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Supporting Information

Factors influencing the catalytic oxidation of benzyl alcohol using supported phosphine-capped gold nanoparticles

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Synthesis of $Au_{101}(PPh_3)_{21}Cl_5$, denoted as Au_{101}

The Au_{101} cluster was synthesized following the method of Hutchison *et. al*.[1] Typically, tetrachloroauric acid, $HAuCl_4 \cdot 3H_2O$ (1.00 g, 2.539 mmol) in Milli-Q water (60 ml) was stirred in a 500 ml flask. Toluene (60 ml) was added to the solution followed by tetraoctylammonium bromide (TOAB, 1.40 g, 2.56 mmol). The mixture was stirred vigorously for 5 min before the addition of triphenylphosphine (2.30 g, 8.76 mmol). The mixture was vigorously stirred for a further 10 min. A solution of sodium borohydride, $NaBH_4$ (2.00 g, 52.9 mmol) in deionised water (10 ml) was added to the mixture *rapidly, with stirring* and the mixture turned reddish-brown. The mixture was stirred for a further 3 h.

The aqueous and organic layers were separated using a 250 ml separating funnel. The organic layer was washed 3 times with 100 ml of Milli-Q water. The organic layer was filtered on a #3 glass frit funnel and the filtrate was evaporated to dryness. The crude product was completely dissolved in chloroform (35 ml) before pentane (300 ml) was added slowly to the solution to precipitate the product. The suspension was filtered through a #3 glass frit funnel to collect the crude product. The product was washed with the following solvents to complete the purification:

- 2 × (100 ml hexanes followed by 100 ml 2:3 MeOH:H_2O)
- 2 × (100 ml hexanes followed by 100 ml 1:1 MeOH:H_2O)
- 100 ml hexanes
- 2 × (150 ml 3:1 pentane:chloroform)
- 2 × (150 ml 2:1 pentane:chloroform)
- 2 × (150 ml 1:1 pentane:chloroform)

The ^1H NMR of the Au_{101} cluster was a single broad band at δ 6-8 ppm (Figure S1). TEM image (Figure S2) shows the average particle size of Au101 around 1.6 ± 0.4 nm. Thermogravimetric showed the decomposition of phosphine ligands at 250 °C (Figure S3).

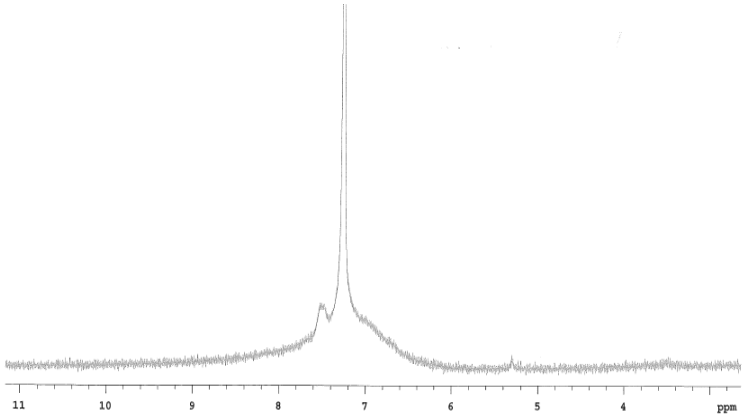

Figure S1 ^{1}H NMR of Au_{101} cluster.

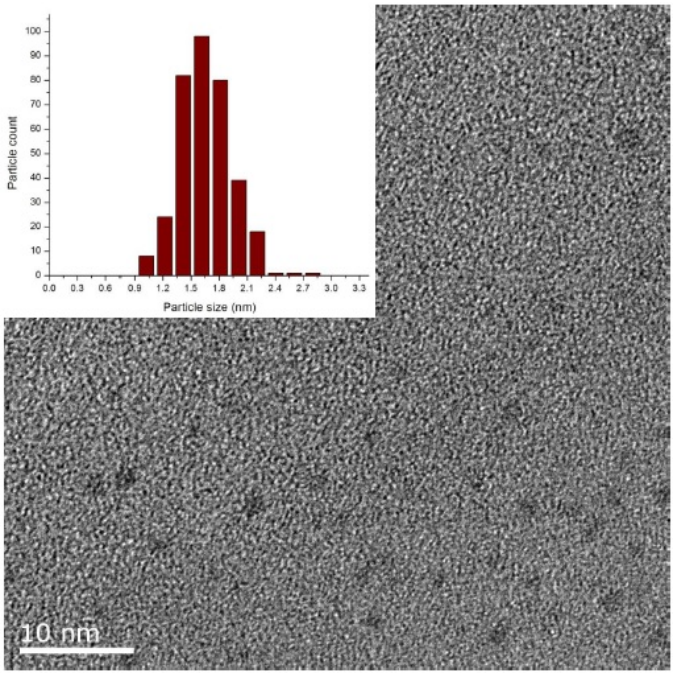

Figure S2 A representative TEM image of Au_{101} cluster on a holey carbon film coated Cu 300 Mesh grid.

