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

Supplementary Information

Foreign atom encapsulated Au_{12} cage clusters for catalysis of CO oxidation

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S1. Adsorption energies of reaction intermediates

We calculated the adsorption energies of molecules and reaction intermediates involved in CO oxidation on the M@Au_{12} clusters, including O_2, CO, co-adsorbed O_2 and CO molecules (*O_2-*CO), and co-adsorbed O atom and CO molecule (*O-*CO). Their adsorption energies are defined as follows:

$$E_{O2} = E_{total} - E_{M@Au12} - E_{O2} \quad \text{(S1)}$$

$$E_{CO} = E_{total} - E_{M@Au12} - E_{CO} \quad \text{(S2)}$$

$$E_{*O2\text{-}*CO} = E_{total} - E_{M@Au12} - E_{O2} - E_{CO} \quad \text{(S3)}$$

$$E_{*O\text{-}*CO} = E_{total} - E_{M@Au12} - 1/2E_{O2} - E_{CO} \quad \text{(S4)}$$

where E_{total} and $E_{M@Au12}$ are the energies of a M@Au_{12} cluster with and without adsorption of the molecule or reaction intermediate, respectively; E_{O2} and E_{CO} are the energies of gaseous O_2 and CO molecules in vacuum, respectively.

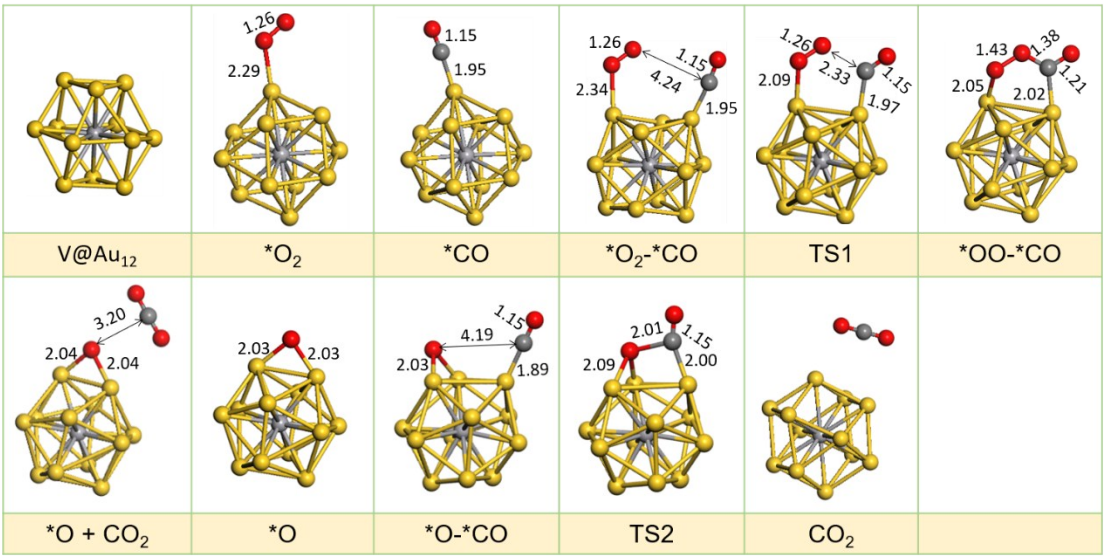

Fig. S1 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $V@Au_{12}$ cluster under the L-H mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

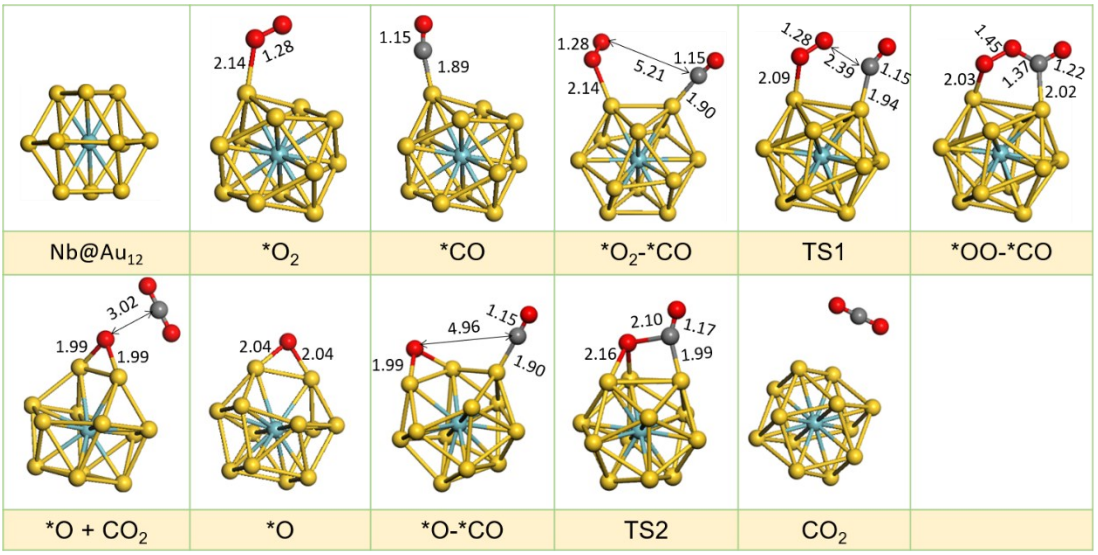

Fig. S2 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Nb@Au_{12}$ cluster under the L-H mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

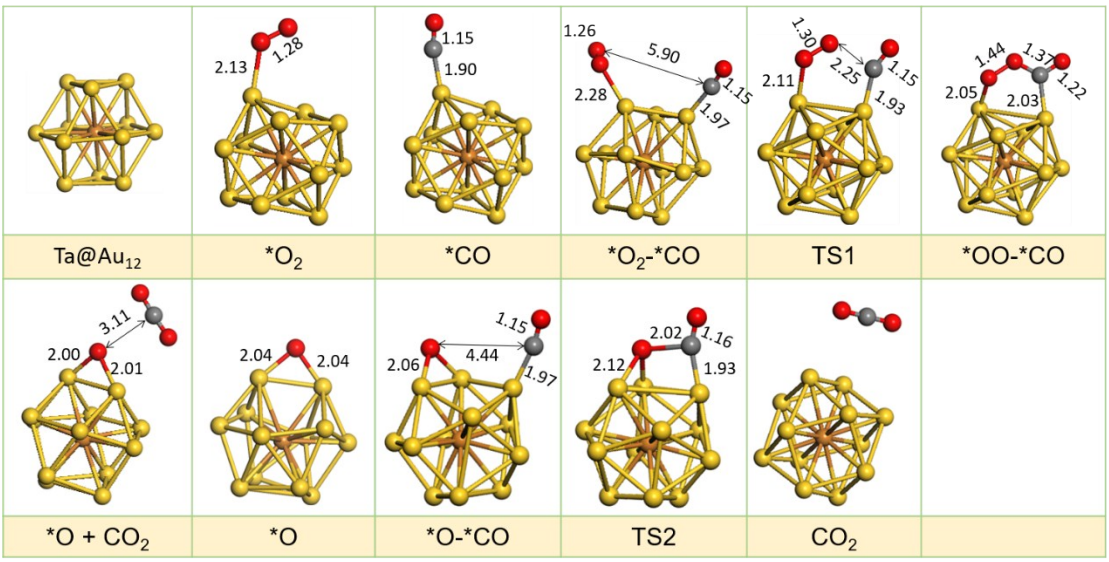

Fig. S3 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Ta@Au_{12}$ cluster under the L-H mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

