Supplementary Information

A Micropacked-Bed Multi-Reactor System with *In Situ* Raman Analysis for Catalyst Evaluation

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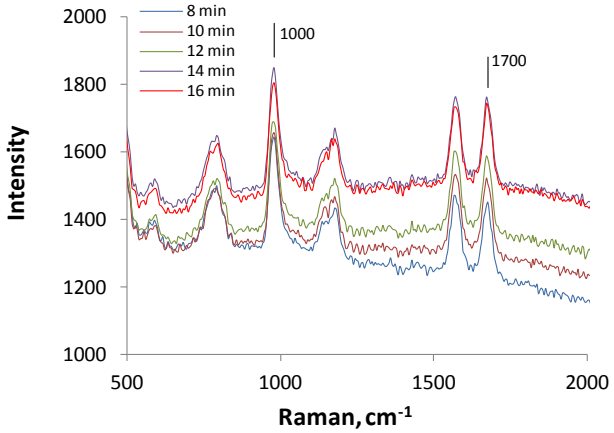
1. Effect of gas-liquid flow on liquid pockets during the acquisition of Raman spectrum

The presence of gas in the flow caused fluctuations of the Raman spectra, as shown in Fig. S1. The measurement was carried out by using a mixture of benzyl alcohol and benzaldehyde (1:1 volume ratio) at 120°C with a liquid flow of 0.005 ml/min and oxygen flow of 1 ml/min. Despite the fluctuations, the peak positions, the shape of the spectra and the peak area ratio of 1700 cm^{-1} to 1000 cm^{-1} were not significantly affected.



Time, min	Peak area ratio
8	0.553
10	0.541
12	0.595
14	0.543
16	0.572
Average	0.561
STDV	0.023

Fig. S1. Raman spectra measured at the same liquid pocket during adjacent gas-liquid slug flow and the peak area ratio of 1700 cm^{-1} to 1000 cm^{-1}.

2. Preparation of micropacked bed reactor

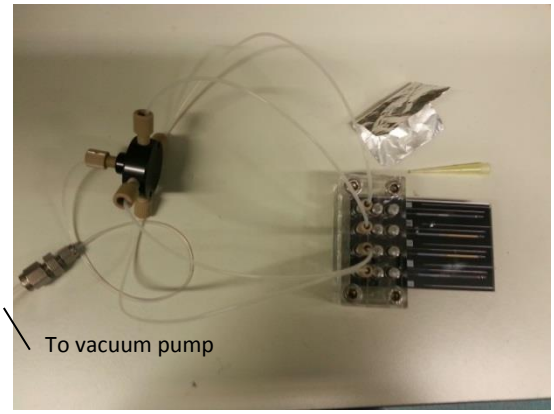


Fig. S2. Catalyst packing using a Perspex connector and a 5-way manifold. A 200 ml pipette tip was used as a funnel to aid packing.

3. Effect of temperature and mixture composition on Raman peak ratio

Effect of temperature

Fig. S3 shows the Raman spectral peak area ratios obtained at room temperature and at 120°C from mixtures of benzyl alcohol and benzaldehyde. The effect of temperature becomes significant with increasing benzaldehyde concentration in the mixture.

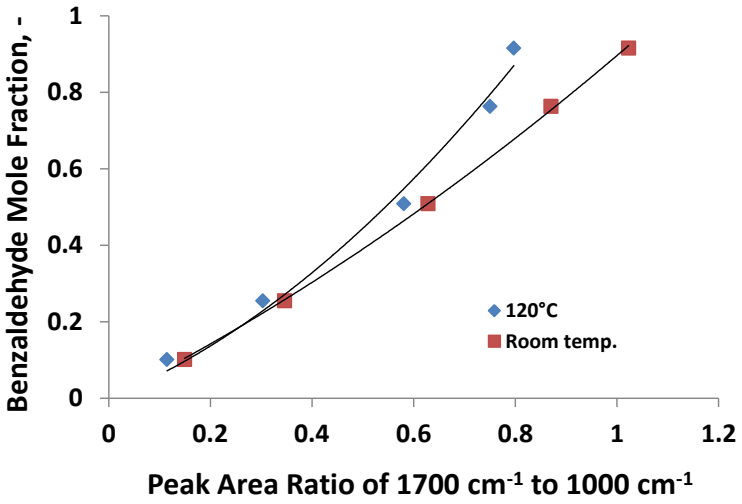


Fig. S3 Raman spectral peak ratios obtained at room temperature and at 120°C with mixtures of benzyl alcohol and benzaldehyde.

