Understanding the Effect of Thermal Treatments on the Structure of $CuAu/SiO_2$ Catalysts and their Performance in Propene Oxidation

Supplementary Information

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ICP and XPS Data

Catalyst	ICP results		Cu/Au molar ratio
	Cu assay / %	Au assay / %	
Cu/SiO_2	4.90	-	-
Cu_3Au/SiO_2	2.33	2.72	2.66
$CuAu/SiO_2$	1.31	4.20	0.97
$CuAu_3/SiO_2$	0.53	4.90	0.34
Au/SiO_2	-	4.5*	-

Table S1. Metal content of calcined catalysts. * high levels of variation in the Au content due to the presence of large clusters.

Catalyst	ICP results		Cu/Au molar ratio
	Cu assay / %	Au assay / %	
Cu/SiO_2	4.84	-	-
Cu_3Au/SiO_2	2.42	2.69	2.79
$CuAu/SiO_2$	1.22	3.98	0.95
$CuAu_3/SiO_2$	0.51	4.38	0.36
Au/SiO_2	-	5.71	-

Table S2. Metal content of reduced catalysts.

Catalyst	ICP results		Cu/Au molar ratio
	Cu assay / %	Au assay / %	
Cu/SiO_2	4.78	-	-
Cu_3Au/SiO_2	2.43	2.20	2.81
$CuAu/SiO_2$	1.15	3.50	1.02
$CuAu_3/SiO_2$	0.48	5.15	0.29
Au/SiO_2	-	5.71	-

Table S3. Metal content of reduced-calcined catalysts.

Heat Treatment	Cu/Au molar ratio				
	Theory	ICP	XPS		
			Fresh	After use in propene oxidation	
				Without H_2 addition	With H_2 addition
Calcination	0.33	0.34	0.83	2.5	11.4
	1	0.97	3.8	0.66	3.2
	3	2.66	6.4	10.1	12.1
Reduction	0.33	0.36	3.5	n.d.	0.45
	1	0.95	3.3	n.d.	5.0
	3	2.79	22.4	n.d.	27.1
Reduction and Calcination	0.33	0.29	0.37	1.4	2.3
	1	1.02	1.6	4.4	1.1
	3	2.81	7.5	8.0	4.2

Table S4. Analysis of Cu/Au molar ratio by ICP and XPS before and after propene oxidation experiments. n.d. = not determined.

Visible Spectra of Catalysts

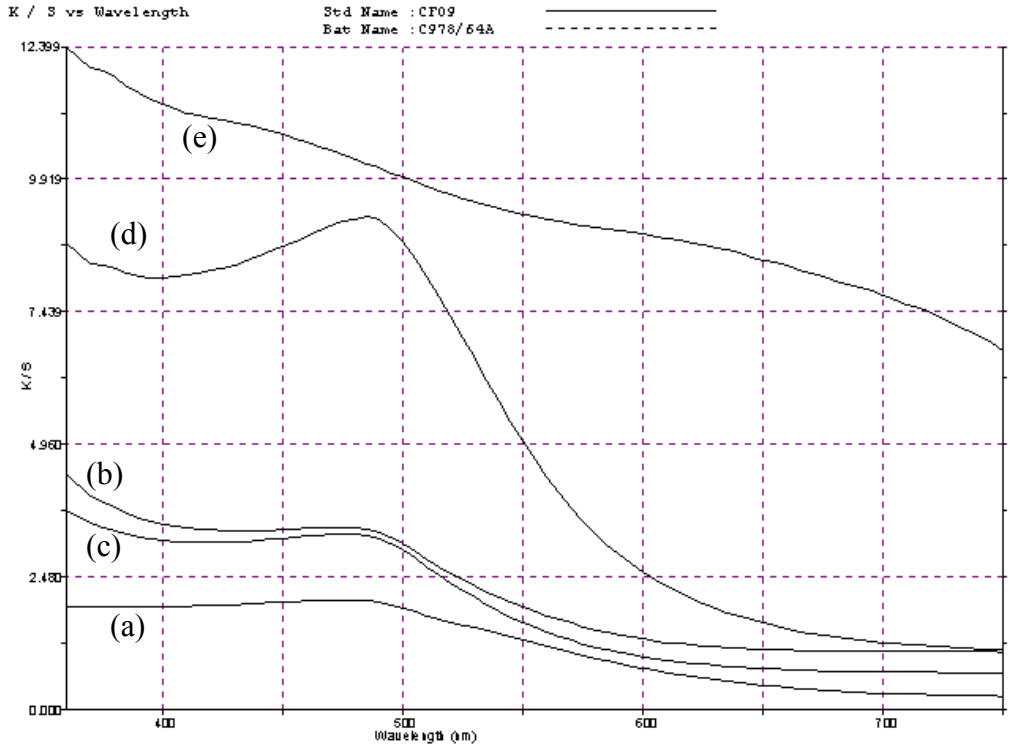

Fig. S1a. Visible spectroscopy of calcined catalysts. (a) Au/SiO_2, $CuAu/SiO_2$ with Cu:Au ratio 1:3 (b), 1:1 (c) and 3:1 (d) and (e) Cu/SiO_2.

