

Supporting Information

**From Small Molecules To Polymeric Catalysts In Oscillatory Carbonylation Reaction:
Multiple Effects of Adding HI**

Anna Isakova,^{1*} Billy Murdoch,² Katarina Novakovic¹

1. School of Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK 2. National EPSRC XPS Users' Service (NEXUS), School of Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK

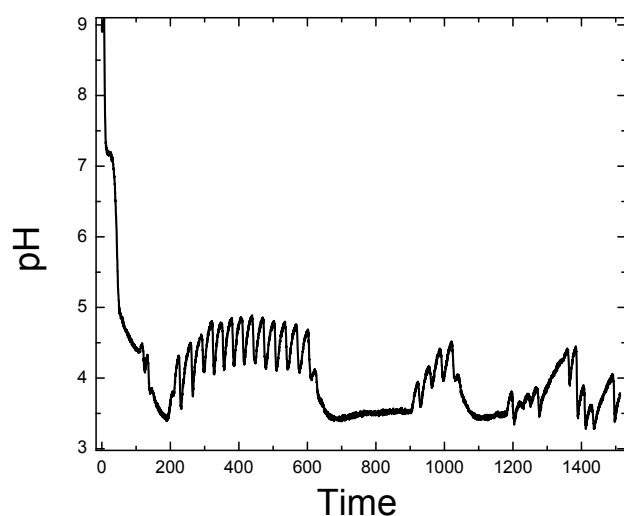


Figure S1. pH recorded in the oxidative carbonylation of phenylacetylene in methanol using PdAc as catalyst, with CO and air (15 ml/min each). Disruptions in oscillations are observed when gas lines get clogged with KI or Pd(0) particles, caused by a high concentration of catalyst in the reaction media.

PdAc catalytic behaviour was studied by UV-Vis absorbance measurements (Figure S2). The pH drop, caused by purging CO/air through the reaction mixture, was accompanied by a rapid discolouration of solution: within 5 min the colour changed from dark red solution (Erlenmeyer denoted with number 1) to light, orange solution (Erlenmeyer denoted with number 2), Figure S2a. The discolouration was accompanied by a dramatic change in absorbance spectra when compared to the spectra for the PdAc/KI/MeOH reaction mixture prior to purging with the gases. A major decrease in the concentration of the highly absorbing Pd²⁺ species (absorbance maximum at 338 nm) was noted (Figure S2a).¹ Similarly, the peak at 450 nm observed prior to purging and attributed to the presence of molecular iodine, I₂,² disappeared. However, two other peaks emerged at 288 nm and 353 nm, attributed to the formation of I₃⁻

($I_2 + I^- \rightarrow I_3^-$).² No metallic Pd was visually observed either, indicating that the palladium species formed from Pd^{2+} was from a different intermediate. Previous studies by other groups suggested conversion of Pd^{2+} into Pd^+ species at this initial stage of the reaction, however, evidence for this species was not solid.^{3,4}

As seen from the absorbance spectrum, in the substrate-initiated reaction mixture (PdAc/KI/MeOH/CO/air/PhAc) during the pH drop iodine existed as I_3^- (a clearly visible shoulder at 288 nm) and only a trace amount of Pd^{2+} was observed at 338 nm. While formation of metallic Pd(0) was visually observed following PhAc addition, this was not picked up by the UV-Vis measurements. When oscillations started, a similar picture was visually observed during pH falling – the majority of Pd species was Pd(0). When pH was rising, the picture was the opposite – a major peak of Pd^{2+} species was noted by UV-Vis measurements, accompanied by an I_2 peak at 450 nm.