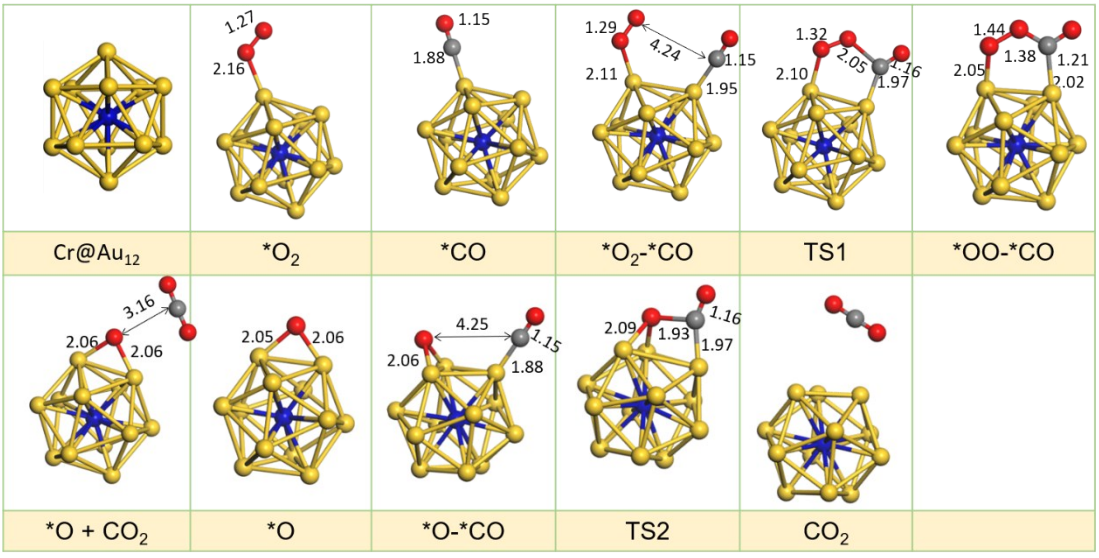

Fig. S4 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Cr@Au_{12}$ cluster under the L-H mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

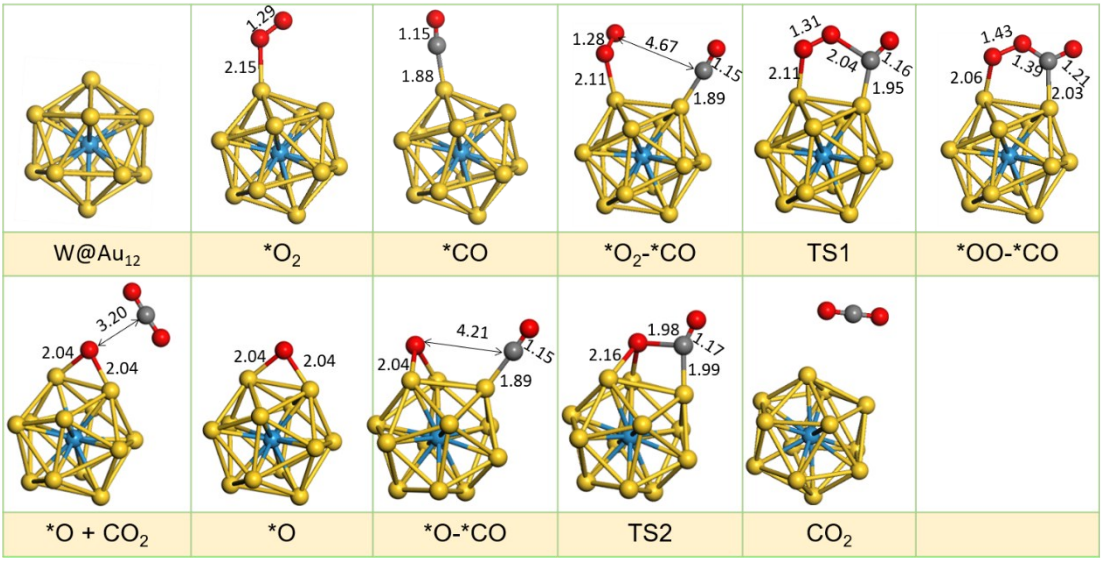

Fig. S5 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Mo@Au_{12}$ cluster under the L-H mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

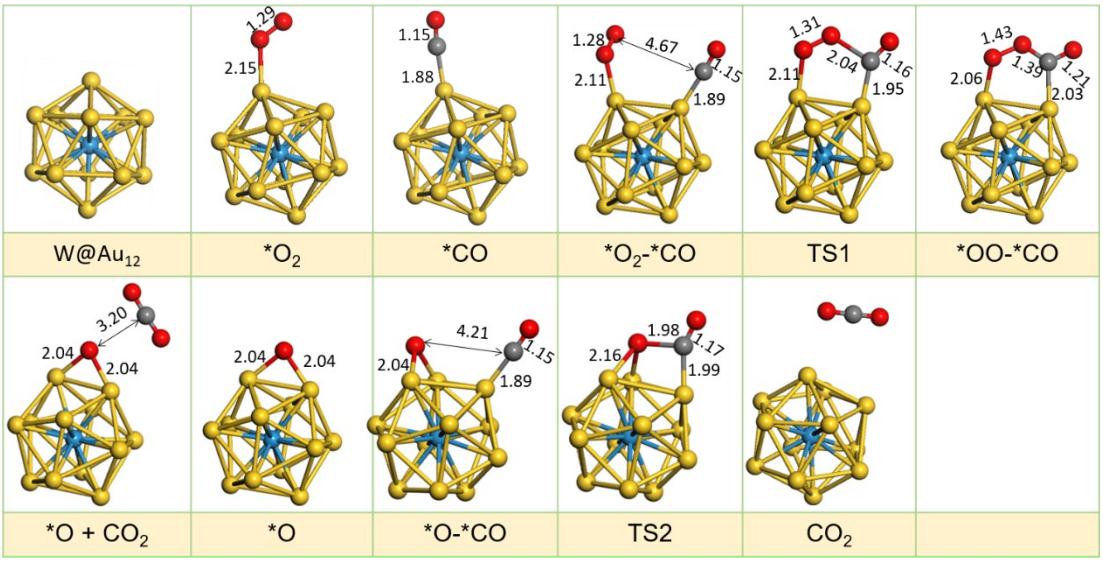

Fig. S6 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $W@Au_{12}$ cluster under the L-H mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

