

## Supporting Information

### **Controlling Palladium Particle Size and Dispersion as a Function of Loading by Chemical Vapour Impregnation: An Investigation Using Propane Total Oxidation as a Model Reaction**

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Table S1. Activity data for the Pd/Al<sub>2</sub>O<sub>3</sub> catalysts synthesised by wet impregnation. T<sub>20</sub> = Temperature at which 20 % conversion was achieved. T<sub>50</sub> = Temperature at which 50 % conversion was achieved. Reaction conditions: 1000 ppm propane/10% O<sub>2</sub>/N<sub>2</sub>, Gas Hourly Space Velocity (GHSV) 50,000 h<sup>-1</sup>, Temperature range 200 – 500 °C.

Catalyst	T <sub>20</sub> (°C)	T <sub>50</sub> (°C)	Decomposition rate at 250 °C (mol <sub>C<sub>6</sub>H<sub>8</sub></sub> h <sup>-1</sup> kg <sub>cat</sub> <sup>-1</sup> )
1.0 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	297	335	2.05x10 <sup>-6</sup>
2.5 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	276	305	1.51x10 <sup>-6</sup>
5.0 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	301	335	4.46x10 <sup>-7</sup>

Table S2. Palladium oxidation state and surface concentration for catalysts synthesised by chemical vapour impregnation as determined by XPS.

Catalyst	Pd oxidation state <sup>a</sup>	Surface concentration (%)
1.0 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	2+	0.19
2.5 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	2+	0.40
5.0 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	2+	0.70

Table S3. Post reaction CO chemisorption data for catalysts synthesised by CVI after 50 hour TOL study

Sample	Palladium surface sites ( $\text{g}^{-1}$ )	Dispersion (%)
1.0 Wt% Pd/ $\text{Al}_2\text{O}_3$	$2.05 \times 10^{19}$	30
2.5 Wt% Pd/ $\text{Al}_2\text{O}_3$	$3.98 \times 10^{19}$	28
5.0 Wt% Pd/ $\text{Al}_2\text{O}_3$	$7.95 \times 10^{19}$	26

Table S4. Physicochemical properties of the Pd/Al<sub>2</sub>O<sub>3</sub> wet impregnation catalysts from MP-AES and BET analysis.

Sample	Pd weight loading (%)	BET (m <sup>2</sup> g <sup>-1</sup> )
1.0 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	0.91	125
2.5 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	2.45	125
5.0 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	4.98	125

Table S5. Physical properties and activity characteristics of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts synthesised by wet impregnation extracted from and based on CO chemisorption characterisation.

Sample	CO adsorbed (mmol g <sup>-1</sup> )	Palladium surface sites <sup>a</sup> (g <sup>-1</sup> )	Dispersion <sup>a</sup> (%)	TOF <sup>b</sup> (10 <sup>-3</sup> )(s <sup>-1</sup> )
1.0 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	5.56x10 <sup>-3</sup>	6.79x10 <sup>18</sup>	12	1.81
2.5 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	1.45x10 <sup>-2</sup>	1.70x10 <sup>19</sup>	8	2.01
5.0 Wt% Pd/Al <sub>2</sub> O <sub>3</sub>	1.71x10 <sup>-2</sup>	1.98x10 <sup>19</sup>	7	6.79

a. Calculated from CO chemisorption assuming a stoichiometry of 2.

