Supporting Information

Theoretical Insights into the CO Dimerization and Trimerization on Pt Nanocluster

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**Fig. S1.** Geometrical structures of icosahedral Pt$_{55}$ cluster (a) and one of the (1 1 1) facets (b). Red atoms are the corner Pt, and blue atoms are edge Pt at the surface.
Fig. S2. Relative energies and geometrical parameters of all the minima and transition states involved in the reactions of CO dimerization on two neighboring corner and edge Pt atoms (Path-A1), CO dimerization on one corner Pt atom (Path-A2), and CO disproportionation on two neighboring corner and edge Pt atoms (Path-B).
Fig. S3. Relative energies and geometrical parameters of all the minima and transition states involved in the reactions of CO trimerization on two edge Pt atoms (Path-C1) and CO trimerization on two neighboring corner and edge Pt atoms (Path-C2).
Fig. S4. Relative energies and geometrical parameters of all the minima and transition states involved in the reactions of CO dimerization on two neighboring corner and edge Pt atoms (Path-A1'), CO dimerization on one corner Pt atom (Path-A2'), and CO disproportionation on two neighboring corner and edge Pt atoms (Path-B') with high CO coverage effect.
**Fig. S5.** Relative energies and geometrical parameters of all the minima and transition states involved in the reactions of an additional free CO adsorbed at B1 site (Path-D), CO dimerization between an free CO molecule and corner CO* on one corner Pt atom (Path-E), and CO trimerization on two edge Pt atoms (Path-C1’) with high CO coverage effect.
Fig. S6. $7\sigma$ (a), $8\sigma$ (b), $9\sigma$ (c), $1\pi$ (d) and (e), $2\pi$ (f) and (g), and $3\pi^\ast$ (h) and (i) orbitals of C$_2$O$_2$ before adsorption. The symbol (*) in $3\pi^\ast$ indicates this orbital contains one electron.
Fig. S7 $7\sigma$ (a), $8\sigma$ (b), $9\sigma$ (c), $1\pi$ (d,e), $2\pi$ (f,g) and $3\pi^{(*)}$ (h,i) orbitals of C$_2$O$_2$ when C$_2$O$_2$ is adsorbed on one Pt atom.