

Supplementary Information

Fig. S1. Cu-K edge XANES spectra of precursors and standard materials. (a) CuAu/SiO₂ impregnated and dried; (b) Cu/SiO₂ deposition dried; (c) CuAu/SiO₂ deposition dried; (d) Copper Nitrate Hemipentahydrate; (e) Copper hydroxycarbonate; (f) Copper (II) Oxide; (g) Copper (I) Oxide; and (h) Copper foil.

Fig. S2. Au-L3 edge XANES spectra of precursors and standard materials. (a) CuAu/SiO₂ impregnated and dried; (b) CuAu/SiO₂ deposition dried; (c) Gold hydroxide; (d) Sodium Gold Tetrachloride; (e) Gold foil.

Fig. S3. Propene conversion for catalysts prepared by impregnation and (a) hydrogen reduced (dashed line) ; (b) hydrogen reduced and calcined (solid line); (c) calcined only (dotted line). The arrows indicate increasing and decreasing temperature.

Fig. S4. Propene conversion for catalysts prepared by impregnation and (a) sodium borohydride reduced; (b) sodium borohydride reduced and calcined. The arrows indicate increasing and decreasing temperature.

Fig. S5. Propene conversion for catalysts prepared by deposition and (a) hydrogen reduced (dashed line); (b) hydrogen reduced and calcined (solid line). The arrows indicate increasing and decreasing temperature.

Fig. S6. Propene conversion for monometallic catalysts prepared by impregnation and calcined: 5% Cu/SiO₂ (dashed line) and 5% Au/SiO₂ (solid line). The arrows indicate increasing and decreasing temperature.

Fig. S7. Temperature-Programmed Reduction of 5% CuO/SiO₂ catalyst.

Table S1. Selectivity Data for CuAu/SiO₂ catalysts in propene oxidation. ^a Oxygenates are propene oxide, acetone and ethanal.

Table S2. Summary of XANES fits using Cu K edge data. ‘-’ means omitted from fit whilst ‘0’ means included in fit but no contribution found.

Table S3. Summary of XANES fits using Au L3 edge data. ‘-’ means omitted from fit whilst ‘0’ means included in fit but no contribution found.

Fig. S1. Cu-K edge XANES spectra of precursors and standard materials. (a) CuAu/SiO₂ impregnated and dried; (b) Cu/SiO₂ deposition dried; (c) CuAu/SiO₂ deposition dried; (d) Copper Nitrate Hemipentahydrate; (e) Copper hydroxycarbonate; (f) Copper (II) Oxide; (g) Copper (I) Oxide; and (h) Copper foil.

