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Use of a rotating disc reactor to investigate the heterogeneously catalysed oxidation of cinnamyl alcohol in toluene and ionic liquids

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Abstract

To evaluate the effect of mass transfer limitations in the three-phase oxidation of cinnamyl alcohol carried out in toluene and an ionic liquid (1-butyl-3-methyl-imidazolium *bis*(trifluoromethylsulphonyl)imide), studies have been performed in a rotating disc reactor and compared with those carried out in a stirred tank reactor where mass transfer effects are considered negligible. High catalyst efficiencies are found in the stirred tank reactor with the use of both ionic liquid and toluene, although there is a decrease in rate for the ionic liquid reactions. In contrast, internal pore diffusion limits the reaction in both solvents in the rotating disc reactor. This mass transfer resistance reduces the problem of overoxidation of the metal surface when the reaction is carried out in toluene, leading to significantly higher rates of reaction than expected, although at the cost of decreased selectivity.

Keywords: Rotating disc reactor; Heterogeneous; Oxidation; Cinnamyl alcohol; Ionic liquid; Mass transfer

1. Introduction

The role of any reactor for use with heterogeneous catalysts is simply to expose an active catalytic area to the reactants at optimised concentrations and temperature. In addition, it must also provide a means by which heat can be removed from or added to the system. Commonly, trickle-bed or slurry reactors are used in industry to perform gas–liquid–solid reactions with heterogeneous catalysts; however, it can be difficult to obtain the necessary engineering data required for scale-up purposes or even to identify the controlling mechanisms of the reaction from these reactor systems. This is due in part to limitations on the sizes of catalyst particles but also to the uneven wetting in the trickle-bed reactors. Three-phase reactions are often limited by the transport of either the liquid or gas-phase reagent to the catalyst surface by one of a number of diffusion resistances through boundaries such as gas to liquid, liquid to solid, and internal diffusion through the pores. Thin-film reactors have been employed to reduce many of these resistances to a minimum, allowing for design information to be extracted, giving the possibility of total reactor optimisation. A variety of designs have been reported for chemical synthesis, including spinning disc [1], falling or rising film [2], wiped film [3], and monolith froth reactors [4]. In general, these employ thin liquid films in contact with a heated surface to permit good thermal and mass transfer characteristics.

Thin-film reactors in the form of rotating biological contactors (RBCs) have been studied extensively in the area of water treatment and are applied on a large scale industrially for aerobic and anoxic destruction of aqueous organics [5]. The RBC operates on the principle of a series of partially submerged discs, covered with organisms, supported on a horizontal shaft, which rotate through the wastewater, drawing a thin film on the surface into the air, where the water becomes aerated, allowing the organisms to degrade

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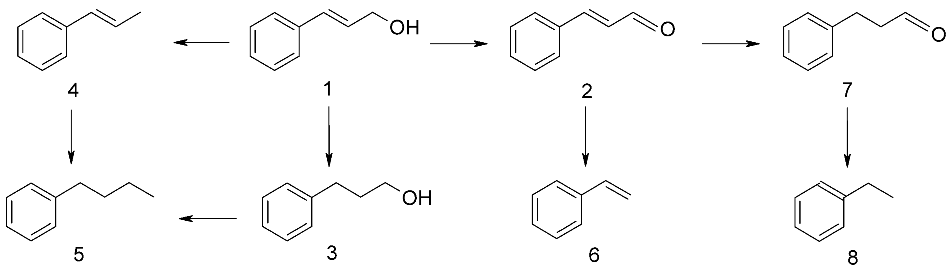


Scheme 1. Schematic of cinnamyl alcohol oxidation pathways.

the waste. They offer a number of advantages over a sludge process, namely high surface area, low power consumption, and shear over the discs as they pass through the water, which prevents clogging [6]. This reactor setup has also been examined for air stripping of hydrocarbons from water [7]. More recently, Dionysiou and co-workers and Hamill et al. have demonstrated the applicability of a rotating disc reactor to photocatalytic degradation of organics in water in a similar design [8,9]. In this case, the vertical catalyst-supporting discs are half-immersed in a bulk liquid reaction medium, and, on rotation, the catalyst disc entrains a thin film of liquid into the gas phase, which is irradiated by UV light where the reaction occurs. Because of its large-scale application, a good understanding of the hydrodynamics and flow characteristics of the rotating disc reactor has been developed [10].

For this paper, we used a similar rotating disc reactor design to allow the study of the kinetics of the selective oxidation of cinnamyl alcohol (Scheme 1). With this arrangement it is possible to extract individual mass transfer effects in such three-phase reactions simply through variation of the experimental parameters. For example, when the rotation speed of the disc is varied, the mixing in the bulk liquid and in the film is changed, allowing the liquid-to-solid mass transfer to be studied. The rotation speed also governs the thickness of the liquid film, which allows control over the gas-to-liquid mass transport. By a change in the number of discs, either the catalyst/substrate ratio can be changed, or, if a blank disc is used, the mixing in the bulk liquid but not within the film can be controlled. Therefore, the Reynolds number of the system and thus the liquid-to-solid mass transfer of the system can be changed without a change in the gas-to-liquid mass transfer. In addition, the more conventional experimental parameters, such as alcohol concentration, temperature, and gas pressure, can readily be varied.

Selective oxidation reactions have been studied extensively with the use of platinum-group metal heterogeneous catalysts in the liquid phase with oxygen [11]. In many cases, the solvent of choice has been water, with the aim of oxidation of alcohols to aldehydes without overoxidation to carboxylic acids. A wide range of substrates have been investigated, including aromatic alcohols and polyols. In particular, Baiker et al. [12,13] and Lee et al. [14,15] have reported the oxidation of cinnamyl alcohol in organic media. The selective oxidation of α,β-unsaturated alcohols is an important step in the synthesis of flavours and fragrances, and the reaction can produce a large number of by-products. Baiker et al. have studied the mechanistic aspects of the oxidation of cinnamyl alcohol over Pd/Al_2O_3 and Pd/Pt/Bi/C in detail and have demonstrated that the presence of oxygen is most probably only required for cleaning the catalyst surface of by-products rather than taking a primary role in the reaction [13].

To date, neither oxidation reactions nor heterogeneously catalysed reactions have been studied extensively in ionic liquids [16–27]. The limited number of examples of homogeneously and heterogeneously catalysed oxidations in ionic liquids have shown high selectivities for a wide range of substrates [23–27]. The study reported herein uses a rotating disc reactor as a system to understand selective oxidation reactions in toluene and ionic liquids over a Pd/Al_2O_3 catalyst to determine mass transfer influences and to evaluate the role of the ionic liquid.