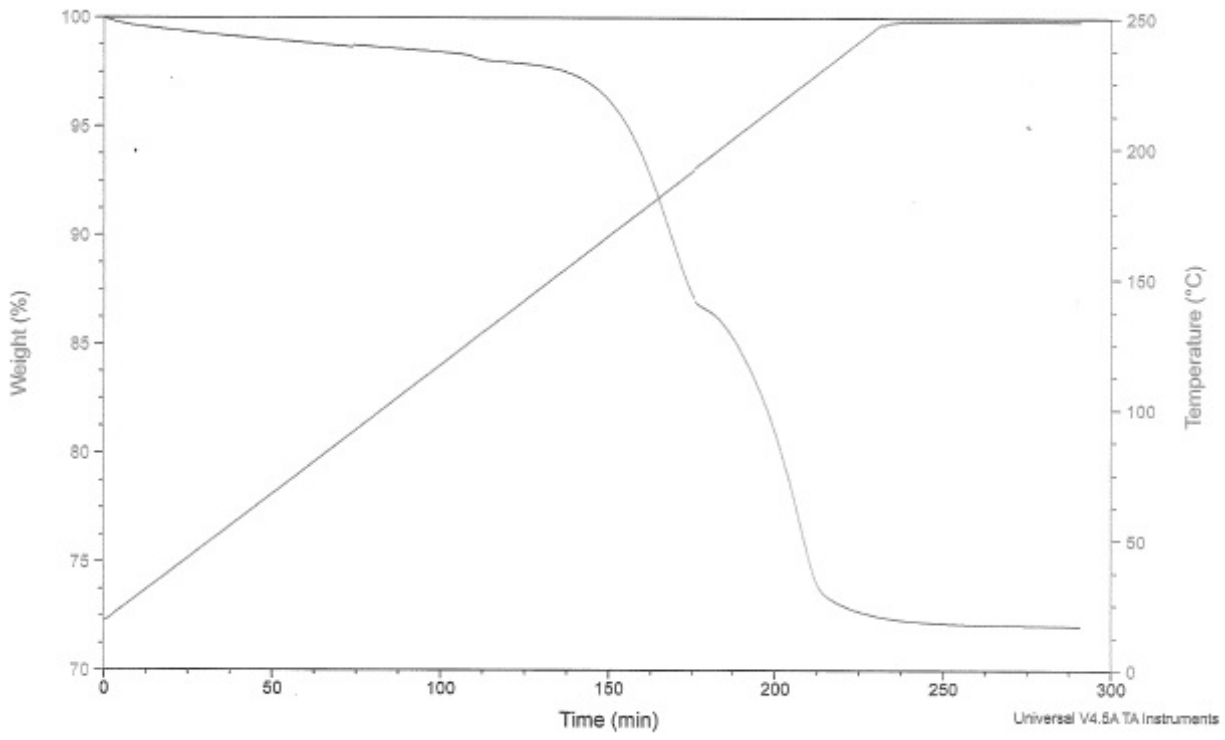

Figure S3 TGA plot of Au_{101} cluster.

Synthesis of $Au_9(PPh_3)_8(NO_3)_3$, denoted as Au_9

The synthesis of Au_9 cluster followed the synthetic procedure from Simon *et. al* with improved yield.[2] Typically, $Au(PPh_3)NO_3$ (0.856 g, 1.642 mmol) was suspended in EtOH (40 ml) while stirring. Then, $NaBH_4$ (0.0159 g, 0.042 mmol) dissolved in EtOH (23 ml) was added dropwise into $Au(PPh_3)NO_3$ solution. The mixture was stirred at room temperature for 2 h and then filtered. The filtrate (dark-red brown solution) was dried *in vacuo* using rotary evaporator. The solid residue was then dissolved in minimum amount of dichloromethane (5 ml). After filtering and solvent removal *in vacuo* using rotary evaporator, the solid residue was washed then dissolved in tetrahydrofuran and left to precipitate overnight. The residue was collected on a fritted funnel #3 and washed with tetrahydrofuran and hexane alternately three times. The solid was then crystallised in methanol by vapour diffusion with diethyl ether. The yield was 0.311 g after crystallisation. The Au_9 cluster was verified using ^{31}P NMR (CD_3OD): δ 56.9 ppm (s) with H_3PO_4 acid as the external reference (Figure S4). The UV/Vis spectrum shown below (Figure S5) is identical to the published data, confirming the pure product as the Au_9 cluster.[2] Thermogravimetric analysis showed the decomposition of phosphine ligands at 230 °C. Elemental analysis showed, the experimentally obtained values and calculated values in parentheses, % C- 42.61 (42.6), %N- 1.01 (1.04), %H- 3.08 (2.99).