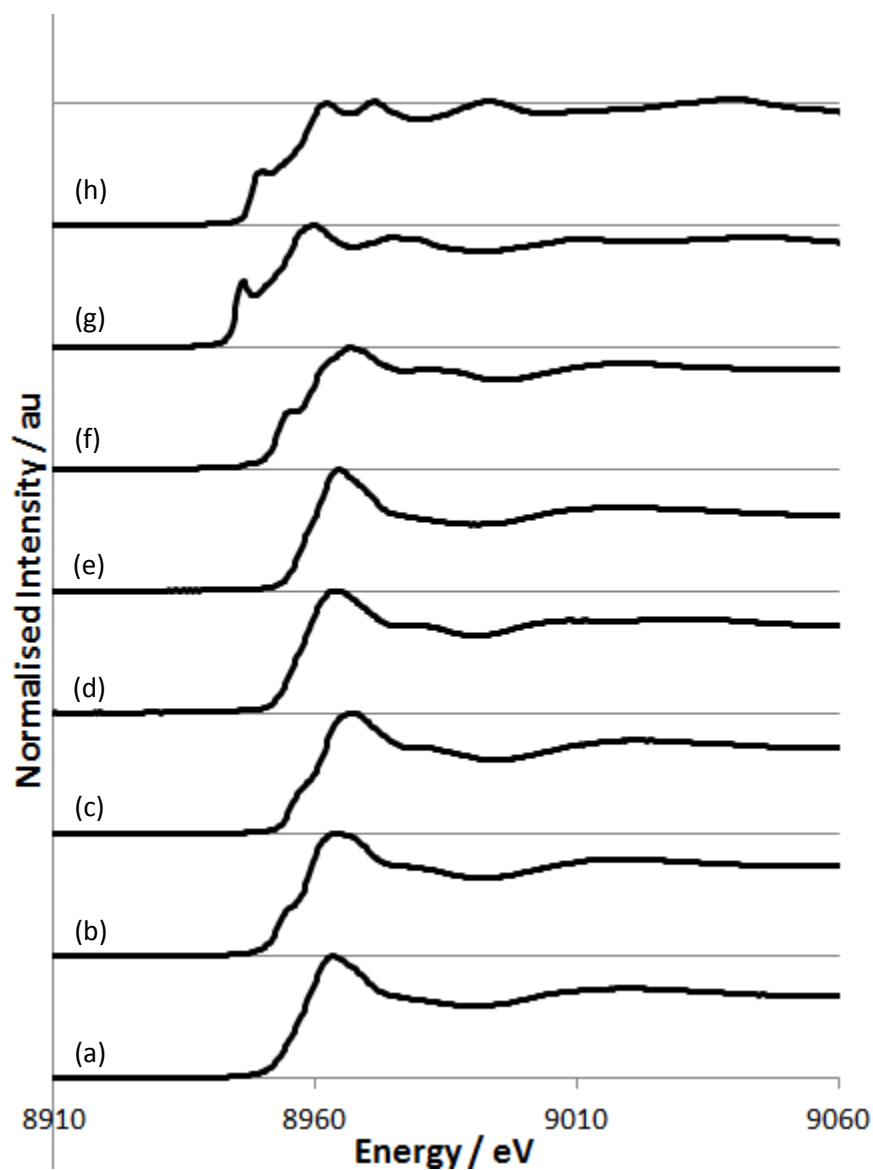


Fig. S2. Au-L3 edge XANES spectra of precursors and standard materials. (a) CuAu/SiO₂ impregnated and dried; (b) CuAu/SiO₂ deposition dried; (c) Gold hydroxide; (d) Sodium Gold Tetrachloride; (e) Gold foil.