b. Calculated at 250 °C

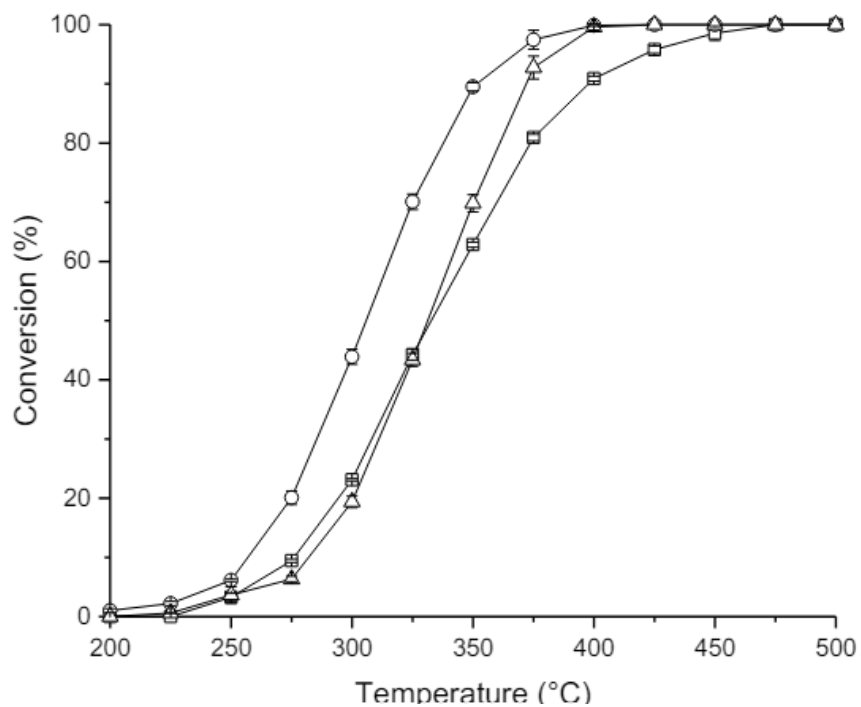


Figure S1. Propane conversion as a function of temperature for the Pd/Al<sub>2</sub>O<sub>3</sub> catalysts synthesised by wet impregnation. (Square) 1.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub>, (Circle) 2.5 Wt% Pd/Al<sub>2</sub>O<sub>3</sub>, (Triangle) 5.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub>. Reaction conditions: 1000 ppm propane/10% O<sub>2</sub>/N<sub>2</sub>, Gas Hourly Space Velocity (GHSV) 50,000 h<sup>-1</sup>, Temperature range 200 – 500 °C.

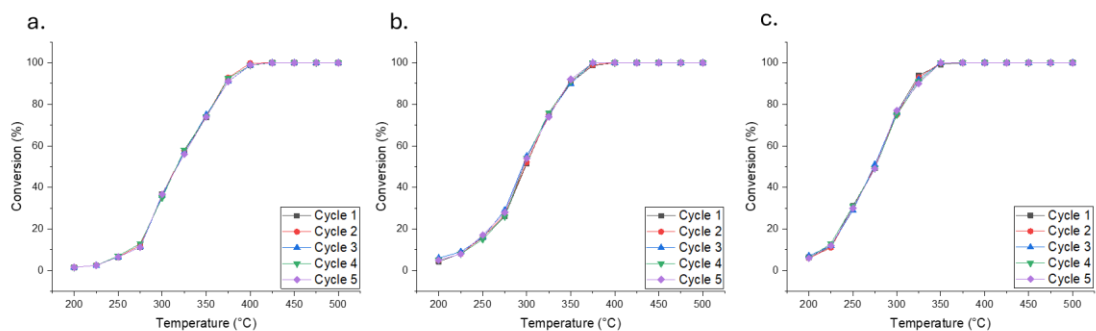


Figure S2. Stability testing for the catalysts synthesised by chemical vapour impregnation showing propane conversion as a function of temperature over multiple tests. A. 1.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub> b. 2.5% Wt% Pd/Al<sub>2</sub>O<sub>3</sub> c. 5.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub> Reaction conditions: 1000 ppm propane/10% O<sub>2</sub>/N<sub>2</sub>, Gas Hourly Space Velocity (GHSV) 50,000 h<sup>-1</sup>, Temperature range 200 – 500 °C.



