. These process advantages demonstrate the potential of the SDR to provide a "greener" approach to catalytic reactions.

Keywords: α-Pinene oxide isomerisation; Campholenic aldehyde; Process intensification; Green chemistry; Spinning disc reactor; Thin film flow

1. Introduction

Rearrangement reaction of α-pinene oxide is a very important reaction in the pharmaceutical industry. Notoriously, under different reaction conditions, over one hundred different products have been reported in literature [1,2]. Many of the products have significant importance as high value chemicals, such as campholenic aldehyde (favoured product if mild Lewis acids are used), *trans*-carveol, *trans*-sobrerol and *p*-cymene (if Brönsted acids are used). Some of the major products that can be formed during the reaction are shown in Fig. 1.

One of the very important products in this reaction is campholenic aldehyde, further used by the fragrance industry in the synthesis of several sandalwood fragrances. Traditionally, campholenic aldehyde is produced on a commercial scale by the Lewis acid catalysed isomerisation of α-pinene oxide in a homogeneously catalysed process [3]. Maximum expected selectivity does not exceed 90% [4] if a reaction is performed in benzene with Lewis acid catalyst $ZnBr_2$. $ZnCl_2$ and $ZnBr_2$ proved to be the most active and selective homogenous systems used in this reaction, however an extraction process required to remove the catalyst from the system causes a huge environmental concern. Recent efforts for the development and application of heterogeneous catalysts stems from these environmental issues.

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Abbreviations: OTf, triflate (trifluoromethanesulphonyl group), $CF_3SO_3^-$; KX, K stands for Kiesel (silica), X for pore size; HMS_x, hexagonal mesoporous silica, with pore size x

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Nomenclature

a	constant
b	constant
c	constant
d	constant
e	constant
I	constant
K	constant
N	rotational speed (rpm)
Q	volumetric flow rate (m^3/s)
r	radial distance (m)
t_{res}	mean residence time (s)
v	velocity (m/s)
x_A	conversion (%)
z	vertical upward distance (m)

Greek letters

δ	average film thickness (m)
$\dot{\gamma}$	shear rate (s^{-1})
ν	kinematic viscosity (m^2/s)
σ_A	selectivity (%)
ω	angular velocity (s^{-1})
ϖ	axial velocity component (m/s)

Subscripts

i	inlet
o	outlet
res	residence

To date, heterogeneous catalysts developed for this reaction have involved the use of mixed oxide solid acids [5] and US-Y zeolites [3,6]. Typically, selectivities towards campholenic aldehyde of 55–80% have been reported. More recently, the use of zeolite titanium beta resulted in observed 95% selectivity [7]. However, a significant drop in selectivity was observed after 6 h. Ravasio et al. [8] reported maximum of 72% selectivity at full conversion using mixed cogels.

Novel heterogeneous Lewis acid catalysts based on silica-supported zinc-triflate have been developed by Wilson et al. [9] for use in the rearrangement of α-pinene oxide to campholenic aldehyde. These catalysts have been shown to exhibit considerable activity and can be recycled without loss of selectivity towards the aldehyde. The selectivity towards the aldehyde can be optimised to 80% (at 50% conversion) when the reaction is performed in batch mode at 25 °C using hexagonal mesoporous silica (HMS_{24}) as the catalyst support.

Often, the high activity of the supported catalysts results in further reaction of the desired product, causing the selectivity to drop during the course of the reaction. It is therefore very important not only to “direct” reaction towards the formation of campholenic aldehyde but to stop the reaction altogether at this point. This may be achieved by processing in an intensified continuous reactor where the residence time is kept short and is tightly controlled.

The spinning disc reactor is an example of such an intensified reactor technology. Centrifugal accelerations generated by rotation of the disc surface cause thin (100–200 μm), highly sheared films to flow on the rotating surface. Rapid mixing in the liquid film, short liquid residence times (of the order or 1–5 s typically) and enhanced heat and mass transfer are characteristics of this reactor technology [10,11]. This makes spinning disc reactors strong contenders for performing fast, exothermic and mixing limited reactions. Recent applications of this reactor technology to polymerisation [12,13], crystallisation [14] and precipitation [15] have indicated its potential to significantly enhance reaction rates and to efficiently control product properties.

In the present study, an intensified reactor/separator integrated unit based on the spinning disc reactor technology was evaluated for the catalytic isomerisation of α-pinene oxide to campholenic aldehyde in terms of reactant conversion and process selectivity. The feasibility of immobilising the catalyst on the reactor surface was also investigated with a view to eliminate the downstream catalyst separation step for a more environmentally friendly and cost-effective process.

2. Experimental procedures

Three catalysts developed and characterised at the University of York [9] were used in this study: 0.05 mmol/g $Zn(OTf)_2$ supported on K60 (silica) (Catalyst 1), 0.01 mmol/g $Zn(OTf)_2$ supported on K100 (silica) (Catalyst 2) and 0.05 mmol/g $Zn(OTf)_2$ supported on HMS_{24} (silica) (Catalyst 3). Kinetic studies that include activation energies for all three catalysts used in this study have also been conducted and are presented in a separate publication [16]. Tests were carried out to investigate the performance of these catalysts in the rearrangement of α-pinene oxide in a spinning disc reactor (SDR) and in a conventional batch vessel for benchmarking. Catalyst performance was measured in terms of conversion and selectivity.

2.1. Spinning disc reactor

A 200 mm diameter spinning disc reactor with a stainless steel reacting surface and equipped with excellent heating and cooling facilities was used in this study (Fig. 2). Details of this SDR system have been reported elsewhere [17]. Prior to reaction, the disc surface was removed and coated with catalyst using epoxy based glue. The amount of catalyst was recorded by weighing the disc prior to coating and after the application of glue and the catalyst coating. The total mass of catalyst used for all the SDR runs was 0.8 ± 0.05 g.

One pass experiments in the SDR were initially performed. A peristaltic pump was used to transfer the reactant mixture containing 1 g of α-pinene oxide (reactant, Aldrich 99%), 100 ml of 1,2-dichloroethane (solvent, Aldrich 98%) and 0.5 g decane (Aldrich 99%, used as internal standard) from a storage vessel to the feed distributor of the spinning disc reactor. The feed outlet of the feed distributor was located at the centre of the disc surface where the feed was introduced. Centrifugal forces created by rotation of the disc forced the liquid to flow over the disc surface in form of very thin, highly mixed film. At the edge of the disc,

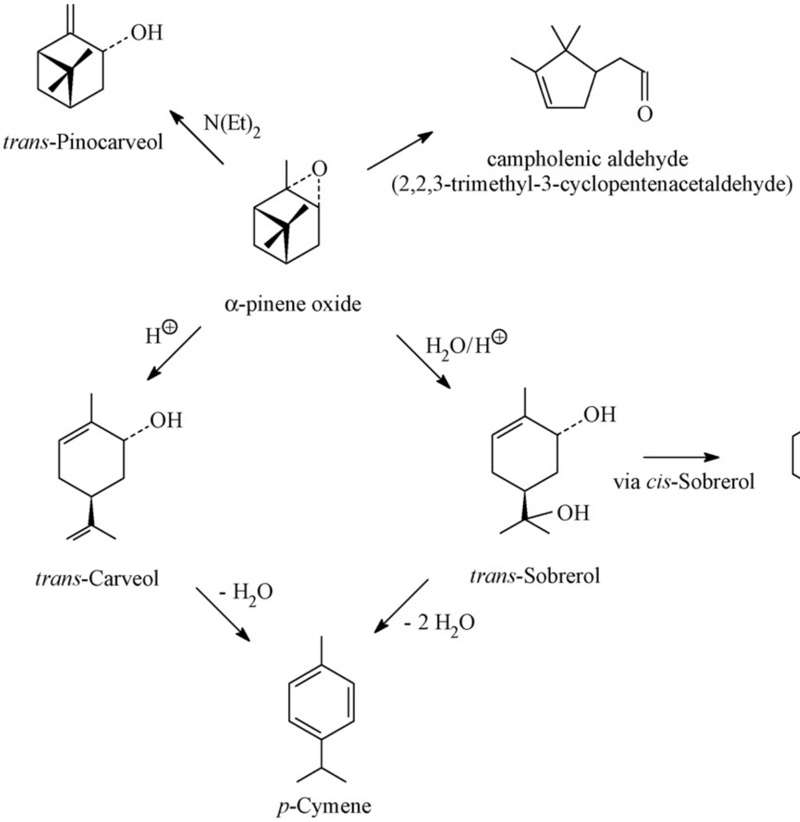


Fig. 1. Main products from the rearrangement of the α-pinene oxide.

the liquid was thrown off the surface, flowed down the water-cooled stationary jacket walls and was collected for analysis. One sample from each run was also taken from the storage vessel to ensure that reaction did not take place before being introduced to SDR. The range of SDR operating conditions studied for each catalyst was as follows: temperatures between 25 °C and 85 °C, disc speeds between 200 rpm and 1500 rpm and reactant flow rates between 3 cm^3/s and 6 cm^3/s.

