Activation and Deactivation of A Robust Immobilized Cp*Ir-Transfer Hydrogenation Catalyst: A Multi-Element *In Situ* XAS Study

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Contents

1. General Procedure

Experiments involving air sensitive reagents or products were performed under an atmosphere of nitrogen, using oven-dried glassware. The XAS flow-cell was assembled and flushed with nitrogen for 30 minutes before experiments. Anhydrous 2-propanol (<50 ppm water) and all other reagents were obtained from commercial suppliers and used without further purification. Reaction solvents were degassed by bubbling nitrogen through for a minimum of 30 minutes. All glassware was dried in oven (120 °C) overnight prior to use. GC analyses were performed using a Bruker 430-GC equipped with a CP-8400 autosampler.

Complexes $[Cp^*IrCl_2]_2$ and $[Cp^*Ir(\mu^2\text{-}Cl)_3IrCp^*]OTf$ were synthesised according to literature procedures.[1, 2] Immobilised catalysts were provided by Yorkshire Process Technology.

2. Synthesis of Materials

Synthesis of [Cp*IrCl$_2$(Py)]

Complex $[Cp^*IrCl_2]_2$ (0.50 g, 0.63 mmole) was dissolved in pyridine (25 mL) and the solution was stirred for 25 hours. The resulting yellow solution was evaporated to dryness and the crude product was recrystallised using layer diffusion from a dichlorometane/hexane solvent system to give the product as a yellow powder (0.54 g, 1.13 mmole, 90% yield).

Anal. Found C: 37.5, H:4.1, N: 2.9, Cl: 14.3%; Anal. Calc. C: 37.7, H:4.2, N: 2.9, Cl: 14.9%;

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.99 (br, d, J = 6.1 Hz, 2H), 7.74 (br, t, J = 7.6 Hz, 1H), 7.35 (dd, J = 6.8 Hz, 2H), 1.54 (s, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 137.7, 125.4, 85.7, 8.5.

3. Typical batch reaction

To the immobilized pre-catalyst $[Cp^{**}IrCl_2]_2$ (0.057 g, 0.035 mmole Ir) in a vial was added KO^{t}Bu (0.50 mg, 0.004 mmole) and anhydrous ^{i}PrOH (5 ml). The mixture was stirred at 60 °C for one hour for catalyst activation. Benzaldehyde (0.05 ml, 0.5 mmole) was then added. The mixture was stirred at 60°C and the reaction was monitored by GC. Further runs were conducted by decanting the solution, and recharging the resin with KO^{t}Bu (0.5 mg, 0.004 mmole), ^{i}PrOH (5 ml) and benzaldehyde (0.05 ml, 0.5 mmole) immediately. After 35 runs, the resin was recovered by filtering, washing with dichloromethane and dried using a vacuum oven. ICP analysis resulted in a very small change in Ir content: 0.034 mmole (3% decrease).

4. Mercury poisoning experiment

Two identical batch reactions were performed at the scale described above at 60 °C. After 3 hours, mercury (2.1 g, 10.5 mmole) was added to one reaction, while the other was left alone. GC samples were taken from both reactions at regular intervals (with 1,1'-biphenyl as internal standard, see section 11). The results are summarised below:

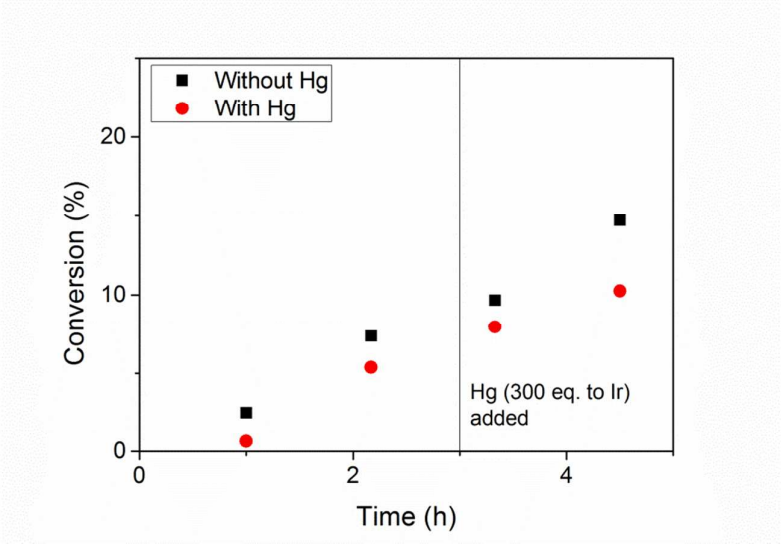


Figure S1. Catalytic conversion *vs* time in mercury poisoning experiment

5. 'Hot filtration' experiment

A batch reaction as described in section 3 was performed at 60 °C. After 3 hours, half of the reaction mixture was taken up by a syringe and filtered through a Whatman® cellulose acetate syringe filter (0.2 mm) into another vial. Both vials were continued to be stirred at and GC samples were taken at regular intervals (with 1,1'-biphenyl as internal standard, see section 11). The results are summarised below:

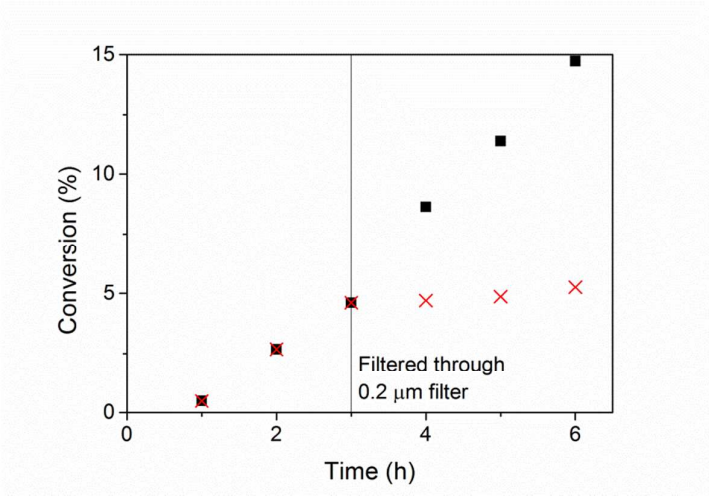


Figure S2. Catalytic conversion in 'hot filtration' experiment

6. Effect of water experiment

Two batch reactions were performed based on the typical anhydrous batch reaction using 57 mg of immobilized catalyst (0.035 mmole Ir), with water (3.3 mL, 0.18 mmole) added to one. Reaction progress was monitored over 6 hours using GC.