2. Experimental

The catalyst, 5 wt% Pd/Al_2O_3 Johnson Matthey 324, had a BET surface area of 134.3 $m^2\ g^{-1}$ and a metal dispersion of 14%, as determined by CO chemisorption. *trans*-Cinnamyl alcohol and toluene (99%) were obtained from Lancaster and Reidel de Haen, respectively, and used as received. Research-grade gases were supplied by BOC. The ionic liquid, 1-butyl-3-methyl-imidazolium *bis*(trifluoromethylsulphonyl)imide ($[C_4mim][NTf_2]$), was synthesised from $[C_4mim]Br$ by standard preparative procedures described in the literature [28]. The ionic liquid was dried in vacuo at 60 °C for more than 4 h before use and contained < 0.01 wt% water, determined by Karl–Fischer analysis. The density of the ionic liquid and reagent mixtures, used to calculate concentrations, were obtained with an Anton Parr DMA4500 densitometer.

The stirred tank reactor (STR) experiments were carried out in a 50 cm^3 Hazards Evaluation Laboratory autoclave equipped with a gasifying impeller and four baffles. Before reaction, the catalyst was pre-reduced under 1 bar of hydrogen for 20 min at room temperature and, following flushing with nitrogen, was exposed to air. The pretreated catalyst (0.25 g) and solvent (20 cm^3) were placed in the reactor and purged with oxygen until the desired temperature was reached, at which point a concentrated solution of cinnamyl

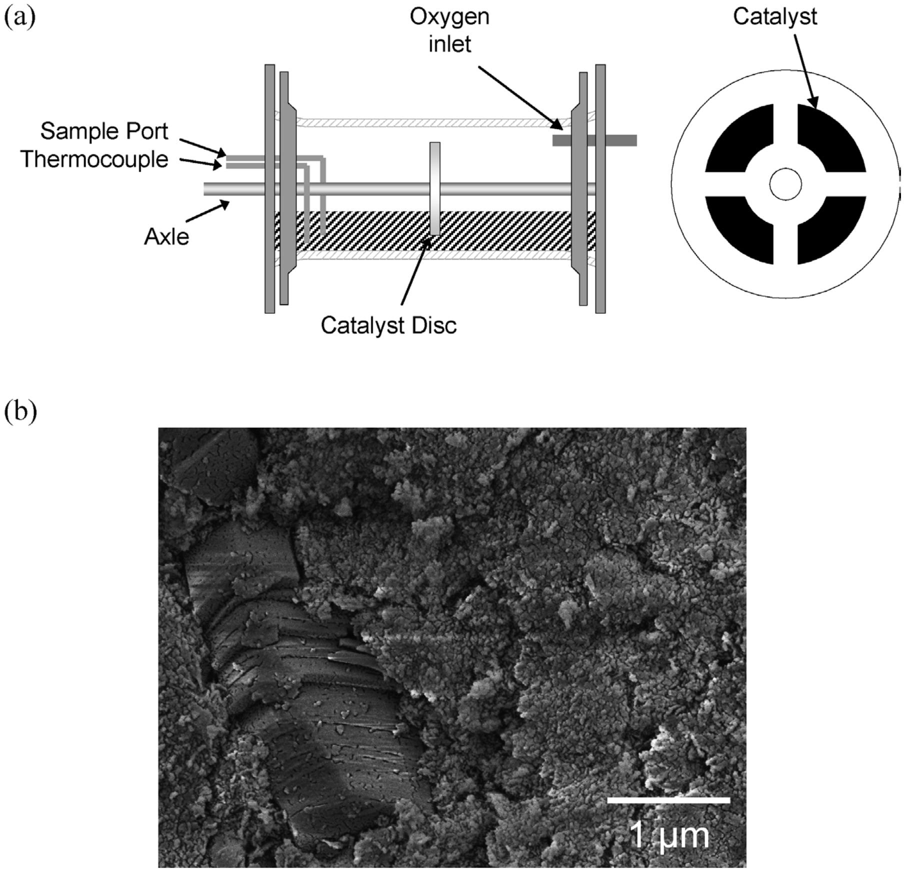


Fig. 1. (a) Schematic diagram of rotating disc reactor and catalyst disc (b) SEM image (magnification: 25,000) of the catalyst pressed into the quadrants.

Table 1
Dimensions of rotating disc reactor

Parameter	
Reactor length	127 mm
Internal diameter	80 mm
Diameter of shaft	10 mm
Diameter of (1.35 mm disc)	72.7 mm
Diameter of (2 and 3 mm discs)	70 mm

alcohol in the solvent (2 cm^3) was added. The reaction was started by rotation of the stirrer at 1000 rpm, and the pressure was maintained throughout with a mass flow controller.

Fig. 1a shows a schematic diagram of the rotating disc reactor and the catalyst disc used in this study; Table 1 summarises the reactor dimensions. The catalyst ($\sim$1 g) was pressed into the quadrants of a stainless-steel disc, at 20 tons of pressure, with a Research and Industrial Instruments Company (RIIC) press; the disc was then supported on a horizontal shaft. Fig. 1b shows an SEM image of the pressed catalyst, taken with a Jeol 6500 FEG scanning electron microscope. Unless otherwise stated, the disc thickness was 1.35 mm. For experiments using discs larger than 1.35 mm, the same mass of catalyst was used and the extra thickness was made up with γ-alumina (Degussa) to ensure a constant substrate/palladium ratio. Variation of the rotation speed of the disc (3.5–496 rpm) was accomplished by the application of a variable voltage (4–24 V) to a Maxon DC motor fitted with one of three gearboxes at stepdown ratios of 6:1, 30:1, or 200:1. The temperature of the reaction mixture was measured in the liquid phase with a thermocouple, and we maintained the temperature of the reactor by immersing the reactor in a thermostatted oil bath up to the liquid level in the reactor. The catalyst pretreatment was performed in the rotating disc reactor by first purging the assembled reactor with dry nitrogen for 10 min and then passing hydrogen at 1 bar and room temperature over the catalyst for 20 min. After reduction, the catalyst was flushed with nitrogen for a further 20 min before the catalyst was exposed to air for 10 min. For reactions in toluene, the prereduction was carried out in the presence of solvent. Because of the low solubility of hydrogen in the ionic liquid and to ensure complete reduction, the catalyst was pretreated in the absence of $[C_4mim][NTf_2]$.