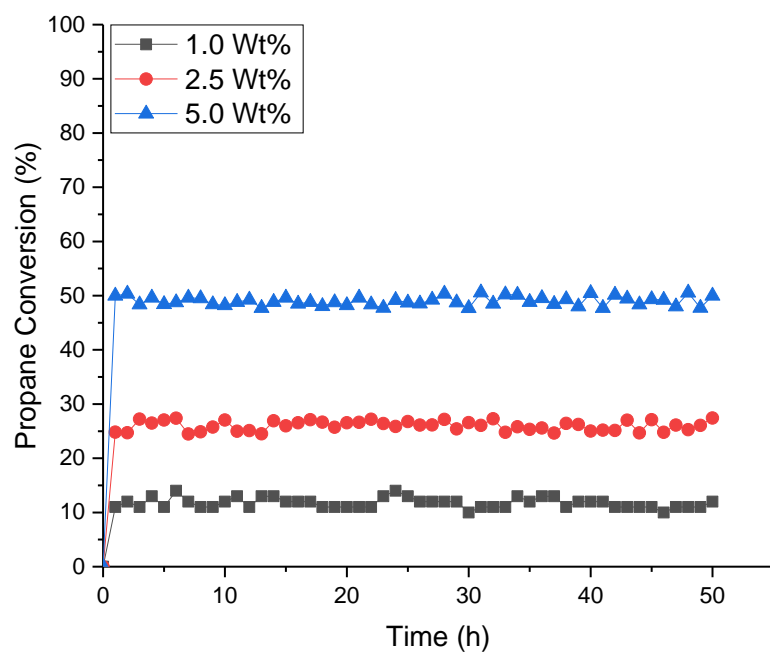


Figure S3. 50 hour time on line study the catalysts synthesised by chemical vapour impregnation showing propane conversion as a function of time. Reaction conditions: 1000 ppm propane/10% O<sub>2</sub>/N<sub>2</sub>, Gas Hourly Space Velocity (GHSV) 50,000 h<sup>-1</sup>, Temperature 275 °C.