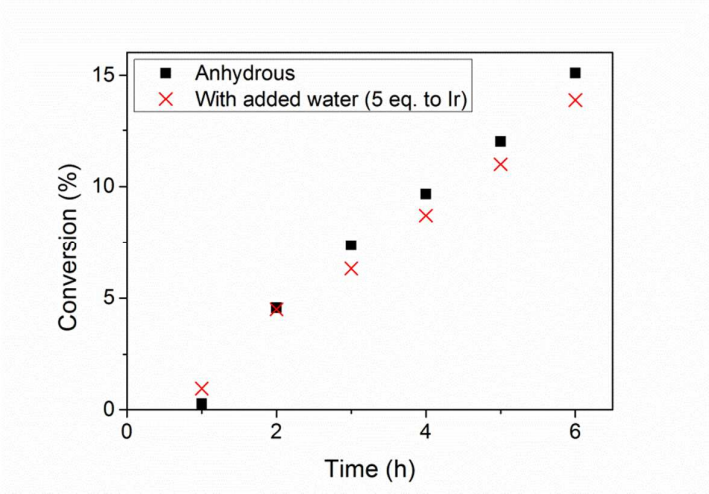


Figure S3. Catalytic conversion vs time in experiments on effect of water

7. Beamline Details

Solid state XAS measurements of various iridium catalysts and standards at the Ir L-edge were acquired on beamline B18 at Diamond Light Source using a Si(111) monochromator at 3 GeV and 300 mA. Samples were prepared as 8 mm cellulose pellets (80 mg of cellulose) with 10 mg of the immobilised catalyst samples and 5 mg for the iridium complexes. Signal was recorded using an ionisation chamber and intensity monitoring.

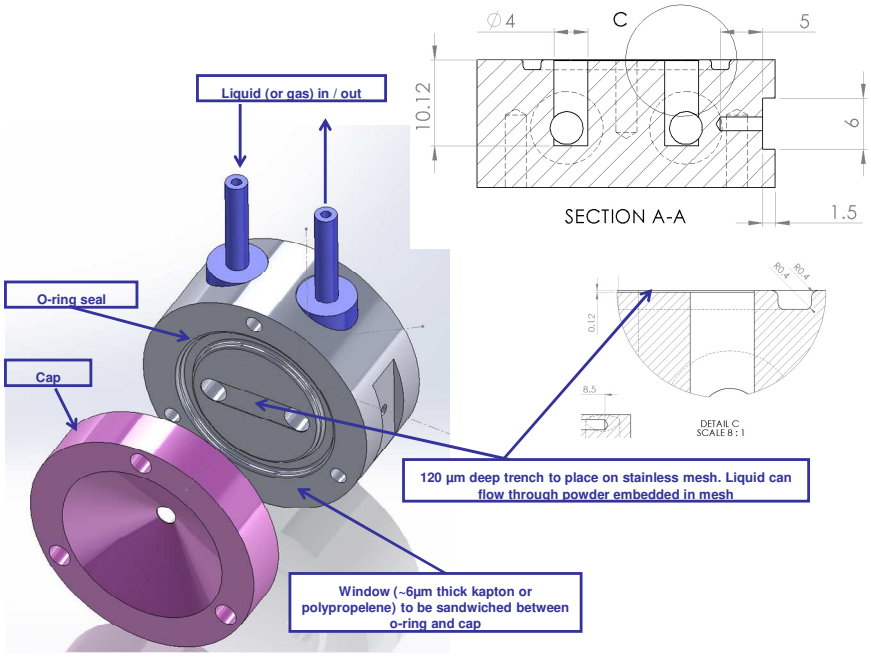
Cl and K K-edge XAS measurements were performed on beamline BM28 of the ESRF using a Si(111) double crystal monochromator at 6 GeV and 200 mA. Ir L-edge, *ex situ* Cl K-edge and K K-edge spectra

were collected in fluorescence mode using solid sample mounted on carbon tape under vaccum. *In operando* experiments are described in more details in section 8 and 11. Signal was recorded using MCA and a Vortex Silicon Drift detector.

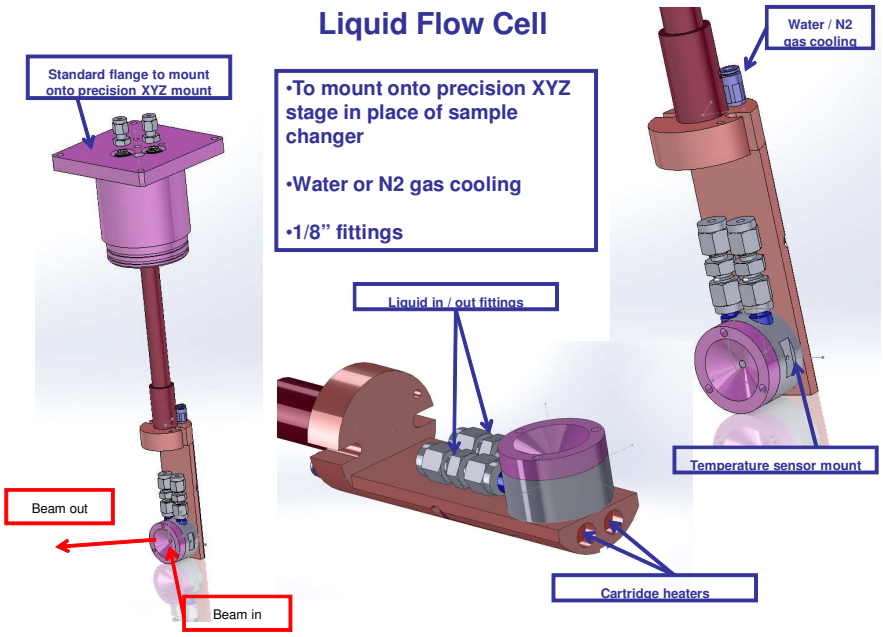
Data processing and analysis were conducted using the IFFEFIT software package.[3]

8. XAFS Spectroscopy Flow-Cell

A flow-cell for XAS at low energy in fluorescence mode was developed for this study. The cell was constructed from stainless steel, with a catalyst bed of 100 µm depth and a polypropylene window (6 µm thickness). The immobilised catalyst was mounted with the help of a stainless steel grid (no. FE200230 from Goodfellow). Two Swagelok connectors were used to connect the cell with a pump for reaction solution and a reservoir for reaction output using 1/8" PTFE tubing. The cell is mounted on a heating unit, for temperature control, which is subsequently connected to a *x,y,z*-motorised mount inside a vacuum/helium chamber. A hole was drilled on the side of the cell for a K-type thermocouple.