The oxidations were carried out in the RDR by charging the solvent (toluene (170 cm^3) or $[C_4mim][NTf_2]$ (148 cm^3)) into the reactor and purging the liquid and the headspace for 30 min with oxygen at a flow rate of 7 $cm^3\,min^{-1}$ until the reaction temperature was reached. A concentrated solution of the cinnamyl alcohol in toluene (30 cm^3) or $[C_4mim][NTf_2]$ (22 cm^3) was then added, and the reaction was started by rotation of the disc. A constant pressure of oxygen was supplied from a balloon fitted to a port into the head space of the reactor.

All of the rates of reaction are expressed as millimoles of alcohol consumed or aldehyde produced per gram of total catalyst per minute. The turnover frequencies (TOFs) are calculated as moles of alcohol consumed per mole of surface palladium per minute.

The continuous-flow experiments were performed in the RDR by pumping in fresh reaction mixture and removing reaction mixture from the reactor at 100 $cm^3\ h^{-1}$ with two Watson–Marlow 101U peristaltic pumps.

In the case of ionic liquid experiments, the $[C_4mim][NTf_2]$ was recycled after reaction by solvent extraction with diethyl ether until no reagents or products could be observed by either ^{1}H-NMR or Raman spectroscopy. The ionic liquid was dried under vacuum, as described above, before re-use. No detrimental effects were observed on re-use of the ionic liquid. Good reproducibility was found with fresh ionic liquid and fresh catalyst compared with recycled ionic liquid and recycled catalyst. No reaction was observed in the absence of catalyst, in either the fresh or recycled ionic liquid.

Samples were taken periodically and analysed with a Hewlett–Packard 6890 GC fitted with an RTX-5 column (30 m, 0.25-µm diameter). The retention times of the peaks were compared against authentic samples. In the case of organic solvents samples were analysed directly after dilution with diethyl ether. When $[C_4mim][NTf_2]$ was used, the samples were extracted with diethyl ether in a volume ratio of 1:10 (IL/diethyl ether), which was repeated two times, and then the extract phase samples were combined, concentrated, and analysed.

For the catalyst recycle experiments the reaction mixture was removed from the reactor, and the RDR was washed thoroughly with diethyl ether (3×250 cm^3), as the disc was rotated rapidly. Compressed air was passed through the reactor to dry it before the catalyst was pre-reduced as described above. When the catalyst was recycled without further pre-reduction, toluene was used for washing, and the reactor was purged with nitrogen before the introduction of fresh reaction mixture, as described above.

3. Results

3.1. Kinetics of reaction in RDR and STR

Typical reaction profiles with respect to time for the oxidation performed in the RDR and in the STR in both toluene and $[C_4mim][NTf_2]$ under 1 bar of oxygen are shown in Fig. 2. The rates in both reactors are similar when the reaction is carried out in toluene; however, in the ionic liquid, the rate of reaction is greatly decreased compared with that observed with toluene. Furthermore, the differential between the rate of reaction in toluene compared with $[C_4mim][NTf_2]$ is much higher in the RDR than in the slurry reactor. It is noticeable that the selectivity towards cinnamaldehyde at a given conversion is higher in the ionic liquid compared with in toluene (Table 2). For example, in the stirred tank reactor at 50% conversion the cinnamaldehyde selectivity is found to be 93% in $[C_4mim][NTf_2]$ and 88% in toluene. Under the conditions used in these reactions, overoxidation to cinnamic acid was not observed; however, in agreement with previous reports [13], a range of hydrogenated and decarbonylated products were obtained (Scheme 1). In the STR under 1 bar of O_2 at $\sim 50\%$ conversion these constituted $< 6\%$ of the total reaction mixture in the case of toluene and $< 4\%$ in $[C_4mim][NTf_2]$, with 3-phenylpropanol found as the major by-product.

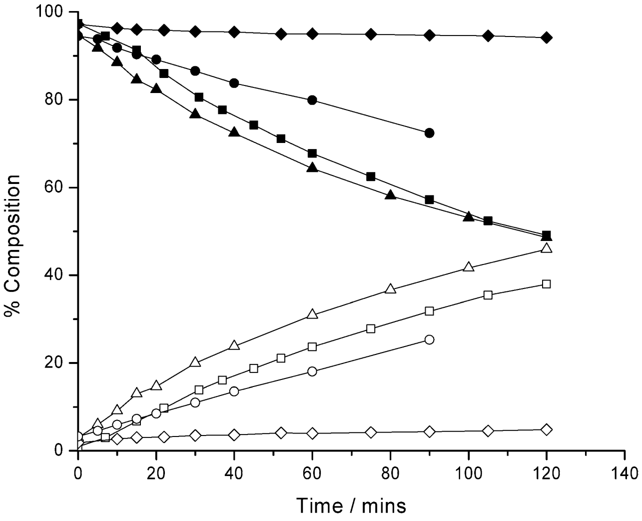


Fig. 2. Kinetic profile for cinnamyl alcohol consumption (closed symbols) and cinnamaldehyde formation (open symbols) obtained in toluene, using the RDR (□, ■) and STR (△, ▲), and in $[C_4mim][NTf_2]$, using the RDR (◇, ◆) and STR (○, ●). The experimental conditions were as follows: rotation speed (RDR) = 496 rpm, stirrer speed (STR) = 1000 rpm, [cinnamyl alcohol] = 0.09 M (toluene), [cinnamyl alcohol] = 0.10 M ($[C_4mim][NTf_2]$), at 80 °C.

3.2. Variation with rotation speed in the RDR

To understand the reasons for the change in rate between the ionic liquid and toluene, we studied the RDR reactions in detail. Fig. 3 shows the variation in initial rate in toluene as a function of rotation speed of the disc. Changes in rotation speed will substantially alter a number of mass transfer characteristics. For example, the turbulence in the bulk solution will increase with higher rotation speeds, as will the mixing in the entrained film [9]. Both of these effects will improve the external liquid-to-solid mass transfer of the liquid-phase reagent. It has been reported that for RBCs, at low rotation speeds the oxygen mass transfer rate (k_L) varies with rotation speed to a power in the range of 0.5–1.039 [29]. Recently Patwardhan has shown that the following expression from Boumansour and Vasel is considered most accurate [10]:

$$\frac{k_L D}{D_m} = 2.673\left(\frac{ND^2\rho}{\mu}\right)^{0.769}\left(\frac{N^2 D}{g}\right)^{0.135}\left(\frac{H}{R}\right)^{0.865}.$$

Table 2
Summary of initial rates of cinnamyl alcohol consumption and aldehyde formation, selectivity and reaction composition as a function of solvent, reactor, cinnamyl alcohol concentration and oxygen pressure at 80 °C. The RDR experiments were performed at 496 rpm using a 1.35 mm thick disc and the STR was stirred at 1000 rpm. The reaction components are as designated in Scheme 1. The balance of the composition is due to components **4**–**7**, unless otherwise stated

