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Electronic Supplementary Information

Platinum-catalysed cinnamaldehyde hydrogenation in continuous flow

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Catalyst synthesis. Fumed Silica (Sigma Aldrich, S5505, 200 $m^2.g^{-1}$) was wetted with aqueous ammonium tetrachloroplatinate (II) solution (16 cm^3 with the precursor concentration adjusted to achieve a nominal 2 wt% Pt loading). The resulting slurry was stirred for 18 h at room temperature before heating to 80 °C. Agitation was ceased after 5 h, and the solid dried at 80 °C for 24 h. The resulting powder was calcined at 500 °C for 4 h in air (ramp 10 $°C.min^{-1}$) prior to reduction at 400 °C for 2 h (ramp 10 $°C.min^{-1}$) under 10 $ml.min^{-1}$ flowing hydrogen.

Catalyst characterisation. Nitrogen porosimetry was undertaken on a Quantachrome Nova 2000e porosimeter, and analysed using NovaWin software version 11. Samples were degassed at 120 °C for 2 h prior to analysis by nitrogen physisorption. Adsorption/desorption isotherms were recorded for both parent and Pt-impregnated silica. BET surface areas were calculated over the relative pressure range 0.01-0.2. Wide angle XRD patterns were recorded on a Bruker D8 Advance diffractometer with Cu K_α (1.54 Å) source calibrated against a Si standard, between 2θ = 20-90° with a step size of 0.02°. The Scherrer equation was used to calculate the volume-averaged Pt particle size from line broadening. XPS was performed on a Kratos Axis HSi X-ray photoelectron spectrometer fitted with a charge neutraliser and magnetic focusing lens employing Al K_α monochromated radiation (1486.7 eV). Spectral fitting was performed using CasaXPS version 2.3.14, with binding energies corrected to the C 1s peak at 284.6 eV. The Pt 4f XP spectrum was fitted using an asymmetric lineshape. Pt dispersion was measured via CO pulse chemisorption on a Quantachrome ChemBET3000 system.The catalyst was outgassed at 150 °C under 20 $ml.min^{-1}$ flowing He for 1 h, prior to 150 °C reduction under 10 $ml.min^{-1}$ flowing hydrogen for 1 h before room temperature analysis: a CO:$Pt_{surface}$ stoichiometry of 0.68 was assumed, since the formation of a fully saturated monolayer is energetically unfavourable under these measurement conditions. Note that this reduction protocol is milder than that employed during Pt impregnation, and hence does not induce additional particle sintering. Metal loading was determined by EDX analysis on a Carl Zeiss Evo-40 SEM operated at 25 kV. High resolution (S)TEM images were recorded on a FEI Tecnai F20 field emission gun TEM operating at 200 kV equipped with a Gatan Orius SC600A CCD camera. The 2wt% Pt/SiO_2 sample was prepared for TEM by dispersion in ethanol and drop-casting onto a copper grid coated with a continuous carbon support film (Agar Scientific Ltd).

Batch cinnamaldehyde hydrogenation. Catalyst testing was performed using a Parr 5513 100 cm^3 stainless steel stirred batch autoclave at 1 and 5 bar H_2 pressure on a 10 cm^3 scale at 90 °C. 100 mg of 2.1 wt% Pt/SiO_2 was added to a reaction mixture containing 8.4 mmol of CinnALD substrate, 0.1 cm^3 mesitylene internal standard and 10 cm^3 anisole solvent under 700 rpm stirring. The absolute Pt content was 10.8 μmol, corresponding to a substrate:catalyst ratio of 780. Reactions were sampled periodically via a dip-tube and analysed by off-line GC using a Varian 3800GC with 8400 autosampler fitted with a (30 m x 0.25 mm x 0.25 μm) VF-5ms factor four column.

