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Supplementary Information

Low Temperature Selective Oxidation of Methane using Gold-Palladium Colloids

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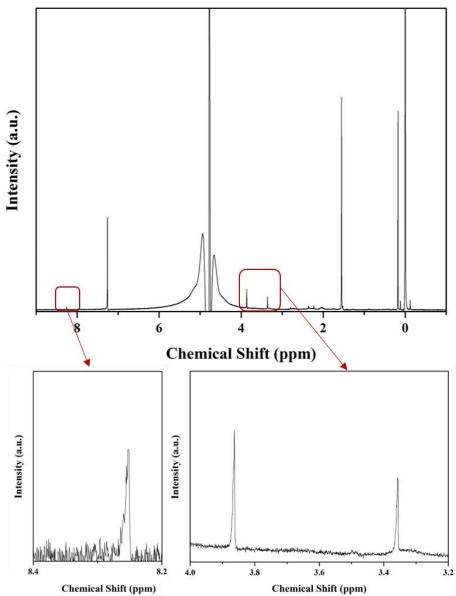
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Figure $S1 - {}^{1}H$ -NMR spectrum obtained from a typical reaction mixture.

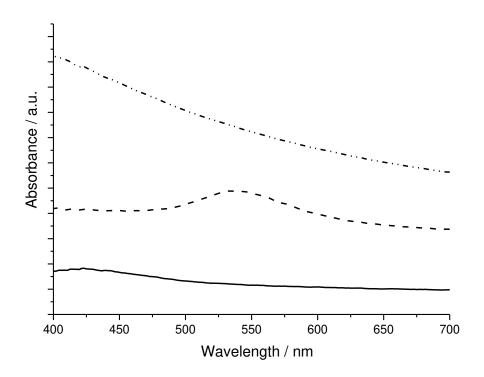


The oxygenated species identified were methylhydroperoxide (s, δ = 3.9) and methanol (s, δ = 3.4) shown in the zoomed inset along with formic acid (s, δ = 8.4). The relative intensities in insets are arbitrarily shown. The other signals present corresponds to tetramethylsilane (s, δ = 0), CHCl₃ (s, δ = 7.3), H₂O in CDCl₃ (s, δ = 1.5) and dissolved CH₄ (s, δ = 0.2).

 $\textbf{Table S1} \ \text{Liquid phase oxygenated products analysed by 1H-NMR for methane oxidation.}$

Species	Abbreviation	δ/ppm		
Methanol	СН₃ОН	3.35, s		
Methyl hydroxyperoxide	СН ₃ ООН	3.9, s		
Formic acid	НСООН	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,

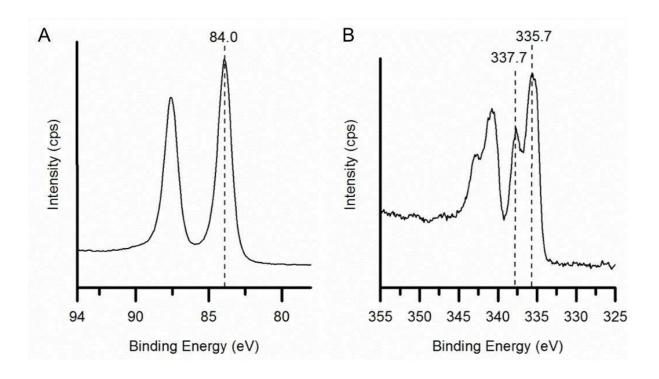


Table S2 - Re-usability of the Au-Pd -PVP colloid over multiple reaction cycles

Entry	Amount of Product (µmol) Time Gy Oy Gy Ooy (1900)				Oxygenate Selectivity	MeOH Selectivity	Productivity (mol kg ⁻¹ cat	TOF (h-1)	H ₂ O ₂ used/ products	
	Time	CH ₃ OH	CH ₃ OOH	НСООН	CO_2	(%)	(%)	h ¹)	(11)	generated
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 μ mol H₂O₂, 50 °C, total volume 10 ml, 30 bar, 1500 rpm, 7.57 μ mol metal per reaction.

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

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

Entry	Catalyst	Amount of Product (µmol)			Oxygenate	МеОН	Productivity	TOE	H ₂ O ₂	
		CH ₃ OH	CH ₃ OOH	НСООН	CO_2	Selectivity (%)	Selectivity (%)	$(\text{mol kg}^{-1}_{\text{cat}} \\ \text{h}^{1})$	TOF (h ⁻¹)	used/ products generated
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 $\mu mol\ H_2O_2,\ 50\ ^\circ C,\ total\ volume\ 10\ ml,\ 30\ bar,\ 0.5\ h,\ 1500\ rpm,\ 7.57\ \mu mol\ metal\ per\ reaction.$

Colloid; PVP: metal = 1.2:1, Au: Pd = 1:1 molar, [metal] = 7.57×10^{-4} M

 $[^]b$ Optimum Condition: 5000 $\mu mol\ H_2O_2,\,60$ °C, total volume 10 ml, 40 bar, 0.5 h, 1000 rpm, 7.57 $\mu mol\ metal\ per\ reaction.$

 $[^]c$ Blank Reaction: 1000 $\mu mol\ H_2O_2,\ 50\ ^oC,\ total\ volume\ 10\ ml,\ 30\ bar\ N_2,\ 0.5\ h,\ 1500\ rpm,\ 7.57\ \mu mol\ metal\ per\ reaction.$