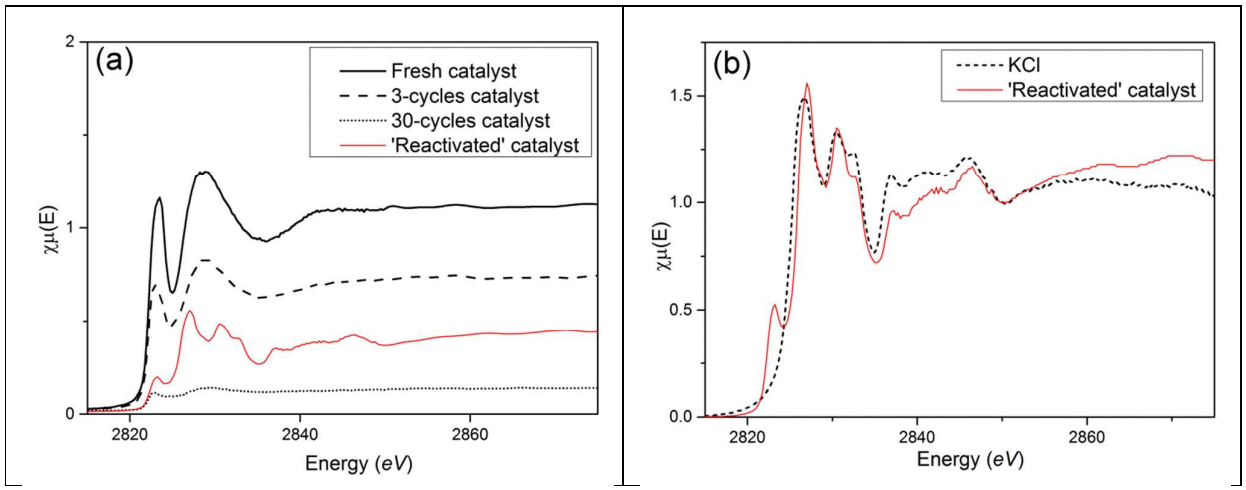
Scheme S1. Flow-cell for *in operando* XAS at low energy



Scheme S2. Mounting assembly for *in operando* XAS at low energy

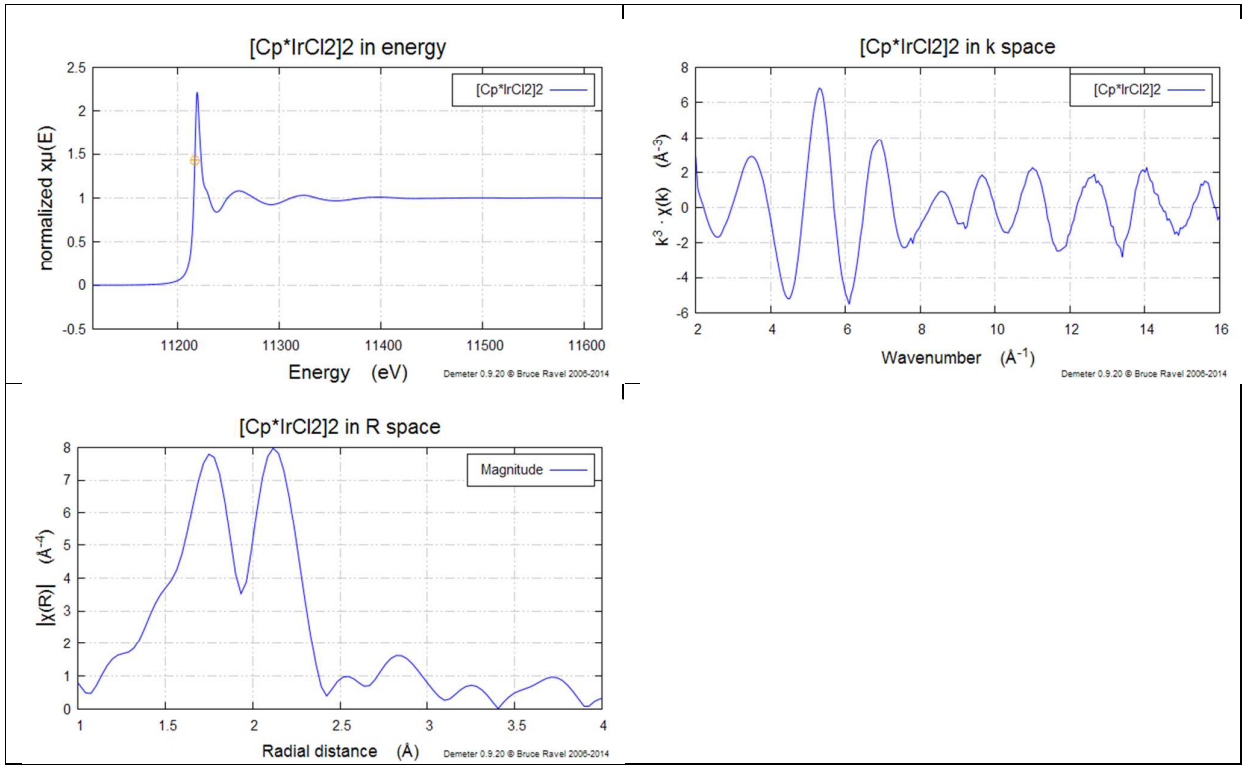
Scheme S3. Flow-cell with catalyst and window