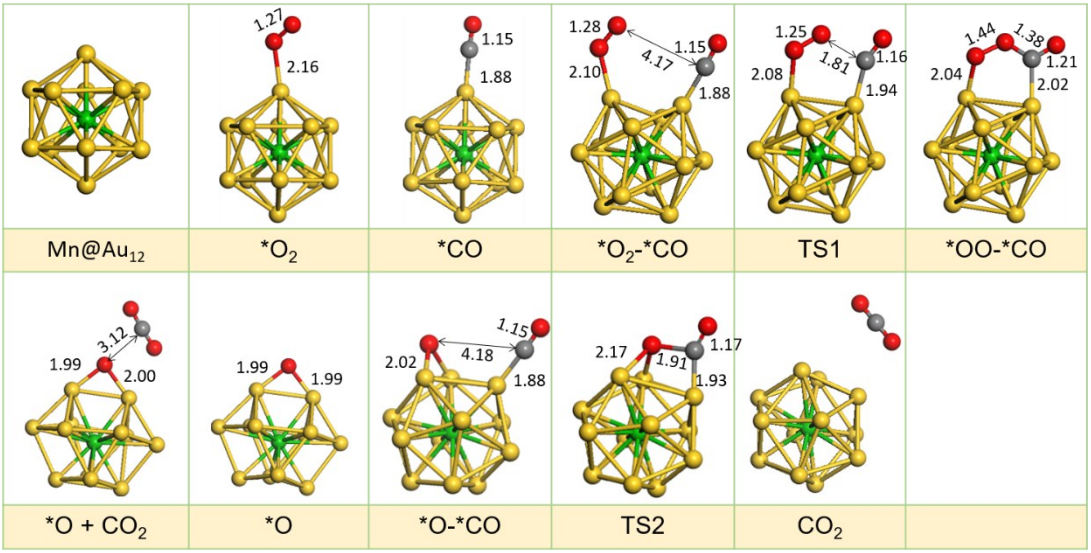

Fig. S7 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Mn@Au_{12}$ cluster under the L-H mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

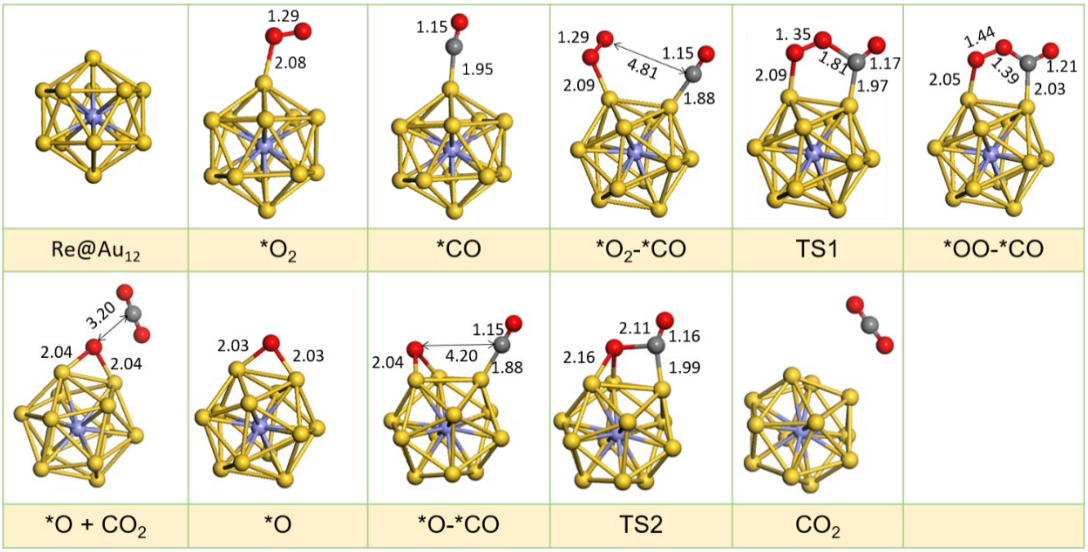

Fig. S8 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Re@Au_{12}$ cluster under the L-H mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

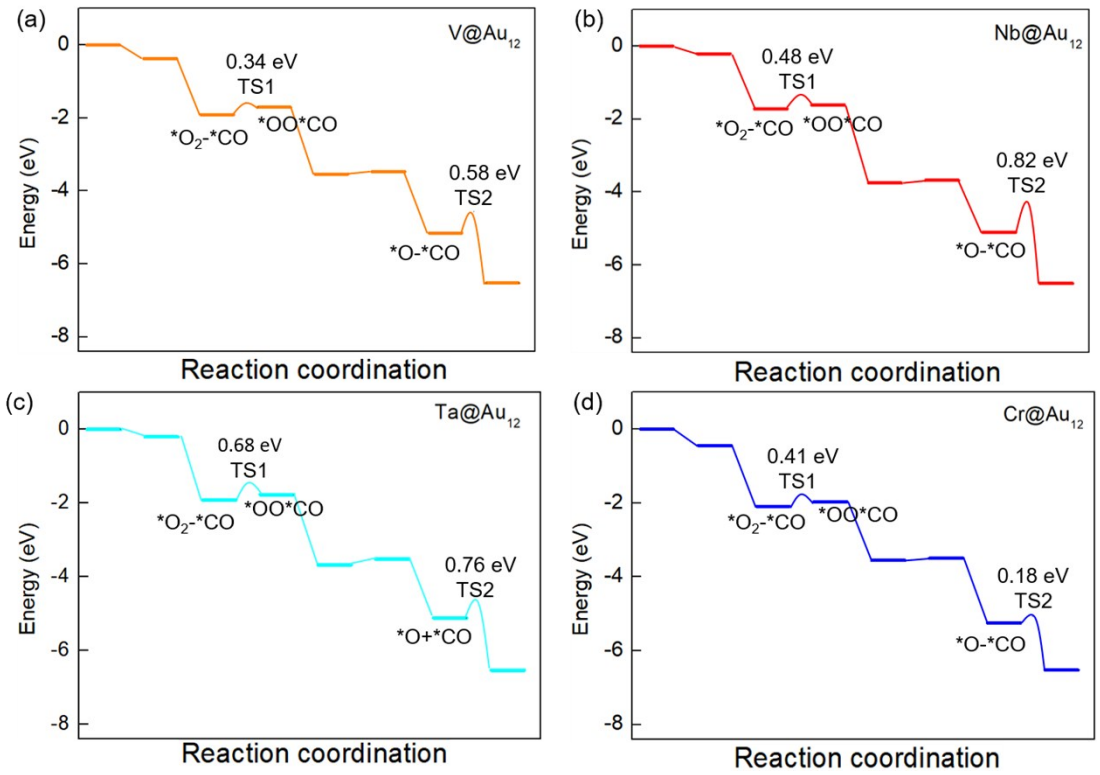

Fig. S9 Reaction pathway of CO oxidation under the L-H mechanism on (a) V@Au_{12}, (b) Nb@Au_{12}, (c) Ta@Au_{12}, and (d) Cr@Au_{12} clusters, respectively. The numbers indicate the kinetic barriers.