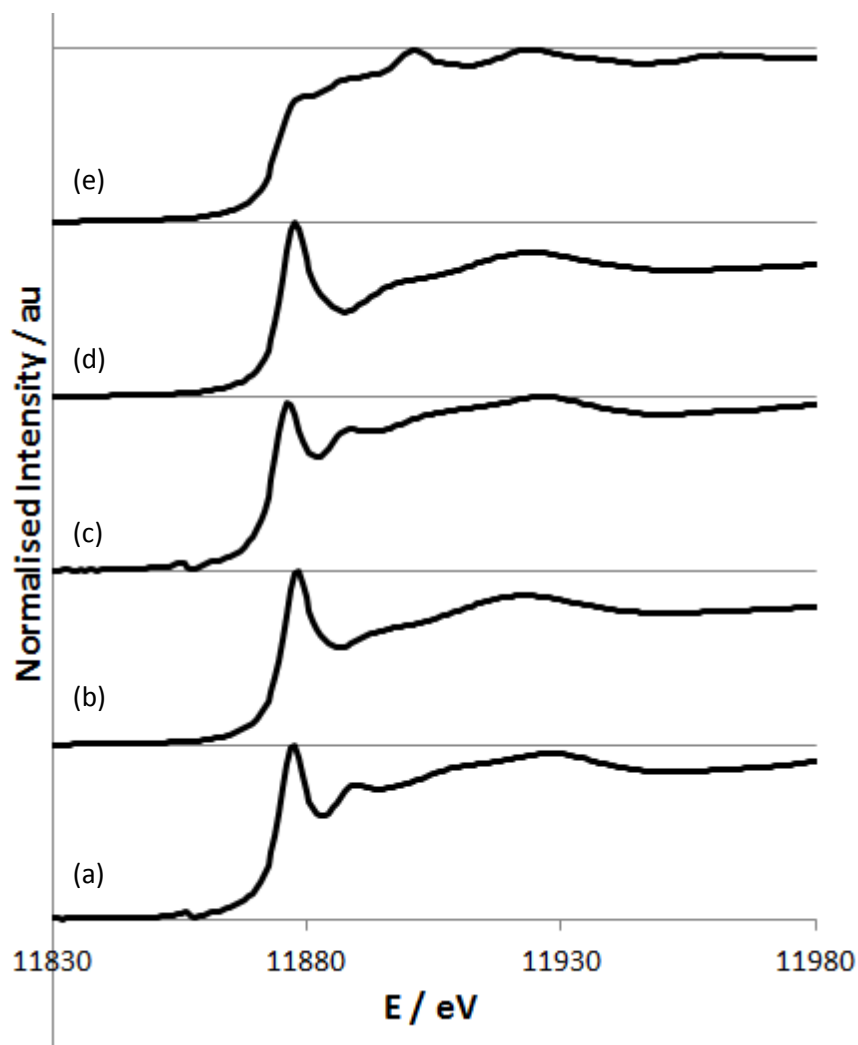


Fig. S3. Propene conversion for catalysts prepared by impregnation and (a) hydrogen reduced (dashed line) ; (b) hydrogen reduced and calcined (solid line); (c) calcined only (dotted line). The arrows indicate increasing and decreasing temperature.

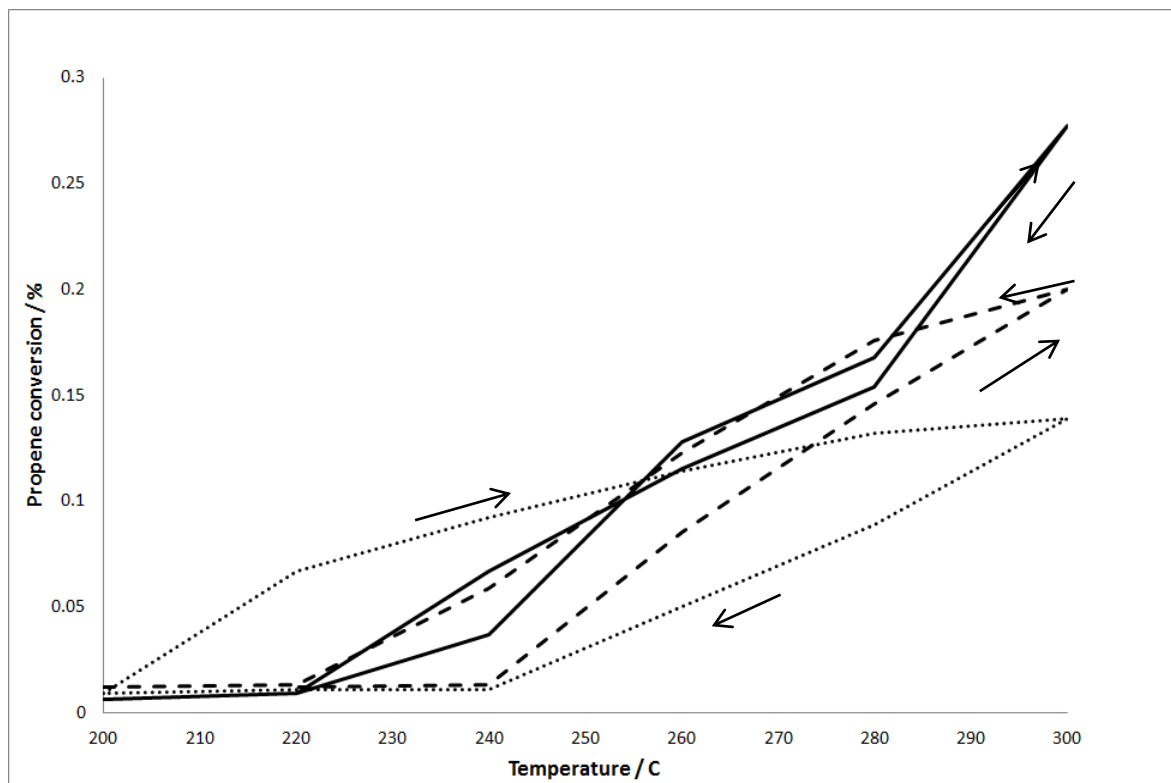


Fig. S4. Propene conversion for catalysts prepared by impregnation and (a) sodium borohydride reduced; (b) sodium borohydride reduced and calcined. The arrows indicate increasing and decreasing temperature.