9. *Ex situ* Cl K-edge XANES Spectrum of Catalysts and KCl

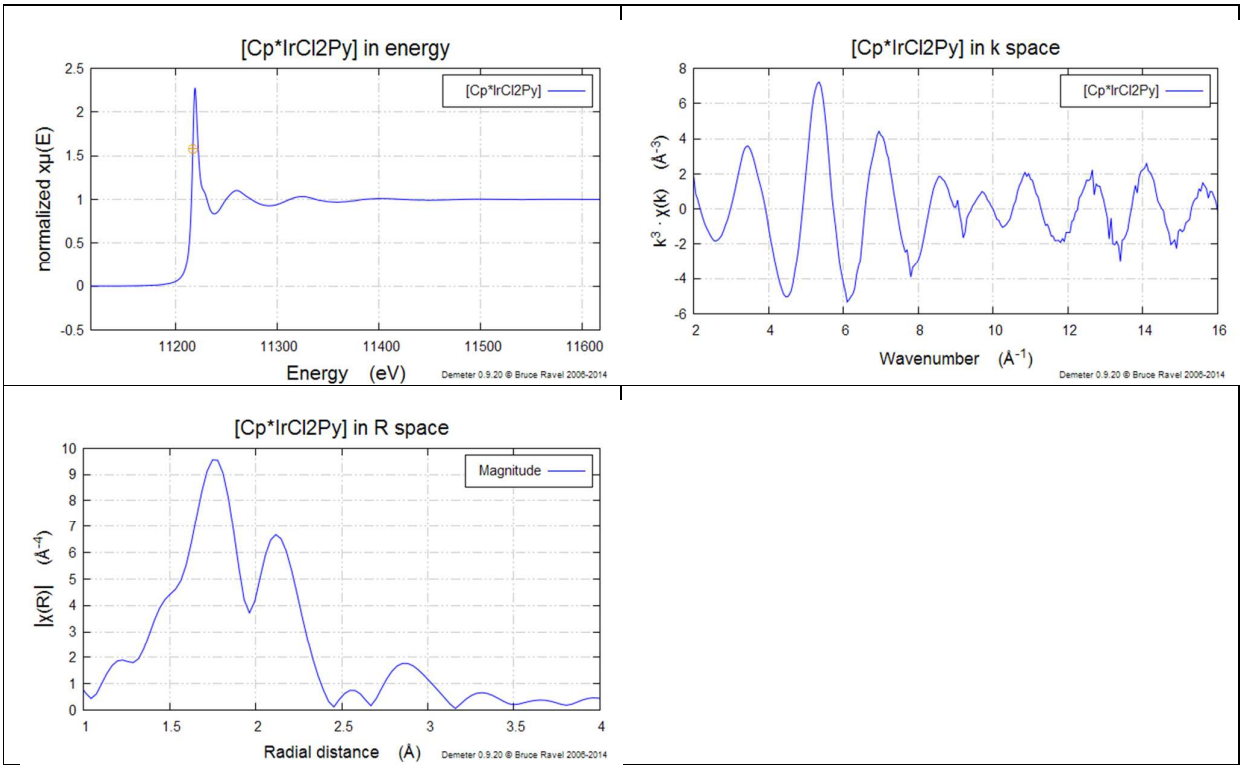


10. *Ex situ* Ir L-edge EXAFS Spectra of Standards and Immobilised Catalysts

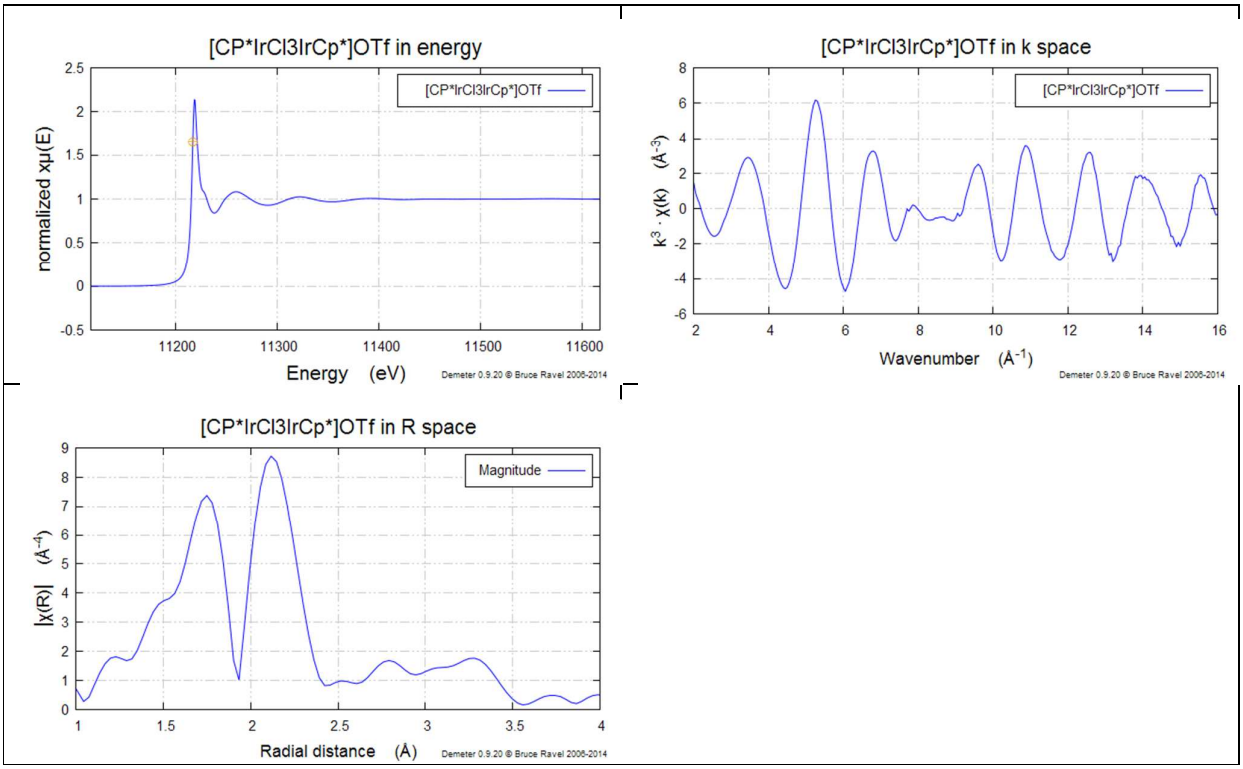
EXAFS spectra of $[Cp^*IrCl_2]_2$