Flow reactor cinnamaldehyde hydrogenation. Catalyst testing was conducted using a commercial Uniqsis FlowSyn reactor, comprising a gas-liquid addition module (GAM II) and packed bed microreactor with downstream backflow pressure regulator (Scheme 2). Hydrogen was delivered via an in-line Brooks mass flow controller and back pressure regulator, while integral HPLC pump delivered an 8.4 mmol anisole/cinnamaldehyde liquid stream at flow rates between 0.08 $mm^3.min^{-1}$ to 2.4 $cm^3.min^{-1}$ Liquid and gas feeds were pre-mixed before introduction to the microreactor packed bed via the GAM II module which features a preheated semi-permeable polymer coil and reactor mandrel to ensure efficient gas-liquid pre-mixing and pre-heating to 90 ˚C prior to contact with the catalyst. The catalyst was diluted with quartz beads (Sigma Aldrich, mesh size = 4-20) to minimise back pressure, and packed within a 10 mm i.d. x 100 mm OMNIFIT® glass column to give a total bed volume of 2.35 cm^3, held in place between quartz wool plugs at either end of the column. The reactor was oriented vertically and the gas-saturated liquid stream fed in an up-flow direction to minimise settling and maximise permeation of the reaction mixture through the catalyst bed. Neither fluidisation nor compaction of the catalyst bed were observed under any conditions. Exit stream passed through a needle valve and backflow regulator with excess gas vented prior to off-line sampling for GC analysis.

Catalyst properties. The bulk and surface properties of the 2 wt% Pt/SiO_2 catalyst are detailed below.

Table S1. Physicochemical properties of 2 wt% Pt/SiO_2 catalyst.

Support	Pt loading / wt%$^{(a)}$	Pt dispersion / %$^{(b)}$	Pt particle size / nm$^{(c)}$	PtO_2 content / %$^{(d)}$	Surface area / m^2 g$^{-1(e)}$	Micropore surface area / m^2 g$^{-1(e)}$
Fumed SiO_2	2.10	10.0	15.6 (16.6)	7.7	176	35

[a]SEM/EDX; [b]from CO chemisorption assuming a CO:$Pt_{surface}$ stoichiometry of 0.68[1, 2]; [c]From CO chemisorption with parenthesis values from XRD via Scherrer analysis; [d]XPS; [e]N_2 BET; [f]BJH desorption isotherm

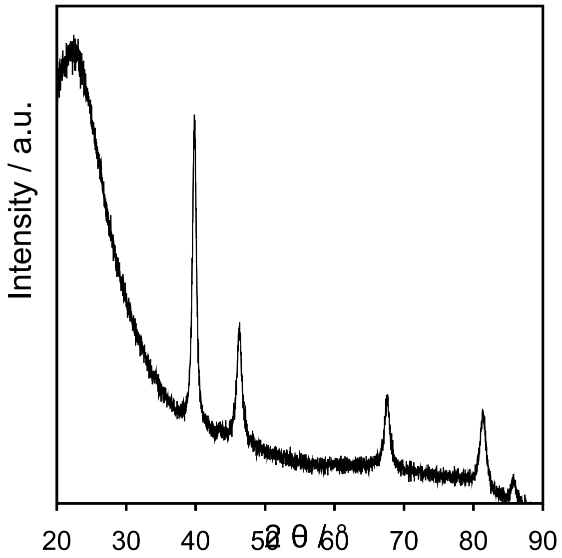

Figure S1. Wide angle XRD pattern of 2 wt% Pt/SiO_2 catalyst evidencing fcc platinum metal crystallites.

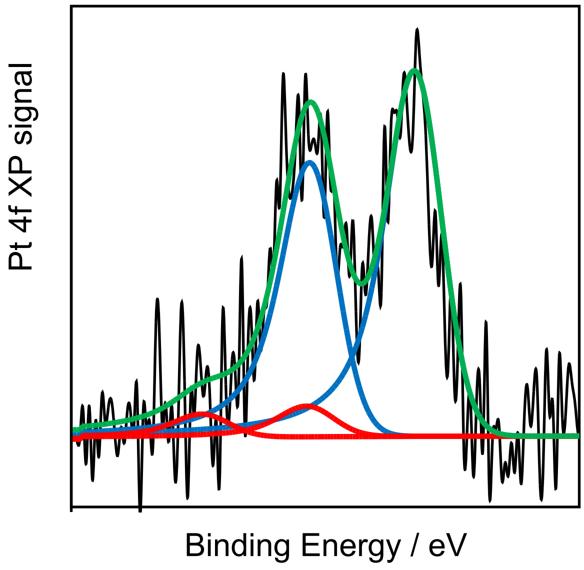

Figure S2. Pt 4f XP spectra of 2 wt% Pt/SiO_2 catalyst. Contributions due to $Pt^{(0)}$ (blue) and PtO_2 (red) fitted components are shown. The solid green line represents the fitted envelope. Offset for clarity.

Cinnamaldehyde hydrogenation.