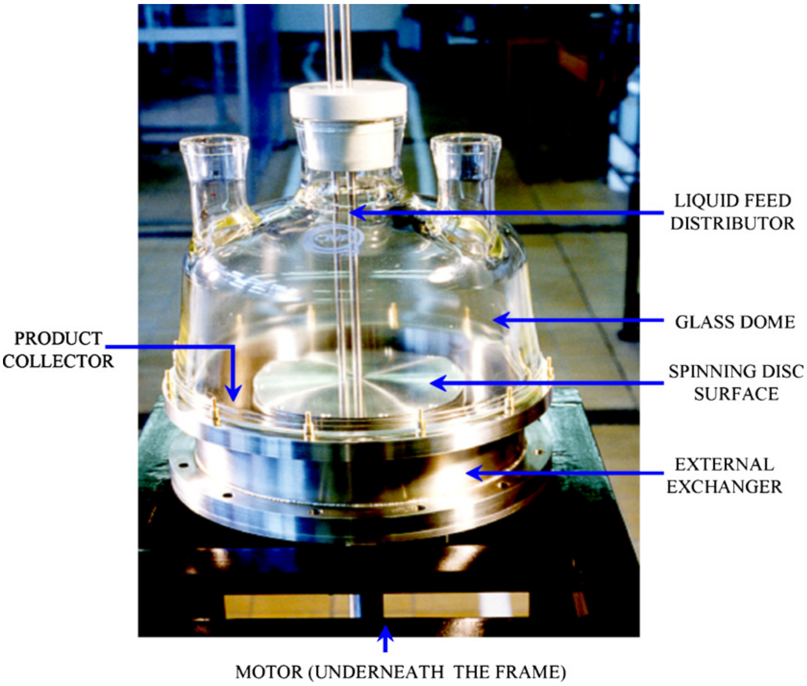


Fig. 2. Outside view on the SDR [18].

In order to asses the possibilities of improving the reactor's performance when unsatisfactory results were achieved, multipass experiments were performed. The procedure for the first pass was as described above for the one pass experiments. The product collected from the first pass was fed onto the disc again and this procedure was repeated for the desired number of passes in the SDR. After each pass a sample was taken from the collected product and analysed. The rotational speed of the disc was kept constant at 500 rpm for the multipass experiments. The SDR was set at the following temperatures for each catalyst: 25 °C for Catalysts 1 and 2 and 85 °C for Catalyst 3. These temperatures were selected on the basis of the low conversions achieved for each catalyst in one pass, with the aim of improving these low conversions over a number of disc passes.

2.2. Batch apparatus

A batch reactor was used to benchmark the performance of the SDR using comparable reaction temperatures. It consisted of a 250 ml capacity volume 'Pyrex' glass vessel surrounded by a water circulator system. The circulating water was pumped from a constant temperature bath which was provided with a digital controller unit for temperature control. The reactor was placed in the centre of a magnetic plate which, together with a magnetic stirrer in the reaction mixture, was used to provide adequate mixing. Manual controls on the magnetic plate allowed the agitation rate in the batch mixture to be regulated. Access to the glass vessel was provided by two stopped arms and a thermocouple was inserted through one of them and connected to the data logger to record the temperature of the mixture. The other arm was used for feeding reactant, solvent and catalyst into the reactor and for taking samples from the reaction mixture as required. The top end of the vessel was fitted with a vertical condenser system to prevent loss of volatile material.

One gram of α-pinene oxide (Aldrich 99%), 100 ml of 1,2-dichloroethane (Aldrich 98%) and 0.5 g decane (Aldrich 99%, internal standard) were introduced in the batch vessel and the mixture preheated to an operating temperature. After 0.2 g of the selected catalyst was added, samples were taken by pipette at intervals of 10 min and analysed immediately after collection.

2.3. Sample analysis

All samples were analysed using a FID UNICAM Series 610 LC-GC system with an HP1 packed column (100% dimethylpolysiloxane). Data obtained from the GC analysis were used to calculate conversion and selectivity towards the campholenic aldehyde.

3. Results and discussion

It was shown experimentally [19] that once a fluid spreads on the disc it quickly adjusts to the rotation rate of the disc in an entrance region of small radii. Under steady state conditions, the liquid is subjected to centrifugal and viscous forces which act in opposite direction and balance out. Shear stress at the free surface of the thin film at low gas/liquid pressures is negligible resulting in a semi-parabolic radial velocity profile as illustrated in Fig. 3.

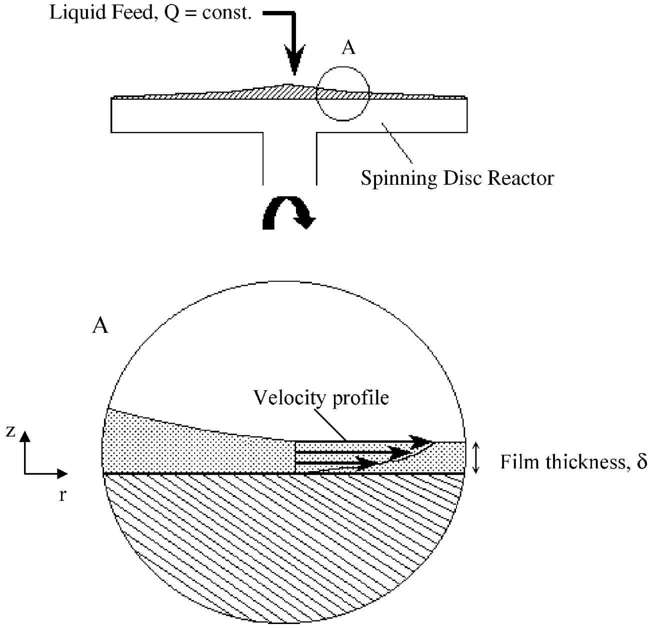


Fig. 3. Thin film liquid flow and velocity profile in the SDR.

The radial velocity field $v(r, z)$ can be expressed as [20]:

$$v(r,z) = \frac{r\omega^2\delta^2}{\nu}\left(\frac{z}{\delta} - \frac{1}{2}\left(\frac{z}{\delta}\right)^2\right) \tag{1}$$

In the above equation, δ is the film thickness which can be calculated using the following equation [20]:

$$\delta = \left(\frac{3}{2\pi}\frac{\nu Q}{\omega^2 r^2}\right)^{1/3} \tag{2}$$

The mean residence time of the liquid film on the disc can be calculated from Eq. (3) [20]:

$$t_{\text{res}} = \left(\frac{81\pi^2\nu}{16\omega^2 Q^2}\right)^{1/3}(r_0^{4/3} - r_i^{4/3}) \tag{3}$$

The rotational speed is a critical parameter which needs to be carefully optimised to achieve the best performance of the spinning disc in terms of mixing, heat transfer rates and disc residence time.

3.1. Effect of SDR temperature

In the initial experimental work, the effects of disc temperature on the conversion of α-pinene oxide and selectivity towards campholenic aldehyde were investigated at a fixed disc speed of 500 rpm and reactant flow rate of 4 cm^3/s. The data are shown in Fig. 4 (conversion) and Fig. 5 (selectivity) for all three catalysts tested. Increased activity at higher disc temperatures was observed for Catalysts 1 and 2 with Catalyst 1 being consistently 10–20% more active at each tried temperature. As for Catalyst 3, increase of temperature to 45 °C increased the conversion to 100%, but beyond this temperature conversion dropped significantly.

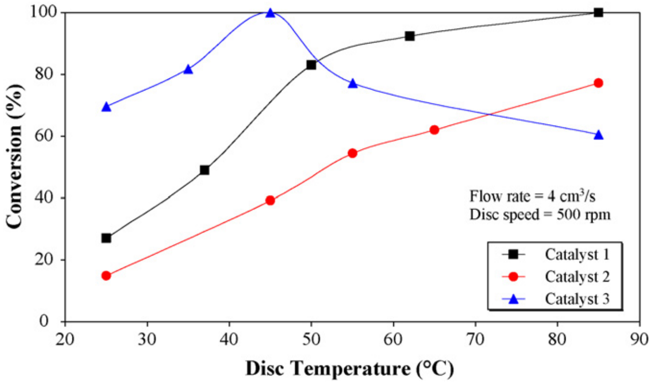


Fig. 4. Influence of temperature on conversion for all catalysts.

In the low and high temperature ranges, Catalyst 1 gave very low selectivities towards campholenic aldehyde in spite of significant conversion at these temperatures. Reactions resulting in the formation of unwanted products rather than campholenic aldehyde were therefore promoted in the lower temperature range. The optimum selectivity of Catalyst 1 was obtained in the temperature range of 40–60 °C. Catalyst 2 gave the highest selectivity of 70% over the whole range of temperatures tested although it also gave the lowest conversion of all three catalysts. The selectivity for Catalyst 3 varied between 55% and 75% at most temperatures except at temperatures around 45 °C where selectivity dropped significantly to 20%.

The optimal temperature for each catalyst was selected on the basis of maximum conversion of α-pinene oxide achieved. All subsequent experimentation was therefore conducted at the following temperatures: 85 °C for Catalysts 1 and 2 and 45 °C for Catalyst 3.

3.2. Effect of disc speed and feed flow rate

Conversion and selectivity results for all three catalysts under a range of disc speeds at a fixed reactant flow rates of 4 cm^3/s and 6 cm^3/s are presented in Figs. 6–9.

As shown in Fig. 6, Catalysts 1 and 3 resulted in complete conversion of α-pinene oxide at a flow rate of 4 cm^3/s regardless of disc speed. This observation suggests that the rate of reactant consumption is so fast with these two catalysts at their operating temperatures of 85 °C and 45 °C, respectively, that complete conversion was obtained even within the minimum residence time provided at the highest disc speed. On the other hand, Catalyst 2 exhibited a lower level of activity even at the operating temperature of 85 °C, causing the rearrangement reaction with this catalyst to be slower. As seen in Fig. 6, lower disc speeds and therefore higher residence times resulted in 90% conversion with Catalyst 2, which gradually dropped to 40% at the highest speeds.

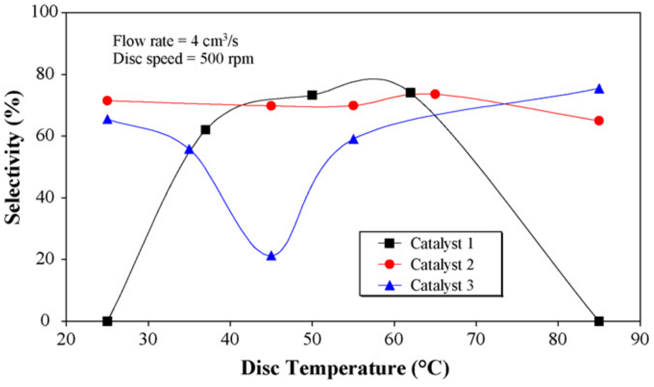


Fig. 5. Influence of temperature on the selectivity for all catalysts.