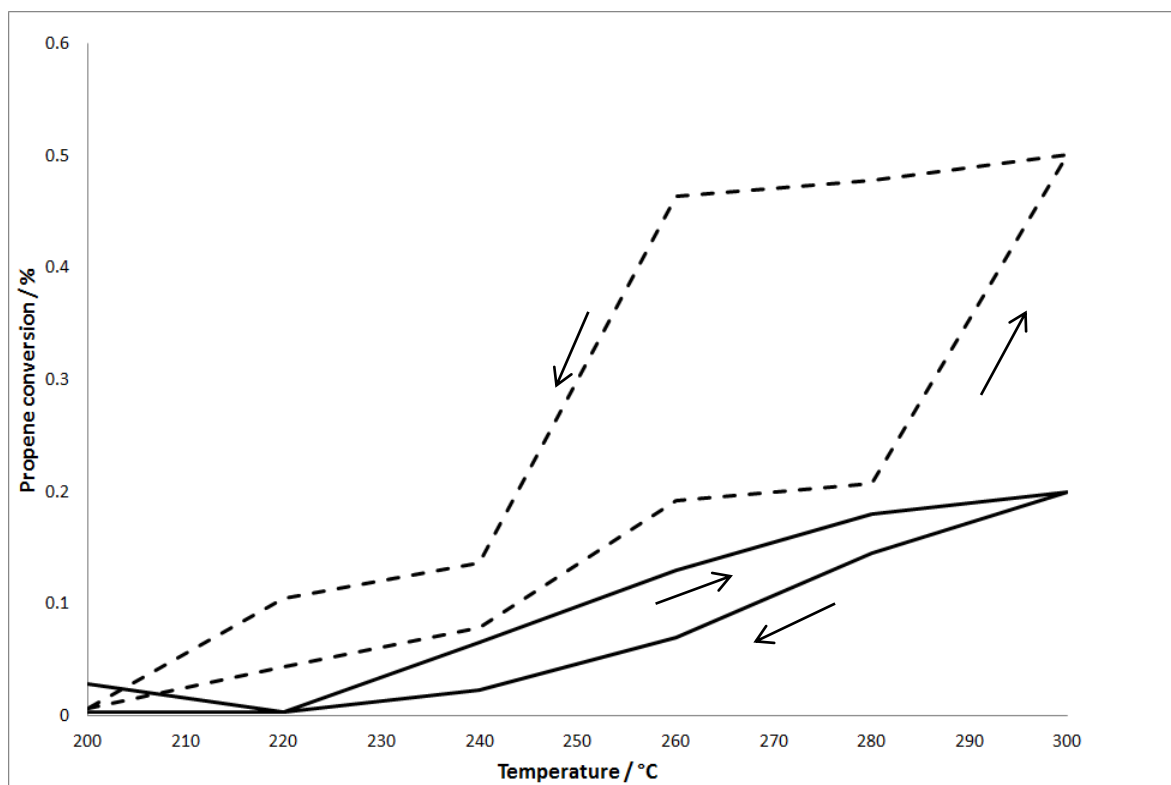


Fig. S5. Propene conversion for catalysts prepared by deposition and (a) hydrogen reduced (dashed line); (b) hydrogen reduced and calcined (solid line). The arrows indicate increasing and decreasing temperature.

