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Experimental studies of nitrobenzene hydrogenation in a microstructured falling film reactor

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Abstract

Nitrobenzene hydrogenation over palladium catalyst was performed in a microstructured falling film reactor at a range of flowrates (0.5–3 ml/min) and pressure (1–6 bar). Confocal microscopy was used to measure liquid film thickness. Comparison with film thickness prediction equations showed an overprediction of 10–30%. The k_La of this system was estimated to be 3–8 s^{-1} with interfacial surface area per reaction volume 9000–15000 m^2/m^3. Conversion was found to be affected by both liquid flowrate and hydrogen pressure, and the reactor operated between the kinetic and mass transfer controlled regimes.

Keywords: Falling film reactor; Microstructured reactor; Nitrobenzene hydrogenation; Confocal microscopy

1. Introduction

Falling film reactors generate thin liquid films that fall under gravity. The thinness of these films results in rapid heat and mass transfer. Conventional falling film systems generate films with thickness 0.5–3 mm (Dabir et al., 1996; Karimi and Kawaji, 1998). A microstructured falling film reactor (μ-FFR) developed by the Institut für Mikrotechnik Mainz can generate stable films less than 100 μm thick, thus offering excellent heat removal capabilities, and has been used safely in the direct fluorination of aromatics (Jähnisch et al., 2000). Our research aims to evaluate the performance of the μ-FFR in solid catalysed gas–liquid hydrogenations, using the hydrogenation of nitrobenzene to aniline as a model system. The development of a suitable catalyst incorporation method is detailed elsewhere (Yeong et al., 2003). Liquid film thickness measurements and reaction studies using an incipient wetness catalyst are presented in this paper.

Gas–liquid–solid hydrogenation in microfabricated reactors has been investigated by Losey et al. (2001, 2002) using micro-packed bed reactors for the hydrogenation of cyclohexene. Mass transfer coefficients (k_La) of 3–15 s^{-1} with gas/liquid interfacial contact area up to 16000 m^2/m^3 were obtained. Födisch et al. (2001, 2002) investigated the liquid phase hydrogenation of p-nitrotoluene using either a stack of porous microstructured aluminium wafers, aluminium wire pieces or conventional fixed bed particles in a microreactor module. Conversion in the wafers ranged from 39–84%, in comparison to 85% conversion with the fixed bed catalyst.

2. Experimental apparatus and procedures

The microstructured stainless steel plate that generates the falling film has 64 straight, parallel channels (300 μm wide, 100 μm deep, 78 mm long separated by 100 μm wide walls) and has been presented in detail elsewhere (Yeong et al., 2003). The microchannels were coated with γ-alumina using a slurry/washcoating process (Cominos et al., 2002). The area surrounding the channels was covered with tape and the channels were covered with an aqueous suspension of γ-alumina powder (20% solids content, average particle size 3 μm), binder (PVA) and acid (acetic acid or nitric acid). Excess suspension was wiped off and the plate was calcined at 700°C for 2 h. This resulted in a 10 μm thick film contained *within* the microchannel, with pore size of about 20 nm and surface area of 58 m^2/g. Due to surface tension and curved channel walls/bottom, the coating was thicker at the 'corners' (Zapf et al., 2003). The channel area was covered with 10 ml of a palladium (II) nitrate (Aldrich,

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Pd 12–16% w/w) solution with ca 1.3 wt% palladium and left to dry in a fume cabinet. The plate was calcined in air at 400°C for 3 h.

To determine the validity of macroscale liquid film thickness predictions, film thickness measurements were performed on a stainless steel plate at a range of flowrates (0.5–2 ml/min) using confocal microscopy (Noran Odyssey) at ca. 1.5 cm downstream of the liquid entrance to the reactor chamber. Experiments were performed with pure ethanol fed using a syringe pump (Razel A-99). For the reaction experiments, a HPLC pump (Knauer K-120, 50 ml pump head) was used to feed the liquid mixture. Prior to entering the reactor, the feed passed through a heating bath (Grant W14). A needle valve was used to control the liquid/gas outlet flowrate and to maintain the desired pressure in the reactor. Experiments were conducted at 60°C, 1–6 bar inlet pressure and liquid flowrates 0.5–3 ml/min nitrobenzene solution (99.5%, Fluka, diluted in ethanol, 0.1 mol/l). Product analysis was performed by an Agilent 6890 GC with an auto-sampler. A PTA-5 capillary column (poly(5% diphenyl/ 95% dimethylsiloxane), 30 m long, 0.32 mm ID, 0.5 μm df, Supelco) was used in conjunction with an FID. Blank experiments showed that stainless steel had no catalytic activity.

