

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

Christopher Hardacre<sup>a,b,\*</sup>, Edel A. Mullan<sup>a,b</sup>, David W. Rooney<sup>b,c</sup>, Jillian M. Thompson<sup>a,b</sup>

<sup>a</sup> School of Chemistry, Queen's University of Belfast, Belfast BT9 5AG, Ireland

<sup>b</sup> QUILL Research Centre, Queen's University of Belfast, Belfast BT9 5AG, Ireland

<sup>c</sup> School of Chemical Engineering, Queen's University of Belfast, Belfast BT9 5AG, Ireland

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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.

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## 1. Introduction

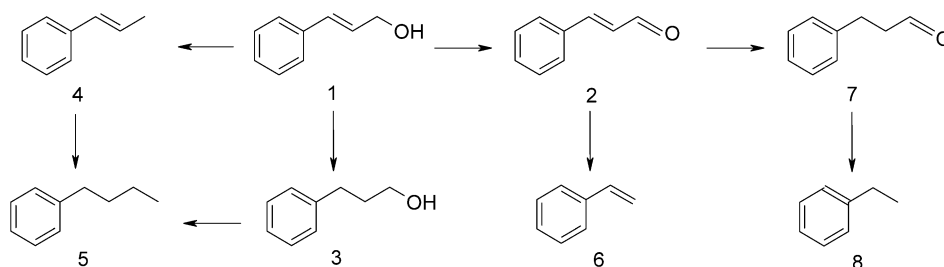
The role of any reactor for use with heterogeneous catalysts is simply to expose an active catalytic area to the reactants at optimised concentrations and temperature. In addition, it must also provide a means by which heat can be removed from or added to the system. Commonly, trickle-bed or slurry reactors 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 sur-

face 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

\* Corresponding author.

E-mail addresses: [c.hardacre@qub.ac.uk](mailto:c.hardacre@qub.ac.uk) (C. Hardacre),  
[d.rooney@qub.ac.uk](mailto:d.rooney@qub.ac.uk) (D.W. Rooney).



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  $\alpha$ ,  $\beta$ -unsaturated alcohols is an important step in the synthesis of flavours and fragrances, and the re-

action 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> catalyst to determine mass transfer influences and to evaluate the role of the ionic liquid.

## 2. Experimental

The catalyst, 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> Johnson Matthey 324, had a BET surface area of 134.3 m<sup>2</sup> g<sup>-1</sup> 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<sub>4</sub>mim][NTf<sub>2</sub>]), was synthesised from [C<sub>4</sub>mim]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<sup>3</sup> 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<sup>3</sup>) were placed in the reactor and purged with oxygen until the desired temperature was reached, at which point a concentrated solution of cinnamyl

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