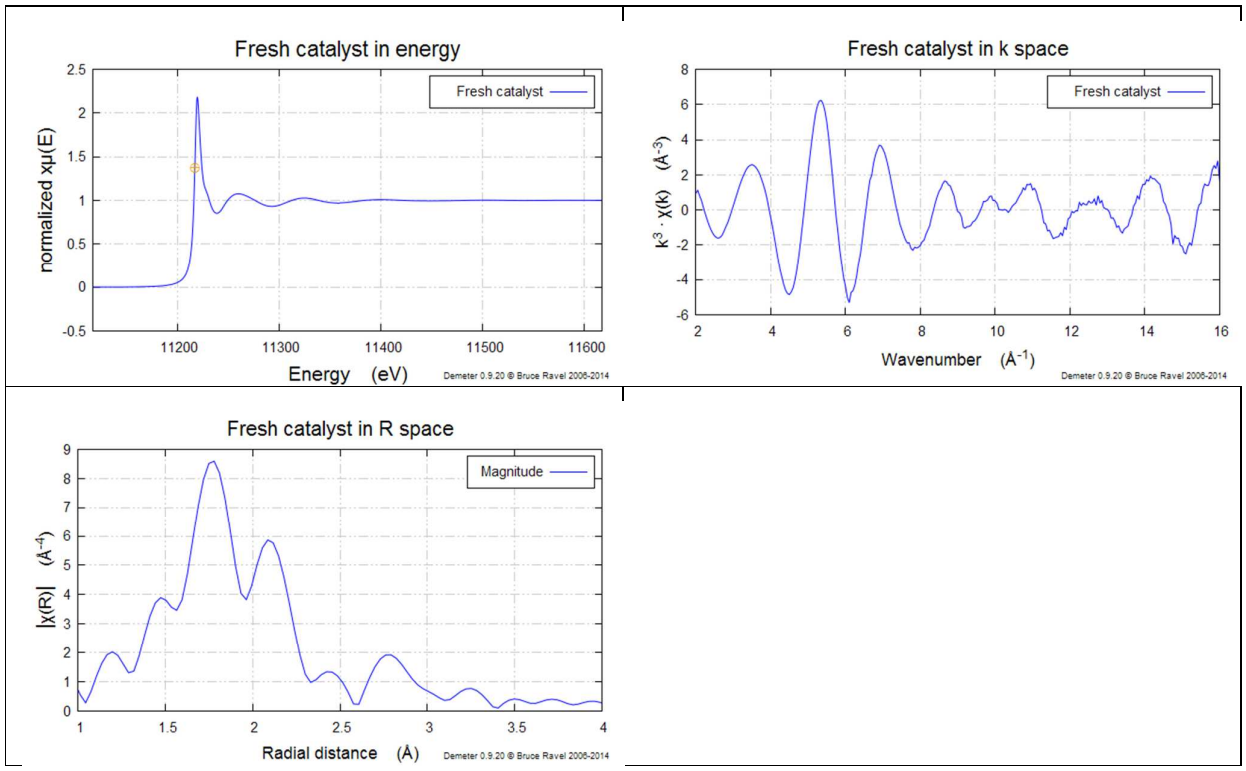
EXAFS spectra of $[Cp^*IrCl_2(Py)]$



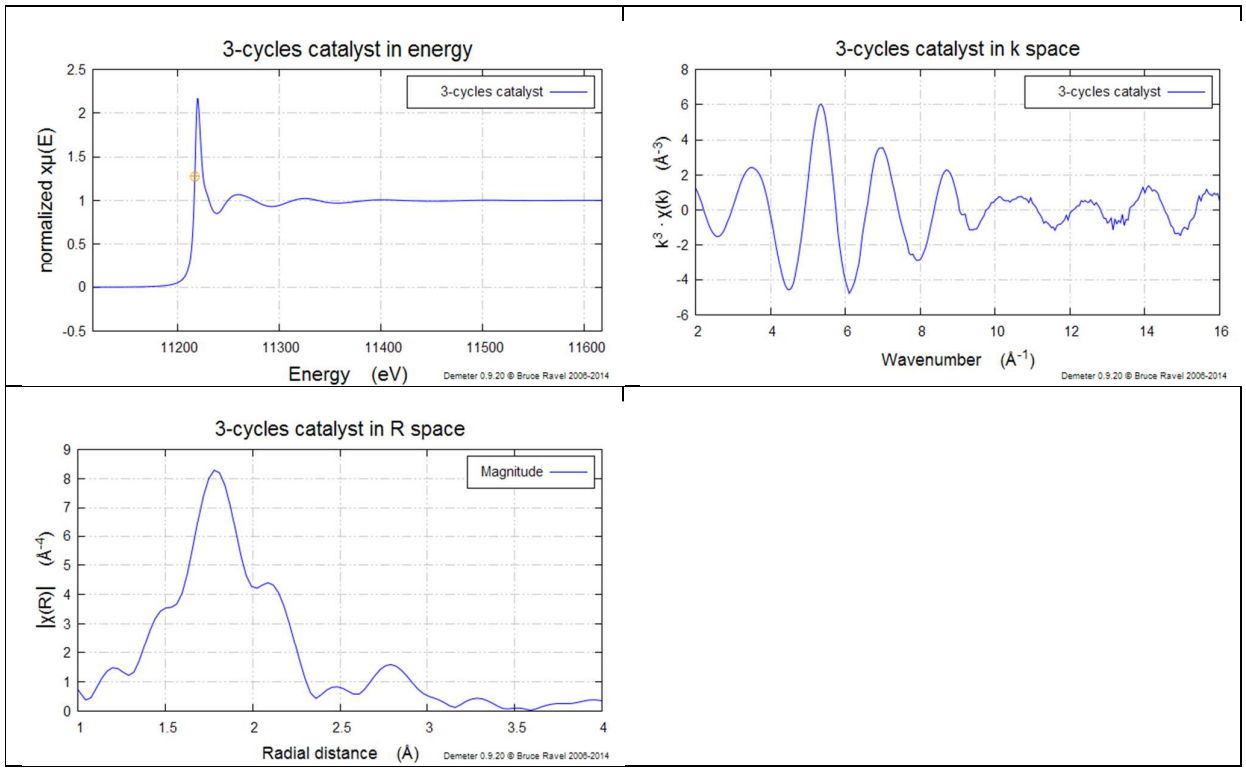
EXAFS spectra of [Cp*Ir(μ^2-Cl)$_3$IrCp*]OTf



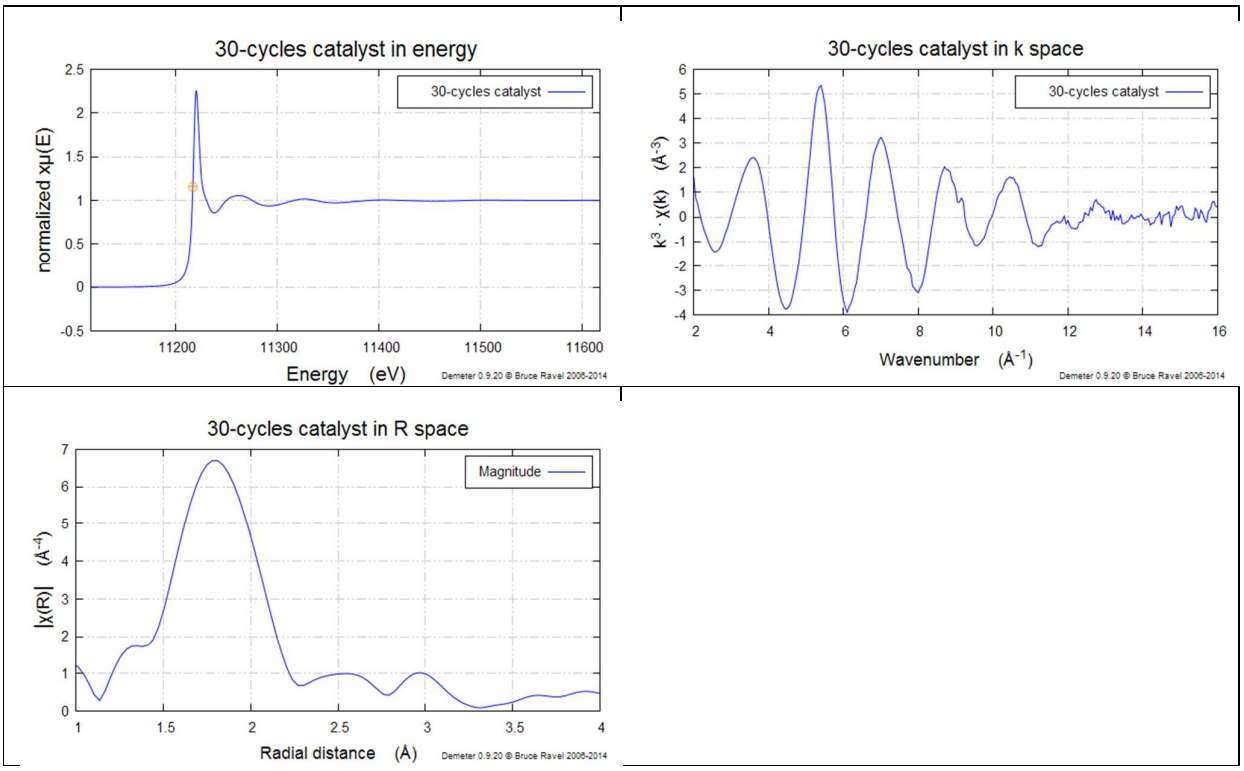
EXAFS spectra of fresh immobilised catalyst