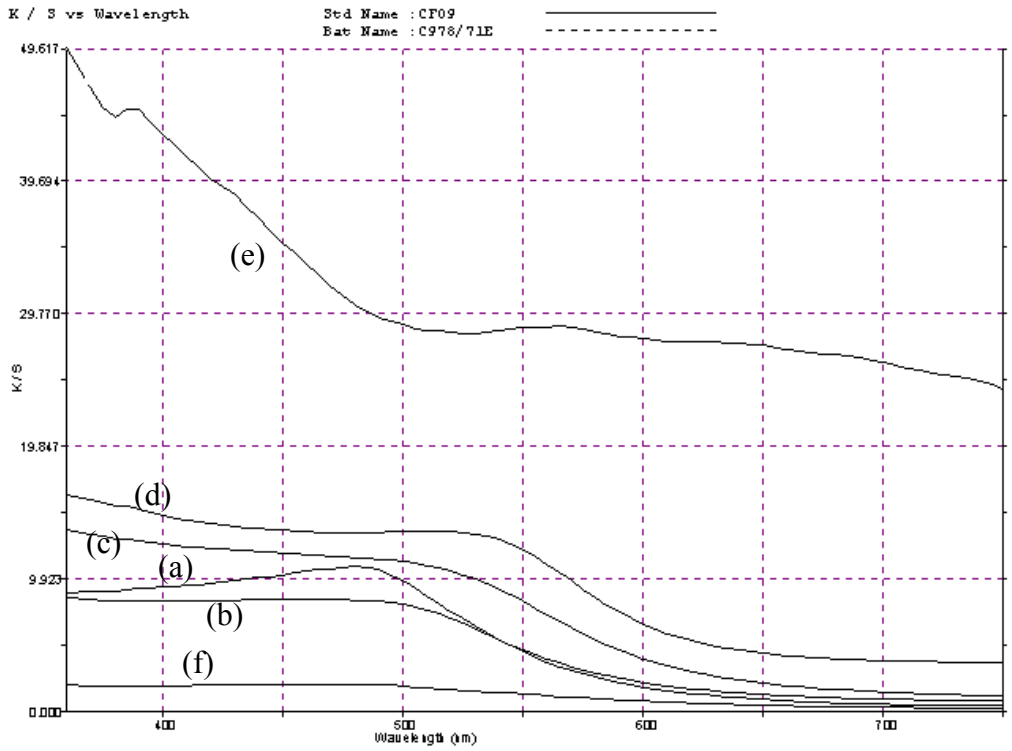

Fig. S1b. Visible spectroscopy of reduced catalysts. (a) Au/SiO_2, $CuAu/SiO_2$ with Cu:Au ratio 1:3 (b), 1:1 (c) and 3:1 (d), (e) Cu/SiO_2 and (f) Au/SiO_2 calcined.

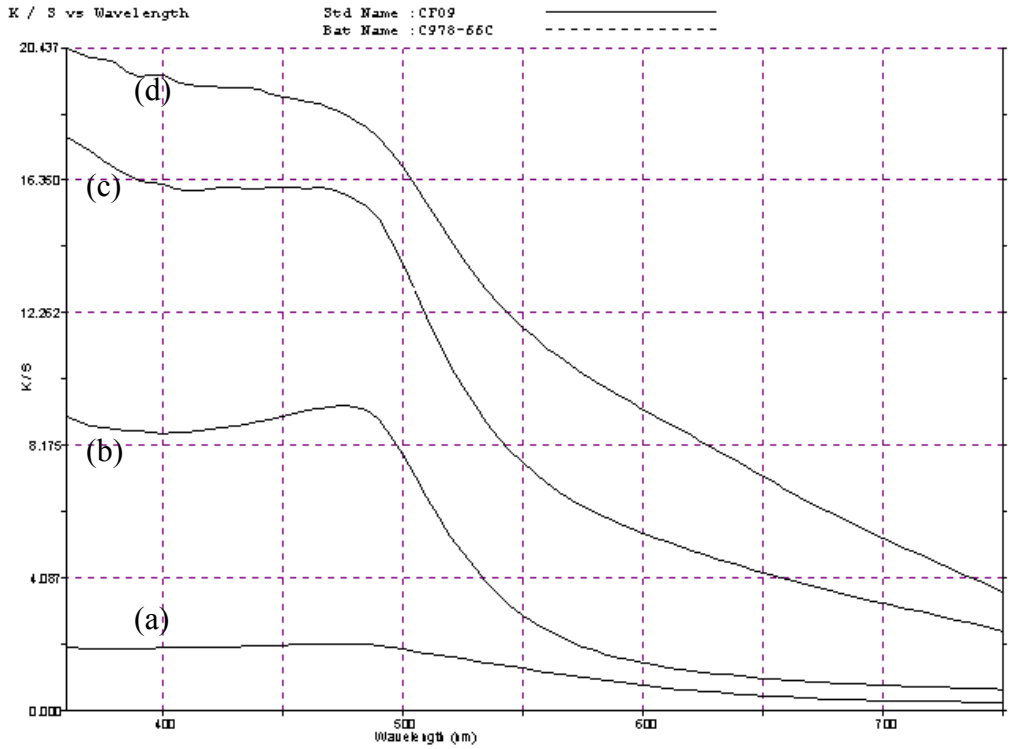

Fig. S1c. Visible spectroscopy of reduced and calcined catalysts. (a) Au/SiO_2, $CuAu/SiO_2$ with Cu:Au ratio 1:3 (b), 1:1 (c) and 3:1 (d).

Visible Microscope Images

Fig. S2a Visible Microscope Image of 1:1 $CuAu/SiO_2$ catalyst direct calcination showing a large gold-rich cluster and pink copper-rich silica particles behind.