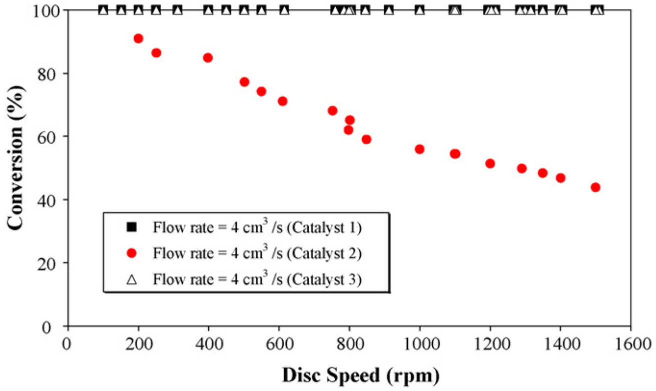


Fig. 6. Effect of disc speed on conversion for all catalysts at 4 cm^3/s. Temperatures: 85 °C (Catalysts 1 and 2); 45 °C (Catalyst 3).

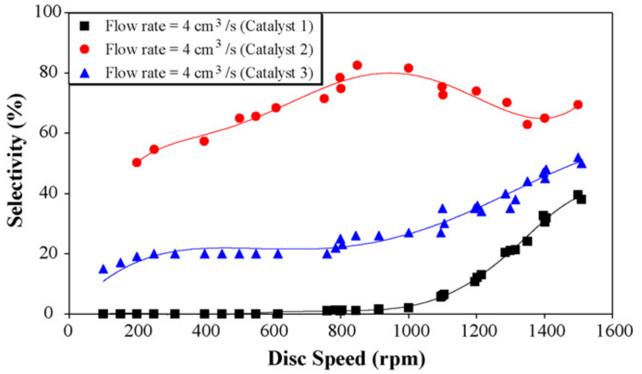


Fig. 7. Effect of disc speed on selectivity for all catalysts at 4 cm^3/s. Temperatures: 85 °C (Catalysts 1 and 2); 45 °C (Catalyst 3).

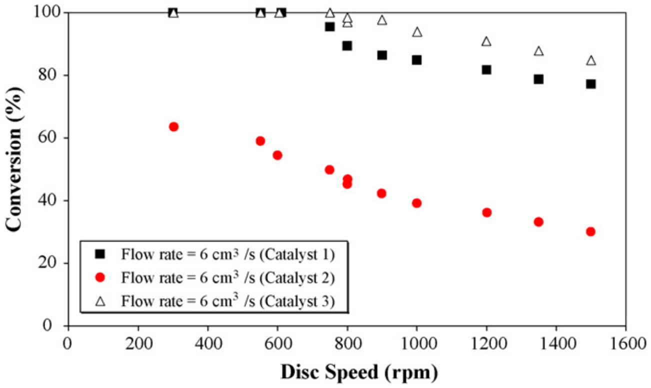


Fig. 8. Effect of disc speed on conversion for all catalysts at 6 cm^3/s. Temperatures: 85 °C (Catalysts 1 and 2); 45 °C (Catalyst 3).

When trends for selectivity results are compared (Fig. 7) it is noticeable that both “fast” catalysts (Catalysts 1 and 3) have very low selectivity towards campholenic aldehyde compared to the less active Catalyst 2; in fact for low disc speeds and correspondingly long residence times, none of the aldehyde was observed when using Catalyst 1. This may be explained in two ways: either Catalysts 1 and 3 were promoting reactions other than that which forms the desired campholenic aldehyde, or consecutive reactions which consume the highly reactive aldehyde after it is produced set in during the process on the disc. The latter explanation appear more plausible and is in fact reinforced by monitoring the selectivity towards the aldehyde in a batch process over a longer period of time, as will be discussed later.

Fig. 7 also indicates that selectivity may be improved for Catalysts 1 and 3 by increasing the disc speed and lowering residence times. It is interesting to also note that whilst Catalyst 2 resulted in lower conversions, its selectivity towards campholenic aldehyde is much higher than that for the other two catalysts. This suggests that high selectivity is achievable if a limitation is imposed on the extent to which the reaction proceeds. One way to control the reaction is by controlling the residence time or contact time between the reactant and the catalyst. The residence time on the disc is influenced by disc speed and reactant flow rate on the disc as indicated in Eq. (3).

The experimental effects of increasing reactant flow rate from 4 cm^3/s to 6 cm^3/s on conversion and selectivity are shown in Figs. 8 and 9, respectively.

At the higher flow rate of 6 cm^3/s, a clear difference in catalyst activity is now observed between Catalysts 1 and 3 which was not immediately apparent in Fig. 6. The drop in conversion with disc speed with Catalysts 1 and 3 occurs as a result of reduced residence time at the higher disc speeds and flow rate. There is a large increase in selectivity in the lower disc speed range at the higher flow rate for these two catalysts which may be attributed to the shorter residence times as indicated in Figs. 10 and 11 for Catalyst 1 and 3, respectively.

It is clear from Figs. 10 and 11 that, at any particular flow rate, selectivity improves significantly at shorter residence times. If residence time is longer than 0.8 s virtually no desired product is formed (as seen in Fig. 10). Selectivity becomes very sensitive to residence times in the range 0.15–0.3 s of the reaction. Highest selectivities of 60% and 75% for Catalysts 1 and 3, respectively, are obtained at residence times shorter than 0.15 s whilst less than 35% selectivity is achieved beyond 0.3 s of residence time. At any given disc speed, shorter residence times are achieved at higher flow rates so that highest selectivity is obtained at the highest flow rates. Such behaviour is clearly depicted in Fig. 12 for Catalyst 3.

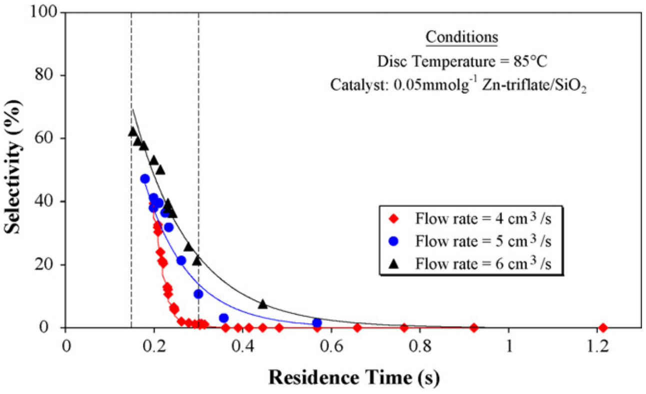


Fig. 10. Effect of disc residence time on selectivity for Catalyst 1.

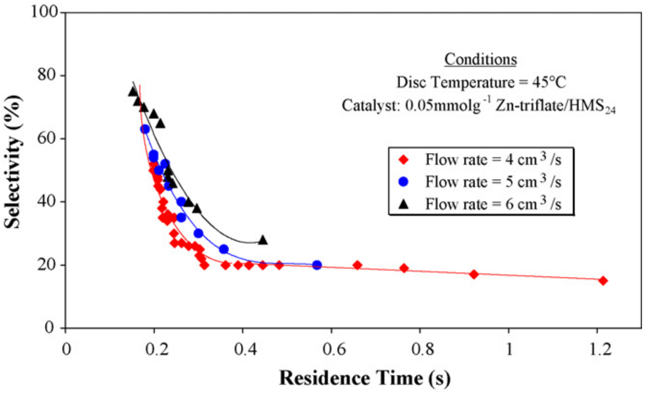


Fig. 11. Effect of disc residence time on selectivity for Catalyst 3.

On the other hand, a decrease in residence time causes reactant conversion to fall, as seen in Figs. 13 and 14 for Catalysts 1 and 3, respectively. Again, conversion exhibits the greatest sensitivity to residence times in the interval 0.15–0.3 s. Beyond 0.3 s, complete conversion is reached.

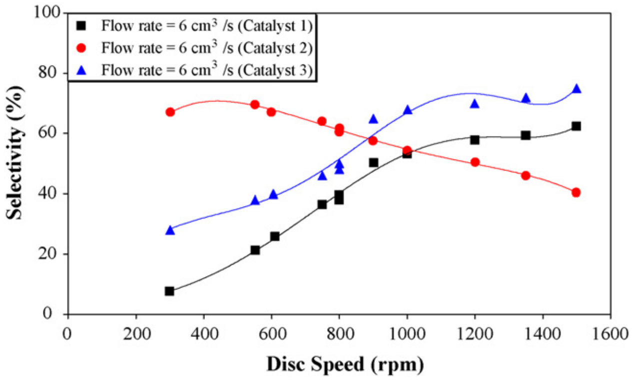


Fig. 9. Effect of disc speed on selectivity for all catalysts at 6 cm^3/s. Temperatures: 85 °C (Catalysts 1 and 2); 45 °C (Catalyst 3).

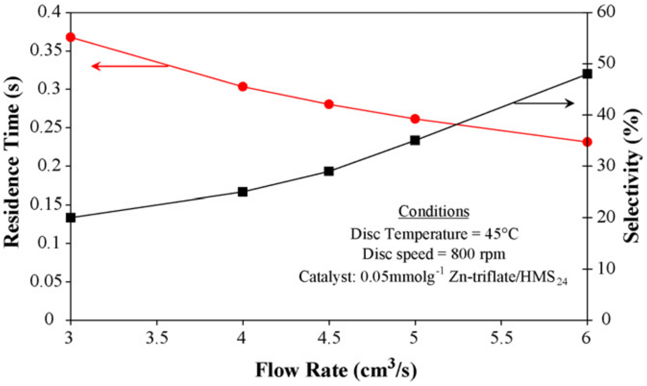


Fig. 12. Effect of reactant flow rate on disc residence time and selectivity at fixed disc speed of 800 rpm for Catalyst 3.