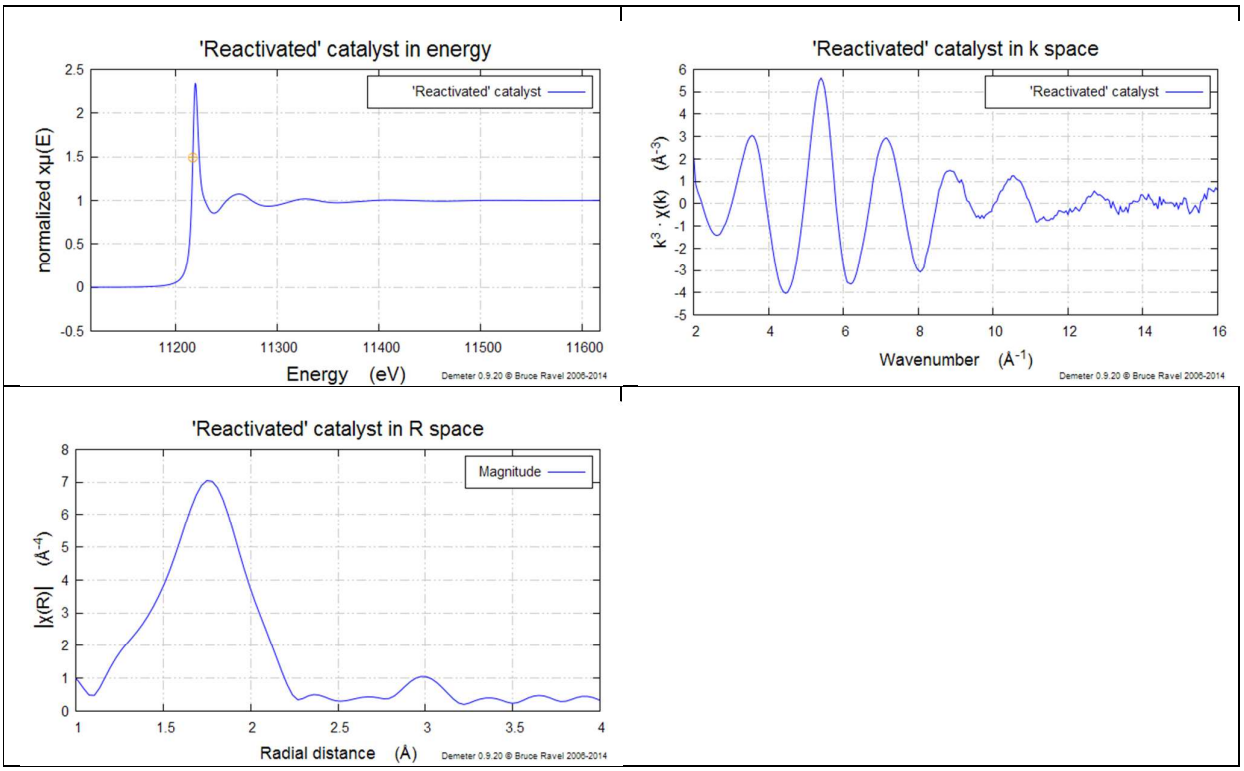
EXAFS spectra of immobilised catalyst after three cycles of use



EXAFS spectra of immobilised catalyst after 30 cycles of use

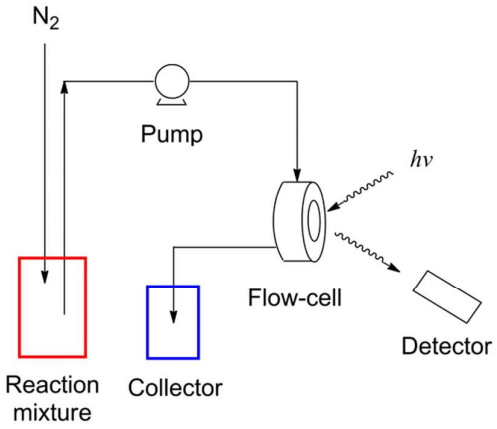


EXAFS spectra of immobilised catalyst after 'reactivation' with HCl



11. *In operando* XAS Experiment at Cl and K K-edge

The reaction solutions were prepared following the protocol outlined below at 60 °C using a milliGAT® positive displacement pump and 1/8" PTFE tubing. A schematic of the experiment set-up is shown in Scheme S4.



Scheme S4. In operando XAS experimental setup

Step 1: A solution of anhydrous 2-propanol was passed through the flow reactor (volume = 6.9 µL) containing a the immobilised catalyst (1 mg, 12% Ir w/w) on a stainless steel mesh support at 10.8 µLmin^{-1} (residence time = 39 seconds) at 60 °C for 30 minutes. XANES spectra at Cl K-edge or K K-edge were collected.

Step 2: A solution of anhydrous 2-propanol (60 mL) containing potassium *tert*-butoxide (6.0 mg, 0.89 mM) was passed through the flow reactor at 10.8 µL.min^{-1} and 60 °C for 30 minutes to generate active catalyst. This was followed by washing with anhydrous 2-propanol (0.33 mL) at flow-rate 10.8 µL.min^{-1}. XANES spectra at Cl K-edge or K K-edge were collected.

Step 3: A solution of anhydrous 2-propanol (60 mL) containing potassium *tert*-butoxide (6 mg, 0.89 mM) and benzaldehyde (0.637 g, 0.10 M) was passed through the flow reactor 10.8 µLmin^{-1} (residence time = 39 seconds) at 60 °C. This was continued for 24 hours, and XANES spectra at Cl K-edge and K K-edge were collected alternatively. The total runtime for each scan was approximately 60 minutes.

Step 4: Anhydrous 2-propanol (30 mL) was passed through the flow-cell at flow rate mL.min-1 to wash off residue of the reaction mixture. XANES spectra at Cl K-edge or K K-edge were collected.

Step 5: The flow-cell was allowed to cool to room temperature. A solution of HCl 1M in 2-propanol (1 mL) was flowed through the cell at 10.8 µL.min^{-1}. This was followed immediately by 2-propanol (30 mL) to remove the acid from the stainless steel flow-cell. XANES spectra at Cl K-edge or K K-edge were then collected.