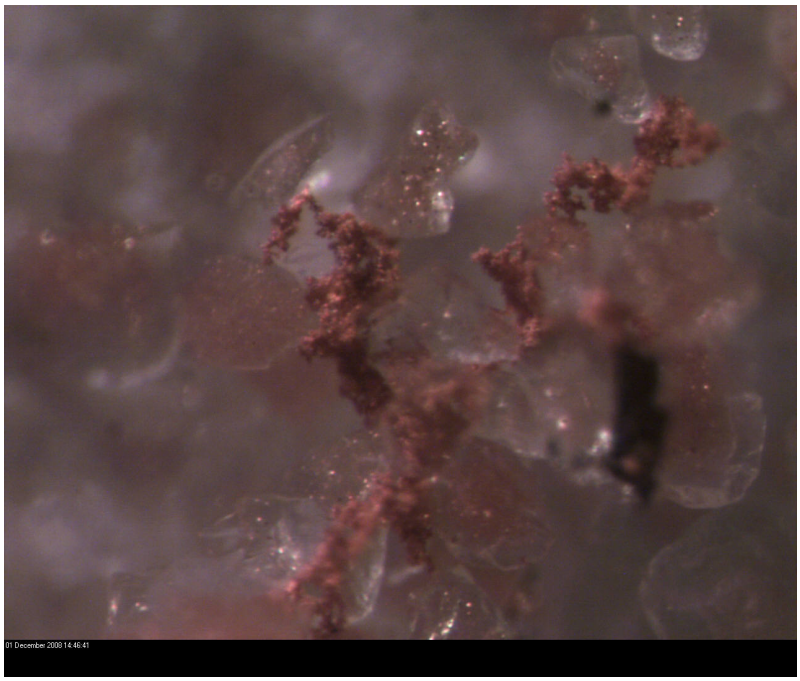

Fig. S2b. Visible Microscope Image of 1:1 $CuAu/SiO_2$ catalyst direct calcination showing a large gold-rich cluster and pink copper-rich silica particles behind.

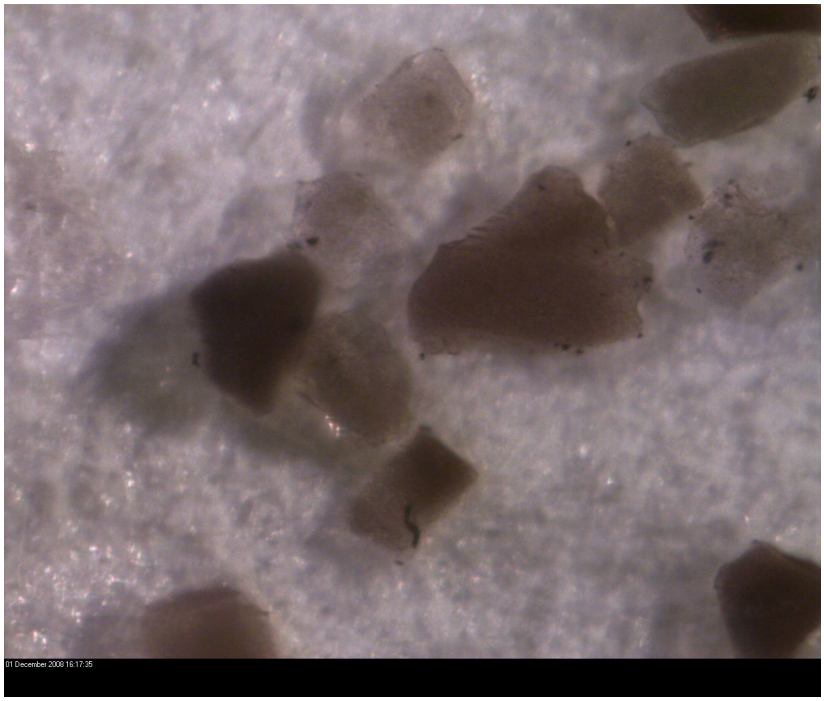

Fig. S2c. Visible microscope image of reduced 1:1 CuAu/SiO_2.

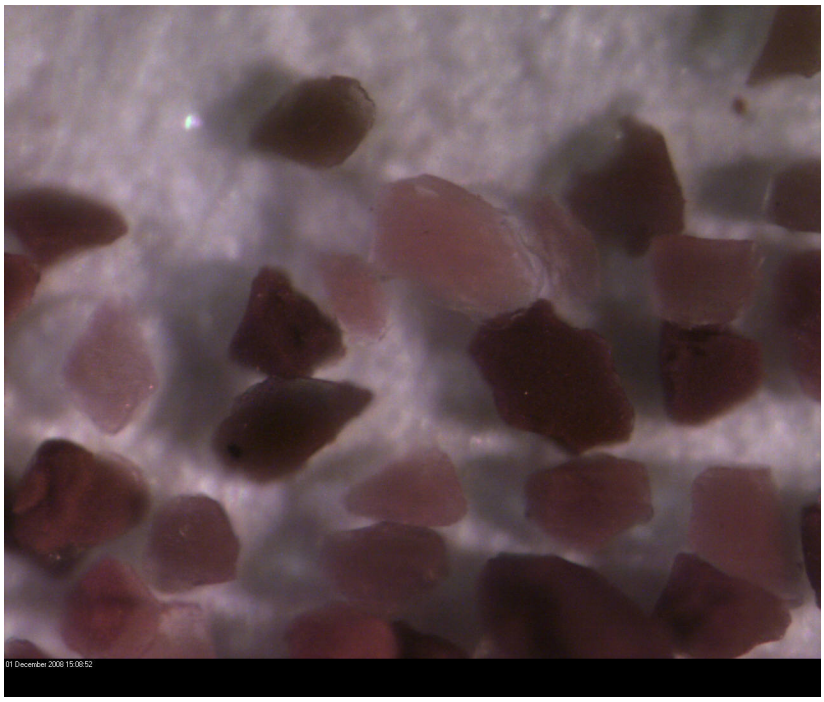

Fig. S2d. Visible microscope image of reduced-calcined 1:1 CuAu/SiO_2.