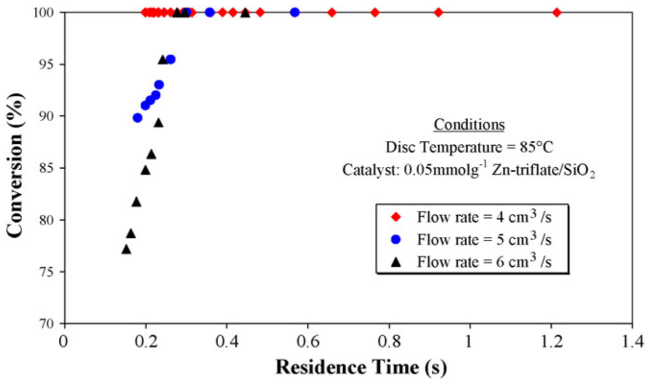


Fig. 13. Effect of residence time on conversion for Catalyst 1.

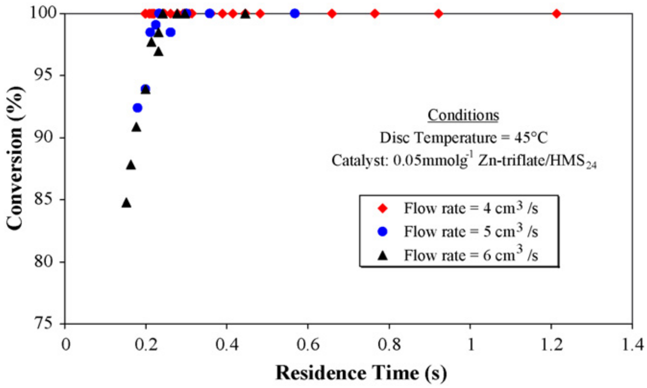


Fig. 14. Effect of residence time on conversion for Catalyst 3.

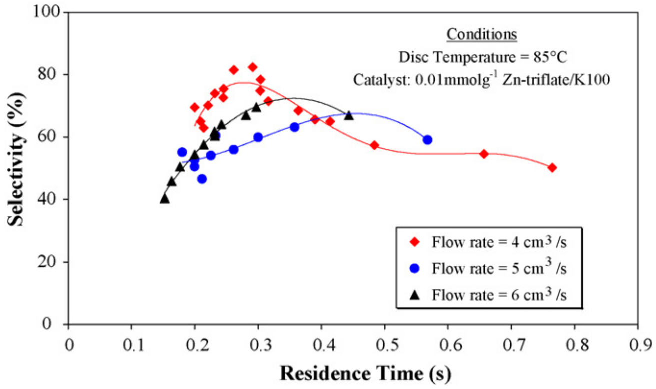


Fig. 15. Effect of residence time on selectivity for Catalyst 2.

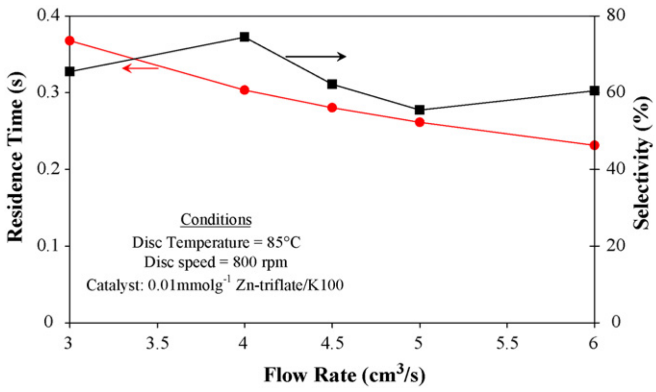


Fig. 16. Effect of reactant flow rate on residence time and selectivity at disc speed of 800 rpm for Catalyst 2.

In sharp contrast to Catalysts 1 and 3, Catalyst 2 exhibits a maximum selectivity at an optimum residence time for each flow rate tested as illustrated in Fig. 15 for the whole range of disc speeds studied (200–1500 rpm). Optimal residence times are seen to be in the range 0.2–0.5 s for flow rates in the range 4–6 cm^3/s. These effects can be more clearly observed for a selected disc speed of 800 rpm in Fig. 16 where a maximum selectivity of 74% is achieved at the optimal flow rate of 4 cm^3/s.

Furthermore, it is apparent from Fig. 17 that the reaction using Catalyst 2 is slower than that with the Catalysts 1 and 3 as much longer residence times (more than four times) are required for 80% conversion to be reached. It can be predicted from Fig. 17 that for complete conversion, residence times of over 1 s would be required.

From the analysis of the selectivity and conversion results for all catalysts, the residence time on the spinning disc has a profound effect on each parameter. Generally, it can be said that for high selectivity, residence time has to be kept short which has an adverse effect on the level of reactant conversion attained. The SDR conditions for achieving maximum selectivity towards the desired campholenic aldehyde for each of the catalysts at the selected operating temperatures are presented in Table 1.

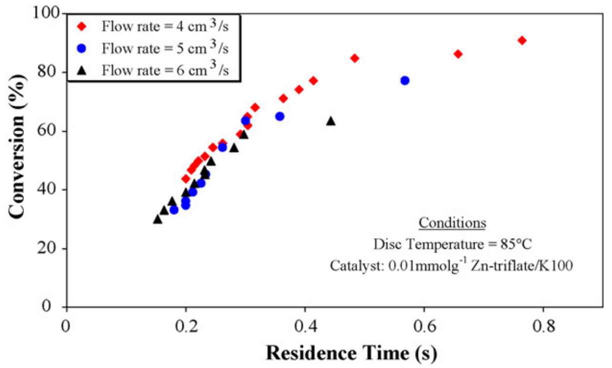


Fig. 17. Effect of residence time on conversion for Catalyst 2.

Table 1

Optimal SDR conditions for each catalyst at selected operating temperatures for achieving maximum selectivity

Catalyst	Disc temperature (°C)	Disc speed (rpm)	Feed flow rate (cm^3/s)	Conversion (%)	Selectivity (%)
1	85	1500	6	77	62
2	85	850	4	59	83
3	45	1500	6	85	75

3.3. Mixing and shear rates in SDR film

It has long been recognised that surface waves play an important role in enhancing mixing in thin films which was initially established for thin films flowing on inclined surfaces under gravity [21]. Significant improvements in heat and mass transfer rates for thin liquid films on a rotating disc under the action of acceleration fields much stronger than the gravitational field have also been reported [22–24]. The level of mixing in the film may also be quantified by the shear rate developed within the film as it flows across the rotating disc surface [13].

Referring to Fig. 3, the shear rate in radial direction $\dot{\gamma}$ is formed by the two velocity gradients:

$$\dot{\gamma}(r,z) = \frac{\partial v}{\partial z} + \frac{\partial \varpi}{\partial z} \tag{4}$$

but since the axial velocity component ϖ is very small, $\dot{\gamma}$ can be expressed as [19]:

$$\dot{\gamma}(r,z) \approx \frac{\partial v}{\partial z} = \left(\frac{3Q\omega^4 r}{2\pi\nu^2}\right)^{1/3}\left(1-\left(\frac{z}{\delta}\right)\right) \tag{5}$$

From Eq. (5) it can be seen that the shear rate is zero when $z=\delta$, it linearly increases with decreasing axial co-ordinate z and has a maximum value at the surface of the rotating disc. Furthermore, it increases in radial direction from the centre to the rim of the rotating disc.

Using Eq. (5), shear rates on the SDR can be calculated at various (r, z) positions. Fig. 18 gives values of shear rates across the disc surface very close to the surface ($z \approx 0$) using the flow rate of 6 cm^3/s.

An increase in disc speed is accompanied by an increase in shear rate and it is also observed that by increasing the speed from 500 rpm to 1500 rpm, shear rate rises by almost an order of magnitude. With the SDR used in this study, shear rates as high as $7.4 \times 10^5\ \text{s}^{-1}$ may be achieved at the edge of the 200 mm diameter disc at disc speeds of 1500 rpm. An arithmetic mean of the shear rate at the inlet and outlet radial positions can be calculated to give an average shear rate across the whole disc surface. Fig. 19 shows that increases in the disc rotational speed and reactant flow rate result in shorter residence times and higher