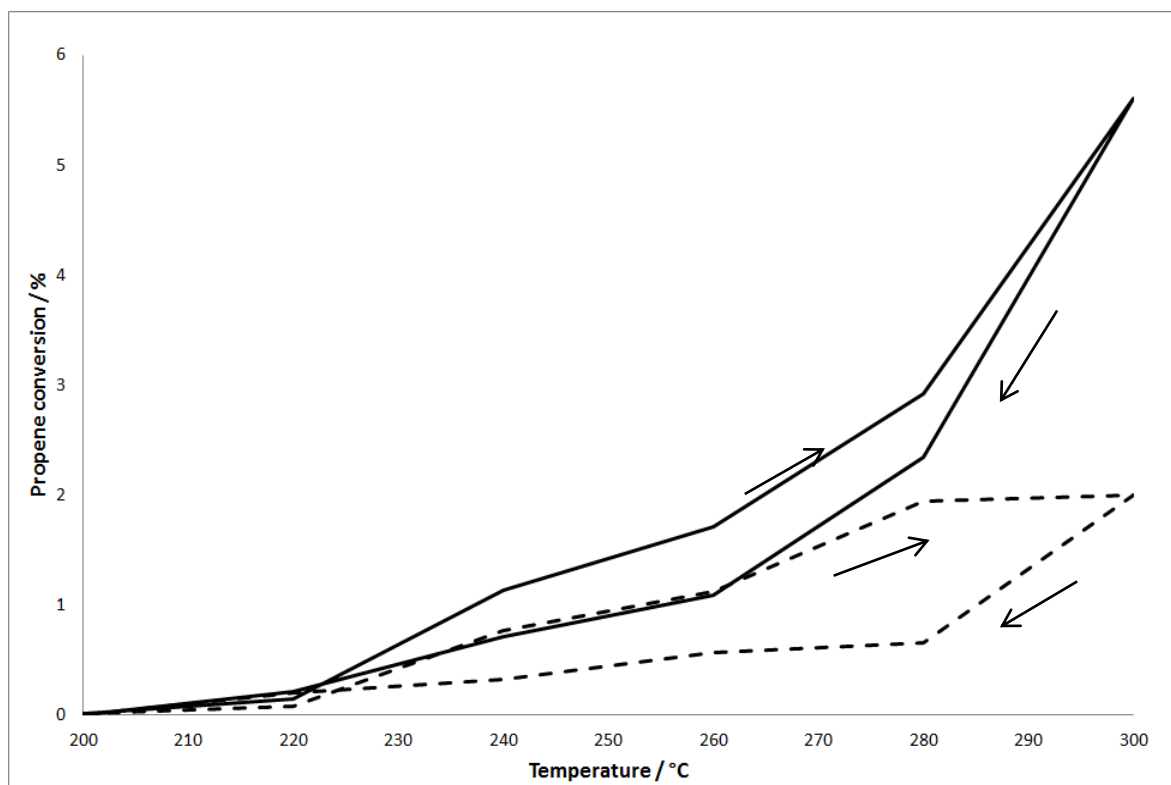


Fig. S6. Propene conversion for monometallic catalysts prepared by impregnation and calcined: 5% Cu/SiO₂ (dashed line) and 5% Au/SiO₂ (solid line). The arrows indicate increasing and decreasing temperature.