SEM Images

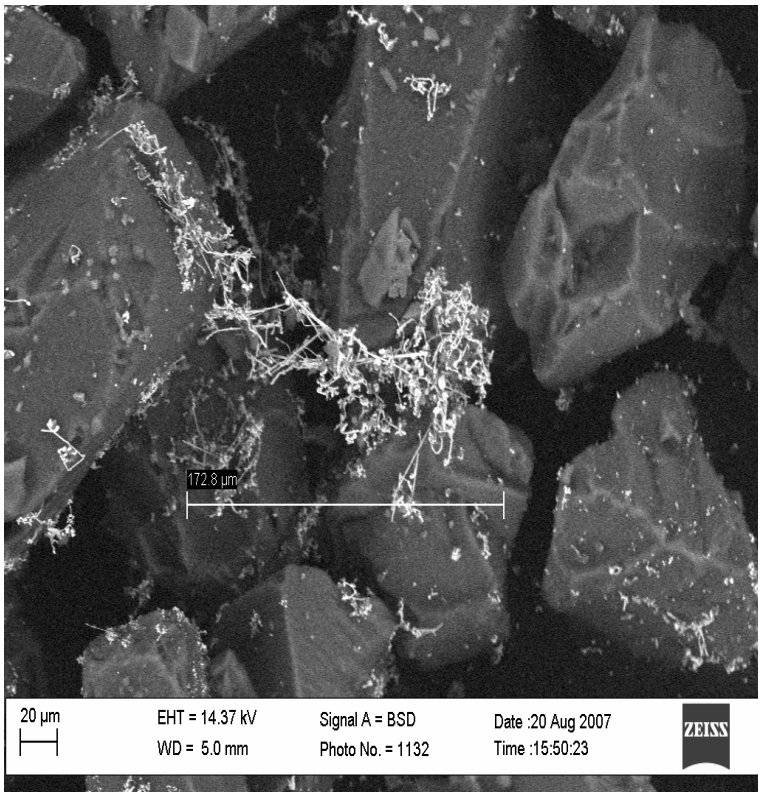

Fig. S3a. SEM analysis of 1:1 CuAu/SiO_2 calcined.

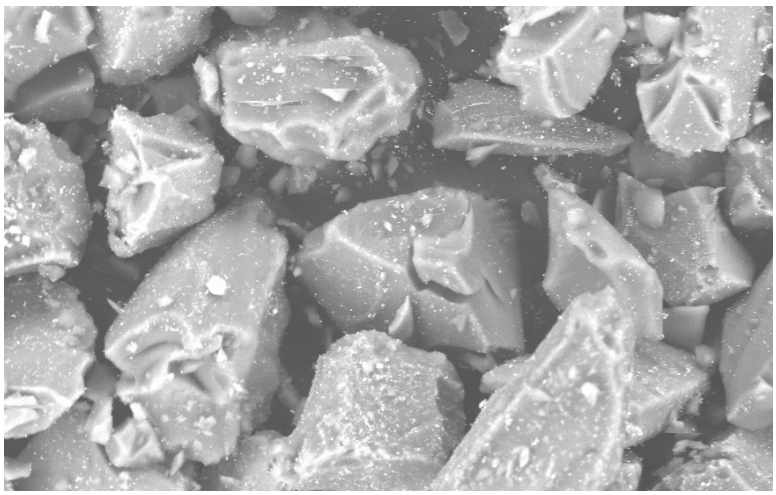

Fig. S3b. SEM analysis of 1:1 CuAu/SiO_2 reduced.

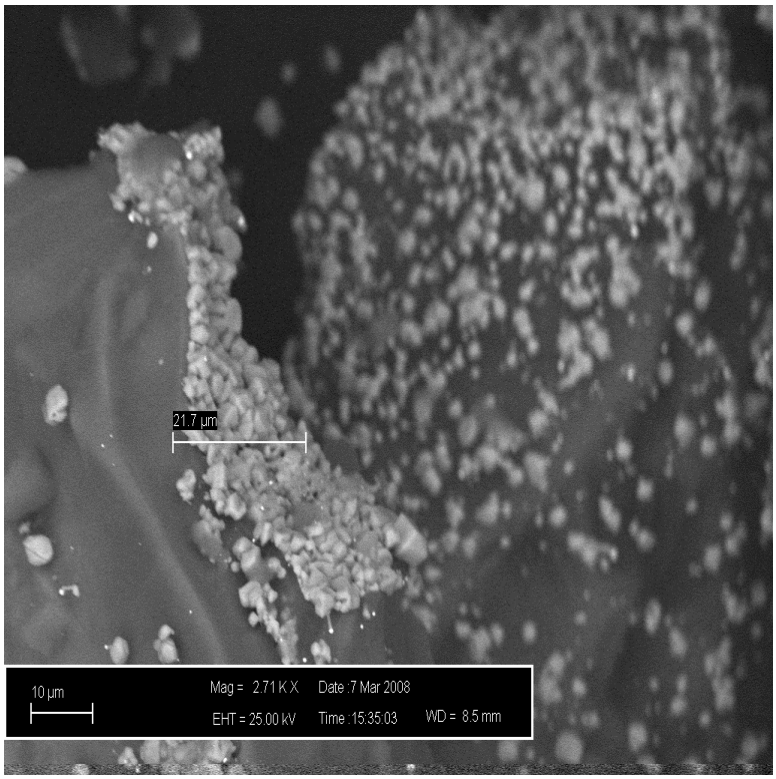

Fig. S3c. SEM analysis of 1:3 CuAu/SiO_2 reduced and calcined.