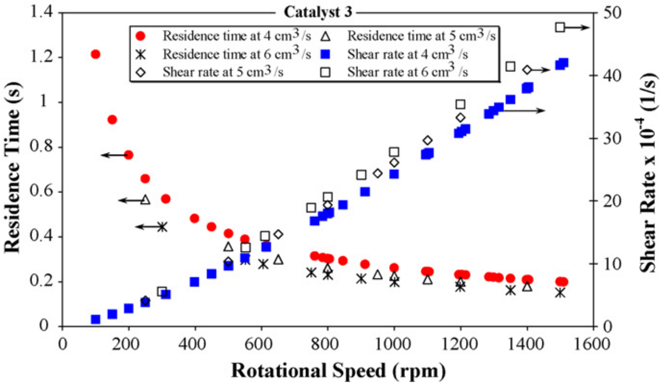
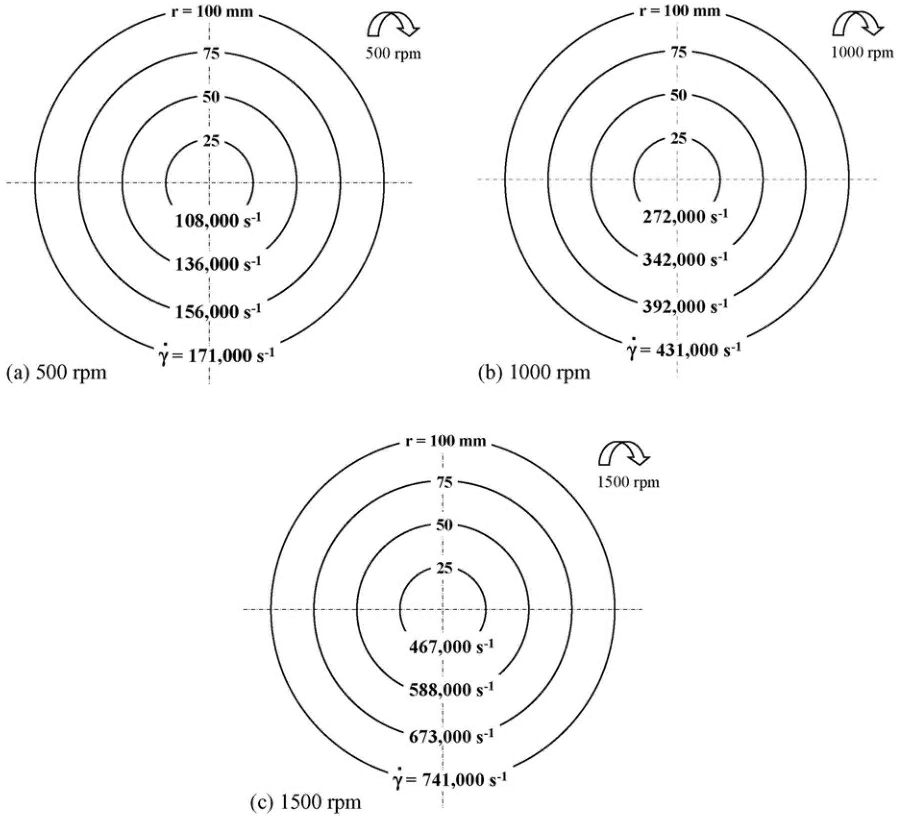


Fig. 19. Residence time and shear rate dependence on rotational speed (Catalyst 3).



(a) 500 rpm

(b) 1000 rpm

(c) 1500 rpm

Fig. 18. Shear rates profile across the disc surface at reactant flow rate of 6 cm^3/s and various disc speeds.

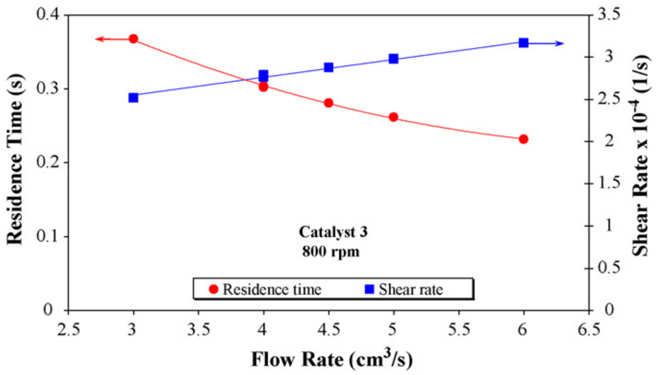


Fig. 20. Residence time and shear rate dependence on flow rates.

shear rates on the SDR. This can be observed more clearly in Fig. 20 for a fixed rotational speed of 800 rpm.

An analysis of the average shear rate effects on the conversion and selectivity results achieved in the SDR reveals opposite trends in the effects of the observed shear rate on these parameters. Overall, high conversion is generally achieved at low shear rates whilst high selectivities are obtained under conditions of high shear rates as seen in Figs. 21 and 22 for Catalyst 1.

The same effect of shear rates on conversion is observed for all three catalysts, although lower conversions were achieved when using Catalyst 2 (as seen in Fig. 23). This showed that by increasing shear rate and hence mixing the reaction rate did not improve and therefore it was the reaction time that was a controlling parameter in this reaction and not the mixing.

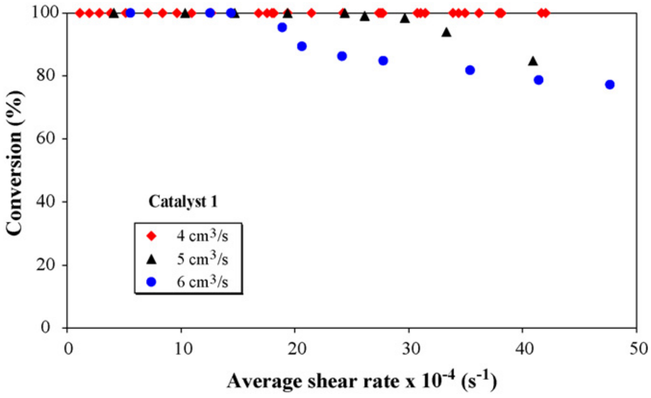


Fig. 21. Effect of average shear rate on conversion of α-pinene oxide in one disc pass (Catalyst 1).

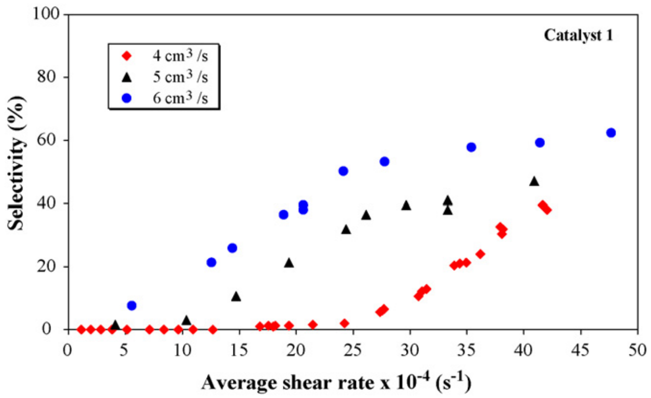


Fig. 22. Effect of average shear rate on selectivity towards campholenic aldehyde in one disc pass (Catalyst 1).

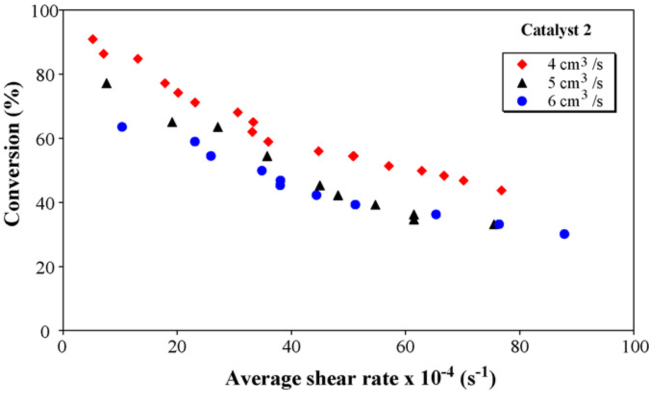


Fig. 23. Effect of average shear rate on conversion of α-pinene oxide in one disc pass (Catalyst 2).

A peculiar effect on selectivity of Catalyst 2 (Fig. 24) is observed in comparison to the other two catalysts. An initial increase in selectivity with decreasing shear rate is noticeable until an optimal shear rate is reached beyond which selectivity drops. This can be explained by considering the two separate “regions” in Fig. 24, lower shear rates (up to the optimum) and higher shear rates (from the optimum onwards). In the region of lower shear rates (where the conversion is higher) the balance between the two opposing reactions (the rate of the formation and the rate of consumption of campholenic aldehyde) goes in favour of the consumption of the aldehyde, which reduces the amount of aldehyde in the final product mixture. In other words, the more reactant is consumed, there are more free active sites available on the catalyst for the product species so consecutive reaction could proceed. This holds true for the other two catalysts where the conversion is much higher and the subsequent trend of lower selectivities is not seen. In the region of lower shear rates there is no time for a consecutive reaction to proceed and all the aldehyde produced mainly stays in the product mixture. The initial rate of formation of campholenic aldehyde when using Catalyst 2 (when conversion is at its lowest) is accelerated

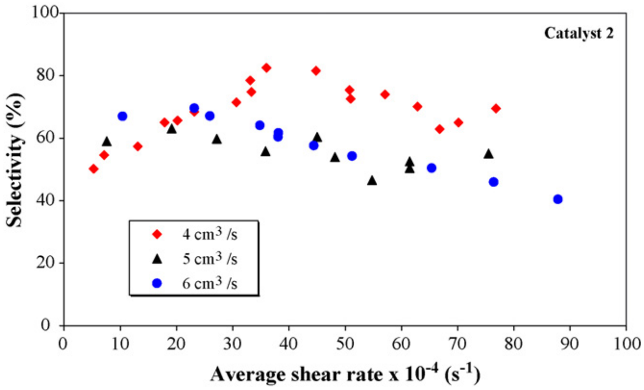


Fig. 24. Effect of average shear rate on selectivity towards campholenic aldehyde in one disc pass (Catalyst 2).

with time, hence lower selectivity is observed at the beginning of reaction. As the rate of reactant consumption accelerates, the rate of formation of aldehyde speeds up, compared to other parallel reactions taking place.

It is interesting to note that an optimum selectivity is also observed in batch reactions using all three catalysts as will be discussed later. The difference with the SDR process is that consumption of aldehyde starts much sooner in the SDR than in a batch reactor as a result of: (a) more catalyst being used in a SDR more efficiently and (b) faster transport rates to/from the active sites. Our experimental results suggest that, if the residence time in the SDR could be lowered below the currently achievable minimum of 0.2 s (by using a much smaller disc in combination with low disc speeds and low flow rates for instance), an optimum selectivity could be expected for Catalysts 1 and 3.