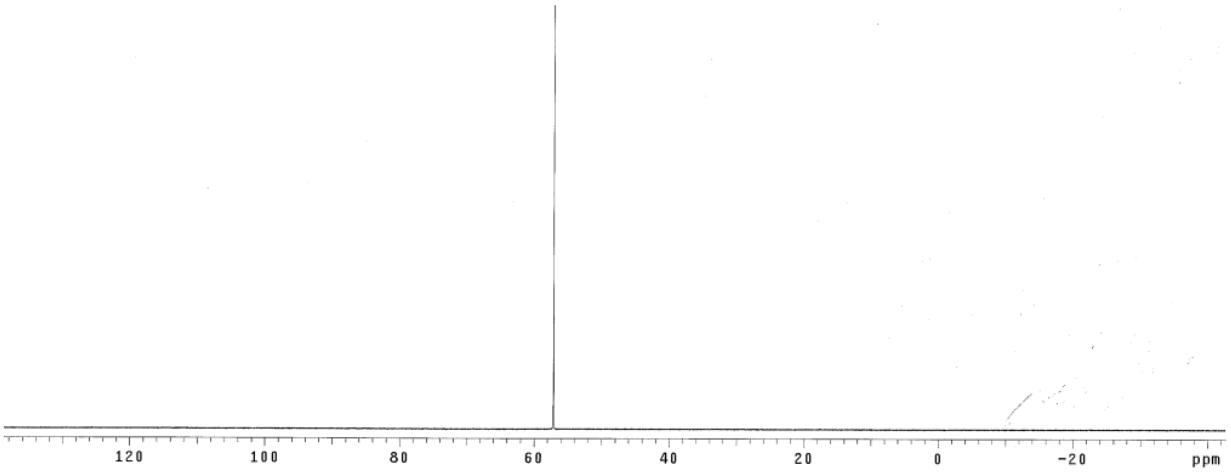

Figure S4 ^{31}P NMR spectrum of Au_9 cluster in CD_3OD.

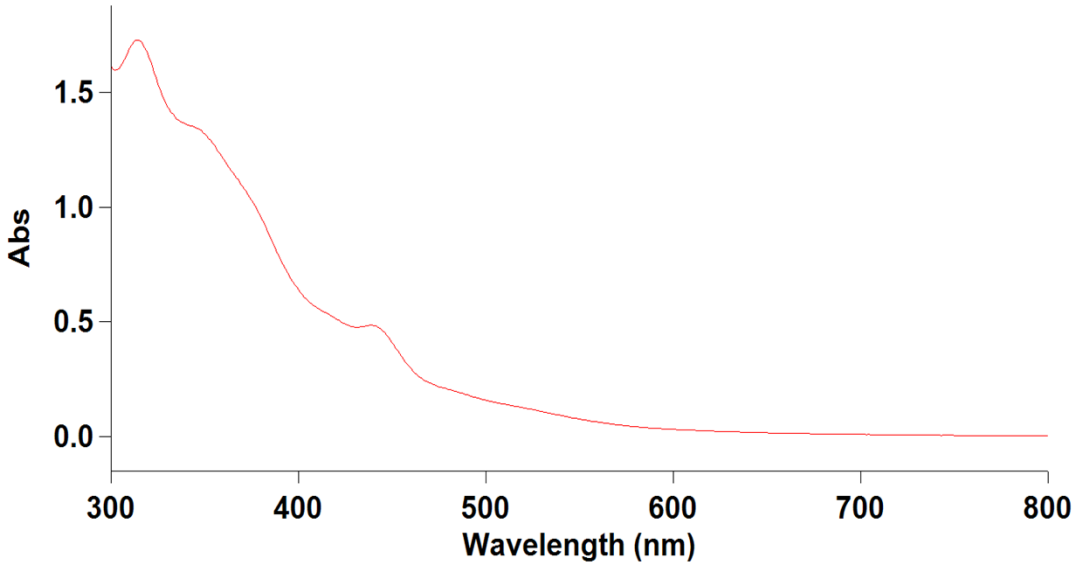

Figure S5 UV-vis spectrum of Au_9 cluster in dichloromethane solution.

