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Supplementary Information

Low Temperature Selective Oxidation of Methane using Gold-Palladium Colloids

Rebecca McVicker¹, Nishtha Agarwal¹, Simon J. Freakley^{1,2}, Qian He¹, Sultan Althahban³, Stuart H. Taylor¹, Christopher. J. Kiely^{1,3} and Graham J. Hutchings^{1*}

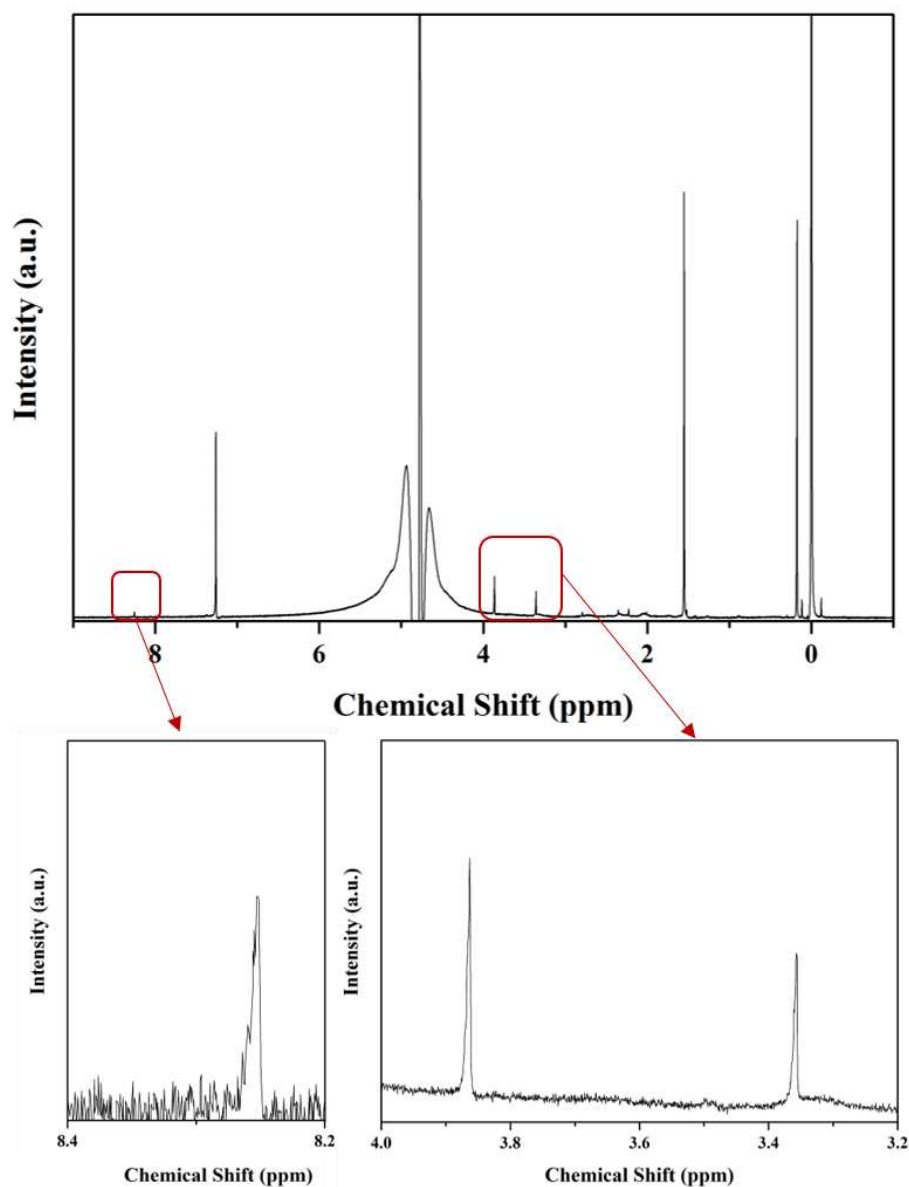
¹ Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK.

³ Department of Chemistry, University of Bath, 1 South, Claverton Down, Bath, BA2 7AY, UK.

³ Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, Pennsylvania, 18015, USA.

* To whom correspondence should be addressed. E-mail: hutch@cardiff.ac.uk

Figure S1 – ^1H -NMR spectrum obtained from a typical reaction mixture.

