Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for:

Jones Oxidation of Glycerol Catalysed by Small Gold Clusters

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✧ Experimental details.

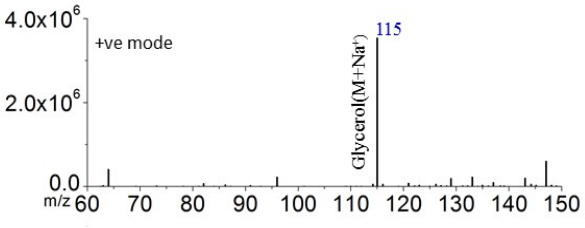

Figure S1. ESI-MS spectra (positive mode) of glycerol after laser ablation without gold rod, (concentrated with rotary evaporation) and at the addition of 0.15 ml volume of H_2O_2 (30%) and 20 mg NaOH (1M).

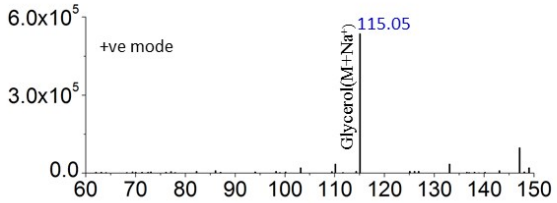

Figure S2. ESI-MS spectra of glycerol after reaction with 0.15 ml volume of H_2O_2 (30%) and 20 mg NaOH (1M), (without laser ablation).

✧ Calculation details

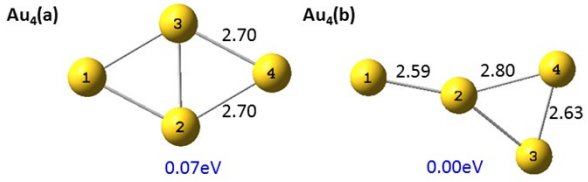

Figure S3. Structures of most stable isomers of Au_4. Inter-atomic distances are given in angstroms.

Table S1. HOMO-LUMO orbitals in Au_4

NAO	Atom	No.	Lang	Type(AO)	Occupancy
38	Au	2	dxz	Ryd(6d)	0.00007
39	Au	2	dyz	val(5d)	1.91151

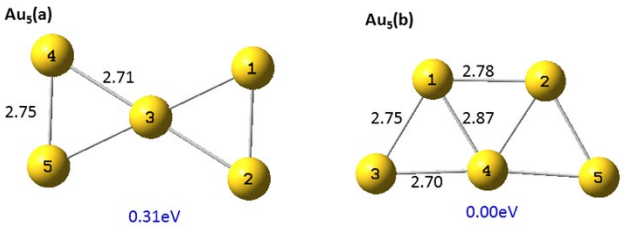

Figure S4. Structures of the most stable isomers of Au_5. Inter-atomic distances are given in angstroms.

Table S2. HOMO-LUMO orbitals in Au_5.

NAO	Atom	No.	Lang	Type(AO)	Occupancy
47	Au	3	S	Ryd(7S)	0.00079
48	Au	3	Px	Cor(5p)	1.99947