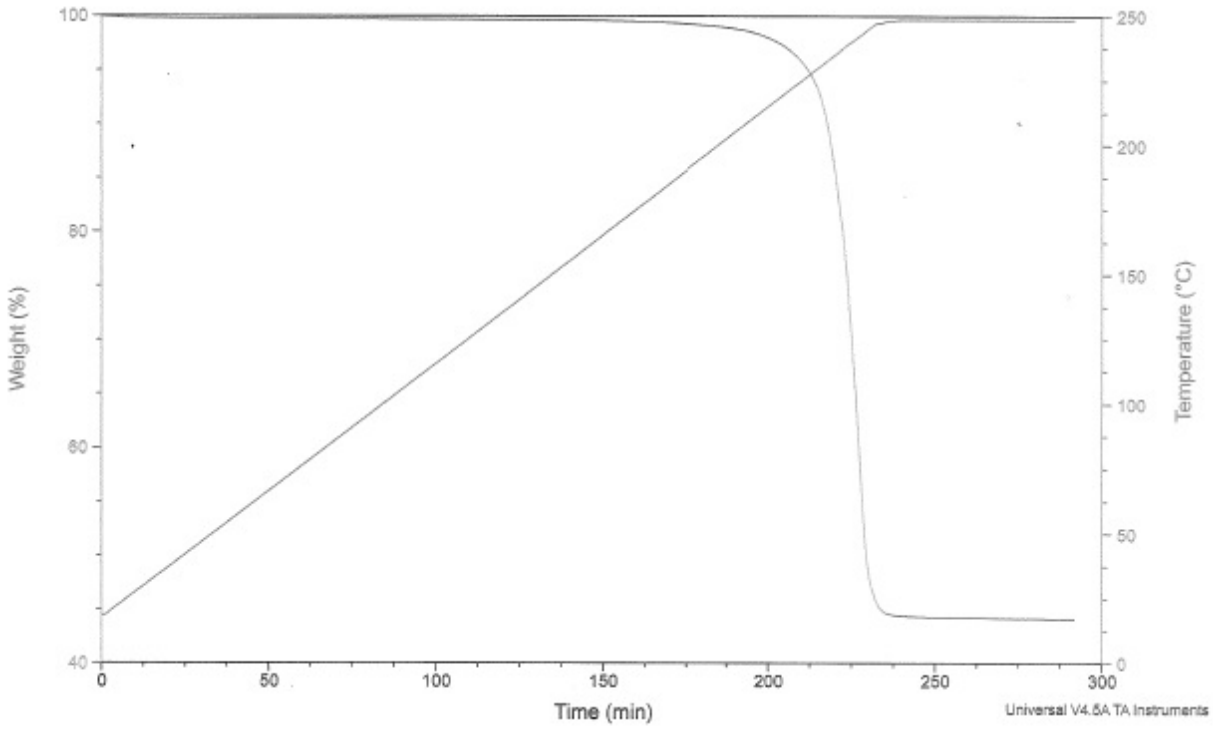

Figure S6 TGA plot of Au_9 cluster.