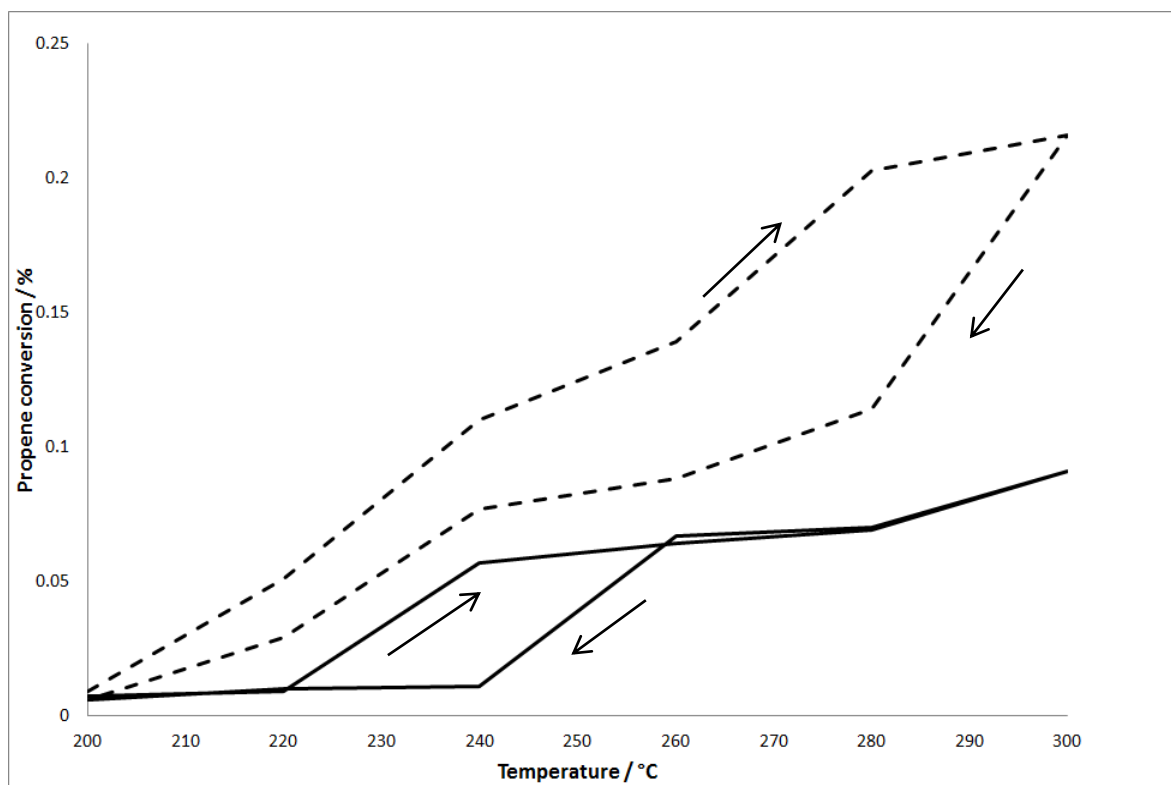


Fig. S7. Temperature-Programmed Reduction of 5% CuO/SiO₂ catalyst.