3. Results and discussion

Liquid film measurements were taken across five adjacent channels and the average film profiles are shown in Fig. 1 (film thickness measurements were within ±4 μm). In the same figure the channel profile is also included, showing the channel had curved walls and rounded corners. At low flowrates, the contact point between the surface of the liquid film and the channel walls could not be observed as the walls were nearly vertical. At ∼ 0.5 ml/min the contact point rose to the top of the channel. Above 0.7 ml/min, the meniscus of the film became increasingly flat. As the flowrate approached 2 ml/min, 'streams' of liquid were observed to flow into defects on the top of the channel walls. At 2 ml/min, the channels flooded. Table 1 compares the measured liquid film thickness with those calculated using the Nusselt equation,

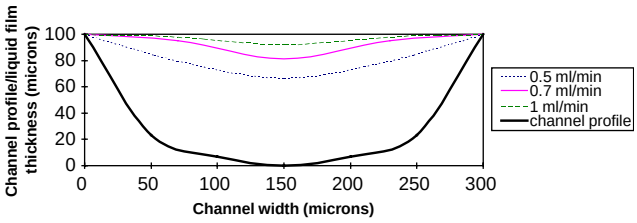

Fig. 1. Average liquid film thickness profile across a channel at various flowrates.

Kapitza equation and Feind correlation (Horoba and Tudose, 2000):

$$\text{Nusselt}: \delta = \left(\frac{3v^2 Re}{g \sin\theta}\right)^{1/3} \left(\frac{\rho}{\rho - \rho_c}\right)^{1/3},$$

$$\text{Kapitza}: \delta = \left(\frac{2.4v^2 Re}{g \sin\theta}\right)^{1/3} \left(\frac{\rho}{\rho - \rho_c}\right)^{1/3},$$

$$\text{Feind}: \delta = \left(\frac{3v^2}{g \sin\theta}\right)^{1/3} \left(\frac{\rho}{\rho - \rho_c}\right)^{1/3} Re^{0.333v'^{-0.11}} v'^{0.025}$$

$$\text{for } 0.72K_F^{-0.1} < Re < 13.5K_F^{-0.1}.$$

There is a some disparity between the experimental and the calculated values, particularly at low flowrates, with the Kapitza prediction being the closest to the experimental values. This is likely because the equations do not take into account the increased importance of evaporation and capillary forces or surface tension in microchannels (note: the *Re* for the flowrates studied was 0.9–3.5, which was smaller than the range of the Feind equation criterion as $K_F^{-0.1} = 8.2$).

As the flowrate increases, the liquid film thickness increases while the residence time decreases. A decrease in residence time will, of course, result in reduced conversion. An increase in film thickness will increase the diffusion time for hydrogen across the liquid film to the catalyst surface, thus reducing conversion as well. Because the effects of film thickness and residence time are coupled, correlating nitrobenzene conversion with Reynolds number (which incorporates both these variables) gives a more complete description of the system. Fig. 2 shows that conversion is linearly dependent on log *Re*.

Table 1
Comparison of measured and calculated liquid film thickness at various flowrates (values at 2.0 ml/min were corrected for spill-over on channel walls due to flooding)

Liquid flowrate (ml/min)	Measured film thickness at channel centre (μm)	Nusselt film thickness (μm)	Kapitza film thickness (μm)	Feind film thickness (μm)
0.5	67	86	80	88
0.7	81	96	89	97
1.0	92	108	100	108
2.0	105 (flood, extrapolated)	127	119	125

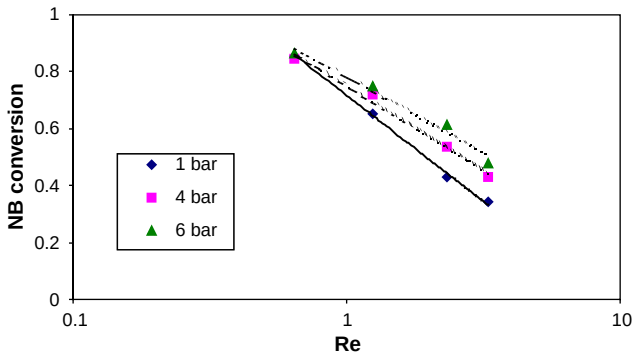

Fig. 2. Nitrobenzene conversion as a function of Reynolds number at various pressures (0.1 mol NB/l, 60°C).