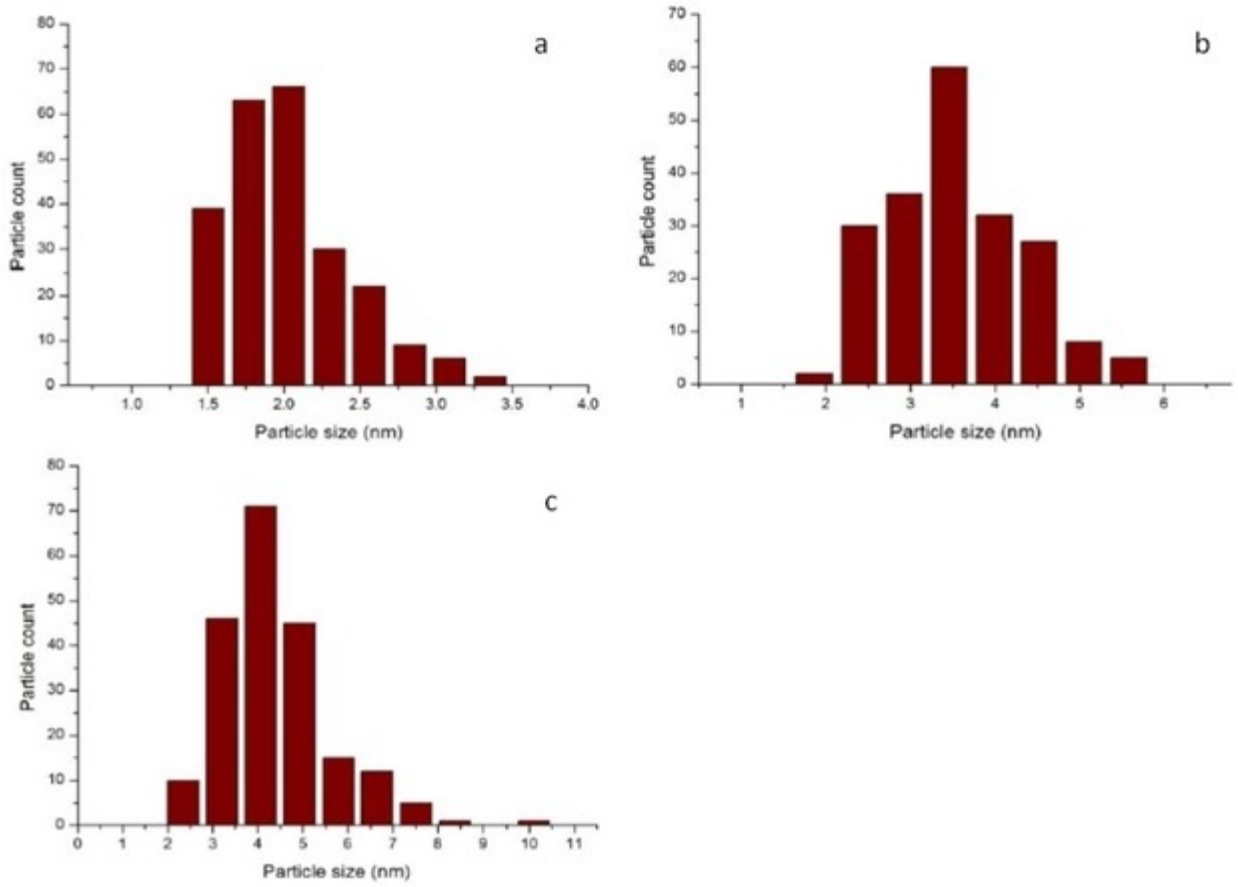

Figure S7 Particle size distribution histograms for 0.17% Au_{101}/TiO_2 catalysts before reaction, a) Au_{101}/TiO_2-untreated, b) Au_{101}/TiO_2-O_2, and c) Au_{101}/TiO_2-O_2-H_2.

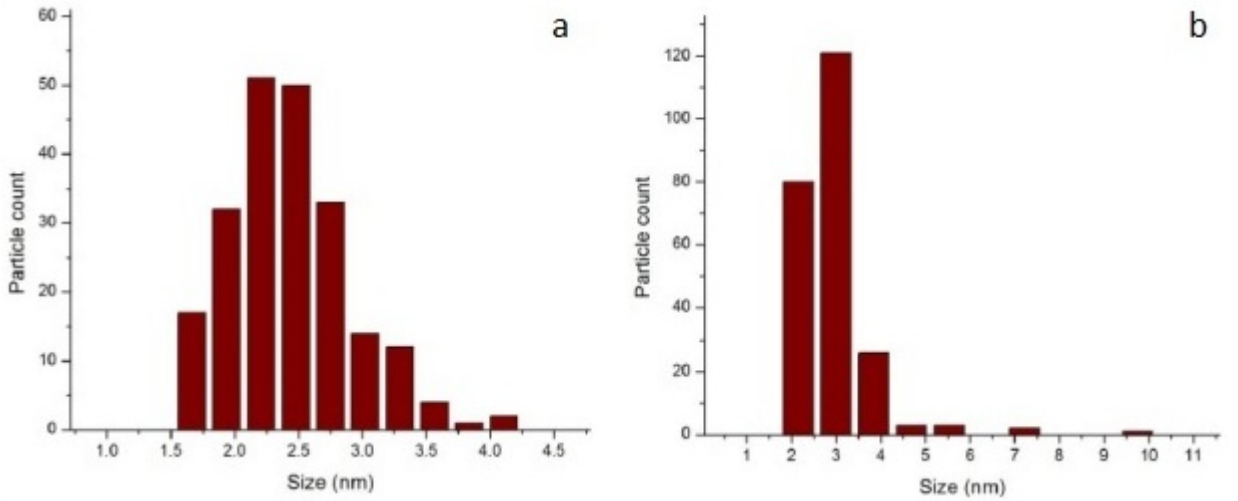

Figure S8 Particle size distribution histograms for 0.17% Au_9/TiO_2 catalysts before reaction, a) Au_9/TiO_2-O_2 and b) Au_9/TiO_2-O_2-H_2. Note that the histogram for Au_9/TiO_2-untreated is not available due to limited resolution of TEM to image very small cluster *ca*. ~ 1 nm.