The observed effects of residence times and shear rates on conversion and selectivity of each catalyst in one pass in the SDR may be summarised as follows:

(1) Minimum residence times of 0.2 s are required for complete consumption of α-pinene oxide when Catalysts 1 and 3 are used at their selected operating temperatures of 85 °C and 45 °C, respectively, indicating that reaction is very fast with these catalysts. At residence times shorter than 0.2 s, there is a marginal decrease in conversion. With an increase in shear rate at higher disc speeds and higher flow rates, no discernible improvement in conversion is seen. These results demonstrate that conversion is controlled solely by residence time and therefore the consumption of α-pinene oxide is kinetically controlled rather than mixing controlled with Catalysts 1 and 3. Furthermore, as reactions with Catalysts 1 and 3 are so fast and no diffusion or mixing limitations are apparent, conditions in the SDR film may be said to give rise to high intensity mixing leading to high rates of mass transfer of the reacting species both within the porous support structure and in the external bulk fluid environment.

(2) A decrease in residence time to below 0.3 s causes a significant rise in selectivity towards campholenic aldehyde for both Catalysts 1 and 3. The shorter the residence time, the less likely it is for the consecutive reaction, which consumes the desired campholenic aldehyde, to proceed to a significant extent, hence the high selectivity. It may also be argued that the high shear rates achieved under conditions that give rise to short residence times (i.e. high disc speed and high flow rates) may enhance the desired reaction. However, it is reasonable to expect that the consecutive reaction may be similarly enhanced in which case the selectivity would be reduced. Hence, we believe that the residence time of the liquid on the disc has a greater influence on selectivity of the catalyst than the shear rate developed within the film.

(3) Catalyst 2 exhibits much slower reaction rates than Catalyst 1 and 3 in spite of the high operating temperature of 85 °C. Residence times in excess of 1 s are required for 100% conversion which could not be attained at the disc speeds and flow rates considered in this study. Conversion is seen to decrease with the increase of shear rates, thus conversion is residence time dependent (kinetically controlled) and not shear rate dependent. Shear rates are already very high in SDR, so there are no mixing limitations imposed on the reaction. Having a consecutive reaction taking place almost at the same time as the main reaction clearly suggests that any diffusion limitations would appear to be minimised in SDR environment.

(4) In sharp contrast to Catalysts 1 and 3, highest selectivity is achieved for Catalyst 2 at an optimal residence time in the SDR observed for each flow rate tested. At these optimal residence times, conversions of 50–55% are obtained. This would seem to suggest that a direct link between conversion and selectivity exists whereby consecutive reactions only kick in (and therefore selectivity drops) when a certain consumption level of the α-pinene oxide is attained. It is likely that similar effects exist with Catalysts 1 and 3, but because these reactions are so fast, the effects on selectivity may not be immediately apparent.

3.4. SDR multipass arrangement

In an attempt to improve the performance of the SDR at 25 °C for Catalysts 1 and 2 and 85 °C for Catalyst 3 where low conversions were achieved in one disc pass as seen in Fig. 4, the effect of multiple passes in the SDR was evaluated. All catalysts showed an improvement in conversion of 10–20% after two and three passes (Fig. 25). Whilst a dramatic improvement in selectivity is also seen with Catalyst 1 (Fig. 26) after the second and third passes (from 0% to 50% after the second pass and to 76% after the third pass), Catalyst 2 and 3 show only a minor change in selectivity. It is particularly interesting to note the considerable drop in selectivity after the third pass with Catalyst 3 when complete conversion of the α-pinene oxide is achieved. As discussed previously, consecutive reactions involving the campholenic aldehyde are promoted during the longer residence times after three disc passes in the absence of α-pinene oxide as the primary reacting species.

With each additional pass in the SDR, the overall residence time is increased. Under the operating conditions of 500 rpm and 4 cm^3/s, each pass on the rotating disc is equivalent to 0.4 s of

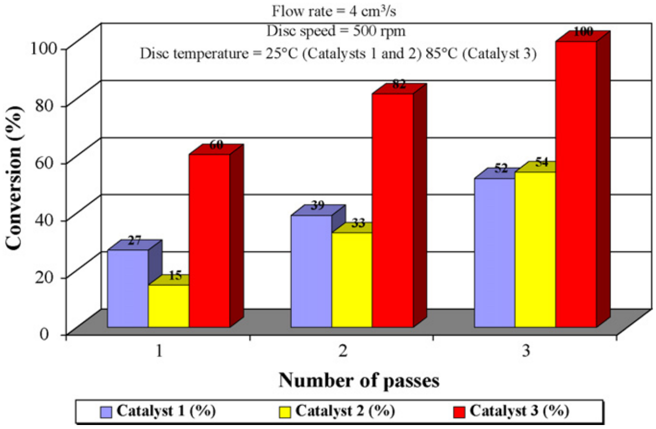


Fig. 25. Conversion change for all catalysts after three passes in SDR.

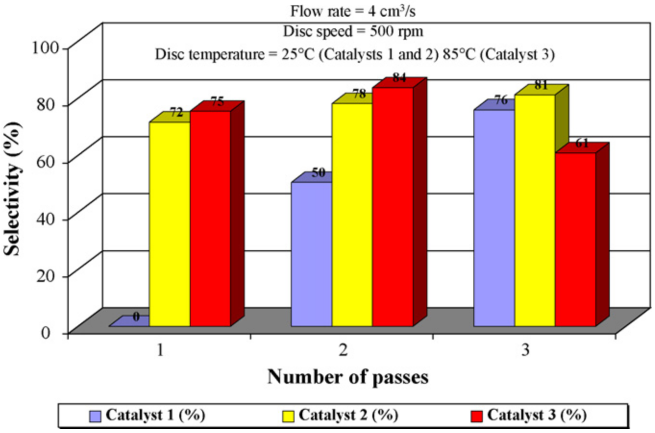


Fig. 26. Selectivity change for all catalysts after three passes in SDR.

residence time. Hence, a total of up to 1.2 s of residence time can be built up over three disc passes. It has to be mentioned that at lower temperatures (i.e. 25 °C) residence times required for a full conversion are much longer than at 45 °C or 85 °C which were tested in previous sections. Once again, these results highlight that residence time is a critical parameter in the catalytic isomerisation reaction in the SDR. Optimisation of conversion and selectivity relies heavily on the contact time between the reactant and the catalyst at a given temperature. Control of the residence time may be achieved by manipulating the SDR parameters such as disc speed and feed flow rate in combination with multiple pass arrangement over the disc surface.

3.5. Regression analysis

3.5.1. Conversion

Conversion data obtained for one pass on the spinning disc for each catalyst were analysed using Microsoft Excel Regression Analysis Tool. Assuming conversion, x_A, can be represented by

$$x_A = I(N)^a(Q)^b \tag{6}$$

or in linearised form:

$$\ln x_A = \ln I + a \ln N + b \ln Q \tag{7}$$

where N is the rotational speed (rpm) of the disc, Q the liquid feed flow rate (cm^3/s) and I, a, b and c are the constants.

Regression analysis results are presented in Table 2.

Table 2
Regression analysis results (conversion)

	Catalyst 1	Catalyst 2	Catalyst 3
$\ln I$	2.81	3.51	0.80
I	16.59	33.5	2.22
a	−0.26	−0.44	−0.08
b	−0.66	−0.77	−0.17
R^2	0.89	0.90	0.64
S.E.	0.03	0.09	0.02

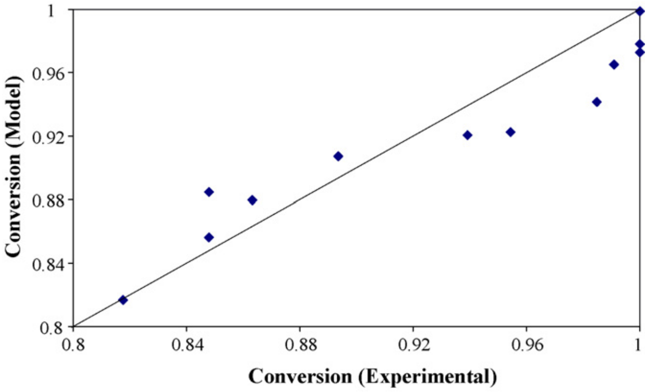


Fig. 27. Evaluation of developed conversion model for Catalyst 1.

The model equations which describe conversion on the spinning disc reactor can be written as

$$\text{Catayst 1}: \quad x_A = 16.59\frac{1}{N^{0.26}Q^{0.66}} \tag{8}$$

$$\text{Catalyst 2}: \quad x_A = 33.53\frac{1}{N^{0.44}Q^{0.77}} \tag{9}$$

$$\text{Catalyst 3}: \quad x_A = 2.22\frac{1}{N^{0.08}Q^{0.17}} \tag{10}$$

The model equations are applicable under the following conditions: $x_A < 1$, $150\,\text{rpm} \le N \le 1500\,\text{rpm}$, $3\,\text{cm}^3/\text{s} \le Q \le 6\,\text{cm}^3/\text{s}$.

In order to check the model equations, x_A values were calculated using (8)–(10) and compared to experimental values by plotting predicted values against experimental data. These graphs are presented in Figs. 27–29 for Catalysts 1–3, respectively.

Model data for all catalysts are generally in reasonable agreement with experimental values, especially for Catalyst 2. Overall, the empirical model equations confirm that decrease of disc rotational speed and feed flow rate (hence the increase of residence time) leads to higher conversions of α-pinene oxide.