Reactor	Solvent	O_2 pressure (bar)	Alcohol concentration (M)	Rate ($\text{mmol min}^{-1}\,g_{cat}^{-1}$)		Reaction composition (%)				Cinnamaldehyde selectivity (%)
				Alcohol consumption	Aldehyde formation	**8**	**3**	**2**	**1**	
RDR	Toluene	1.0	0.09	0.102	0.070	3.8	9.2	38.0	49.1	74.6
RDR	$[C_4mim][NTf_2]$		0.10	0.005	0.003	0.0	1.0	4.0	95.0	79.9
STR	Toluene		0.09	0.092	0.084	1.4	3.8	41.6	53.1	88.8
STR	$[C_4mim][NTf_2]$		0.10	0.043	0.042	1.5	1.6	43.1	53.8	93.3
RDR	Toluene		0.58	0.278	0.190	1.1	13.4	33.9	49.2	66.7
RDR	$[C_4mim][NTf_2]$		0.66	0.028	0.014	0.0	2.1	6.0	85.3	40.8[a]
STR	Toluene		0.57	0.380	0.344	1.2	4.9	38.6	55.3	86.3
STR	$[C_4mim][NTf_2]$		0.66	0.160	0.157	1.2	2.6	35.8	60.4	90.4
RDR	Toluene	0.2	0.09	0.073	0.054	2.8	11.4	37.5	48.3	72.5
STR	Toluene	1.0	0.35	0.192	0.177	0.6	3.2	44.7	49.3	88.1
STR	Toluene	0.2	0.35	0.190	0.161	0.8	5.8	38.7	52.3	81.2
STR	Toluene	0.0	0.35	0.487	0.219	0.7	11.8	20.0	53.0	42.6
STR	$[C_4mim][NTf_2]$	1.0	0.35	0.074	0.074	0.0	1.8	48.5	49.7	96.5
STR	$[C_4mim][NTf_2]$	0.2	0.35	0.090	0.088	0.0	2.3	49.0	48.7	95.4
STR	$[C_4mim][NTf_2]$	0.0	0.35	0.008	0.002	0.0	2.8	3.1	88.0	24.9

[a] Balance in composition is 6.7% of which the coupling products constitute 87%.

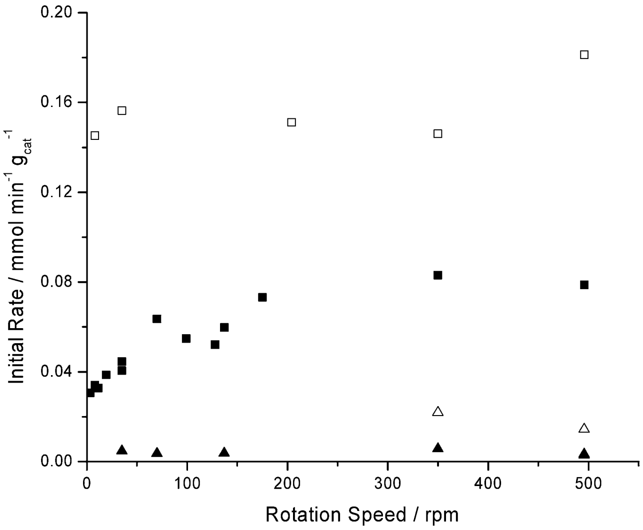


Fig. 3. Variation in initial rate of aldehyde formation with rotation speed in the RDR. The experimental conditions were as follows: in toluene, [cinnamyl alcohol] = 0.09 M (■) or 0.57 M (□) and in $[C_4mim][NTf_2]$, [cinnamyl alcohol] = 0.11 M (▲) or 0.66 M (△), at 80 °C.

The expression $\{ND^2\rho\mu^{-1}\}$ is the Reynolds number (R_e) for the rotating disc reactor. From Fig. 3, although there is an increase in TOF from 0.05 min^{-1} at 3.5 rpm ($R_e = 370$) to 1.38 min^{-1} at 175 rpm ($R_e = 20603$), further increases in rotation speed showed little change with 0.09 M cinnamyl alcohol. At higher alcohol concentrations, the initial rate remained approximately constant between 8 rpm ($R_e = 942$) and 496 rpm ($R_e = 58397$) with TOFs of 2.85 and 3.96 min^{-1}, respectively. Similarly, the rate in $[C_4mim][NTf_2]$ did not change significantly with varying rotation speed, 35 to 496 rpm, with a concomitant change in TOF from 0.07 to 0.05 min^{-1} in the RDR. This is contrary to the results reported by Hamill et al. for photocatalytic oxidation over titania films, for which a strong rate dependence on rotation speed was reported [9]. Therein a number of discontinuities in the reaction rate were found at particular values of R_e. For example, a step in the rate was shown to occur between $R_e = 2060$ and 3740, which was attributed to the transition between laminar and turbulent flow. For a smooth surface, this transition is known to occur at $R_e \sim 2100$ for a Newtonian fluid [30]. However, in the present study the disc cannot be considered as smooth, and the point of transition from laminar flow to turbulent flow will occur much more gradually at much lower Reynolds numbers.

3.3. *Effect of oxygen partial pressure*

A comparison of the initial rate of alcohol conversion at 0.2 and 1 bar of oxygen partial pressure in the STR at a cinnamyl alcohol concentration of 0.35 M in toluene and in $[C_4mim][NTf_2]$ shows a weak dependence (Table 2). These observations are consistent with the results described by Baiker et al. [12,31]. Lee et al. reported for 5 wt% Pt/3 wt% Bi on graphite that the order with respect to oxygen is close to zero [14]. Although the rate dependence on the oxygen pressure is weak for the aldehyde formation, the presence or absence of oxygen has a significant influence on the initial rate of alcohol conversion and cinnamaldehyde selectivity. In toluene under N_2, although the rate of alcohol conversion is significantly higher than in the presence of oxygen, lower selectivity is observed. Only 43% selectivity at 47% conversion is found because of transfer hydrogenation reactions, whereas high selectivity (> 80%) is observed in the presence of oxygen, even in air. In contrast, under nitrogen, little reaction was observed in [C_4mim][NTf_2]. Above 2 bar of oxygen, overoxidation to cinnamic acid is observed in toluene, whereas in [C_4mim][NTf_2] little carboxylic acid was observed at all oxygen pressures studied. Similar results are observed in the RDR.