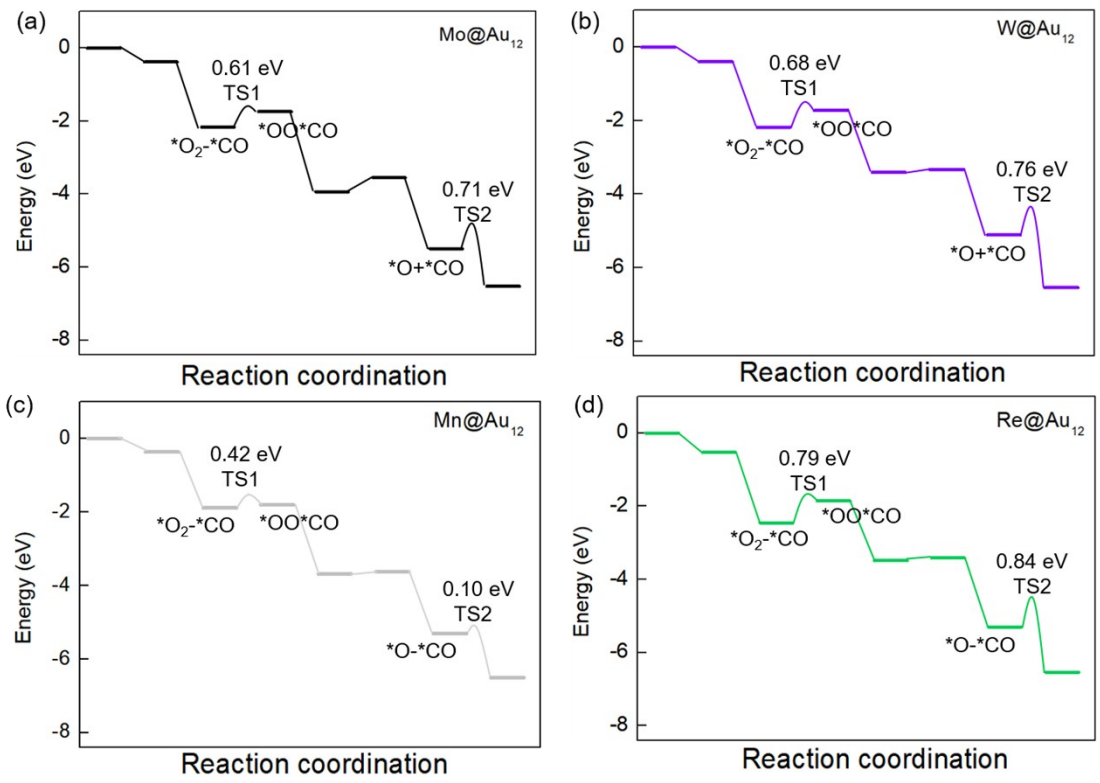

Fig. S10 Reaction pathway of CO oxidation under the L-H mechanism on (a) $Mo@Au_{12}$, (b) $W@Au_{12}$, (c) $Mn@Au_{12}$, and (d) $Re@Au_{12}$ clusters, respectively. The numbers indicate the kinetic barriers.

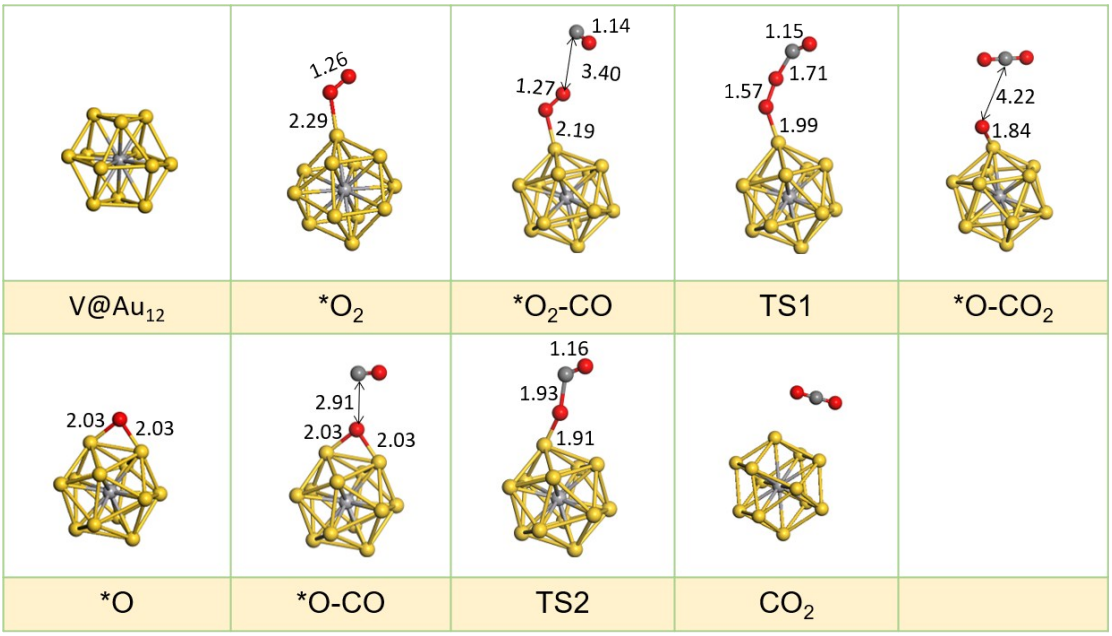

Fig. S11 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $V@Au_{12}$ cluster under the E-R mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