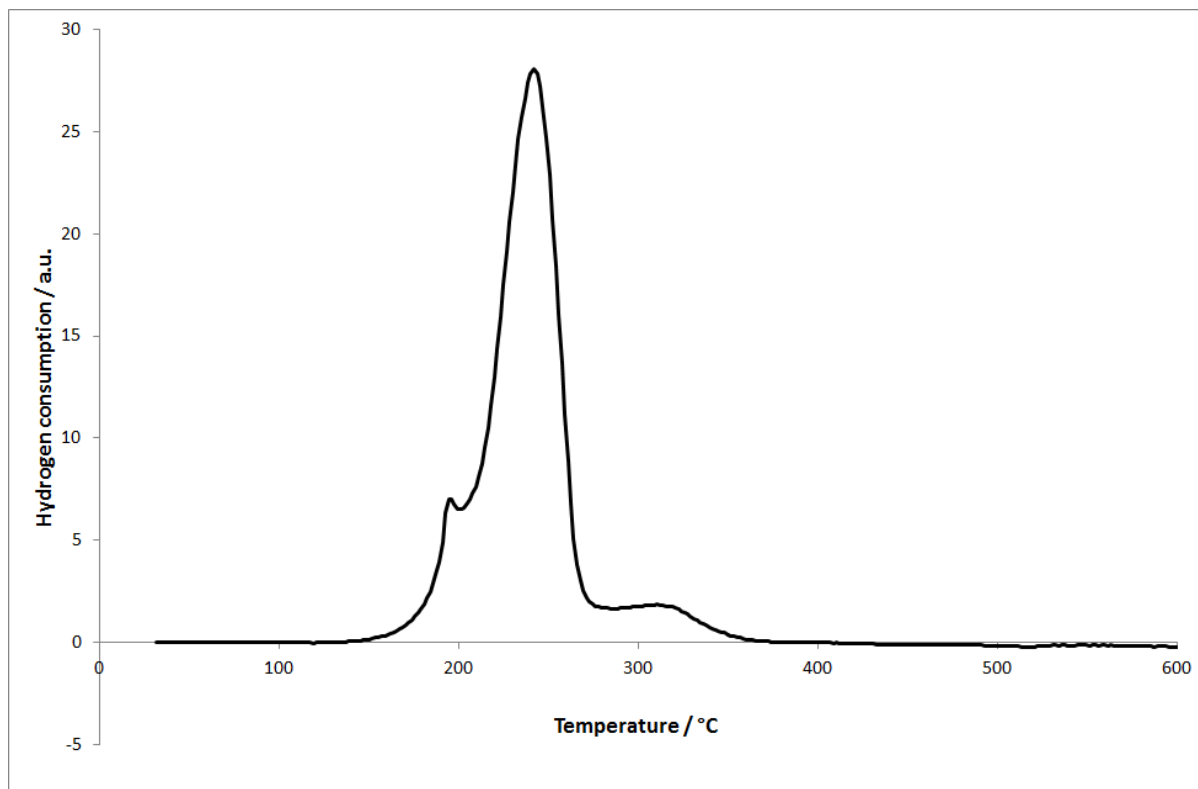


Table S1. Selectivity Data for CuAu/SiO₂ catalysts in propene oxidation. ^a Oxygenates are propene oxide, acetone and ethanal.

Temperature Regime	Temperature / °C	Conversion / %	Selectivity / %		
			Acrolein	Carbon Dioxide	Oxygenates ^a
<u>CuAu/SiO₂ impregnation calcined</u>					
Increasing	200	0.067	0	100	0
	220	0.067	84	16	0
	240	0.092	83	17	0
	260	0.114	80	20	0
	280	0.132	40	28	31
Decreasing	300	0.139	45	21	34
	280	0.089	84	16	0
	260	0.050	82	18	0
	240	0.011	0	100	0
	220	0.011	0	100	0
<u>CuAu/SiO₂ impregnation reduced with hydrogen</u>					
Increasing	200	0.006	0	100	0
	220	0.009	0	100	0
	240	0.037	0	40	60
	260	0.128	55	22	23
	280	0.168	49	28	23
Decreasing	300	0.277	41	36	23
	280	0.154	62	38	0
	260	0.115	85	42	0
	240	0.067	75	25	0
	220	0.009	0	100	0
<u>CuAu/SiO₂ impregnated, reduced with hydrogen and calcined</u>					
Increasing	200	0.012	0	100	0
	220	0.013	0	100	0
	240	0.059	75	25	0
	260	0.123	87	13	0
	280	0.176	81	19	0
Decreasing	300	0.200	83	17	0
	280	0.146	83	17	0
	260	0.085	70	30	0
	240	0.013	0	100	0
	220	0.012	0	100	0
<u>CuAu/SiO₂ impregnated and reduced with NaBH₄</u>					
Increasing	200	0.006	0	100	0
	220	0.043	84	16	0
	240	0.078	60	18	22
	260	0.192	51	23	26
	280	0.207	86	8	6
Decreasing	300	0.501	84	16	0
	280	0.478	76	10	14
	260	0.464	53	9	38
	240	0.136	72	28	0
	220	0.105	48	36	16

<u>CuAu/SiO₂ impregnated, reduced with NaBH₄ and calcined</u>					
Increasing	200	0.002	0	100	0
	220	0.003	0	100	0
	240	0.065	72	28	0
	260	0.130	84	16	0
	280	0.180	83	17	0
Decreasing	300	0.200	82	18	0
	280	0.145	78	22	0
	260	0.070	70	30	0
	240	0.023	0	100	0
	220	0.003	0	100	0
<u>CuAu/SiO₂ deposition, reduced with hydrogen</u>					
Increasing	200	0.008	0	100	0
	220	0.081	0	46	54
	240	0.764	86	6	8
	260	1.115	93	3	4
	280	1.937	64	2	34
Decreasing	300	2.002	93	6	1
	280	0.651	97	3	0
	260	0.565	96	4	0
	240	0.318	94	6	0
	220	0.196	92	8	0
<u>CuAu/SiO₂ deposition, reduced with hydrogen and calcined</u>					
Increasing	200	0.007	0	100	0
	220	0.139	0	55	45
	240	1.131	83	6	11
	260	1.705	83	5	12
	280	2.920	81	5	14
Decreasing	300	5.603	84	7	9
	280	2.34	92	6	2
	260	1.092	93	4	3
	240	0.712	84	2	14
	220	0.209	79	7	14
<u>Cu/SiO₂ impregnation, calcined only</u>					
Increasing	200	0.009	0	100	0
	220	0.051	79	21	0
	240	0.110	46	22	32
	260	0.139	48	12	40
	280	0.203	56	10	34
Decreasing	300	0.216	85	15	0
	280	0.114	72	8	20
	260	0.088	42	7	51
	240	0.077	33	8	59
	220	0.029	78	22	0
<u>Au/SiO₂ impregnation, calcined only</u>					
Increasing	200	0.007	0	100	0
	220	0.009	0	100	0
	240	0.057	73	27	0
	260	0.064	68	32	0
	280	0.069	69	31	0