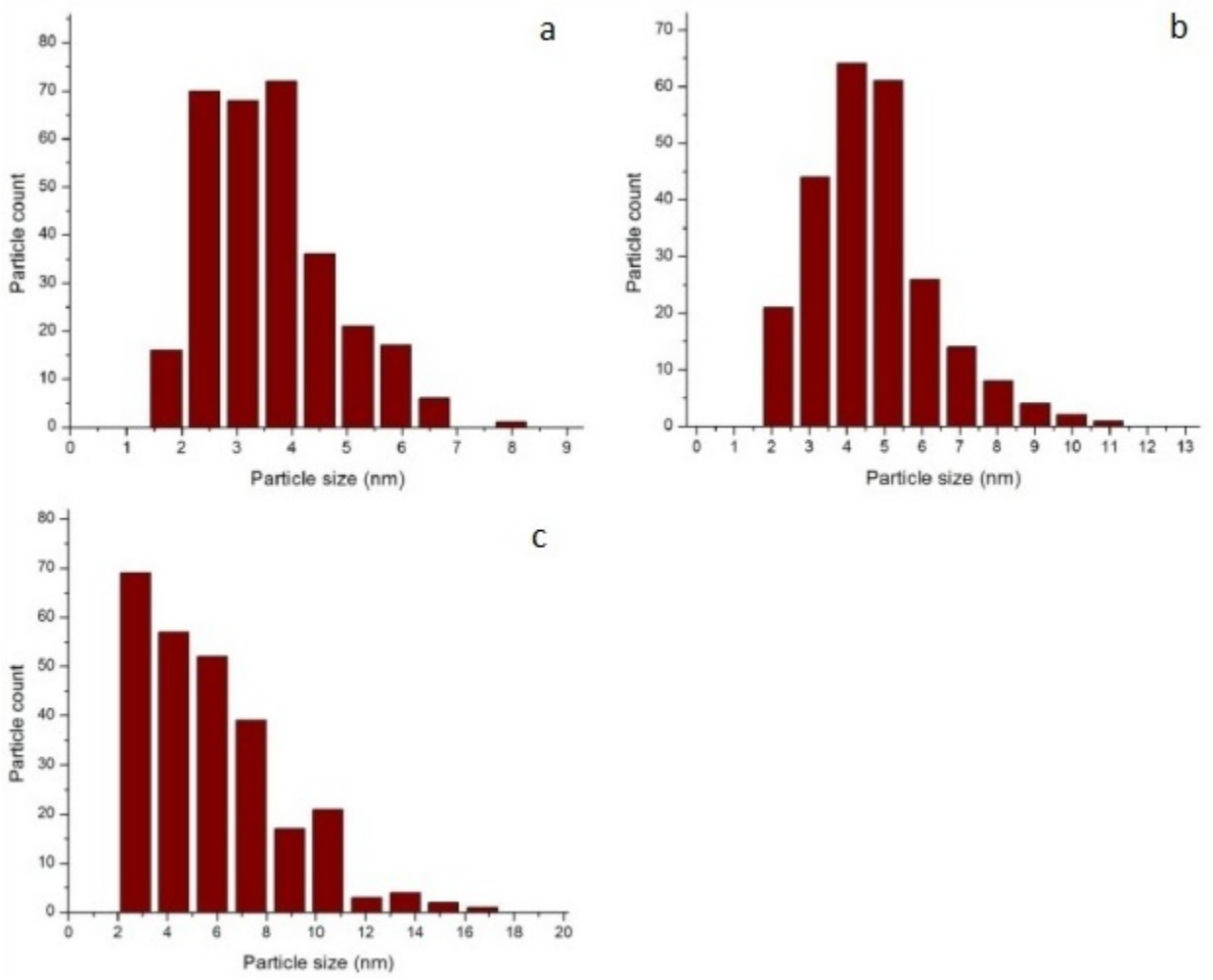

Figure S9 Particle size distribution histograms for 0.5% Au_{101}/SiO_2 catalysts before reaction, a) Au_{101}/SiO_2-untreated, b) Au_{101}/SiO_2-O_2, and c) Au_{101}/SiO_2-O_2-H_2.