Table S2. First order dependence of CinnALD hydrogenation on 2 wt% Pt/SiO_2 catalyst charge (at fixed bed volume). Reaction conditions: 100 or 200 mg of Pt/SiO_2, liquid flow 0.11 $cm^3.min^{-1}$ (84 mM in anisole), 40 cm^3 hydrogen gas flow at 5 bar and 90 °C catalyst

Catalyst mass / mg	**Rate of CinnALD hydrogenation / $mmols.min^{-1}$**
100	0.008
200	0.019

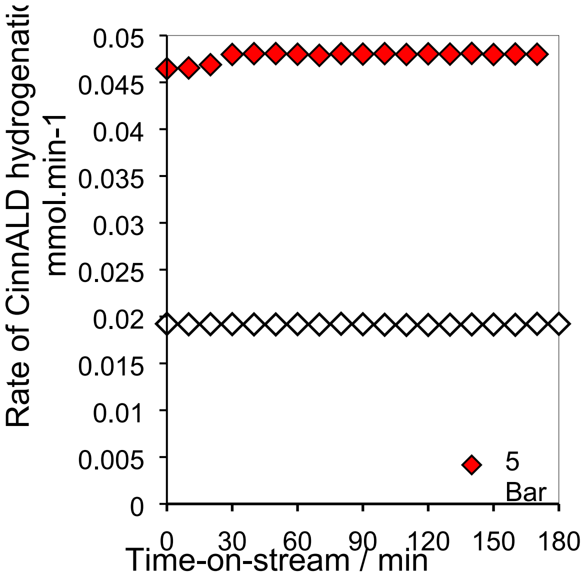

Figure S3. Rate of CinnALD hydrogenation over 2 wt% Pt/SiO_2 catalyst as a function of pH_2. Reaction conditions: 200 mg of Pt/SiO_2, liquid flow 0.11 $cm^3.min^{-1}$ (84 mM in anisole), 40 cm^3 hydrogen gas flow at 5 bar and 90 °C catalyst

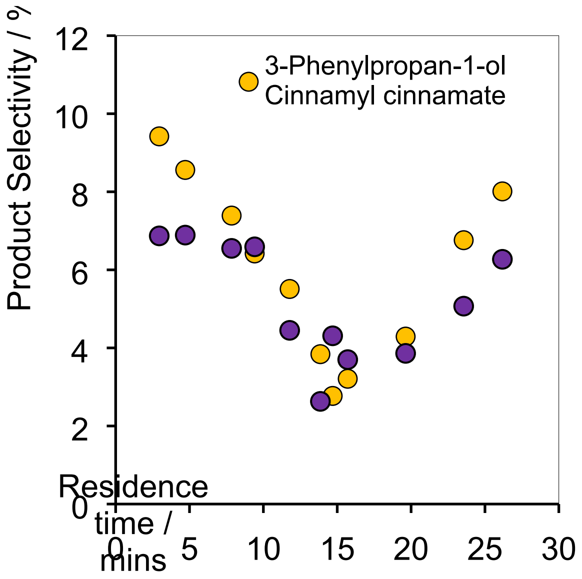

Figure S4. Residence time dependence of minority products during CinnALD hydrogenation over 2 wt% Pt/SiO$_2$ catalyst. Reaction conditions: 200 mg of Pt/SiO$_2$, liquid flow 0.08 to 2.35 cm^3.min^{-1} (84 mM in anisole), 40 cm^3 hydrogen gas flow at 5 bar and 90 °C catalyst.

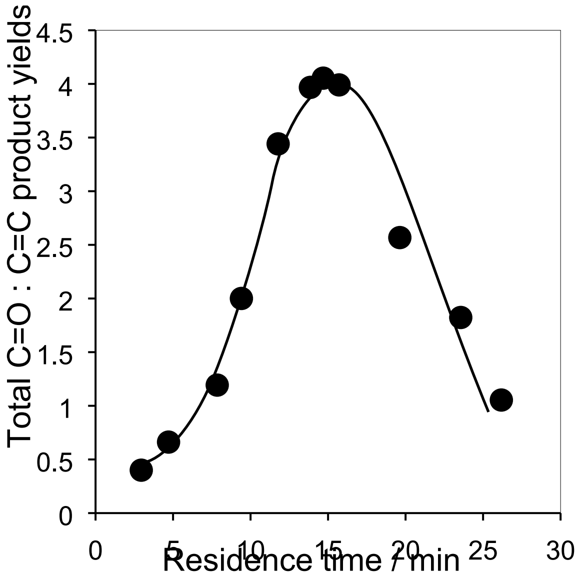

Figure S5. Relative yield of C=O versus C=C hydrogenated products during CinnALD hydrogenation over 2 wt% Pt/SiO$_2$ catalyst. Reaction conditions: 200 mg of Pt/SiO$_2$, liquid flow 0.08 to 2.35 cm^3.min^{-1} (84 mM in anisole), 40 cm^3 hydrogen gas flow at 5 bar and 90 °C catalyst.