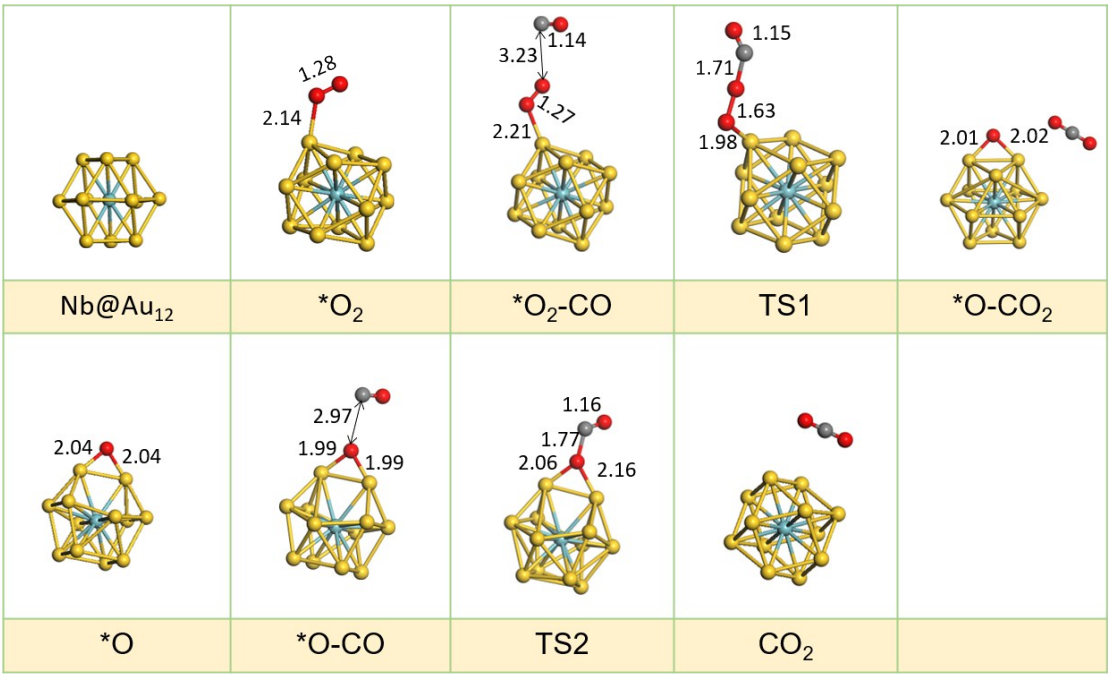

Fig. S12 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Nb@Au_{12}$ cluster under the E-R mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

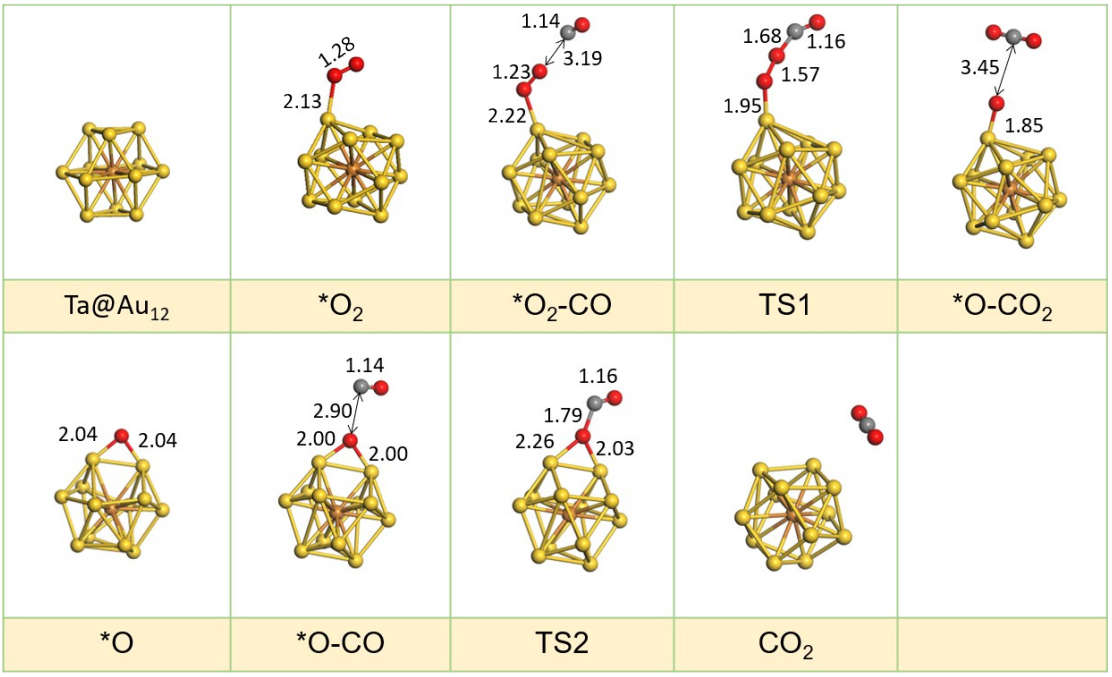

Fig. S13 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Ta@Au_{12}$ cluster under the E-R mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

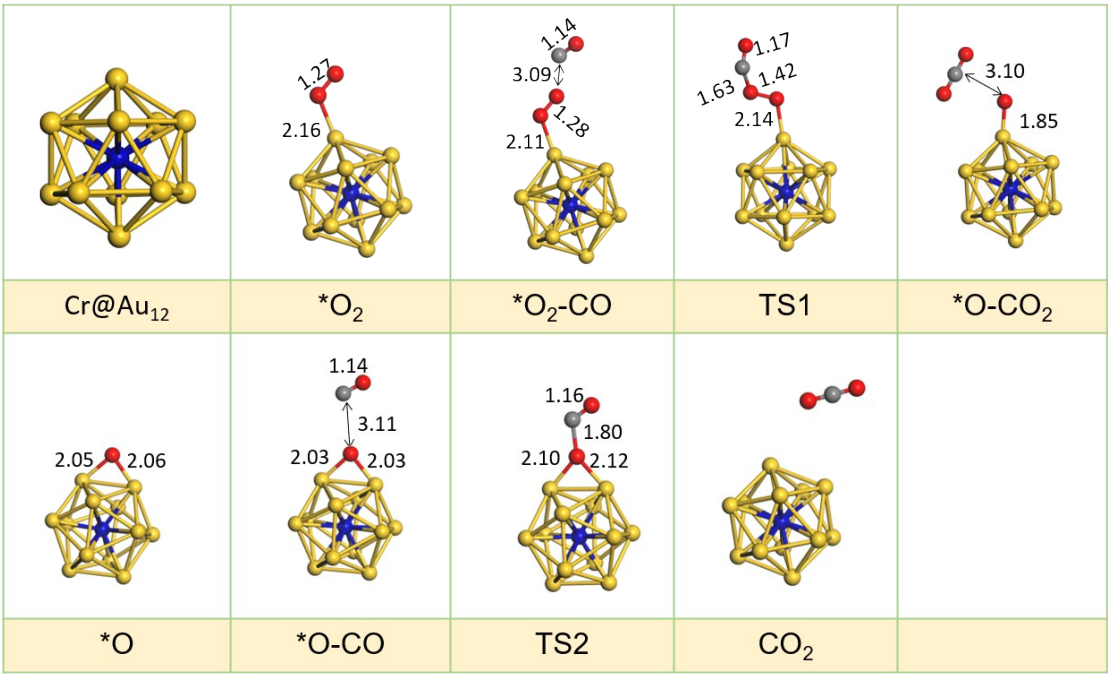

Fig. S14 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Cr@Au_{12}$ cluster under the E-R mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