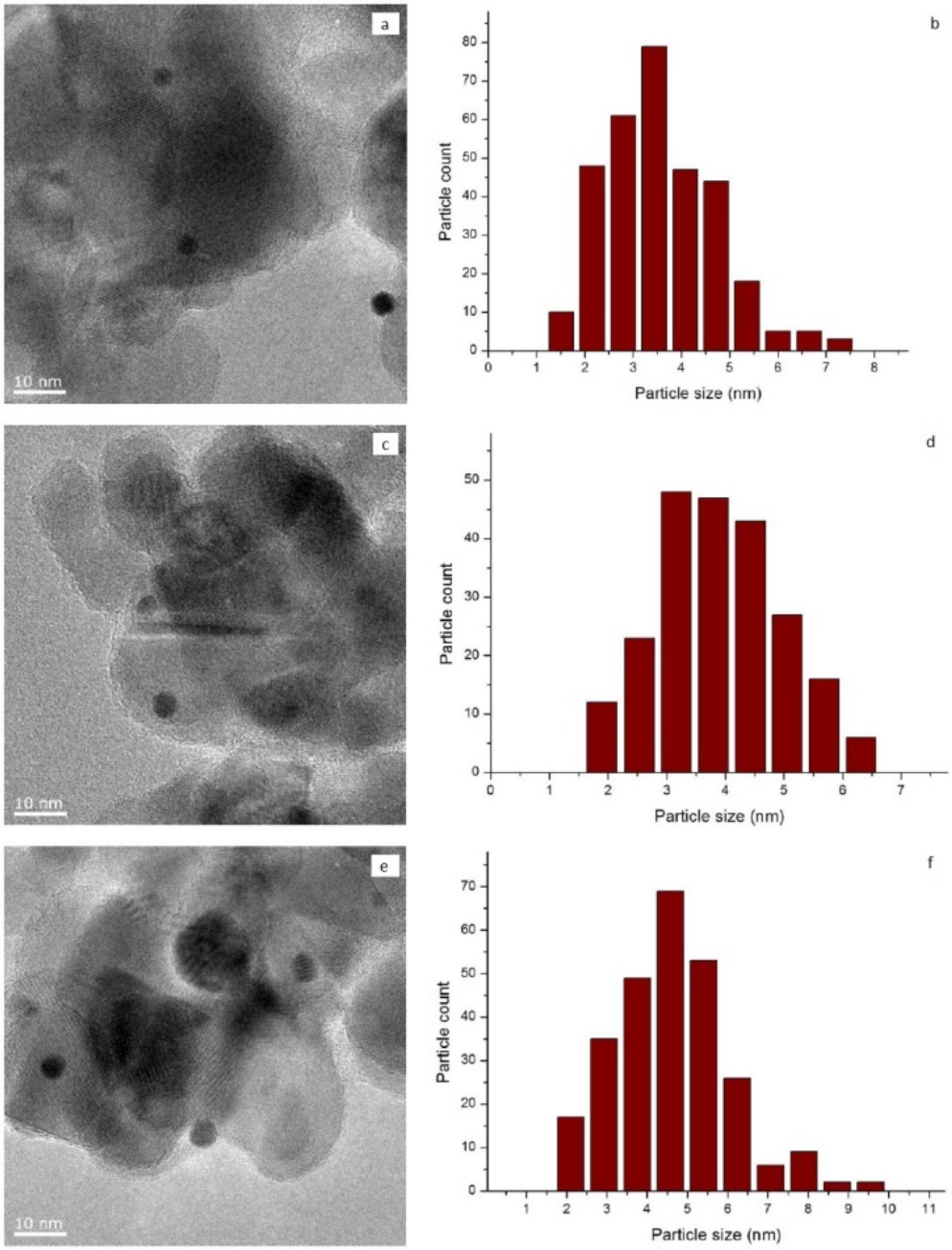

Figure S10 Particle size distribution histograms for 0.17% Au_{101}/TiO_2 catalysts after reaction, a) Au_{101}/TiO_2-untreated, b) Au_{101}/TiO_2-O_2, and c) Au_{101}/TiO_2-O_2-H_2.