3.5.2. Selectivity

The data for selectivity of each catalyst towards campholenic aldehyde were analysed using the same methodology as for

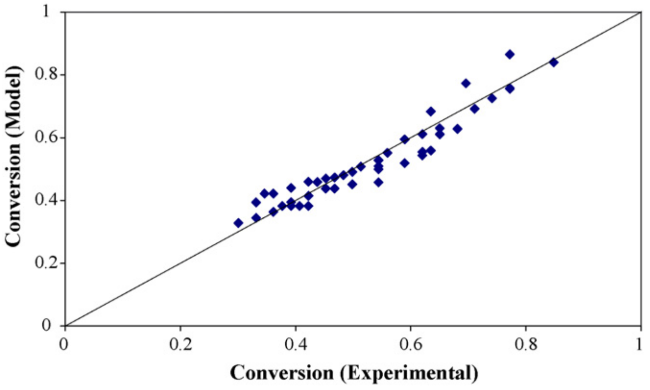


Fig. 28. Evaluation of developed conversion model for Catalyst 2.

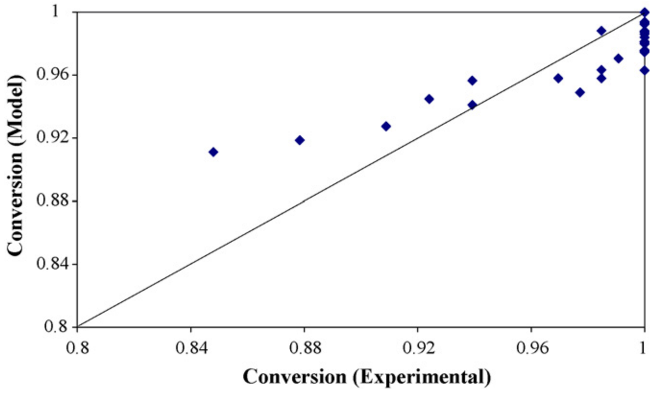


Fig. 29. Evaluation of developed conversion model for Catalyst 3.

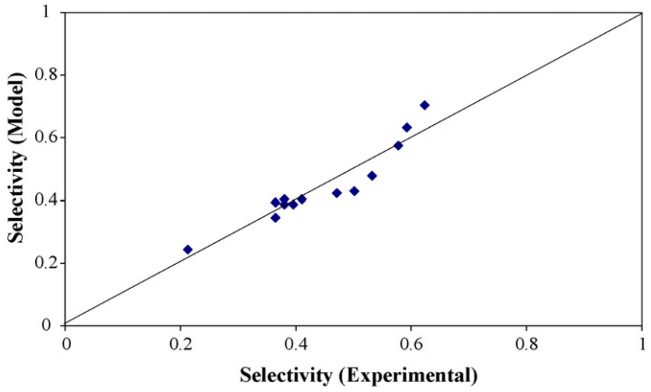


Fig. 30. Evaluation of developed selectivity model for Catalyst 1.

conversion. It is assumed that selectivity, σ_A, is dependent on rotational speed, flow rate and conversion, x_A, according to Eq. (11):

$$\sigma_A = K(N)^c(Q)^d(x_A)^e \tag{11}$$

or in linearised form:

$$\ln\sigma_A = \ln K + c\ln N + d\ln Q + e\ln x_A \tag{12}$$

where K, c, d and e are the constants.

Regression analysis results are presented in Table 3.The model equations that link selectivity with the spinning disc reactor operating parameters can therefore be written as

$$\text{Catalyst 1}: \quad \sigma_A = 3.05\times10^{-7}N^{1.3}Q^{3.09}x_A^{1.52} \tag{13}$$

$$\text{Catalyst 2}: \quad \sigma_A = 3.65\times10^{-2}N^{0.44}Q^{0.34}x_A^{1.01} \tag{14}$$

$$\text{Catalyst 3}: \quad \sigma_A = 6.13\times10^{-6}N^{1.13}Q^{2.17}x_A^{2.19} \tag{15}$$

The model equations are applicable under the following conditions: $\sigma > 0$, $150\,\text{rpm} \leq N \leq 1500\,\text{rpm}$, $3\,\text{cm}^3/\text{s} \leq Q \leq 6\,\text{cm}^3/\text{s}$.

The developed empirical models confirm the experimentally observed opposite effect that disc speed and reactant flow rate has on conversion and selectivity. Whilst conversion is inversely proportional to both disc rotational speed and feed flow rate, it can be seen from Eqs. (13)–(15) that selectivity is directly proportional to these parameters (and hence inversely proportional to the residence time according to Eq. (3)).

As for conversion, the model equations were tested by calculating σ_A values using Eqs. (13)–(15) and compared to experimental values by plotting predicted values against experimental data. These graphs can be seen in Figs. 30–32 for Catalysts 1–3, respectively.

Table 3
Regression analysis results (selectivity)

	Catalyst 1	Catalyst 2	Catalyst 3
$\ln K$	−15.00	−3.31	−12.00
K	3.05×10^{-7}	3.65×10^{-2}	6.13×10^{-6}
c	1.30	0.44	1.13
d	3.09	0.34	2.17
e	1.52	1.01	2.19
R^2	0.90	0.57	0.95
S.E.	0.10	0.11	0.08

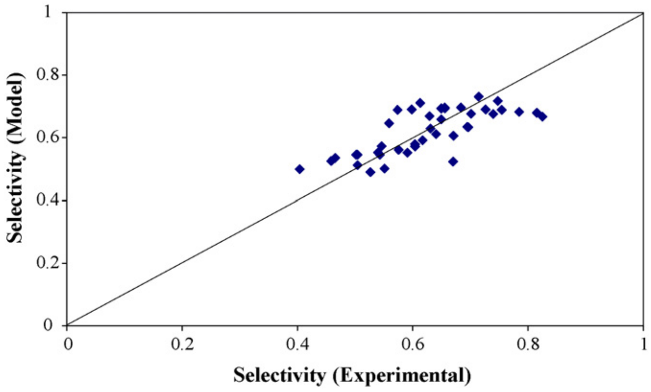


Fig. 31. Evaluation of developed selectivity model for Catalyst 2.

3.6. Batch reactions

The conversion results from the batch reactions for all catalysts are presented in Fig. 33. The slowest rate of conversion is observed with Catalyst 2, as already identified from the SDR experiments. It is also seen in Fig. 34 that for all catalysts, there is an initial increase of selectivity in the first stage of the reaction.

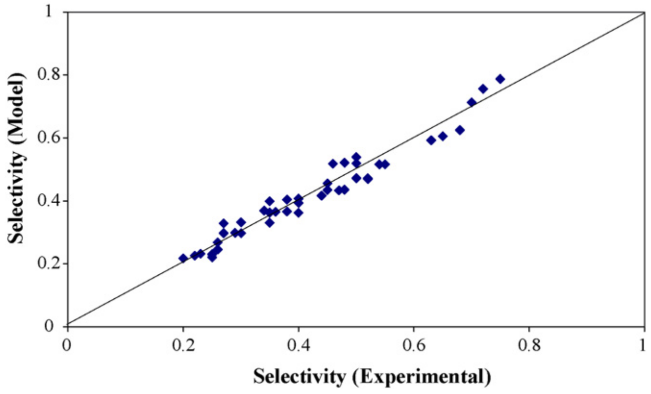


Fig. 32. Evaluation of developed selectivity model for Catalyst 3.

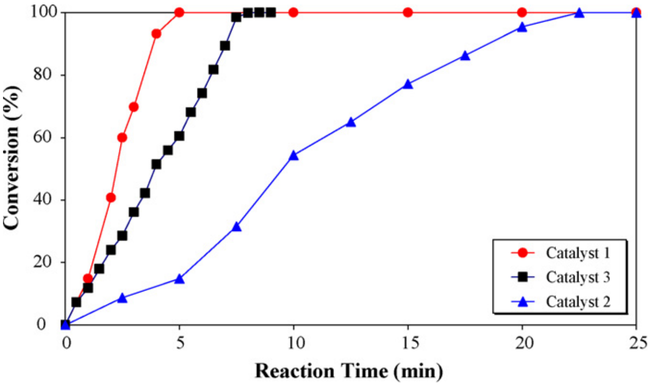


Fig. 33. Conversion results obtained in a batch reactor for all catalysts at operating temperature of 85 °C for Catalysts 1 and 2 and 45 °C for Catalyst 3.

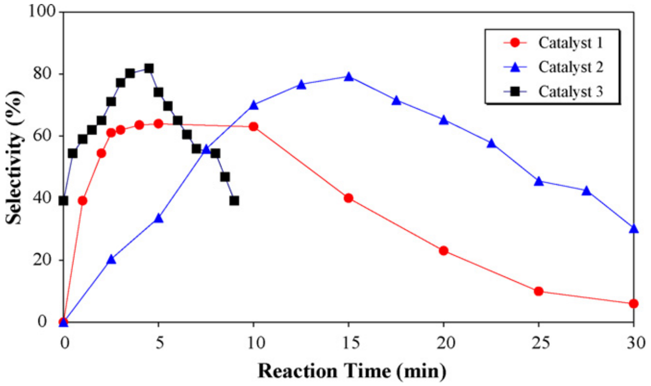


Fig. 34. Selectivity results obtained in a batch reactor for all catalysts at operating temperature of 85 °C for Catalysts 1 and 2 and 45 °C for Catalyst 3.

Beyond a certain residence time in the batch which is catalyst dependent, selectivity drops. In order to understand more clearly these residence time effects on selectivity, it is necessary to study the combined influences of conversion and residence time as shown in Fig. 35 for Catalyst 1. It is observed that selectivity towards the campholenic aldehyde reaches an optimum value at a certain residence time in the batch vessel. This suggests that a consecutive reaction which consumes the desired product sets in beyond this point in the process. Initially, the rearrangement of α-pinene oxide proceeds at a faster rate than the isomerisation of campholenic aldehyde due to the high concentration of α-pinene oxide in the reaction mixture. As more campholenic aldehyde is formed and no α-pinene oxide is left the consecutive reaction takes over and consumes the aldehyde present, causing the selectivity to drop. It would therefore appear that, when very high conversions are achieved on the disc and selectivity is very low, the consecutive reaction step has already consumed a large amount of the campholenic aldehyde. The final product collected from the disc in such cases would be equivalent to that achieved somewhere around Point B (or after Point B) in a batch process.