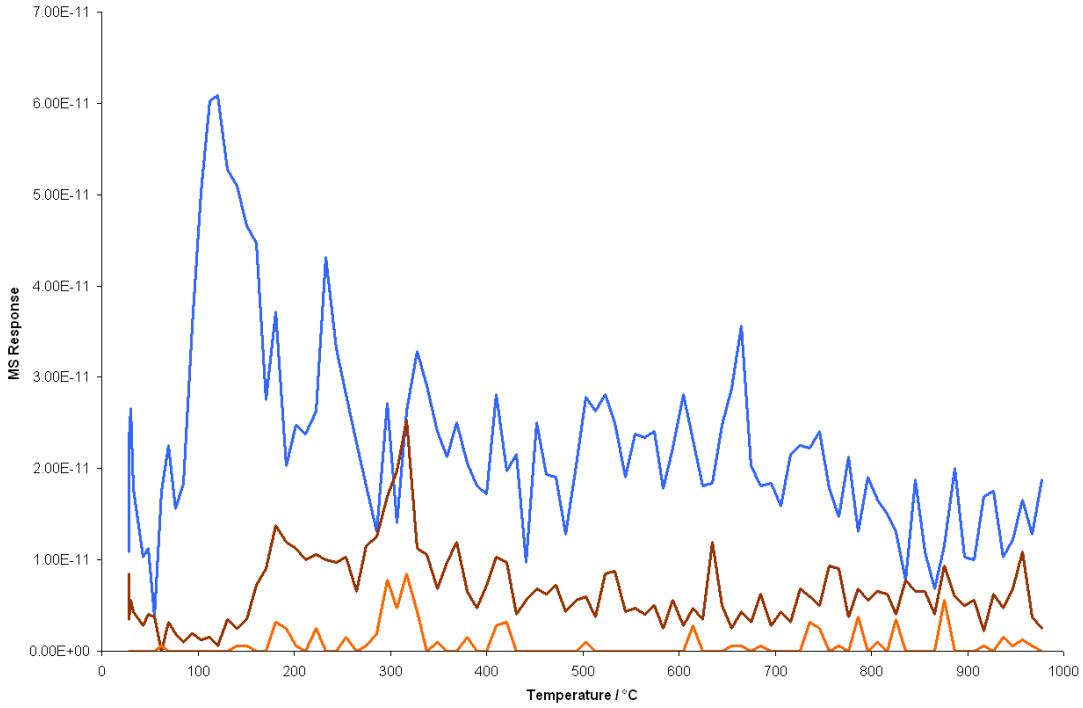

Fig. S4a. MS Profile of gases formed in the decomposition of the dried precursor under 5% O_2/He. Masses are 30 (NO, blue), 36 ($H^{35}Cl$, brown) and 38 ($H^{37}Cl$, orange).

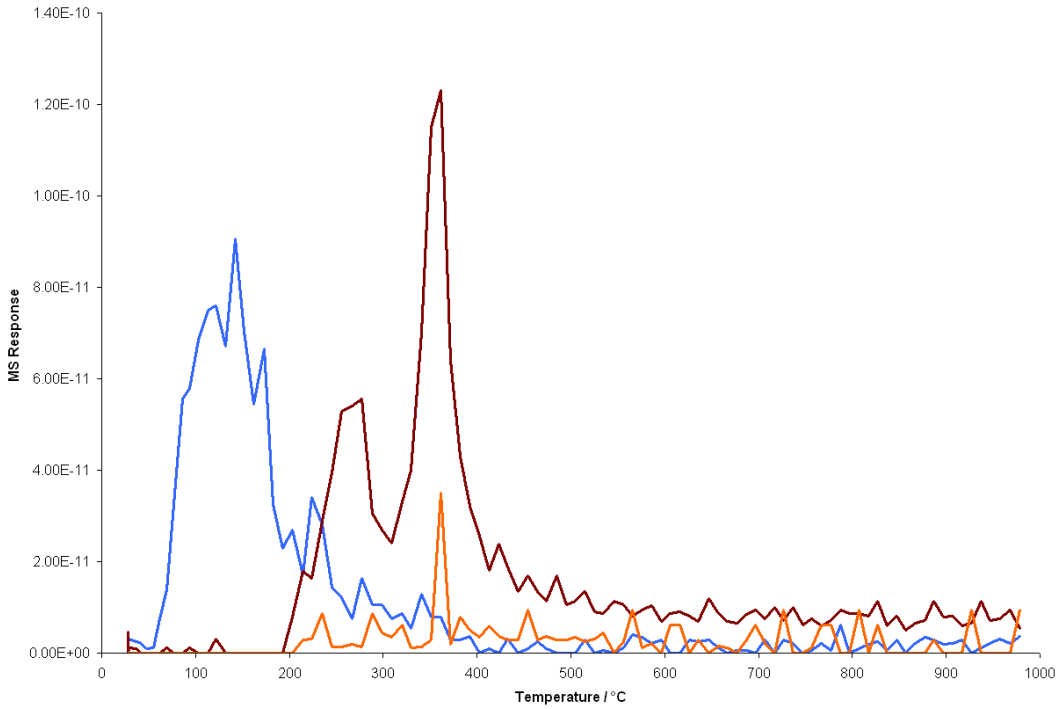

Fig. S4b. MS Profile of gases formed in the decomposition of the dried precursor under 5% H_2/N_2. Masses are 30 (NO, blue), 36 ($H^{35}Cl$, brown) and 38 ($H^{37}Cl$, orange).