Despite the large number of investigations, the role of oxygen in these oxidation reactions is still a matter of debate. Many studies have shown that oxygen can cause overoxidation of the catalyst surface, which poisons the catalyst and reduces the rate of oxidation [32–34]. With the addition of promoters such as lead and bismuth, which may prevent overoxidation, the rate is enhanced [35]. Recently, Baiker et al. reported that deactivation of the catalyst in the absence of air may be due to strongly adsorbed CO formed by the decarbonylation reaction of hydrocinnamaldehyde and cinnamaldehyde forming ethylbenzene and styrene, respectively [12]. The strong adsorption of CO blocks the surface, and the main role of oxygen is to act as a cleaning agent, removing the CO and freeing catalyst sites for further reaction. In addition, oxygen can help to improve the selectivity of the reaction by reacting with the hydrogen formed from the initial dehydrogenation of the cinnamyl alcohol, thereby reducing the likelihood of a transfer hydrogenation reaction. The catalyst is only considered to be overoxidised if oxygen is supplied at a rate greater than that required by the reaction. Oxygen can also improve the selectivity by blocking sites used for the decarbonylation reaction; however, this is likely to be detrimental to the rate, as the catalyst may also be considered to be overoxidised.

3.4. *Effect of alcohol concentration*

In contrast to the variation with oxygen, the rate of reaction in toluene was found to be first order with respect to the concentration of alcohol in the RDR below 0.17 M, with an order of 0.6 observed between 0.17 and 1.10 M (Fig. 4). Similar results were obtained in the STR, although the final order was increased to 0.7. The above data are in contrast to the zero-order dependence for the alcohol reported by Lee et al., who used platinum. It should also be noted that with an increasing alcohol concentration, selectivity to the aldehyde decreases, as expected from the dependence of selectivity on oxygen pressure (Table 2) for both reactors, although only to a smaller degree in the STR.

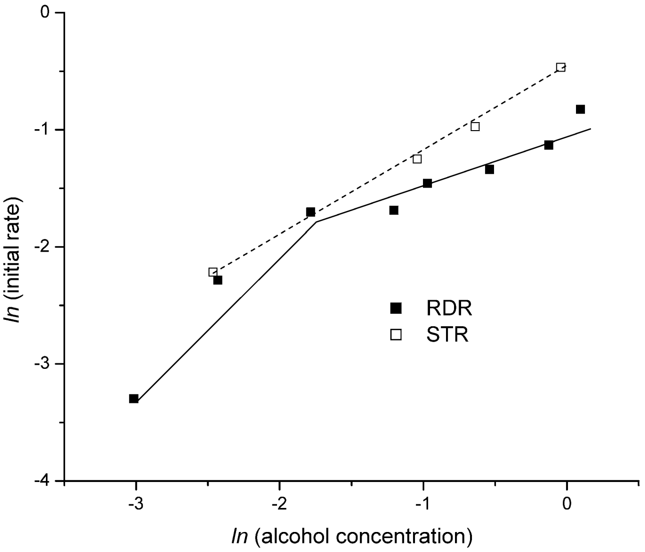
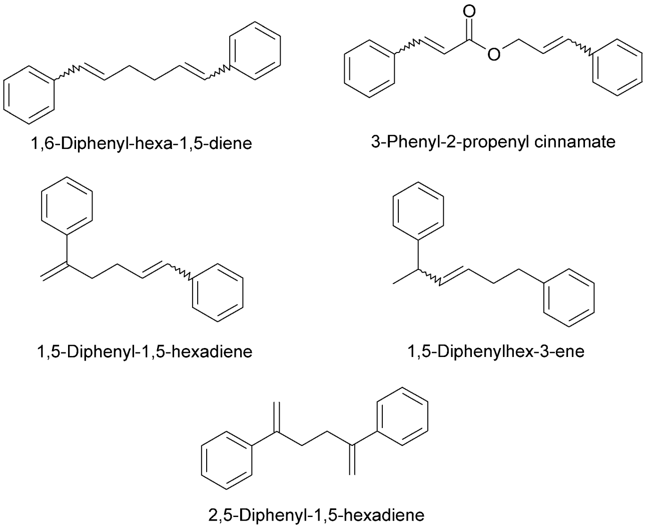


Fig. 4. ln−ln plot of rate of cinnamyl alcohol consumption versus alcohol concentration in the RDR and STR in toluene. The experimental conditions were as follows: rotation speed (RDR) = 496 rpm, stirrer speed (STR) = 1000 rpm, at 80 °C.



Scheme 2. Coupling products formed in the RDR following extended reaction time in [C_4mim][NTf_2].

In the STR, although cinnamaldehyde selectivity is slightly higher in the ionic liquid than in toluene, a similar distribution of by-products is observed at all alcohol concentrations at comparable conversion. However, in the RDR, significant differences are observed between [C_4mim][NTf_2] and toluene, particularly at cinnamyl alcohol concentrations above 0.55 M. In [C_4mim][NTf_2], there is a significant formation of high-boiling-point coupling products even at low conversion; for example, at 15% conversion, these constitute $\sim 40\%$ of the products formed. Scheme 2 shows the compounds that have been identified by GC-MS. At extended reaction times these species increase significantly in concentration. It is not clear how these materials form in the present system, as, although similar coupling reactions of α,β-unsaturated alcohols have been reported previously, these reactions have been radical initiated (for example [36]). The formation of the ester is likely to be via a Tishchenko reaction in which two aldehydes undergo a disproportionation reaction. Reactions of this type have been observed over solid bases and may be catalysed by the basic sites on the alumina, although it should be noted that much stronger bases are normally required [37]. It is reasonable that the coupling products are formed only at high alcohol concentrations, as the rate of their formation is likely to be greater than first order in the substrate. The fact that the coupling products are observed only in the reaction mixture from the RDR and not the STR may be the result of increased residence time in the catalyst pores.

4. Discussion

In the RDR, as the initial rate does not vary significantly with rotation speed, it can be assumed that the transport of oxygen to the catalyst is not a significant limiting factor. (Between 3.5 and 500 rpm the average liquid film thickness [38] changes from 12 to 138 µm in toluene and from 86 to 1031 µm in [C_4mim][NTf_2], which would change the diffusion rate of O_2 significantly but does not greatly change the rate of reaction.) This is not surprising, as it has already been shown that the gas has little effect on the rate of reaction. Therefore, any change could be assumed to reflect the transport of the liquid-phase reagent. At low alcohol concentrations in toluene, a small increase with rotation speed was observed, which indicates that liquid-to-solid mass transfer is determining. However, at higher concentrations of alcohol in toluene and at all alcohol concentrations in [C_4mim][NTf_2], a change in rotation speed in the RDR did not have any significant effect. Under these conditions, although the concentration of alcohol is rate determining, mass transfer of the liquid-phase reagent is not a significant external resistance to reaction and is not affected by rotation speed. There is also only a small difference in the initial rates of reaction observed between the STR and RDR with toluene as the solvent, despite an eightfold change in the interfacial area, showing that the reaction is unlikely to be limited by liquid-to-solid mass transfer. Since external diffusion effects are not rate limiting, the difference in the initial rate of reaction between the two reactors is likely to be due to internal diffusion of the alcohol and/or oxygen through the pores of the catalyst. This can be examined by calculation of the catalyst efficiency for each reactor/solvent system.