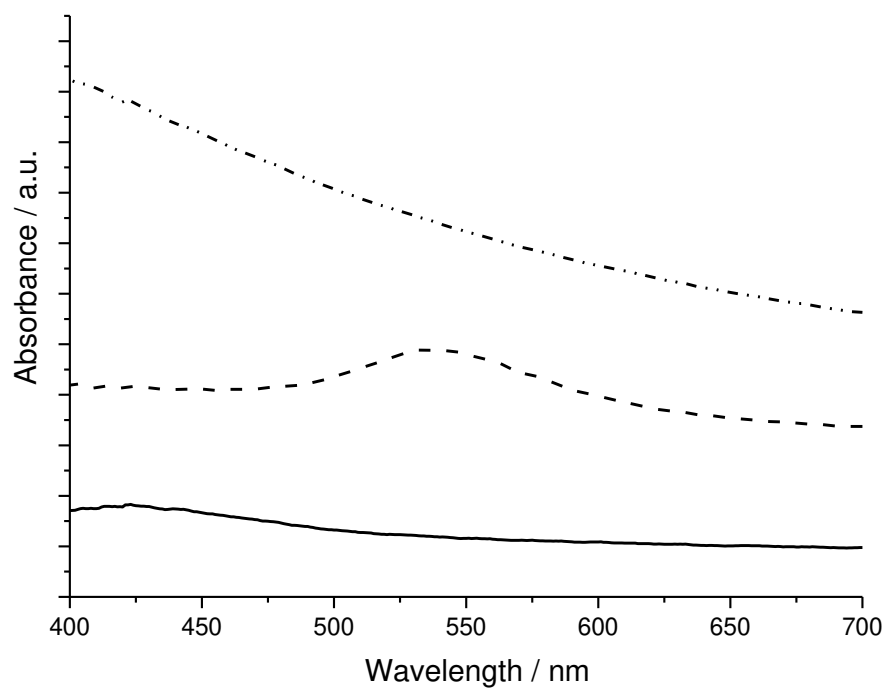


The oxygenated species identified were methylhydroperoxide (s, $\delta=3.9$) and methanol (s, $\delta=3.4$) shown in the zoomed inset along with formic acid (s, $\delta=8.4$). The relative intensities in insets are arbitrarily shown. The other signals present corresponds to tetramethylsilane (s, $\delta=0$), CHCl_3 (s, $\delta=7.3$), H_2O in CDCl_3 (s, $\delta=1.5$) and dissolved CH_4 (s, $\delta=0.2$).

Table S1 Liquid phase oxygenated products analysed by ^1H -NMR for methane oxidation.

Species	Abbreviation	δ/ppm
Methanol	CH_3OH	3.35, s
Methyl hydroxyperoxide	CH_3OOH	3.9, s
Formic acid	HCOOH	8.4, s

Figure S2 – UV-vis spectrometry of Au-only, Pd-only and Au-Pd colloids



Key: Solid line – palladium-only colloid, dashed line – gold-only colloid, dashed/dotted line – gold/palladium colloid.

All colloids: PVP (10kDa) : Metal = 1.2 : 1, Au : Pd = 1:1 molar, [metal] = 7.57×10^{-4} M.

Figure S3 – XPS spectra of monometallic (A) Au(4f) for Au colloid, (B) Pd(3d) for Pd colloid,