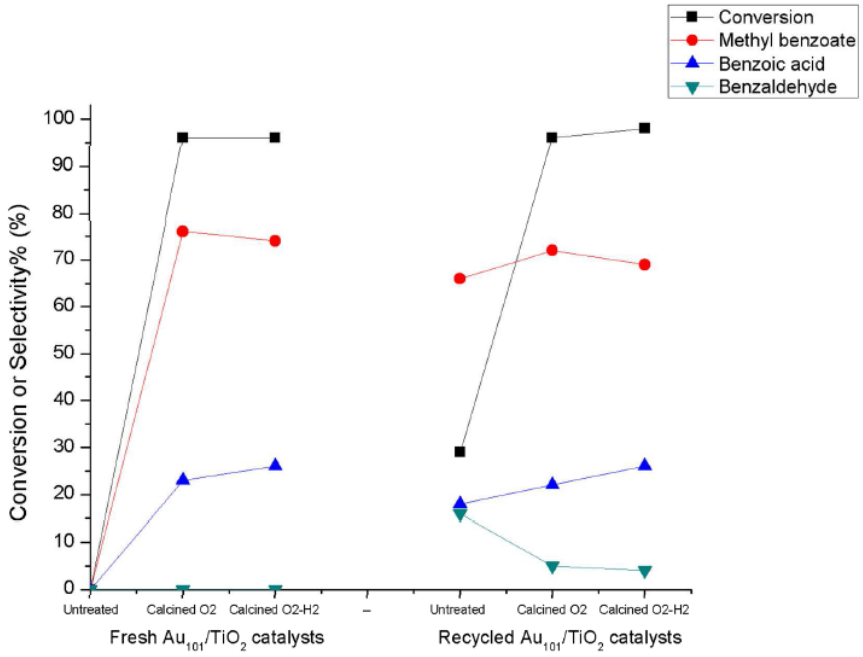

Figure S11 Conversion and selectivity of benzyl alcohol oxidation using recycled 0.17% Au_{101}/anatase catalysts. O_2 (left: fresh catalysts, right: recycled catalysts). Reaction conditions: 2.5 mmol benzyl alcohol, 25 ml MeOH (solvent), 1.25 mmol anisole (internal standard), 2.5 mmol K_2CO_3, 5 bar O_2, 80 °C, 4 hrs.

Table S1 The Au content of the Au_{101}-based catalysts as measured using AAS.

Catalyst	Target loading (%)	Experimental measurement (%)		
		Before reaction	After 1st test	After 2nd test (recycled)
0.17% Au_{101}/TiO_2-untreated	0.17	0.14 ± 0.01	0.11 ± 0.02	0.11 ± 0.02
0.17% Au_{101}/TiO_2-O_2	0.17	0.13 ± 0.01	0.13 ± 0.02	0.13 ± 0.02
0.17% Au_{101}/TiO_2-O_2-H_2	0.17	0.13 ± 0.01	0.11 ± 0.02	0.13 ± 0.01
0.17% Au_9/TiO_2-untreated	0.17	0.17 ± 0.01	0.15 ± 0.02	0.14 ± 0.02
0.17% Au_9/TiO_2-O_2	0.17	0.15 ± 0.01	0.16 ± 0.01	0.15 ± 0.02
0.17% Au_9/TiO_2-O_2-H_2	0.17	0.17 ± 0.01	0.16 ± 0.02	0.16 ± 0.02
0.17% Au_{101}/SiO_2-untreated	0.17	0.18 ± 0.01	0.17± 0.01	0.17 ± 0.02
0.17% Au_{101}/SiO_2-O_2	0.17	0.19 ± 0.01	0.17 ± 0.02	0.18 ± 0.02
0.17% Au_{101}/SiO_2-O_2-H_2	0.17	0.18 ± 0.02	0.18 ± 0.01	0.17 ± 0.02
0.5% Au_{101}/SiO_2-untreated	0.5	0.50 ± 0.01	0.49 ± 0.01	0.48 ± 0.02
0.5% Au_{101}/SiO_2-O_2	0.5	0.48 ± 0.02	0.49 ± 0.02	0.48 ± 0.01
0.5% Au_{101}/SiO_2-O_2-H_2	0.5	0.46 ± 0.02	0.45 ± 0.02	0.47 ± 0.01

Table S2 Comparison of catalytic performances of gold nanoparticles in the oxidation of benzyl alcohol

Catalysts	Au content (mol %)	Au size (nm)	T (K)	Pressure (bar)	Solvent	Time (h)	Conversion (%)	TOF (s^{-1})	Reference
Au/MOF-5	1	4.8	353	5	Methanol	3	>99	0.01	3
Au/Al-MIL53	1	~1.0	353	5	Methanol	23	98	0.001	3
Au/CPL-2	1	2.1	353	5	Methanol	23	55	0.0007	3
Au_{25}/CNT calcined 370 °C	1	n/d	353	5	Toluene	8	33	0.011	4
$Au_{13}Cu_8$/CNT calcined 370 °C	1	n/d	353	5	Toluene	8	47	0.016	4
Au_{101}/TiO_2 calcined O_2	0.13	3.5	353	3	Methanol	3	93	0.65	This work
Au_{101}/TiO_2 calcined O_2	0.13	3.5	353	5	Methanol	4	96	0.51	This work
Au_{101}/TiO_2 calcined O_2-H_2	0.13	4.4	353	5	Methanol	4	97	0.51	This work
Au_{101}/SiO_2 calcined O_2-H_2	0.46	5.7	353	5	Methanol	4	99	0.15	This work

References

1. W. W. Weare, S. M. Reed, M. G. Warner and J. E. Hutchison, *Journal of the American Chemical Society*, 2000, **122**, 12890-12891.
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