The Weisz–Prater criterion, C_{WP}, is often used to estimate the efficiency of a catalyst pellet, as it is based on known values, such as the observed rate of reaction [39]. Values of C_{WP} much less than 1 indicate the absence of internal mass transfer limitation, whereas a value of C_{WP} greater than 1 indicates that the reaction is strongly limited by internal pore diffusion. The Weisz–Prater criterion is given by

$$C_{WP} = \eta\phi^2 = -\frac{r'_{a(obs)}\rho_{cat}R^2}{D_e C_{as}},$$

$$\eta\phi^2 = 3\big(\phi\coth(\phi) - 1\big), \quad \text{for a sphere,}$$

$$\eta\phi^2 = \phi\tanh(\phi), \quad \text{for a slab.}$$

By calculation of C_{WP}, the catalyst efficiency (η) may be determined, and consequently an estimation of the reaction rate for different particle sizes may be calculated.

In the case of the ionic liquid, few experimentally determined bulk diffusivities are available; however, the bulk diffusivity for benzaldehyde (which would have approximately the same molar volume as cinnamyl alcohol) has been measured at $3 \times 10^{-11}\ m^2\,s^{-1}$ in [C_4mim][NTf_2] with cyclic voltammetry [40]. This was measured at 20 °C, and, therefore, it would be expected that the diffusivity for cinnamyl alcohol would be much higher under the reaction conditions used here. At 80 °C, the bulk diffusivity of cinnamyl alcohol is estimated to be $2.3 \times 10^{-10}\ m^2\,s^{-1}$, assuming a direct inverse dependence of diffusivity with viscosity. Using this assumption and a tortuosity coefficient of 0.2 to give the effective diffusivity [41], catalyst efficiencies of 99% ($C_{WP} = 0.095$) in the case of the slurry reactor and 19% ($C_{WP} = 5.298$) for the 1.35-mm disc in RDR have been determined for a concentration of 0.66 M. Therefore, the rate in the RDR rate is predicted to be 5.2 times lower than in the STR, assuming that the catalyst condition is similar in each case. From Table 2, the relative rate between the STR and RDR at this concentration is 5.7, indicating that the Weisz–Prater criterion is generally applicable.

However, in the case of toluene, the Weisz–Prater criterion does not hold. The bulk alcohol diffusivity has been approximated as $2.6 \times 10^{-9}\ m^2\,s^{-1}$ from the Wilke–Chang correlation [42]. Again using a tortuosity coefficient of 0.2, C_{WP} was found to be 0.087 for the case of the slurry reactor, indicating no internal pore diffusion and a catalyst efficiency of 99.7%. From these values, the slurry reactor appears to give the true kinetic rate for toluene. For the RDR (1.35 mm disc) C_{WP} was calculated as 14.12, and the catalyst efficiency was reduced to 7%. These values do not match the rates observed in each reactor. A comparison of the rate of reaction between the RDR and the STR at the same catalyst loading and alcohol concentration shows that the rate of reaction observed in the RDR is $> 70\%$ of that in the STR (Fig. 4), not the 7% predicted by the Weisz–Prater criterion. This suggests that the true rate in the RDR is approximately 12.6 times higher than that of the slurry. It should be noted that if one uses oxygen diffusivity and concentration, the results are similar, although if the oxygen diffusivity is an order of magnitude higher than that of the alcohol, its concentration is an order of magnitude lower.

Although the catalyst efficiencies in toluene are not predicted by the Weisz–Prater criterion for the STR compared with the RDR, for a given reactor setup, such as the RDR, the Weisz–Prater criterion does follow the experimental values. For example, for values of $C_{WP} > 1$ (indicating strong diffusion resistance), the catalyst efficiency is proportional to the inverse of the disc thickness [43]. Fig. 5 shows the variation in the initial rate of reaction as a function of the reciprocal of the disc thickness for toluene in the RDR. As predicted from the theory, a linear relationship is found, indicating that the behaviour of the reaction kinetics can be represented qualitatively by the catalyst efficiency calculations but not quantitatively.

The analysis indicates that the rate of reaction in toluene in the RDR is significantly faster than expected. For example, the 1.35-mm disc is estimated to have a rate constant that is 12.6 times faster than the estimated value based on alco-

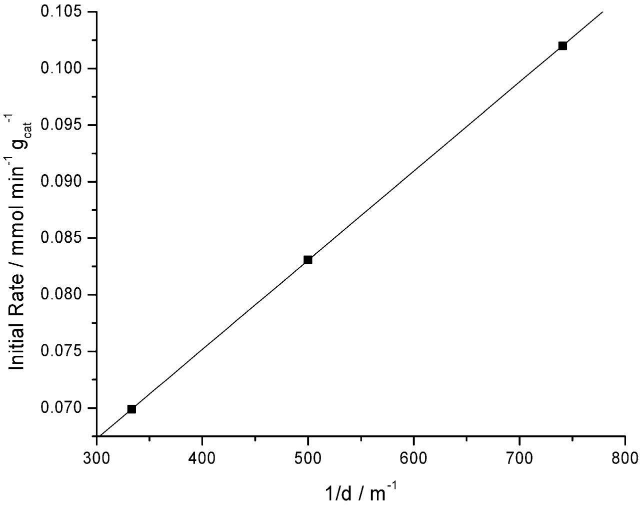


Fig. 5. Variation in initial rate of cinnamyl alcohol consumption with disc thickness (1.35, 2, and 3 mm) in the RDR using toluene. The experimental conditions were as follows: rotation speed = 496 rpm, [cinnamyl alcohol] = 0.09 M, at 80 °C.