Conversion appears to be weakly dependent on hydrogen pressure. At low flowrates, increase in pressure had negligible effect, while at higher flowrates, increasing pressure brought about small increase in conversion. Pressure had no effect at 0.5 ml/min partly because the conversion had already reached very high values and nitrobenzene became the limiting reactant partway through the reactor, while the liquid film thickness towards the side walls was smaller than the middle, thus providing a faster route for hydrogen transfer. The effect of pressure indicated that either the kinetics were not first order (if one assumes that operation is under kinetic control) or that the system was not mass transfer limited. The ratios between hydrogen diffusion time through the liquid film (τ_D) to the residence time within the reactor (τ) at the flowrates employed was calculated to be in the range 0.02–0.2. Because τ_D is much smaller than τ, the system was not likely to be operating in the mass transfer controlled regime. A simple model of the system (beyond the scope of this short communication) showed that the hydrogen concentration ratios between the solid/liquid and gas/liquid interfaces were in the range 0.07–0.93, indicating that the system was not operating under a kinetically-controlled regime either. Therefore, it was concluded that the system was operating in between mass transfer and kinetic control regimes. A proper representation of the system would need to take into account the channel and interface geometry, evaporation effects, as well as potential mass transfer enhancement factors which can be encountered in thin films (Sternling and Scriven, 1959; Wasden and Dukler, 1990; Boyadjiev et al., 1996).

According to film theory, for low concentration of A, the mass transfer coefficient is, $k_L = D_{AB}/\delta$, where D_{AB} is the diffusion of component A through B (Welty et al., 1984). This leads to

$$k_L a = \frac{D_{AB}}{\delta}\,\frac{\text{interfacial surface area}}{\text{liquid volume}} = \frac{D_{AB}}{\delta^2}.$$

The $k_L a$ and interfacial surface area per liquid volume, a, encountered in this system for the range of flowrates studied are conservatively estimated to be in the range 3–8 s^{-1} and 9000–15000 m^2/m^3, respectively, based on the film thickness in the middle of the channels where it was at its maximum value due to channel curvature (values were extrapolated for flooded conditions). In comparison, the values for the micropacked bed reactors studied by Losey et al. (2001, 2002) were in the range 3–15 s^{-1} with surface area per volume ratio as high as 16000 m^2/m^3. Further reducing the flowrate, and therefore the liquid film thickness, would obviously increase the $k_L a$ values. However, the need to avoid liquid film dry-out imposes a minimum practical flowrate.

4. Conclusions

It was shown that conventional equations for fluid flow may not always be applicable on the microscale and must be verified prior to use. Three equations for predicting liquid film thickness were found to overpredict by 10–30%. The Reynolds numbers encountered in the microstructured falling film reactor were much smaller than those in conventional systems, ranging from 0.9 to 3.5. As such, this discrepancy may be due to the increased significance of surface effects at the microscale. The $k_L a$ values of the system were estimated to be in the range 3–8 s^{-1}, with interfacial surface area per reaction volume in the range 9000–15000 m^2/m^3. Typical values for common industrial gas–liquid contactors are 0.0007–3 s^{-1} and 20–7000 m^2/m^3, respectively (Lee and Tsui, 1999). Both liquid flowrate and hydrogen pressure affected conversion. The results indicate that the reactor operated between the kinetic and mass transfer controlled regimes. Compared to other multiphase microreactors, the microstructured falling film reactor is unique in that flow conditions are well-defined as liquid film thicknesses can be measured and controlled. Thus it represents a new tool in reaction engineering studies.

Notation

A	liquid film cross section in a microchannel
a	interfacial surface area per liquid volume
b	channel width
D_{AB}	diffusivity of A in B
g	gravitational acceleration
K_F	$\frac{\mu^4 g}{\rho\sigma^3}$
$k_L a$	overall mass transfer coefficient
n	number of channels
P	wetted perimeter of a microchannel
Re	Reynolds number $=\frac{\rho u}{\mu}\left(\frac{4A}{P}\right)$
V	volumetric flowrate

Greek letters

δ	liquid film thickness
θ	inclination angle from the horizontal
μ	dynamic viscosity

v	kinematic viscosity
v'	$\frac{v}{0.6\times10^{-6}}$
ρ	liquid density
ρ_c	density of adjoining phase
σ	surface tension
τ	residence time
τ_D	diffusion time across liquid film

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