Catalyst Test Data

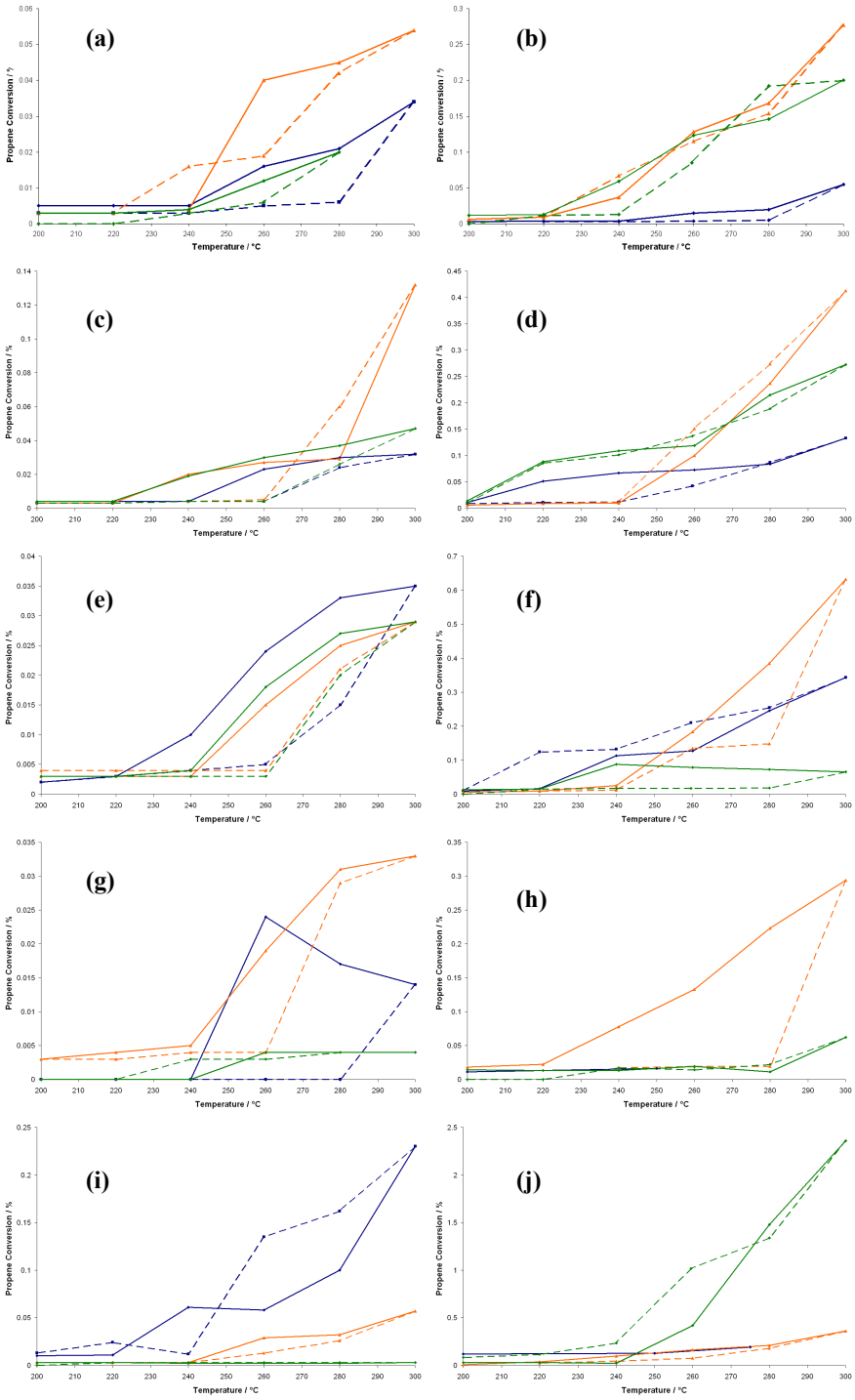

Fig. S5. Propene conversion in propene oxidation for 1:1 $CuAu/SiO_2$ (a) without and (b) with added hydrogen; 1:3 $CuAu/SiO_2$ catalysts (c) without and (d) with added hydrogen; 3:1 $CuAu/SiO_2$ catalysts (e) without and (f) with added hydrogen; Au/SiO_2 catalysts (g) without and (h) with added hydrogen; Cu/SiO_2 catalysts (i) without and (j) with added hydrogen. The catalysts are direct calcined (blue), reduced (orange) and reduced-calcined (green). The solid lines represent increasing temperature and the dashed lines represent decreasing temperature.