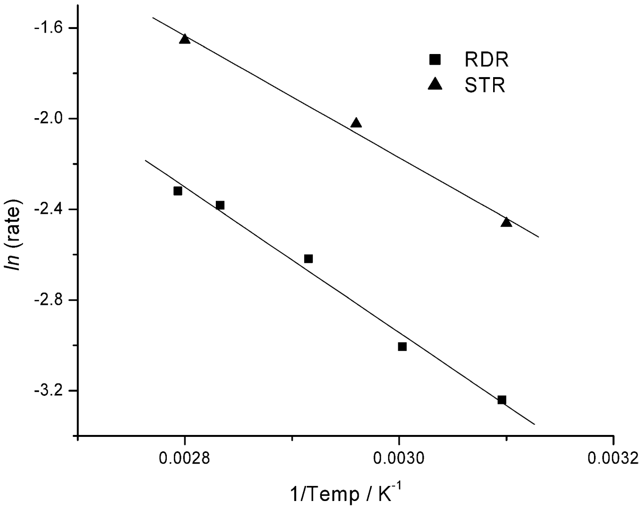


Fig. 6. Arrhenius data for the temperature range 50–85 °C. The experimental conditions were as follows: rotation speed (RDR) = 496 rpm, stirrer speed (STR) = 1000 rpm, [cinnamyl alcohol] (RDR) = 0.09 M, (STR) = 0.35 M.

hol diffusion for the 100 µm slurry. Similarly, for the 2- and 3-mm discs the rates are 20 and 22 times higher, respectively. These unexpectedly high rates may be due to oxygen transport limitations. As discussed above, there is a fine balance between providing enough oxygen to clean the surface and too high an oxygen pressure, which results in site poisoning. Baiker et al. have shown that if the reaction is initially carried out in an inert atmosphere and then switched to air, the rate under aerobic conditions is considerably faster than when the reaction occurs in an oxygen atmosphere from the outset [12]. The thickness of the disc in the rotating disc reactor (1.35 mm compared with 100 µm in the STR) means that in the centre of pellets in the RDR, the oxygen transport is severely limited and its concentration is likely to be low. In this case the system mimics the conditions where the STR is run under inert gas. Without oxygen, the rate of alcohol conversion is much higher than in the presence of oxygen, and therefore the surface conditions in the STR and RDR are different and cannot be compared using the Weisz–Prater criterion. Further evidence for this comes from the fact that the proportion of transfer hydrogenation product in the RDR is considerably higher than that observed for similar reactions performed in a STR (Table 2). This indicates that there is insufficient oxygen present to remove the hydrogen, formed in the dehydrogenation reaction, from the surface of the catalyst.

To distinguish between reaction or adsorption limitations as opposed to diffusion limitations, the apparent activation energy was measured for both the STR and RDR. Fig. 6 shows the Arrhenius plots in each case, and apparent energies of activation of 26 and 22 kJ mol^{-1} were obtained for the RDR and STR, respectively. The similarity between the activation parameters implies that the two reactions are limited by the same step, which is thought to be the dehydrogenation step. Similar activation barriers have been reported by Nicoletti et al. and Schwartz et al. for 2-propanol oxidation (38 and 53 kJ mol^{-1}, respectively) and by Nagai et al. for methanol oxidation (41 kJ mol^{-1}) [44].

Considering the similarities of the activation barriers for the reaction in toluene in the STR and RDR and the inability of the Weisz–Prater criterion to predict the rates, the RDR can be considered to be operating under internal diffusion control. From the selectivity data, oxygen diffusion is likely to be controlling, with the catalyst in RDR having a much lower surface oxygen coverage on average than that in the STR. The catalyst in the STR may therefore be considered to be slightly poisoned, with respect to oxygen, whereas the RDR will eventually become poisoned by CO. The latter condition is not reached in these experiments because of the high catalyst-to-substrate ratio and the relatively low rate of decarbonylation reaction.

Obviously, the catalyst–solvent–reactor system chosen is critical in determining the aldehyde selectivity, as it is strongly dependent on the rate of reaction and surface oxygen coverage on the catalyst. Fig. 7 shows that there is a linear relationship between the rate and aldehyde selectivity for the reactions carried out in toluene in the RDR. Interestingly, if the ionic liquid rates are superimposed on this graph, the points are also found to lie on the trend line plotted through the points from the experiments carried out in toluene. The lower rates and correspondingly higher selectivities found in the ionic liquid are possibly due to the ionic liquid reducing the surface alcohol concentration as the result of strong solvation of the alcohol. It has been shown that aromatics are highly soluble in ionic liquids, and they can strongly hydrogen bond to hydroxyl groups, which may result in a deactivation of the molecule [45]. The decrease in surface coverage of alcohol both reduces the rate of reaction and increases the relative concentration of surface oxygen, resulting in increased selectivity for the aldehyde.

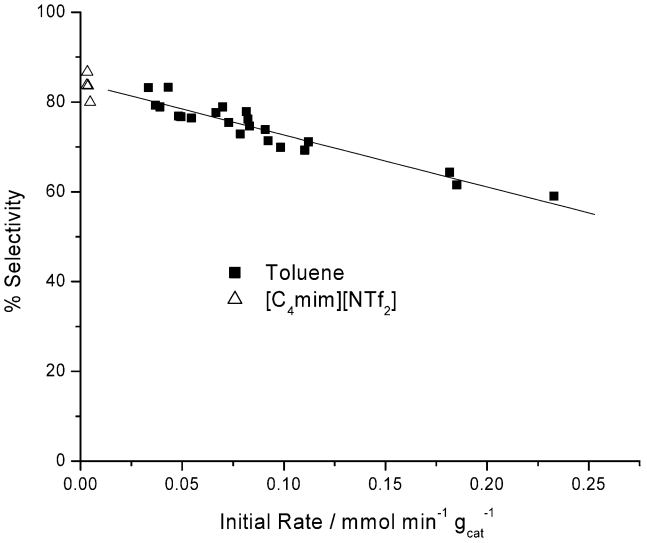


Fig. 7. Variation in cinnamaldehyde selectivity with initial rate of cinnamyl alcohol consumption in the RDR. The selectivity was measured at ~ 20% conversion for toluene and ~ 10% conversion for [C_4mim][NTf_2].

As the Weisz–Prater criterion is dependent on the diffusivity and therefore the viscosity of the solvent, and it is able to predict the rates in both reactors for [C_4mim][NTf_2], it can be assumed that the alcohol is strongly solvated in the ionic liquid and is, as a consequence, somewhat deactivated. The strong solvation decreases the probability that alcohol will stick to the surface, which reduces the rate and permits an increase in selectivity. This is unlike the heterogeneously catalysed hydrogenation reactions previously reported for ionic liquids, where the much higher selectivities observed, compared with conventional molecular solvents, could not be explained simply by the deactivation of the substrate. In this case, the enhanced selectivity was thought to be due to a change in adsorption geometry as a result of the ionic liquid–aldehyde interaction [18].