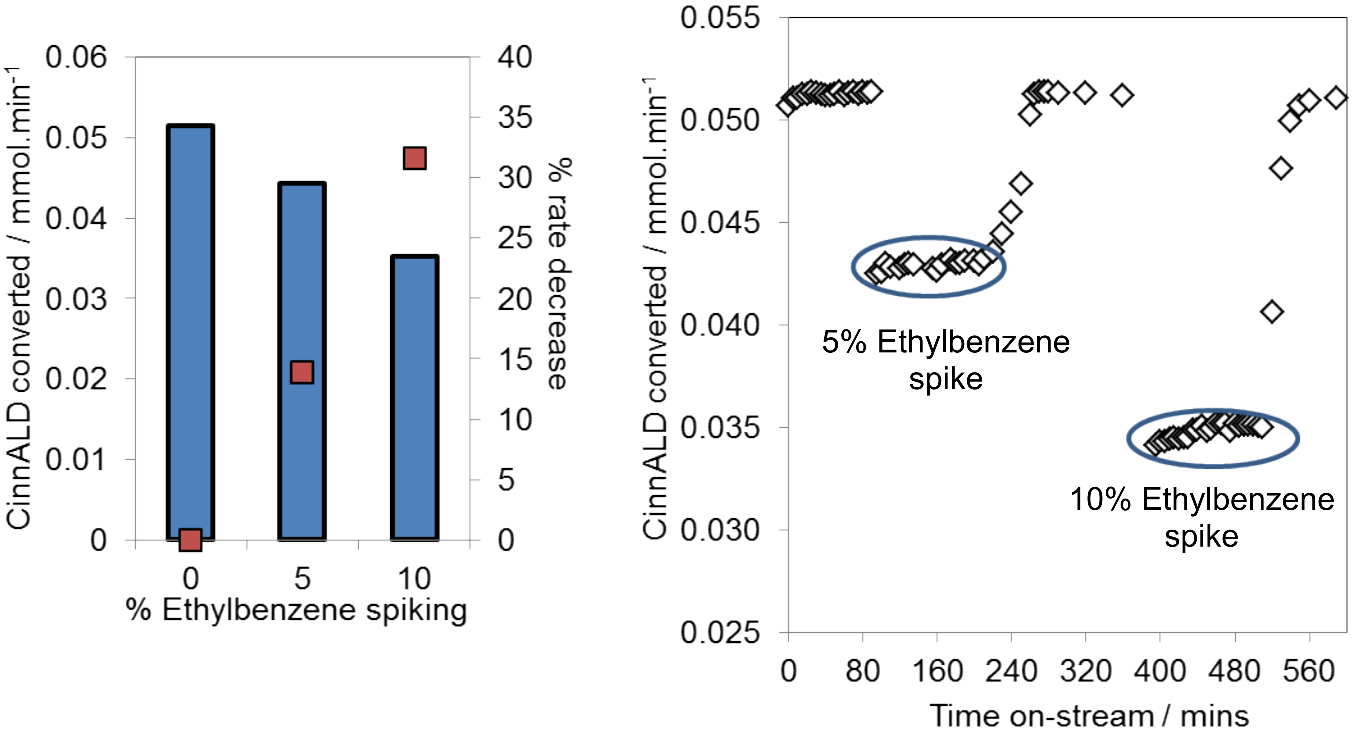

Figure S6. Effect of ethylbenzene spiking on CinnALD hydrogenation rate over 2 wt% Pt/SiO_2 catalyst. Reaction conditions: 200 mg of Pt/SiO_2, liquid flow 0.17 cm^3.min^{-1} (84 mM in anisole), 40 cm^3 hydrogen gas flow at 5 bar and 90 °C catalyst. CinnALD reactant stream spiked with anisole solution containing 5% and 10% ethylbenzene (0.007 mmol min^{-1} and 0.0143 mmol min^{-1}) respectively for 90 minutes whilst periodically sampling.