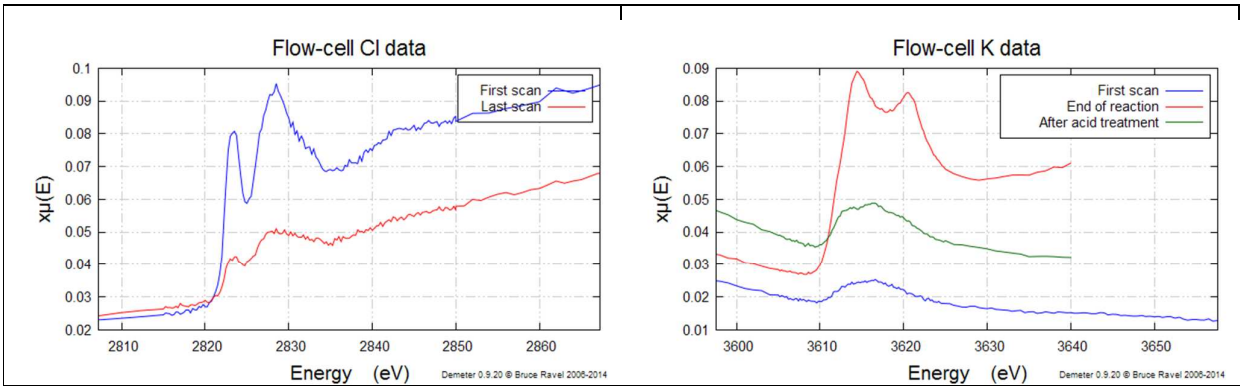


Table 1. *In operando* edge jump data at Cl K-edge and K K-edge *vs* time

Time (h)	Cl edge-jump	K edge-jump
0.05	0.0141	
1.00		0.0192
1.85	0.0165	
2.80		0.0307
3.51	0.0119	
4.47		0.0336
5.59	0.0146	
6.54		0.0306
7.61	0.0117	
8.80		0.0349
9.64	0.0119	
10.59		0.0422
11.30	0.0141	
12.26		0.044
12.97	0.014	
13.92		0.0485
14.64	0.0136	
15.60		0.017
16.39	0.0108	
17.34		0.0549
18.09	0.0112	
19.04		0.05

12. GC Calibration and Calculations

GC was performed using a BR-5 column (30 m x 0.25 mm (ID) x 0.25 µm film thickness) with carrier gas flow rate of 2.0 $mL.min^{-1}$ and a temperature ramp from 50 to 310 ^{o}C at 20 $^{o}C.min^{-1}$. The injection volume was 5 µL with a split ratio of 10. The response factors for the internal standard, substrate and product were calculated using an appropriate calibration for this GC and column.

Calibration was performed for the reaction product, i.e. benzylalcohol, using 0.001 M biphenyl as an internal standard (Table 2). All calibration samples were made up using 0.001 M biphenyl solution in 2-propanol.

Table S2. GC calibration of benzylalcohol against 1,1'-biphenyl as internal standard

[BnOH] (M)	0.0001	0.00025	0.0005	0.001	0.00125
Peak Area (BnOH)	54.0	168.7	350.7	638.9	757.3
Peak Area (PhPh 0.001 M)	165.7	170.9	145.8	121.6	123.6
Peak Area ratio (BnOH/PhPh)	0.326	0.987	2.405	5.254	6.127

The calibration curve is shown below:

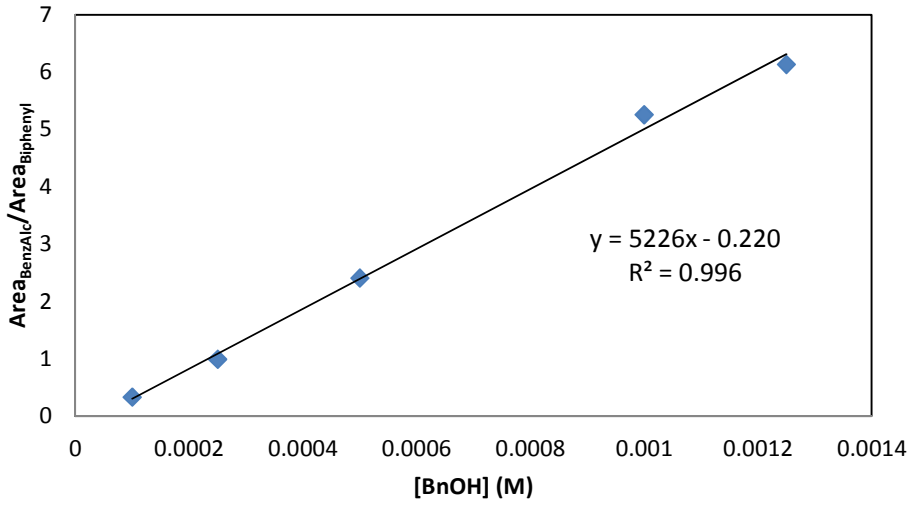


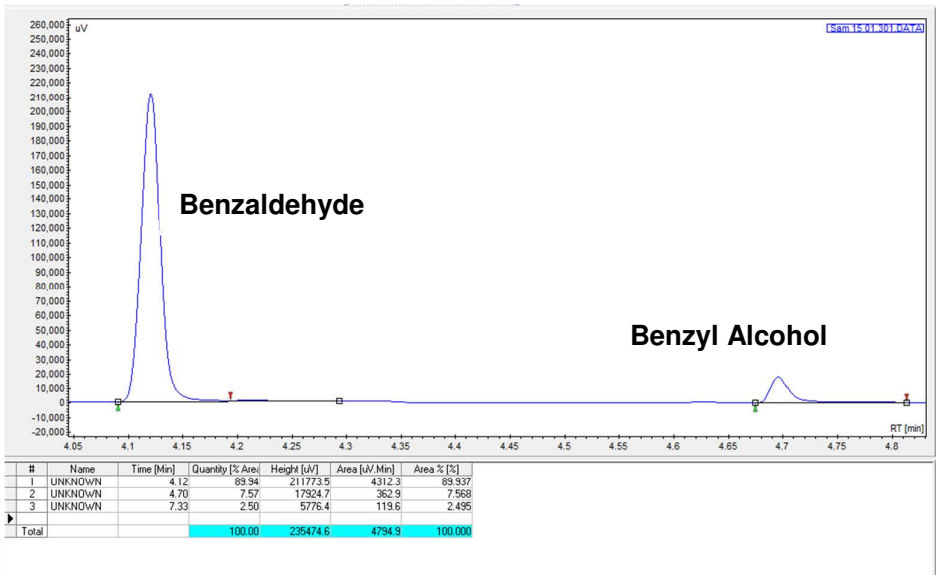
Figure S4. Calibration curve for BnOH response factor against 1,1'-biphenyl as internal standard

Consequently, the concentration of benzylalcohol was calculated as:

$$[\text{BnOH}] = \frac{(\text{Area}_{\text{BenzAlc}}/\text{Area}_{\text{Biphenyl}}) + 0.2206}{5226.6}$$

13. Catalytic Activity *vs* Time Experiment

The experiment was carried out as described in Section 11, to monitor the conversion of benzaldehyde to benzylalcohol over time. 1,1'-Biphenyl (0.001 M) was added to the reaction mixture as internal standard for GC. Samples were collected for every 60 minutes (0.65 mL) for 21 hours and analysed by GC without further purification. Conversion data was calculated based on the concentration of the product against the concentration of starting material flown into the cell (0.01 M benzaldehyde).