Although this reactor was designed and constructed primarily as a tool for the study of mass transfer effects in three-phase reactions, from a process point of view it offers the possibility of simple isolation of the catalyst from the liquid reaction mixture. A single catalyst disc was used over four runs with the reactor in a batch mode and toluene as the solvent. The catalyst was pre-reduced before the first, second, and third reactions; however, no pre-reduction was performed before the fourth reaction. Fig. 8 shows that after 60 min of reaction there is no loss in conversion or selectivity. It should be noted that the conversion appears to increase slightly because of increased formation of propenyl benzene, such that although the selectivity for cinnamaldehyde remains constant at ~ 58%, at 30% conversion the distribution of the other products changes slightly over the four runs. As the catalyst remained active over four runs even with no pre-reduction, the reactor was modified, so that after being run as a batch system it could be changed to CSTR operation, where fresh feed stock was pumped into the reactor while the outlet concentration was monitored by GC. The change in the outlet concentration with time observed with the change to CSTR operation after 120 min of operating under batch mode is shown in Fig. 9. Clearly, there is a drop in conversion from ~ 50 to 25%; however, after ~ 125 min under CSTR operation, a region of steady-state reaction was observed.

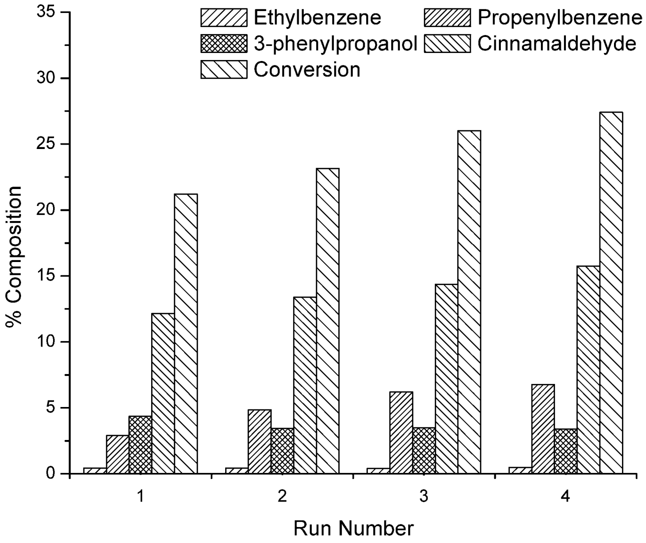


Fig. 8. Composition of toluene reaction mixture as a function of recycle in the RDR. The experimental conditions were as follows: rotation speed = 496 rpm, [cinnamyl alcohol] = 0.38 M, at 80 °C over 60 min reaction time.

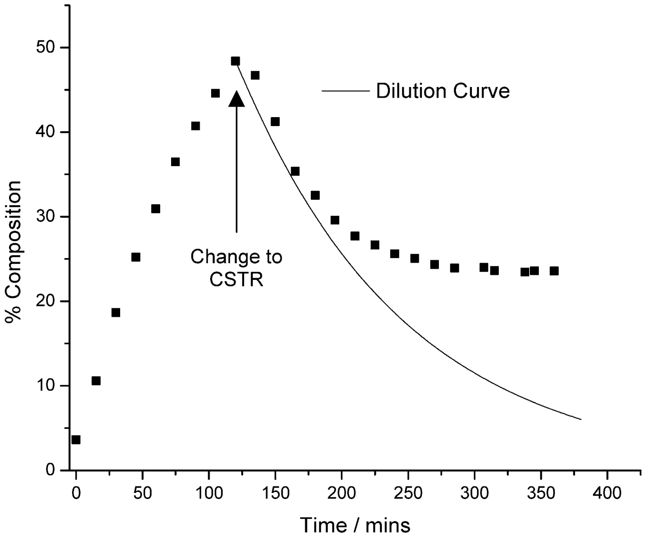


Fig. 9. Percentage aldehyde in the reaction mixture in the RDR operated as a batch reactor for 120 min and, thereafter, in the outlet stream of the RDR operating as a CSTR at a liquid flow rate of 100 cm^3 h^{-1}. The experimental conditions were as follows: rotation speed = 128 rpm, [cinnamyl alcohol] = 0.09 M, at 80 °C.

5. Conclusions

The RDR has been shown to facilitate the three-phase oxidation of cinnamyl alcohol in toluene and [C_4mim][NTf_2]

in the presence of 5 wt% Pd/Al_2O_3 with an atmosphere of either oxygen gas or compressed air. In general, the ionic liquid gave better cinnamaldehyde selectivity than toluene; however, this was only a consequence of the lower rate. In toluene, similar rates were achieved in the RDR and STR, in the presence of oxygen, despite a large difference in the interfacial catalyst area. Estimations of the Weisz–Prater criterion and catalyst efficiency showed that for $[C_4mim][NTf_2]$, the catalyst was operating under similar conditions in the STR and RDR, whereas in toluene the catalyst was less poisoned by oxygen in the RDR than in the STR. This is thought to be due to oxygen diffusion limitations in the RDR, which reduce the surface coverage of oxygen, giving a less poisoned surface and a higher rate than predicted.

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Appendix A. Nomenclature

k_L = mass transfer coefficient for the liquid film exposed to air, $\mathrm{m\,s^{-1}}$
D = diameter of the disc, m
D_m = molecular diffusivity of oxygen, $\mathrm{m^2\,s^{-1}}$
N = speed of rotation, $\mathrm{s^{-1}}$
g = acceleration due to gravity, $\mathrm{m\,s^{-2}}$
H = height of submergence of disc from the bottom, m
R = radius of disc, m
C_{WP} = Weisz–Prater criterion
$r'_{a(obs)}$ = observed rate of reaction, $\mathrm{mmol\,min^{-1}\,g_{cat}^{-1}}$
R^2 = characteristic length = volume/surface area, m
D_e = effective diffusivity of oxygen or alcohol, $\mathrm{m^2\,s^{-1}}$
C_{as} = external surface concentration of oxygen or alcohol, $\mathrm{mol\,m^{-3}}$
ρ = density of liquid, $\mathrm{kg\,m^{-3}}$
ρ_{cat} = density of catalyst pellet, $\mathrm{kg\,m^{-3}}$ (4000 $\mathrm{kg\,m^{-3}}$—STR; 750 $\mathrm{kg\,m^{-3}}$—RDR)
μ = viscosity, Pa s
η = catalyst effectiveness
Φ = Thiele modulus

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