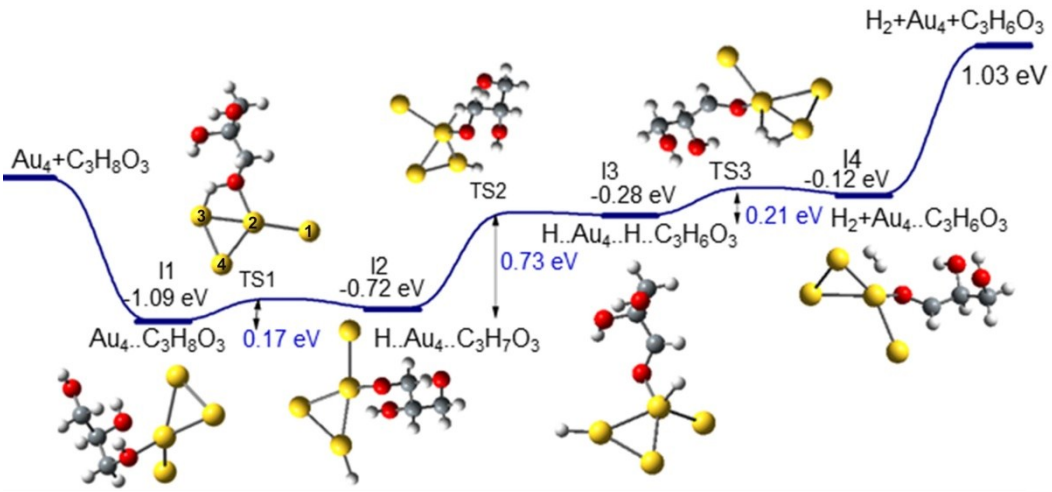

Figure S5. Alternative reaction coordinate of "glycerol+Au_4" involving elimination of two hydrogen atoms on glycerol over Au_4 to form glyceraldehyde. H atom from the -OH group of the terminal carbon atom adsorbs onto No.3 Au atom site. Atoms in yellow, red, grey and white colour represent Au, O, C and H respectively.

We have also compared with the reaction pathways for glycerol dehydration to form 3-hydroxylpropionaldehyde, and followed by oxidation to produce glyceraldehyde, as shown in Figure S6. As results, the calculated activation energy for the initial dehydration step is 0.03 eV, allowing the middle carbon of 3- hydroxylpropionaldehyde to be attached to the oxygen atom of Au_4O*. The following reaction step is the insertion of an oxygen atom into the C-H bond, showing an energy gain of 0.03 eV ($E_{f\text{-}e}$), while desorption of glyceraldehyde from Au_4 has an activation energy, △G, equaling to -1.18 eV.

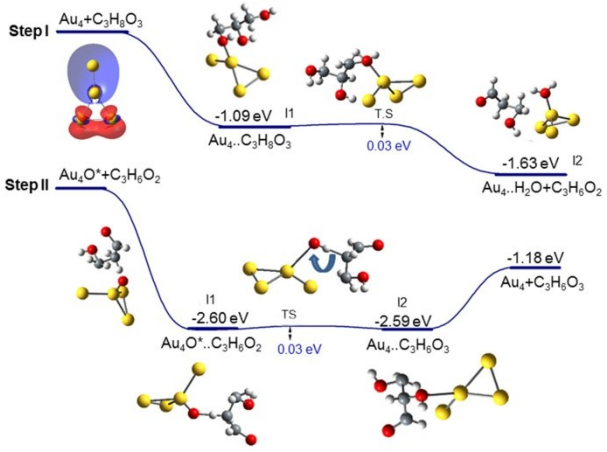

Figure S6. Reaction coordinates involving, step I: glycerol dehydration over Au_4 to 3-hydroxylpropionaldehyde, step II: oxidation of 3-hydroxylpropionaldehyde by Au_4O* to form glyceraldehyde. Atoms in yellow, red, grey and white colour represent Au, O, C and H respectively.

Considering that the reactivity in catalysis could change dramatically with the addition or removal of even a single atom, we have also investigated the interaction H_2O_2 over Au_5.

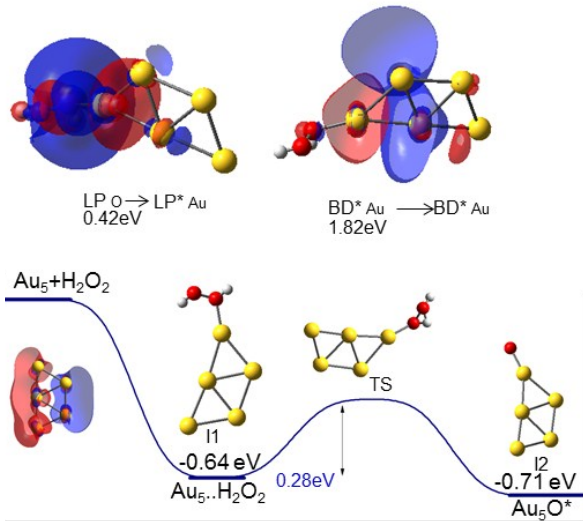

Figure S7: (Upper) SOP theory analysis of Fock matrix in NBO donor–acceptor (overlap) interactions in Au_5–H_2O_2 complex, and (Below) the reaction coordinate of O-transfer from H_2O_2 to Au_5 to form Au_5O^*. Atoms in yellow, red, grey, and white colours represent Au, O, C and H respectively.

