Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

for

CO Oxidation Catalyzed by Silver Nanoclusters: Mechanism and Effects of Charge

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S1. Validation of Theoretical Method

To support our choice for the combination of the functional and basis sets described in the computational details, we provide benchmark calculations of the electron affinities (EAs) and ionization potentials (IPs) for Ag, Ag_2, Ag_3, and O_2, and of the geometrical parameters for O_2, CO, and CO_2. As shown in Table S1, the calculated IPs and EAs are in good agreement with the previous experimental values. The Ag-Ag bond length and bond energies of Ag_2 are predicted to be 2.578 Å and 1.66 eV, which are in fair agreement with experimental findings (2.480 Å and 1.69 eV).[1] The predicted ground state of Ag_3 cluster is $^2B_2$ state with C_{2v} point group, which is in line with the CCSD(T) resuts.[2] The Ag-Ag bond length of the Ag_3 ground state is 2.648 Å , which is close to that (2.643 Å) obtained at CCSD(T)/aVQZ level.[2] The experimental and computational values of the atomization energy [3**E*(Ag)-*E*(Ag_3)] for Ag_3 cluster are 2.62±0.13 and 2.34 eV, respectively.[3] The calculated (experimental) bond lengths of C-O in CO, O-O in O_2, and C-O in CO_2 are 1.138(1.128), 1.226(1.207), and 1.176(1.169) Å,[4] respectively. The calculated (experimental) bond lengths of Ag-O in AgO are 1.995(2.005) Å.[5] In summary, these facts indicate the acceptable accuracy and reliability of the level of theory used.

Table S1 Calculated and Experimental Electron Affinities (EAs, eV) and Ionization Potentials (IPs, eV) for Ag, Ag_2, Ag_3, AgO, and O_2

Species	*calculated*		*experiment*	
	EA	IP	EA	IP
Ag	0.17	7.75	1.302[a]	7.576[b]
Ag_2	0.38	7.67	1.028[c]	7.56[d]
Ag_3	1.71	5.76	2.27±0.1[e]	5.65[f]
O_2	0.84	12.76	0.45[g]	12.05[h]
AgO	1.06	9.10	1.654[i]	-

[a] ref. 6 [b] ref. 7 [c] ref. 8 [d] ref. 9 [e] ref.10 [f] CCSD(t)/ aVQZ level in ref.2
[g] ref.4 [h] ref.11 [i] ref.12