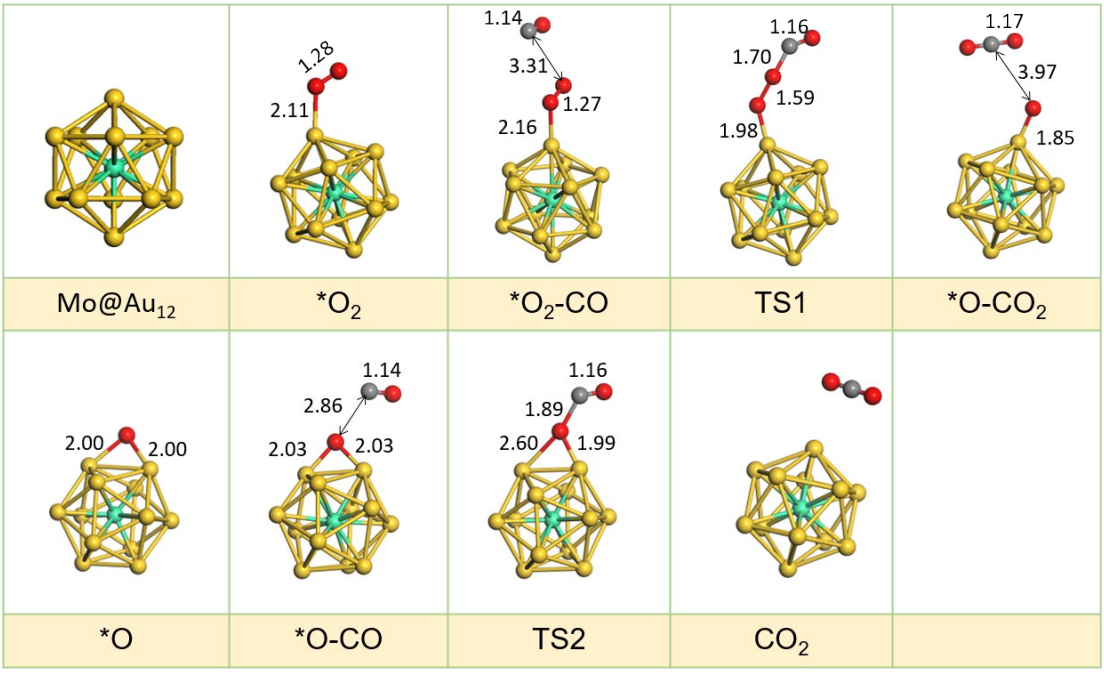

Fig. S15 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Mo@Au_{12}$ cluster under the E-R mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

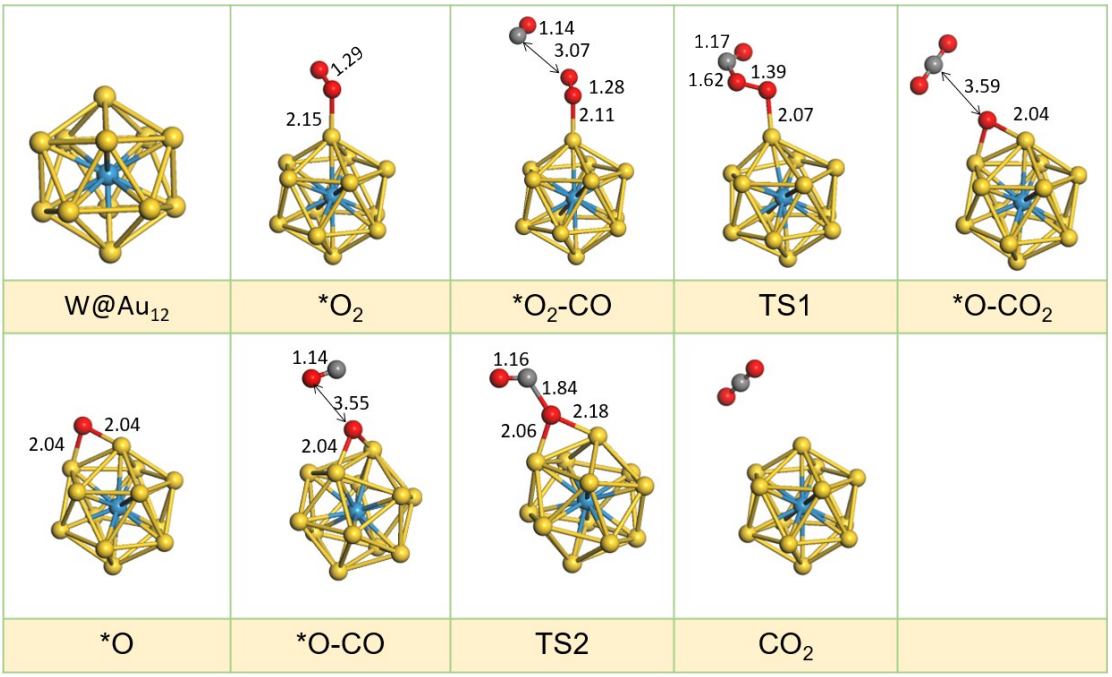

Fig. S16 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $W@Au_{12}$ cluster under the E-R mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