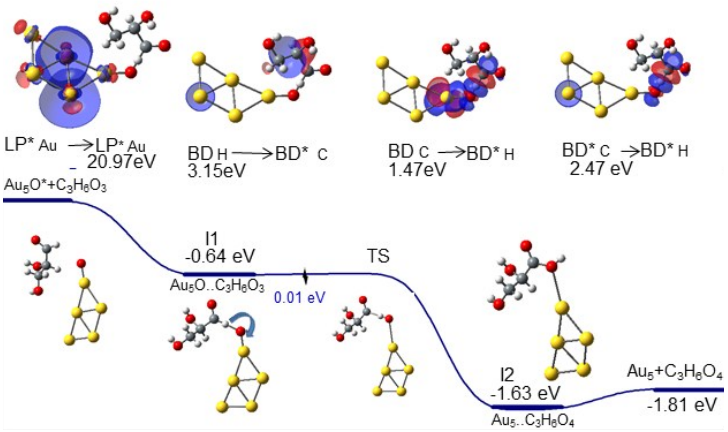

Figure S8: (Upper) Second-order-perturbation theory analysis of Fock matrix in NBO donor–acceptor (overlap) interactions in Au_5o^*–glyceraldehyde complex, and **(below)** the reaction coordinate involving oxidation of glyceraldehyde to glyceric acid over Au_5. Atoms in yellow, red, grey and white colours represent Au, O, C and H respectively.

Table S3. The Sum of electronic and zero point energies (a.u.) of gold clusters, reactants and products, calculated with different methods and basis sets.

	HF/Lanl2dz	B3lyp/ Lanl2dz	B3lyp/6-31G
Au_3	-403.62673	-406.41899	
Au_4	-538.19208	-541.932	
Au_5	-672.75481	-677.43267	
Au_{20}	-2691.2344	-2710.0991	
Glycerol	-342.62875	-344.63154	-344.54804
Glyceraldehyde	-341.46472	-343.4293	-343.35138
Glyceric acid	-416.2463	-418.60322	-418.57338
Hydrogen	-1.113708	-1.164262	-1.165337
H_2O_2	-150.71256	-151.49989	-151.44956
Water	-75.988276	-76.393557	-76.365578

Enlarged NBO patterns

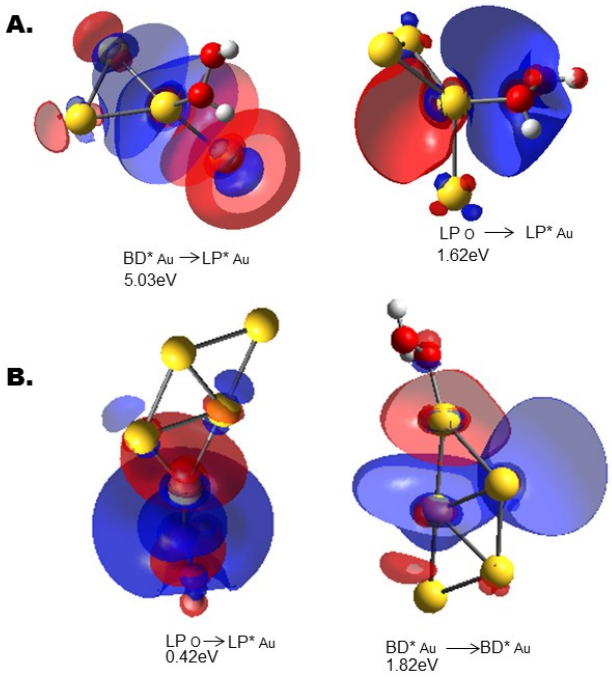

Figure S9. Enlarged NBO patterns. **A:** Second–order–perturbation (SOP) theory analysis of Fock matrix in NBO donor–acceptor (overlap) interactions in Au_4–H_2O_2 complex. **B:** SOP theory analysis of Fock matrix in NBO donor–acceptor (overlap) interactions in Au_5–H_2O_2 complex. Atoms in yellow, red, grey, and white colours represent Au, O, C and H respectively.