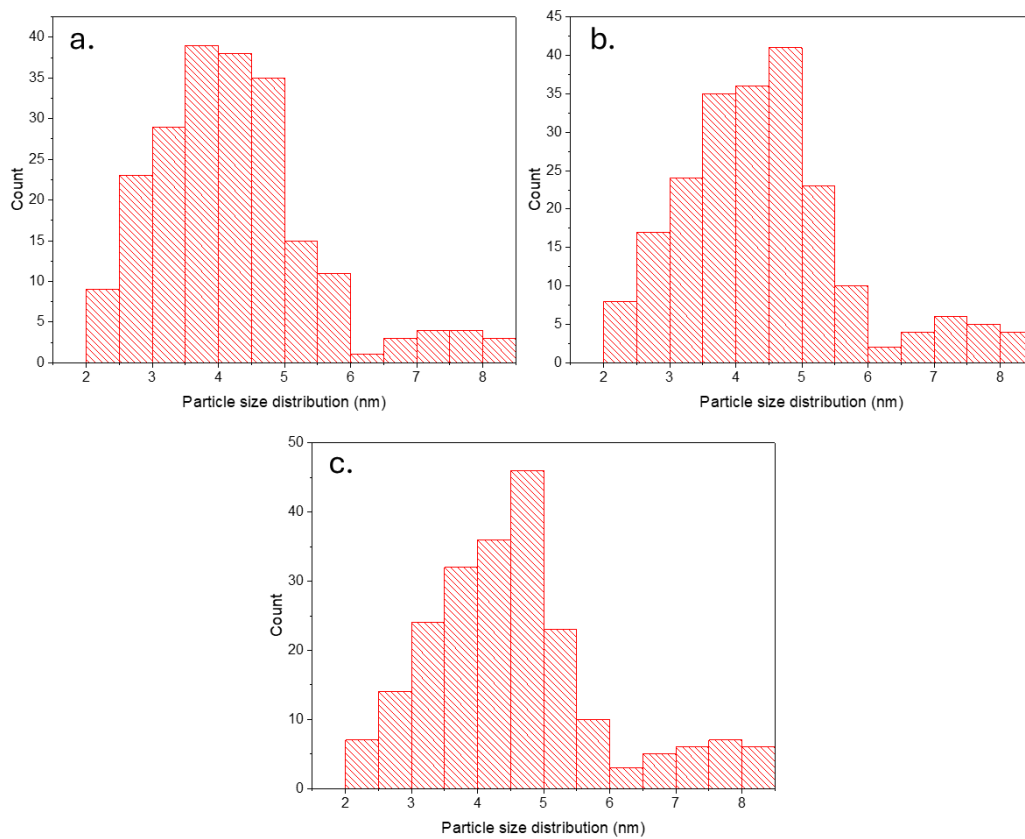


Figure S4. Palladium nanoparticle size distribution for catalysts synthesised by chemical vapour impregnation a. 1.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub> b. 2.5 Wt% Pd/Al<sub>2</sub>O<sub>3</sub> c. 5.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub>

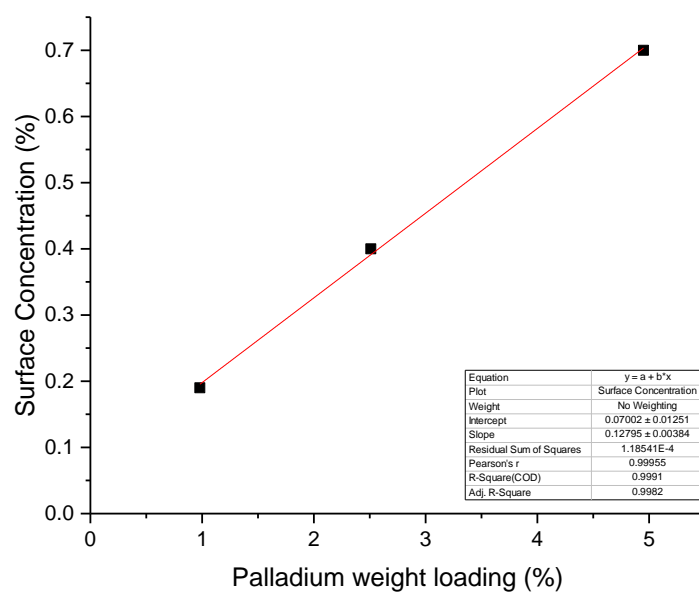


Figure S5. Figure demonstrating the linear relationship between the palladium weight loading calculated by MP-AES, and the surface concentration of palladium (calculated from XPS data), for catalysts synthesised by CVI.