Effect of mixture composition

The effect of mixture composition was examined by preparing samples mimicking reaction mixtures at ~10% and 80% conversions, using the selectivity to benzaldehyde and toluene from previous work [1]. At each conversion level, three samples were prepared: (1) benzyl alcohol and benzaldehyde only; (2) based on (1), benzyl alcohol mole number was reduced and replaced by toluene to keep the total mole number and sample volume constant; (3) water

was added into (2). After adding water, the sample was sonicated to form emulsion, in order to simulate the reaction mixture leaving the catalyst packed bed. Raman peak ratios were obtained and shown in Table S1. It can be seen that at low conversion, the small amount of toluene and water did not affect the Raman peak area ratio significantly. However, increasing toluene and water affected the peak ratio. With mixture composition representative of 80% conversion, the Raman peak area ratio decreased ~3% due to the increased amount of toluene and increased ~14% with the increased water content.

Table S1 Effect of toluene and water content on Raman spectral peak area ratio of 1700 cm^{-1} to 1000 cm^{-1}

	Aromatics concentration mol/L			Added H_2O mol/L	Peak area ratio
	Benzaldehyde	Benzyl alcohol	Toluene		
Samples simulating low conversion	1.28	8.40	-	-	0.154
	1.28	7.89	0.51	-	0.152
	1.28	7.89	0.51	1.28	0.152
Samples simulating high conversion	5.51	4.21	-	-	0.655
	5.51	2.02	2.19	-	0.627
	5.51	2.02	2.19	5.51	0.747

4. Correlation of Raman spectra to benzaldehyde yield

Calibration was carried out by packing the four microreactors with different amounts of a catalyst (1% AuPd/TiO_2) from previous work and run the reaction at different oxygen and benzyl alcohol flow rates at 120°C to generate different benzaldehyde yields. Raman spectra were collected at steady state at each condition over a period of time, while liquid samples were also collected from the gas-liquid separators and analysed by GC. A calibration curve was obtained by plotting the Raman spectral peak area ratio against the benzaldehyde yield measured by GC and shown in Fig. S4.

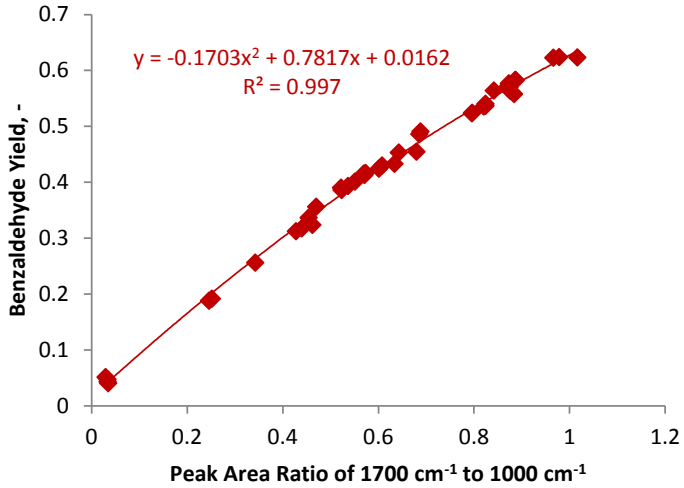


Fig. S4 Correlation of Raman spectral peak area ratio of 1700 cm^{-1} to 1000 cm^{-1} against benzaldehyde yield.

Reference

[1] E. Cao, M. Sankar, S. Firth, K.F. Lam, D. Bethell, D.K. Knight, G.J. Hutchings, P.F. McMillan, A. Gavriilidis, *Chemical Engineering Journal*, **167** (2011) 734-743.