Decreasing	300	0.091	74	26	0
	280	0.07	80	20	0
	260	0.067	80	20	0
	240	0.011	0	100	0
	220	0.010	0	100	0

Table S2. Summary of XANES fits using copper edge data. ‘-’ means omitted from fit whilst ‘0’ means included in fit but no contribution found.

Preparation Method	Pretreatment	Fit / %				Fit Quality	
		CuO	Cu(NO ₃) ₂ ·2.5H ₂ O	Cu ₂ O	Cu(0)	Reduced χ^2	R _{fac}
Impregnation	Calcination	51.0	48.2	0.8	0	0.000500	0.000720
		51.9	48.1	-	-	0.000502	0.000719
	Reduction in H ₂	36.1	53.2	8.5	32.2	0.000824	0.001125
		88.9	11.1	-	-	0.00170	0.00233
	Reduction in H ₂ and calcination	55.4	39.5	5.1	0	0.000271	0.000391
		61.6	38.4	-	-	0.000278	0.000391
	NaBH ₄ reduction	44.3	50.4	4.5	0.8	0.000755	0.00106
		50.8	49.2	-	-	0.000761	0.00108
<u>Deposition</u>	Reduction in H ₂	47.3	46.8	5.0	0.9	0.000508	0.000723
		54.6	45.4	-	-	0.000517	0.000739
	Reduction in H ₂ and calcination	41.7	22.5	17.1	18.7	0.000767	0.001129
		53.2	21.0	-	25.8	0.000831	0.001226
		87.2	12.8	-	-	0.00125	0.001848

Table S3. Summary of XANES fits using gold edge data. ‘-’ means omitted from fit whilst ‘0’ means included in fit but no contribution found.

Preparation Method	Pretreatment	Fit / %			Fit Quality	
		Au(0)	Na ₃ Au(S ₂ O ₃) ₂	NaAuCl ₄	Reduced χ^2	R _{fac}
Impregnation	Calcination	64.9	28.2	6.9	0.000356	0.000575
		67.7	32.3	-	0.000367	0.000600
		100	-	-	0.000457	0.000743
	Reduction in H ₂	59.8	38.8	1.4	0.0000700	0.000114
		60.4	39.6	-	0.0000703	0.000114
		100	-	-	0.0002020	0.000330
	Reduction in H ₂ and calcination	91.2	8.0	0.8	0.0000127	0.000021
		91.5	8.5	-	0.0000129	0.000021
		100	-	-	0.0000169	0.000031
	NaBH ₄ reduction	89.8	8.7	1.5	0.0000572	0.000094
		90.4	9.6	-	0.0000577	0.000096
		100	-	-	0.0000654	0.000109
	NaBH ₄ reduction and calcination	85.9	12.7	1.5	0.0001791	0.000254
		86.5	13.5	-	0.0001789	0.000255
		100	-	-	0.0001966	0.000280
<u>Deposition</u>	Reduction in H ₂	73.8	24.8	1.3	0.0002211	0.000360
		74.4	25.6	-	0.0002206	0.000361
		100	-	-	0.0002756	0.000451
	Reduction in H ₂ and calcination	95.8	4.2	0	0.0000100	0.000016
		100	-	-	0.0000114	0.000019