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S2. Figs. S1 and S2

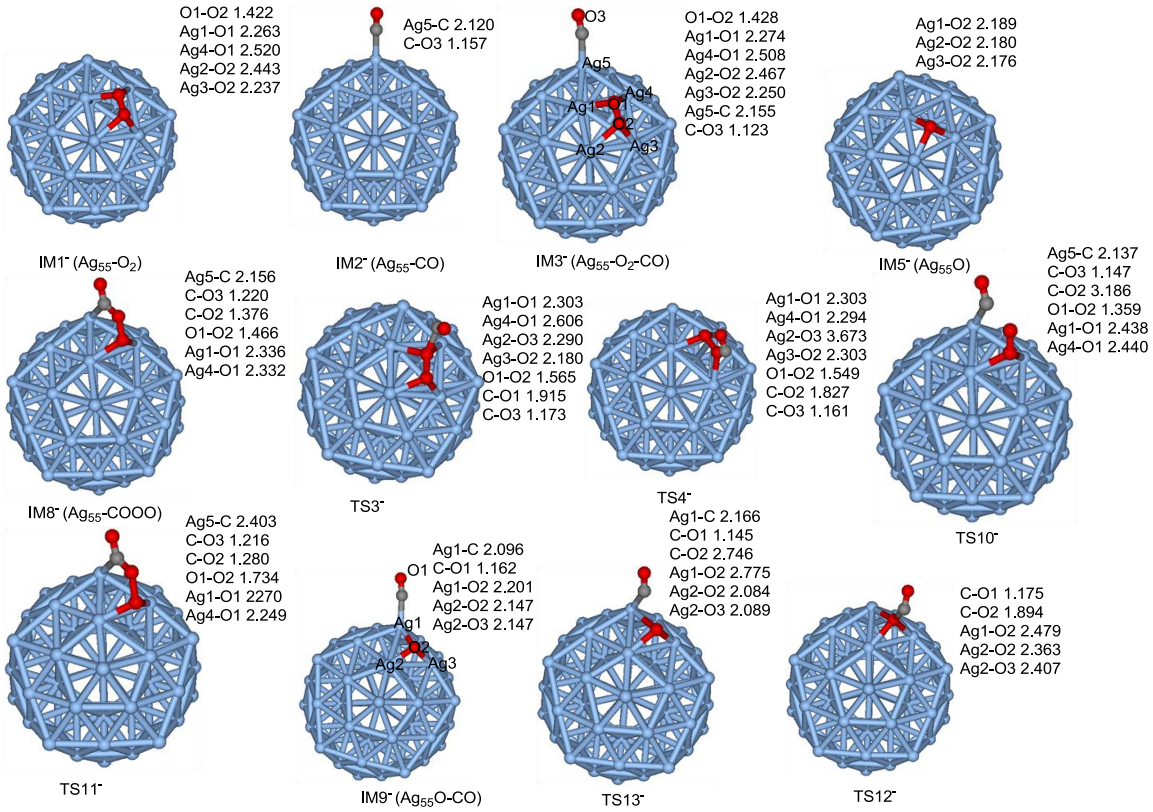

Fig. S1. Optimized structures and the related parameters of the Ag_{55}^--catalyzed CO oxidation.

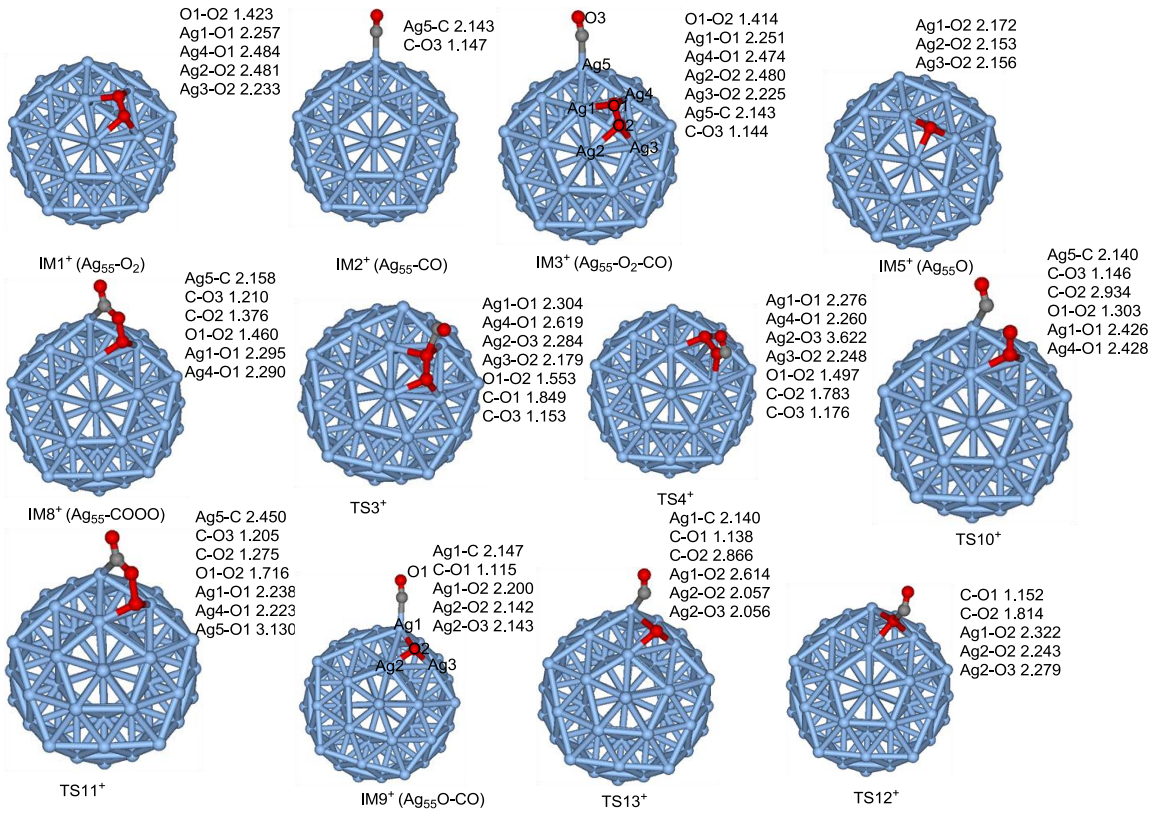

Fig. S2. Optimized structures and the related parameters of the Ag_{55}^{+}-catalyzed CO oxidation.