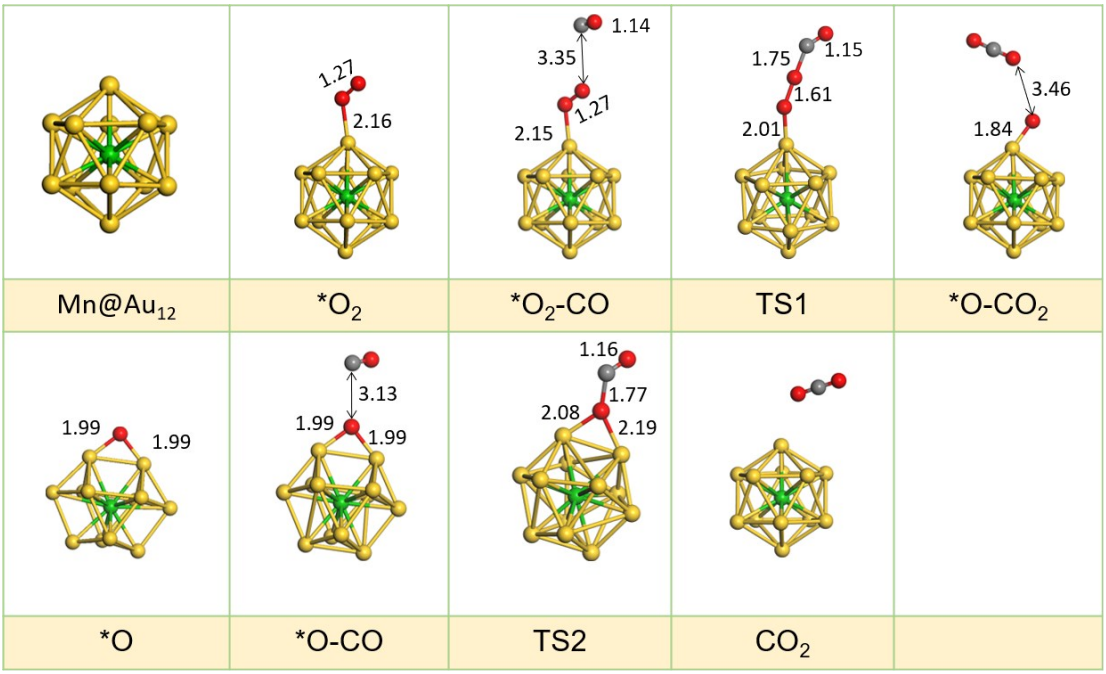

Fig. S17 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Mn@Au_{12}$ cluster under the E-R mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

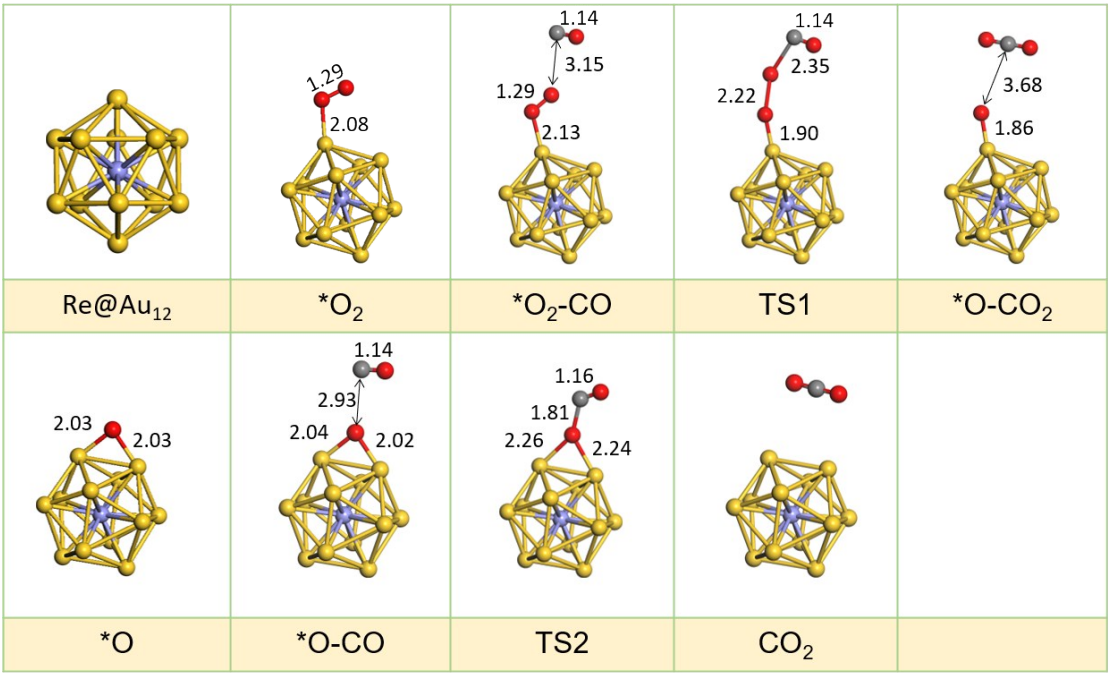

Fig. S18 Atomic structures of reaction intermediates and transition state (TS) of CO oxidation on the $Re@Au_{12}$ cluster under the E-R mechanism. Some key bond lengths and interatomic distances are presented in unit of Å.

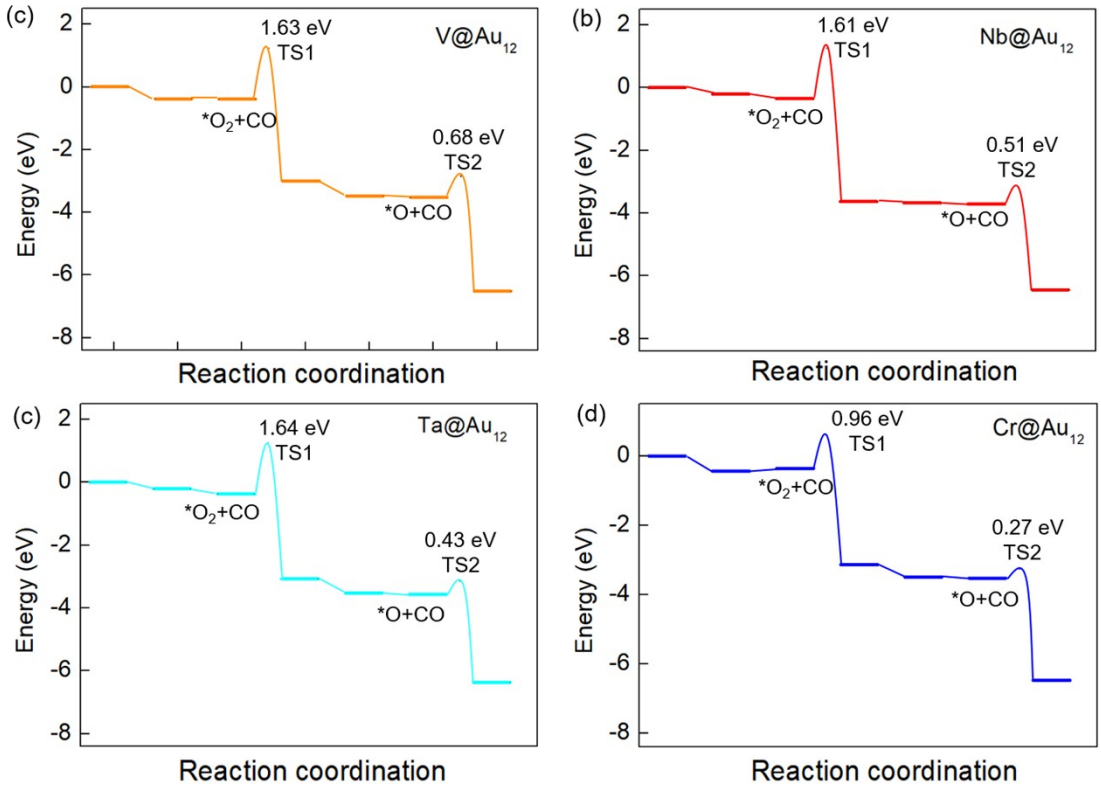

Fig. S19 Reaction pathway of CO oxidation under the E-R mechanism on (a) $V@Au_{12}$, (b) $Nb@Au_{12}$, (c) $Ta@Au_{12}$, and (d) $Cr@Au_{12}$ clusters, respectively. The numbers indicate the kinetic barriers.