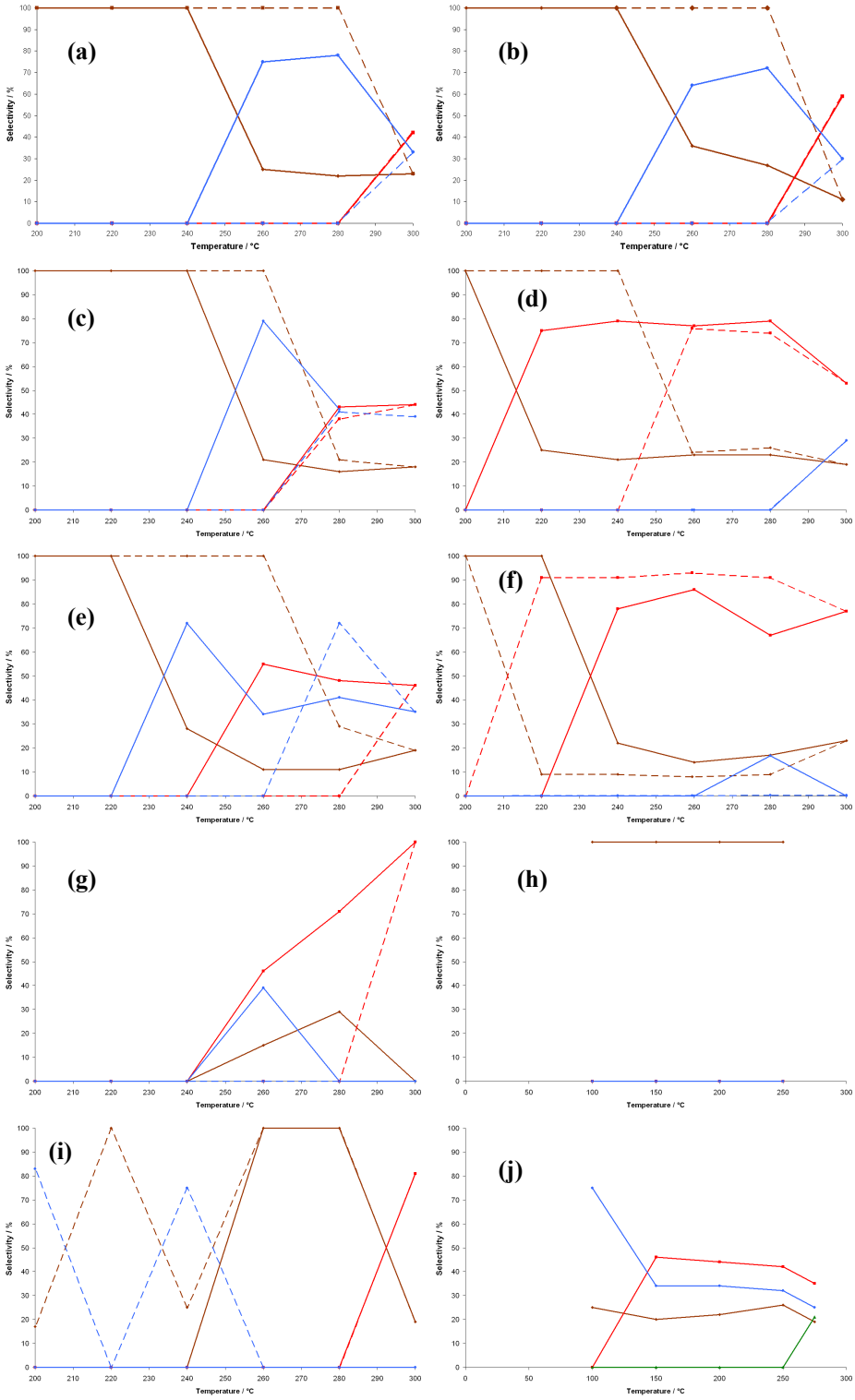

Fig. S6. Selectivity observed with a direct calcined catalyst 1:1 $CuAu/SiO_2$ (a) without and (b) with the addition of hydrogen; 1:3 $CuAu/SiO_2$ (c) without and (d) with the addition of hydrogen; 3:1 $CuAu/SiO_2$ (e) without and (f) with the addition of hydrogen; Au/SiO_2 (g) without and (h) with the addition of hydrogen; and Cu/SiO_2 (i) without and (j) with the addition of hydrogen. The products are carbon dioxide (brown), acrolein (red), ethanal (green) and propene oxide (blue).