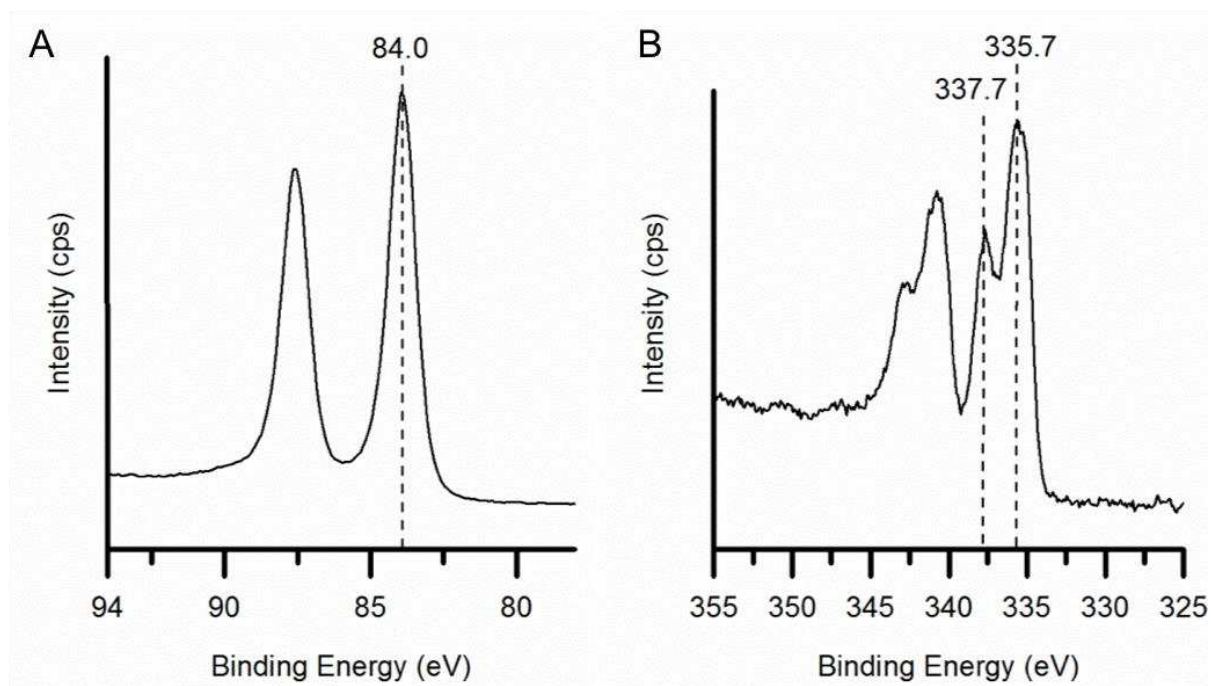


Table S2 – Re-usability of the Au-Pd -PVP colloid over multiple reaction cycles

Entry	Time	Amount of Product (μmol)				Oxygenate Selectivity (%)	MeOH Selectivity (%)	Productivity ($\text{mol kg}^{-1}_{\text{cat}} \text{h}^{-1}$)	TOF (h^{-1})	H_2O_2 used/ products generated
		CH_3OH	CH_3OOH	HCOOH	CO_2					
1	1 x 10	2.14	4.43	2.14	1.31	87	21.4	52.6	7.8	80
2	2 x 10	2.86	4.00	9.29	3.65	82	14.4	51.9	7.6	100

Reaction Conditions; 1000 μmol H_2O_2 , 50 $^\circ\text{C}$, total volume 10 ml, 30 bar, 1500 rpm, 7.57 μmol metal per reaction.

Colloid; Au: Pd = 1:1 molar, $[\text{metal}] = 7.57 \times 10^{-4} \text{ M}$.

Table S3 – Methane oxidation under optimized conditions with Au-Pd colloids with H₂O₂

Entry	Catalyst	Amount of Product (μmol)				Oxygenate Selectivity (%)	MeOH Selectivity (%)	Productivity (mol kg ⁻¹ _{cat} h ⁻¹)	TOF (h ⁻¹)	H ₂ O ₂ used/ products generated
		CH ₃ OH	CH ₃ OOH	HCOOH	CO ₂					
1	Au-Pd colloid – PVP ^a	2.29	10.86	2.57	1.09	94	14	29.4	4.2	40
2	Au-Pd colloid – PVP ^b	11.00	13.86	9.57	8.11	81	26	74.4	11	110
3	Au-Pd colloid – PVP ^c	0.00	0.00	0.00	0.17	-	-	-	0.06	46

^a *Reaction condition:* 1000 μmol H₂O₂, 50 °C, total volume 10 ml, 30 bar, 0.5 h, 1500 rpm, 7.57 μmol metal per reaction.

^b *Optimum Condition:* 5000 μmol H₂O₂, 60 °C, total volume 10 ml, 40 bar, 0.5 h, 1000 rpm, 7.57 μmol metal per reaction.

^c *Blank Reaction:* 1000 μmol H₂O₂, 50 °C, total volume 10 ml, 30 bar N₂, 0.5 h, 1500 rpm, 7.57 μmol metal per reaction.

Colloid; PVP: metal = 1.2:1, Au: Pd = 1:1 molar, [metal] = 7.57×10⁻⁴ M