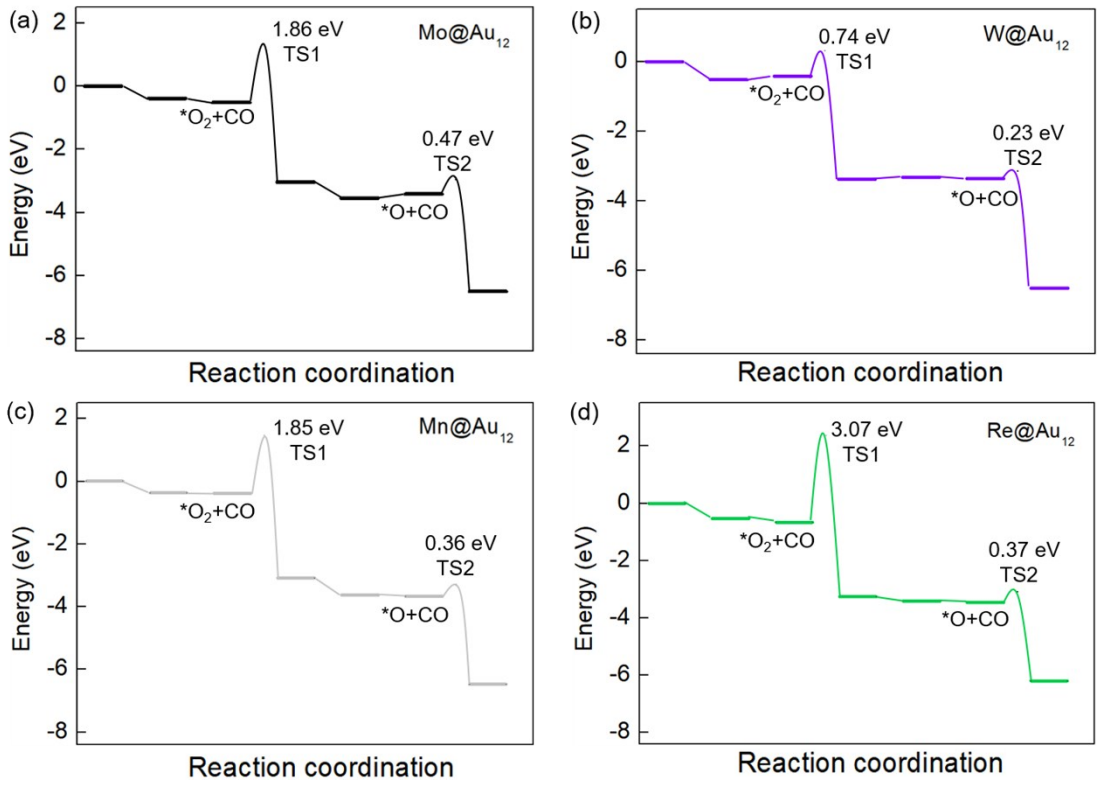

Fig. S20 Reaction pathway of CO oxidation under the E-R mechanism on (a) $Mo@Au_{12}$, (b) $W@Au_{12}$, (c) $Mn@Au_{12}$, and (d) $Re@Au_{12}$ clusters, respectively. The numbers indicate the kinetic barriers.

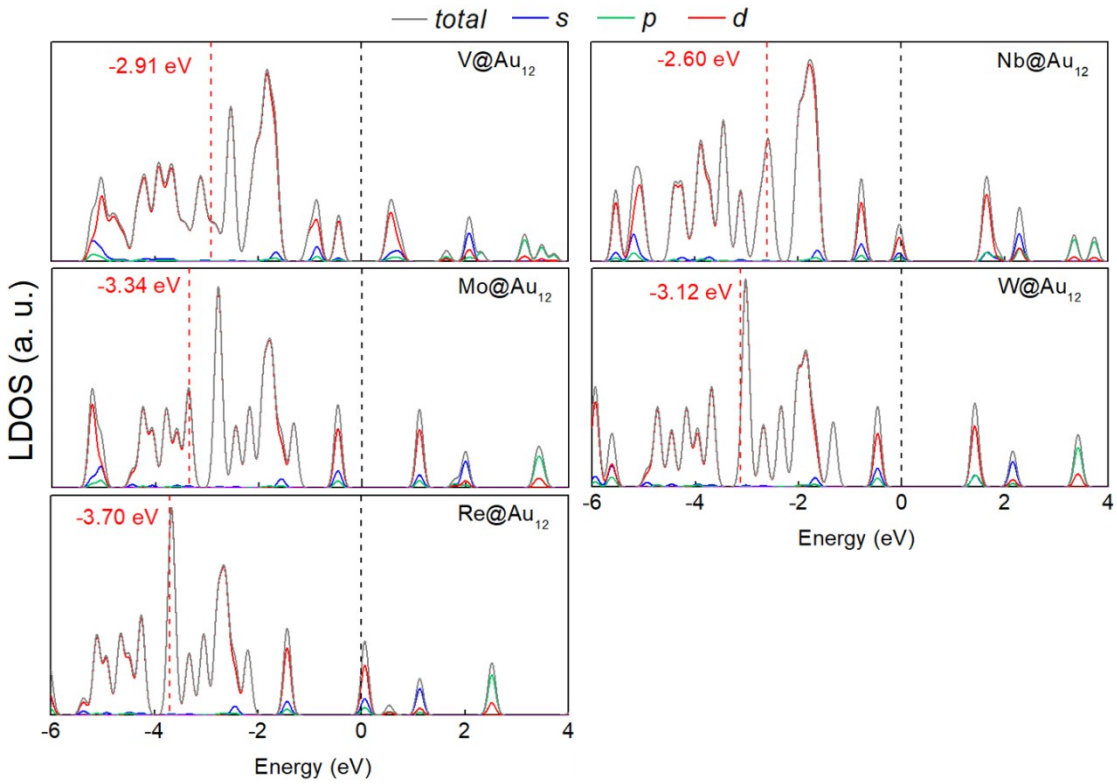

Fig. S21 Local density of states (LDOS) of various M@Au_{12} clusters (M = V, Nb, Mo, W, and Re). For each system, the HOMO level marked by the black dashed line is shifted to zero, and the red dashed lines and the numbers next to them indicate the *d* band center relative to HOMO.