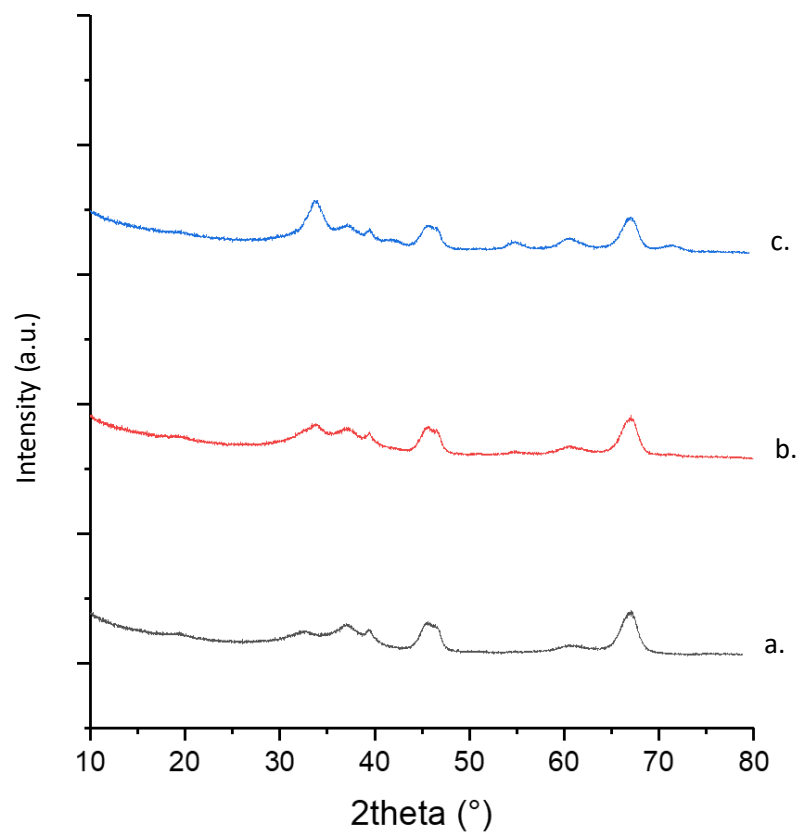


Figure S6. XRD scattering patterns of the samples synthesised by chemical vapour impregnation taken after a 50 hours time on line reaction. a. 1.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub> b. 2.5% Pd/Al<sub>2</sub>O<sub>3</sub> c. 5.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub>

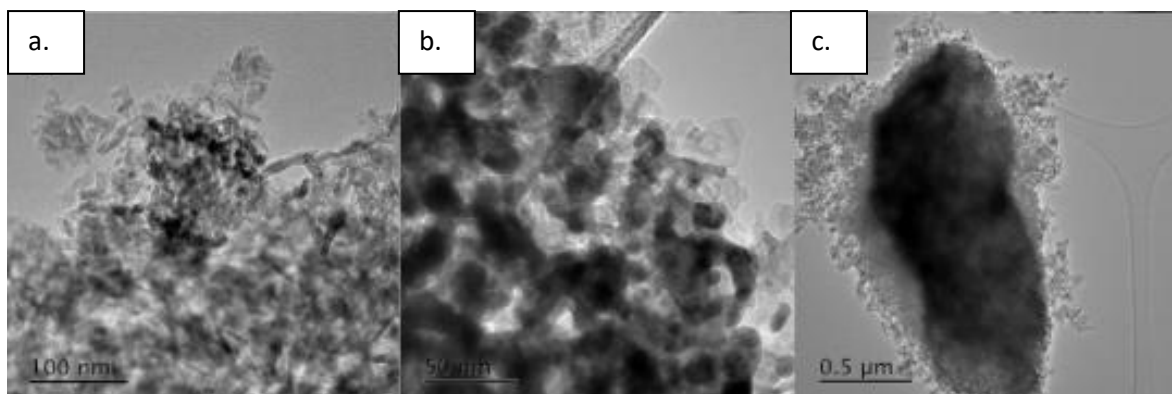


Figure S7. TEM micrographs of the catalysts prepared by wet impregnation. a. 1.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub>, b. 2.5 Wt% Pd/Al<sub>2</sub>O<sub>3</sub>, c. 5.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub>