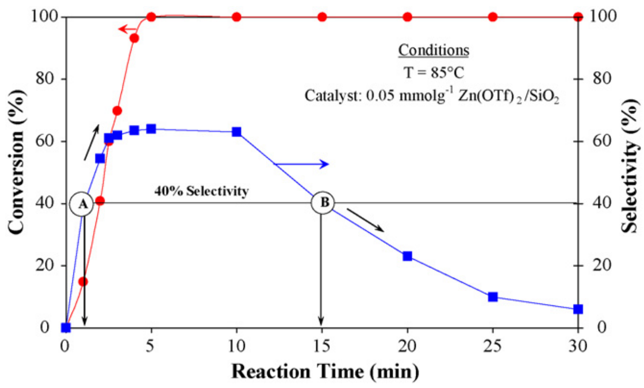


Fig. 35. Conversion and selectivity profiles for the catalytic rearrangement of α-pinene oxide in batch reactor using Catalyst 1.

3.7. Comparison of SDR and batch processes

We have identified important advantages in the SDR process compared to the batch process for the heterogeneous catalytic formation of campholenic aldehyde from α-pinene oxide. These are summarised as follows:

- *Reaction rate and selectivity enhancement*: Improved mass transfer rates in the thin film formed on the rotating disc surface allows the catalytic reaction to proceed at its inherent rate. Reaction is completed within half a second in one SDR pass compared to a timescale of at least 5 min in the batch process, representing at least a two-fold increase in the average rate of conversion in the SDR. This enhancement calculation takes into account the higher catalyst concentration in the SDR which amounts to a total of 1.8 g of catalyst/cm^3 of solution (assuming that the minimum volume of material present at any one time on the disc surface is 0.45 cm^3 on the basis of a reactant flow rate of 3 cm^3/s and a disc residence time of 0.15 s) in comparison with a catalyst concentration of 0.002 g/cm^3 in the batch process. We also assume that by immobilising the catalyst on the disc surface, only half of the active sites are available for reaction. Furthermore, high selectivity in the SDR is encouraged by the short and controllable residence times achieved on the disc which severely limits the extent of the consecutive reactions taking place at high conversions.
- *Catalyst activity*: Catalyst deactivation by product accumulation and blocking of active sites was a problem encountered in batch processes as reported by Wilson and Clark [9]. Catalyst activity in the SDR, on the other hand, can be prolonged as a result of the high shear rates prevailing in the thin film shifting product molecules away from active sites. Our re-use studies indicated that conversion and selectivity remain unchanged when each catalyst was tested over an experimental period of 1 month when 15 separate experimental runs were performed under a fixed set of operating conditions (Figs. 36 and 37).
- *Catalyst immobilisation*: With the catalyst fixed onto the surface of the rotating disc, no downstream catalyst separation from the product mixture is required. Leaching of catalyst from the disc surface was not an issue as confirmed by the observation that no further reaction took place in the collected samples during storage. Although physical immobilisation may be possible in the batch reactor, it is expected that this may give rise to severe diffusion limitations under the

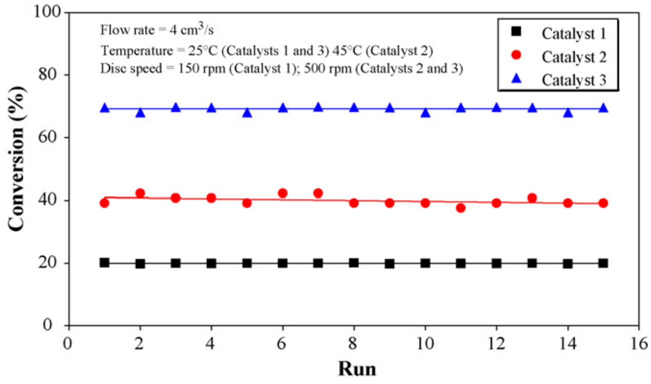


Fig. 36. Reproducibility and re-usability of catalysts in SDR: conversion data.

comparatively poor mixing conditions prevailing in the batch reaction environment.

3.8. *Catalyst loading and support*

The difference in performance of each of the catalysts used in this study may be explained in terms of the catalyst loading and the types of support used. As expected, the loading of the catalyst has significant influence on the reaction rate. When tested in batch reactions, higher loadings of the zinc triflate catalyst (typically 2 mmol/g) result in a very fast, uncontrollable reaction, with complete conversion being attained in less than 30 s [9]. On the other hand, lower loadings (typically 0.05 or 0.01 mmol/g) result in reaction times of around 60 min. In the present study, lower catalyst loadings (0.05 mmol/g loading for Catalysts 1 and 3 and 0.01 mmol/g for Catalyst 2) were chosen in order to deliberately slow down the reaction in conventional batch systems and to better assess any rate enhancements in the SDR. The slower rate of reaction consistently observed in the SDR with Catalyst 2 is clearly attributable to its lower catalyst loading whilst the fast reactions with Catalysts 1 and 3 are the result of their higher loading. These effects can clearly be seen for the batch reactions in Fig. 33: using Catalyst 1 reaction proceeds to completion within 5 min, whilst using Catalyst 2 it takes more than 20 min for the reaction to achieve 100% conversion at 85 °C.

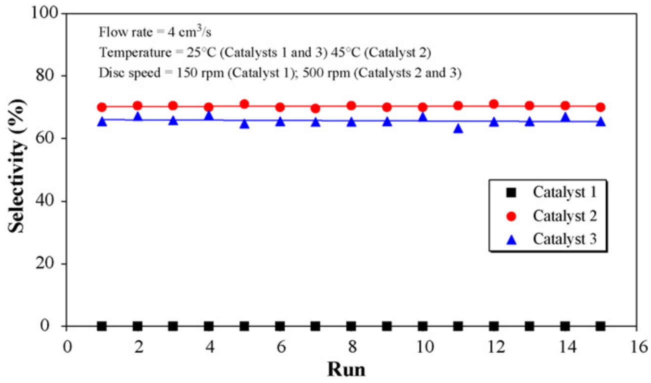


Fig. 37. Reproducibility and re-usability of catalysts in SDR: selectivity data.

The main difference between the different types of silica supports was their pore size as previously reported in the detailed characterisation of each catalyst used in this study [9]. The porous supports can be regarded as a complex maze which may be approximated as uniformly sized pores for the purpose of mathematical modelling of mass transport inside the particles. Diffusion limitations in a porous catalyst may have an important effect on the overall reaction rate. Both the size of the pores in the silica support and the tortuosity of the pore structure [25] are therefore critical in determining the extent of limitations in the diffusion process. With its more regular and smaller pore (24 Å pore size) structure, HMS_{24} is expected to allow more rapid diffusion of the reactants to the active sites of the catalyst embedded within the pore and therefore give faster reaction rates in comparison with the other two supports silica (K100) and silica (K60) of 100 Å and 60 Å pore sizes, respectively. Enhanced in-pore catalytic activity and molecular diffusion are also expected to result in better control of selectivity as the desired product species can rapidly diffuse away from the active site thereby reducing the likelihood of consecutive reactions [26]. The results in the present study using the SDR confirms this view, since Catalyst 3, which is based on HMS_{24} as support, gave the best performance both in terms of conversion and selectivity.

4. Conclusions

The spinning disc reactor (SDR) has been successfully used to perform the heterogeneously catalysed isomerisation of α-pinene oxide using silica-supported zinc triflate catalysts of varying catalyst loadings and pore sizes of support. The overall rate of reaction in the SDR at 85 °C was doubled in comparison to reaction in a batch reactor [16], due to an intense mixing mechanism within the thin film in a SDR. Additionally, the selectivities towards campholenic aldehyde are not only as high those reported in literature for batch processes, but are also more easily controlled by residence time in the SDR through disc speed and reactant flow rate manipulation.

It was generally observed that high conversions of α-pinene oxide achieved in one pass in the SDR compromised the level of selectivity towards campholenic aldehyde which was attributed to consecutive reactions setting in and using up the desired campholenic aldehyde. This was further emphasised by the conventional batch process where selectivity towards campholenic aldehyde dropped significantly at 100% conversions of the α-pinene oxide with longer reaction times. Enhancement in selectivity was seen when residence times in the SDR were kept short. Generally, a rise in selectivity from 0 to 75% was achieved by increasing the disc speed and increasing the reactant flow rate on the disc which have the combined effect of reducing the residence time.

By using a batch reactor there is a need for an additional separation step (filtering of the catalyst from the product mixture) after the reaction has finished, which usually takes about 30–60 min. In contrast, not only are reaction times very low in the SDR (in order of seconds, rather than minutes or hours), but, as importantly, there is no need for the catalyst to be separated from the product as it is immobilised on the surface of the SDR.

The use of spinning disc surfaces is further associated with several other important benefits. It is envisaged that exceptionally good heat transfer characteristics that can be achieved on the rotating disc will allow the use of much smaller discs, hence in case of isomerisation reaction described here it will be possible to achieve even better selectivities. Furthermore, as the process described will be operated under continuous mode with reaction times drastically reduced, the amount of inventory in the reactor at any given time will be small and as a result the intrinsic safety of the process will be improved. This applies to all processes carried out in spinning disc reactors. Other potential benefit to be gained from the proposed process, apart from enhanced reaction rate and an improvement in intrinsic safety of the process, include minimal risk of thermal runaways at high operating temperatures due to short residence times and enhanced heat removal rates.

We hope that we have demonstrated that SDR process provide a greener, flexible environment for the α-pinene oxide rearrangement reaction with no catalyst losses and no inorganic waste stream.

Acknowledgements

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