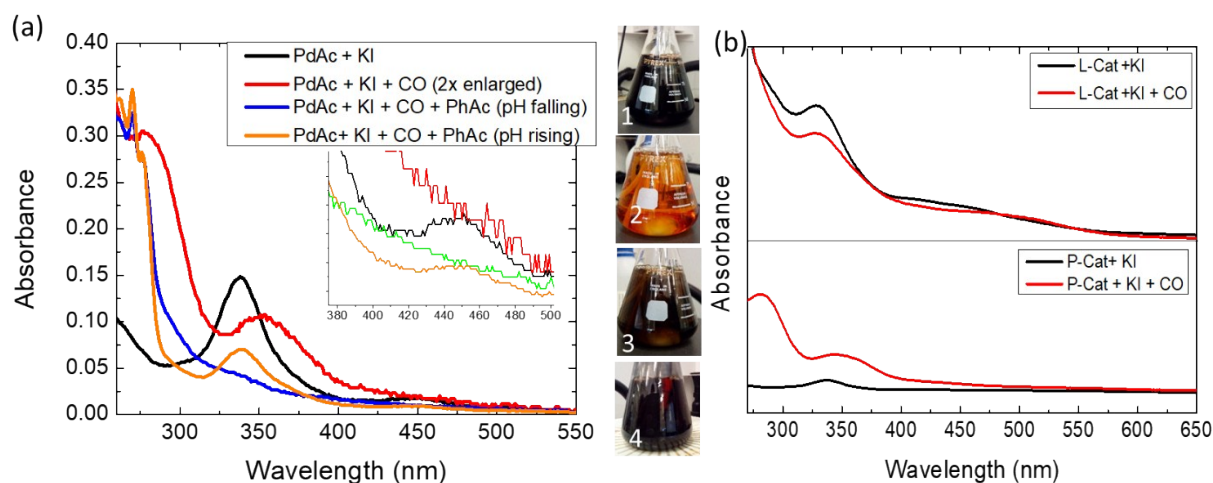


Figure S2. (a) Absorbance spectra of the reaction mixture at different stages of the PCOC of PhAc, employing PdAc as catalyst and while purging with CO (15 ml/min) and air (15 ml/min) at room temperature. The inset shows the enlarged region where I_2 peak absorbance is observed ($\lambda_{max} = 450\text{nm}$). (b) Absorption spectra of the reaction mixture with different catalysts after 15 min of purging with CO (15 ml/min) and air (15 ml/min).

Absorbance measurements of other catalysts, however, demonstrated that incorporation of CO into L-Cat did not result in release of I_3^- (Figure S2b) or disappearance of the Pd^{2+} absorbance. P-Cat exhibited only a trace absorbance of Pd^{2+} species, indicating that some leakage of palladium into the solution occurred, although not dramatic enough to cause pH oscillations in solution.

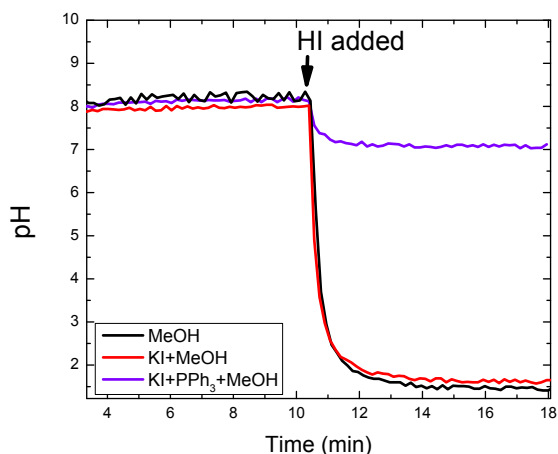


Figure S3. Monitoring of pH in various conditions, including pure methanol (black line), potassium iodide solution in methanol (red line) and a solution of potassium iodide with added triphenylphosphine ligands (purple line, PPh_3) after addition of 0.0228 mmol of hydroiodic acid.

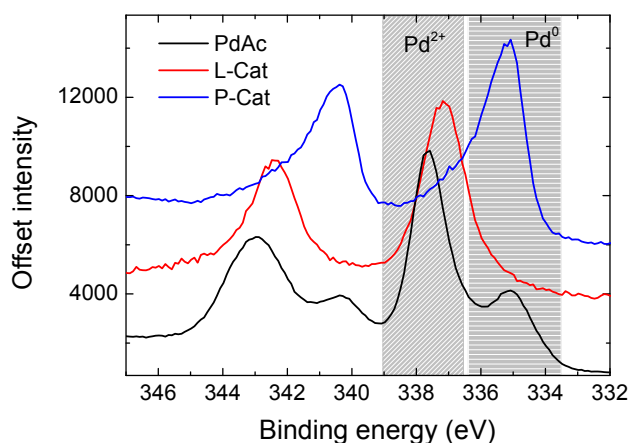


Figure S4. XPS Pd 5d spectra of various fresh catalysts: PdAc (black), L-Cat (red) and P-Cat (blue). The regions, attributed to Pd^0 and Pd^{2+} $5d_{5/2}$, are highlighted with horizontal and diagonal line patterns, respectively.

References

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