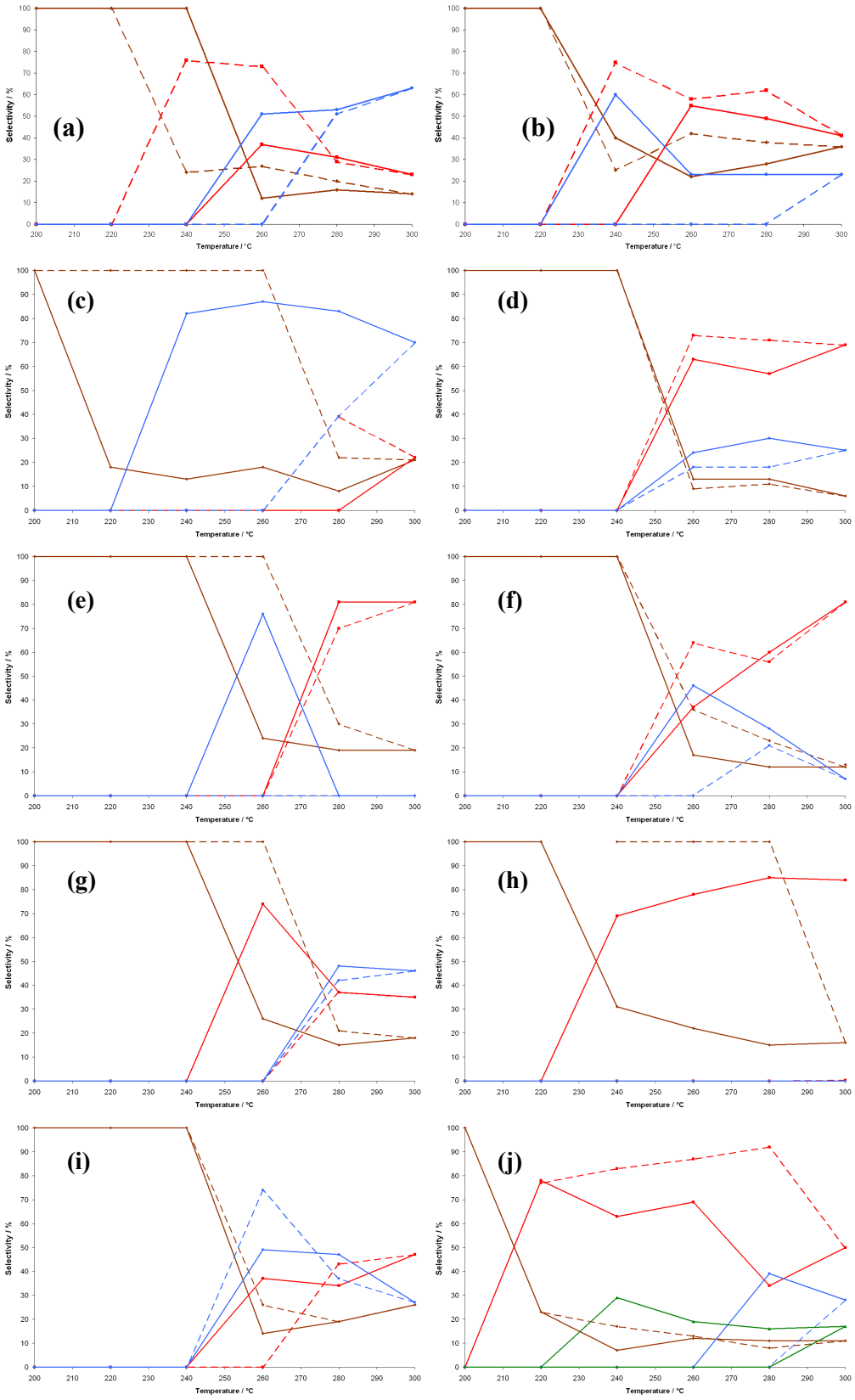

Fig. S7. Selectivity observed with a reduced catalyst 1:1 $CuAu/SiO_2$ (a) without and (b) with the addition of hydrogen; 1:3 $CuAu/SiO_2$ (c) without and (d) with the addition of hydrogen; 3:1 $CuAu/SiO_2$ (e) without and (f) with the addition of hydrogen; Au/SiO_2 (g) without and (h) with the addition of hydrogen; and Cu/SiO_2 (i) without and (j) with the addition of hydrogen. The products are carbon dioxide (brown), acrolein (red), ethanal (green) and propene oxide (blue).

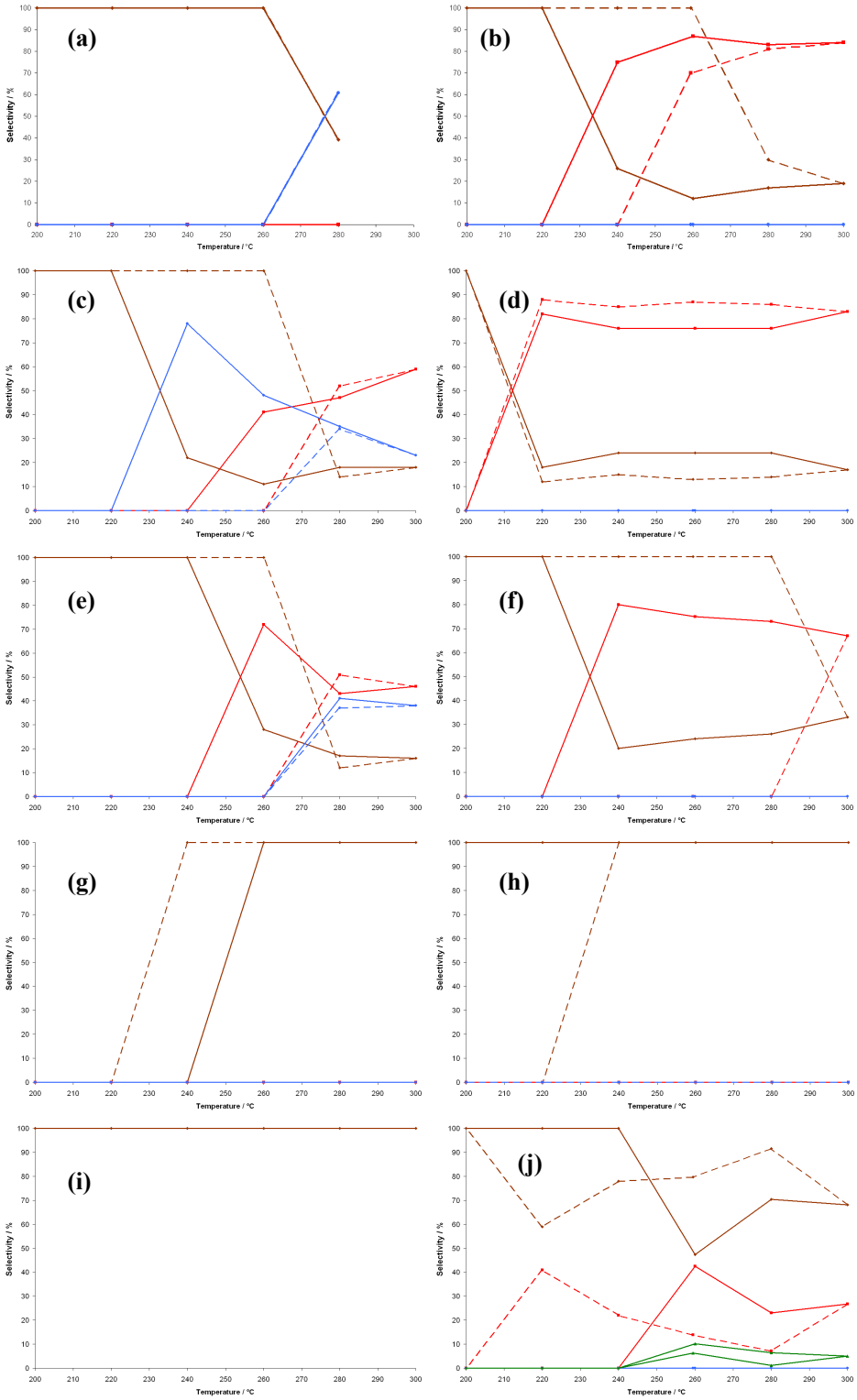

Fig. S8. Selectivity observed with a reduced and calcined catalyst 1:1 $CuAu/SiO_2$ (a) without and (b) with the addition of hydrogen; 1:3 $CuAu/SiO_2$ (c) without and (d) with the addition of hydrogen; 3:1 $CuAu/SiO_2$ (e) without and (f) with the addition of hydrogen; Au/SiO_2 (g) without and (h) with the addition of hydrogen; and Cu/SiO_2 (i) without and (j) with the addition of hydrogen. The products are carbon dioxide (brown), acrolein (red) and propene oxide (blue).