#	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	4.12	89.94	211773.5	4312.3	89.937
2	UNKNOWN	4.70	7.57	17924.7	362.9	7.568
3	UNKNOWN	7.33	2.50	5776.4	119.6	2.495
Total			100.00	235474.6	4794.9	100.000

Figure 5. Example GC chromatogram from catalytic activity *vs* time experiment

Table 3. Results from catalytic activity *vs* time experiment

Sample	Time (Minutes)	Time (Hours)	$Area_{BenzAlc}/Area_{Biphenyl}$	[BnOH] (mM)	Conversion (%)
1	60	1	3.034281	0.623	0.623
2	120	2	2.798548	0.578	0.578
3	180	3	2.397136	0.501	0.501
4	240	4	2.150478	0.454	0.454
5	300	5	1.78777	0.384	0.384
6	360	6	1.555456	0.340	0.34
7	420	7	1.466791	0.323	0.323
8	480	8	1.380987	0.306	0.306
9	540	9	1.164112	0.265	0.265
10	600	10	1.105163	0.254	0.254
11	660	11	0.980291	0.230	0.23
12	720	12	1.094952	0.252	0.252
13	780	13	1.100872	0.253	0.253
14	840	14	1.015635	0.237	0.237
15	900	15	0.941104	0.222	0.222
16	960	16	0.852471	0.205	0.205
17	1020	17	0.912715	0.217	0.217
18	1080	18	0.885246	0.212	0.212
19	1140	19	0.843333	0.204	0.204
20	1200	20	0.735398	0.183	0.183
21	1260	21	0.789517	0.193	0.193

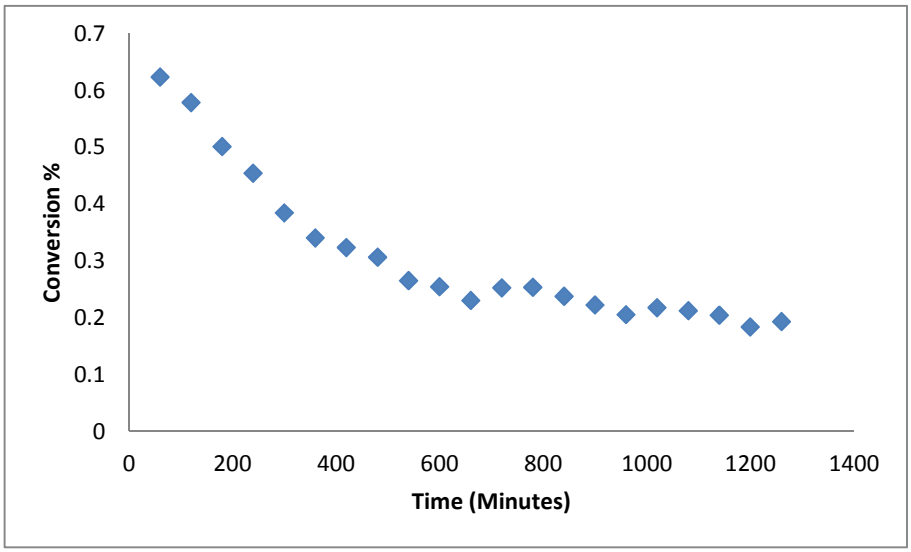


Figure S6. Conversion *vs* time in catalytic activity *vs* time experiment

14. Fitting of catalyst deactivation

Kinetic modelling was performed using the DynaFit package from Biokin.[4] Simple fitting using a single deactivation equation (assuming constant concentrations of other reactants under continuous conditions):

$$A \rightarrow B \quad ; \qquad d[A]/dt = k_1 \times [A]$$

where A is the active catalyst and B is the deactivated catalyst, failed to find a good fit with the experimental data in section 12.

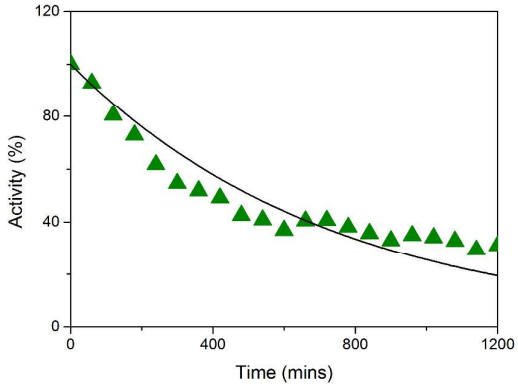


Figure S7. Fitting of catalyst deactivation using one species and first order deactivation pathway

Consequently, a two species model was adopted:

$$A \rightarrow B \quad ; \qquad d[A]/dt = k_1 \times [A]$$

$$C \rightarrow B \quad ; \qquad d[C]/dt = k_2 \times [C]$$

where B is the deactivated catalyst and A and C are catalysts on the surface and at the core of the resin support. These two type of catalysts were given different deactivation rate constants based on different mass transfer rates of solution species to these different catalytic centres. After some initial fitting, an assumption of $[A]_0 = [C]_0$ (at $t = 0$) was made as up to 20% variation in their relative ratio did not seem to significantly

affect the outcome. Fitting was then performed for k_1 and k_2 and the results are summarised in Figure S6. The best fit values for the rate constants are:

$$k_1 = 4.36 \pm 0.29 \times 10^{-3}\ \text{min}^{-1}$$

$$k_2 = 4.50 \pm 0.31 \times 10^{-4}\ \text{min}^{-1}$$

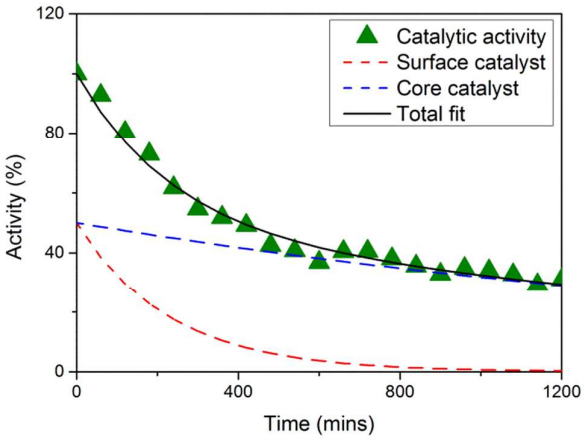


Figure S8. Fitting of catalyst deactivation using two species and first order deactivation pathways

15. References

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3. Newville, M., *J. Synchrotron Rad.* **2001,** *8*, 322-324.
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