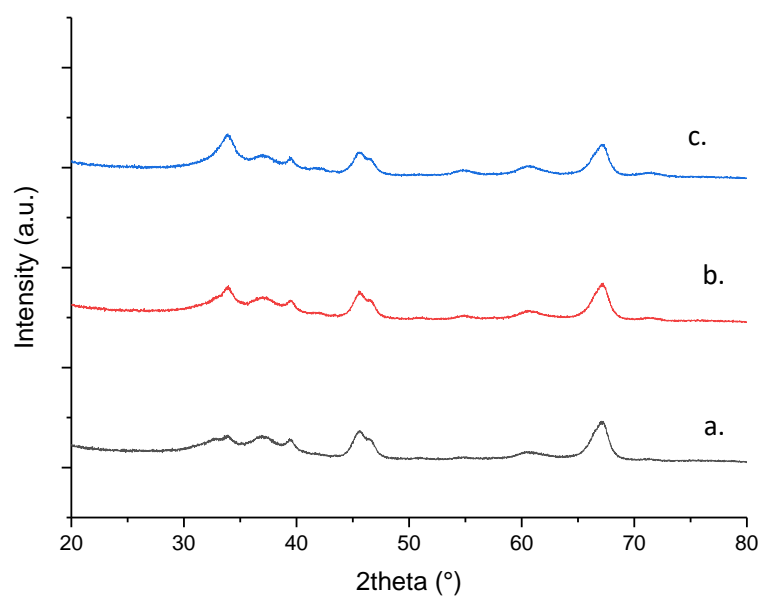


Figure S8. XRD scattering pattern for catalysts synthesised by wet impregnation. (a.) 1.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub>, (b.) 2.5 Wt% Pd/Al<sub>2</sub>O<sub>3</sub> and (c.) 5.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalysts.

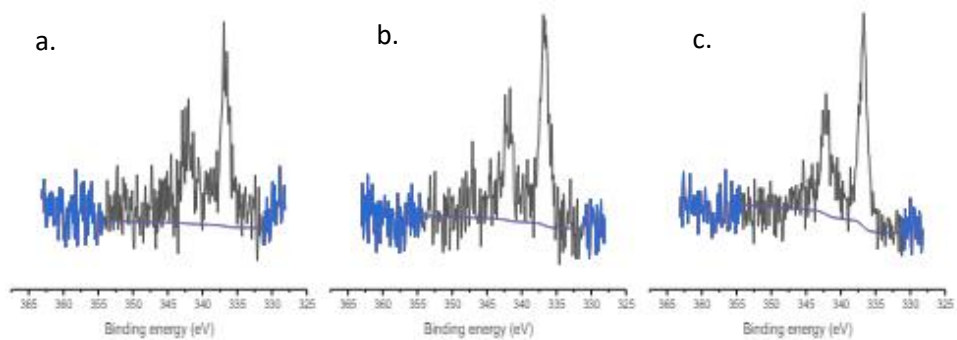


Figure S9. Pd 3d core-level XPS spectra for (a.) 1.0Wt.% Pd/Al<sub>2</sub>O<sub>3</sub>, (b.) 2.5Wt.% Pd/Al<sub>2</sub>O<sub>3</sub> and (c.) 5.0Wt.% Pd/Al<sub>2</sub>O<sub>3</sub> catalysts synthesised by wet impregnation.

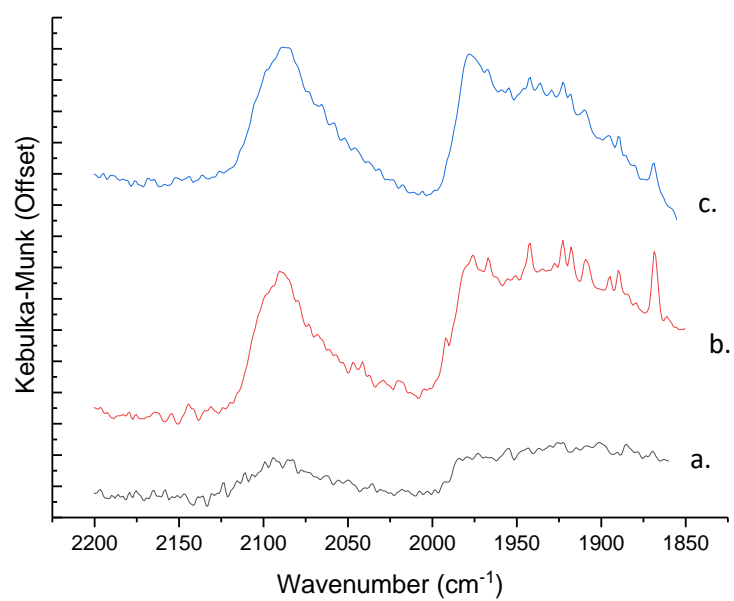


Figure S10. DRIFT spectra of CO adsorbed at room temperature for (a.) 1.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub>, (b.) 2.5 Wt% Pd/Al<sub>2</sub>O<sub>3</sub> and (c.) 5.0 Wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalysts for samples synthesised by wet impregnation.