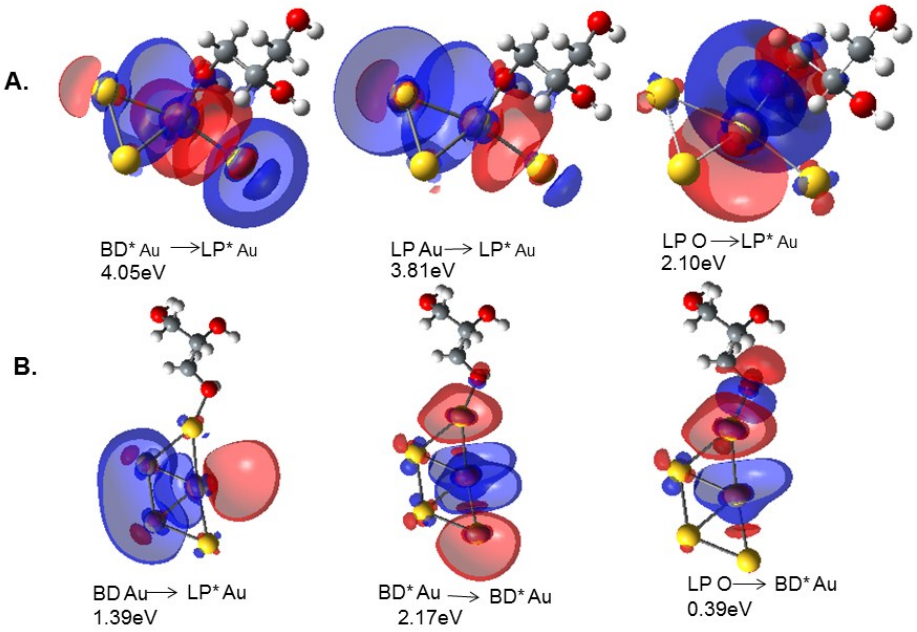

Figure S10. Enlarged NBO patterns. **A:** Second-order-perturbation theory analysis of Fock matrix in NBO donor–acceptor (overlap) interactions in Au_4–glycerol complex **B:** Second-order-perturbation theory analysis of Fock matrix in NBO donor–acceptor (overlap) interactions in Au_5–glycerol complex. Atoms in yellow, red, grey and white colours represent Au, O, C and H respectively.

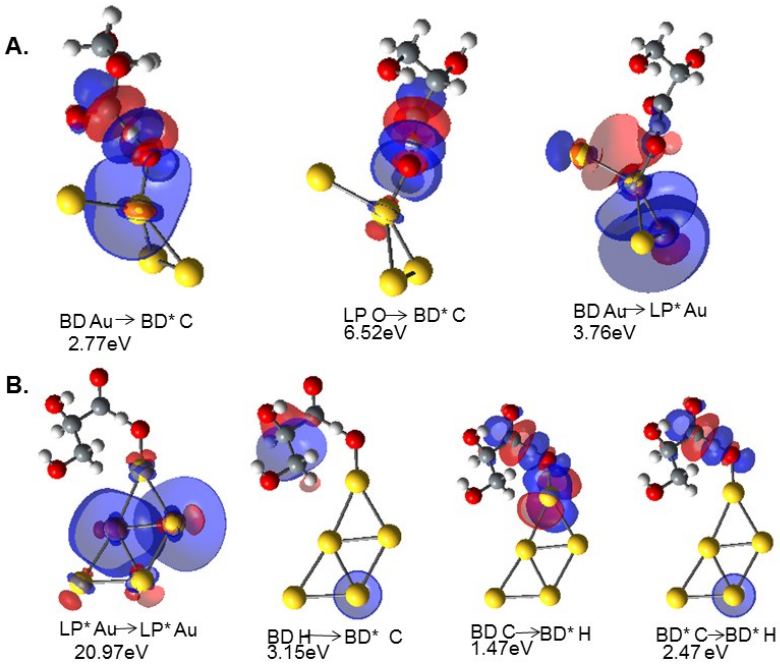

Figure S11. Enlarged NBO patterns. **A:** Second-order-perturbation theory analysis of Fock matrix in NBO donor–acceptor (overlap) interactions in Au_4o*–glyceraldehyde complex **B:** Second-order-perturbation theory analysis of Fock matrix in NBO donor–acceptor (overlap) interactions in Au_5o*–glyceraldehyde complex. Atoms in yellow, red, grey and white colours represent Au, O, C and H respectively.