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

Supporting Information

Theoretical Insight into Single-Atom Catalytic Mechanism of CeO_2 Supported Ag Catalyst in CO Oxidation

Yongli Shen, Kangjuan Yin, Zihui Xiao *

Tianjin Key Laboratory of Advanced Functional Porous Materials, Institute for New Energy Materials & Low-Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China.

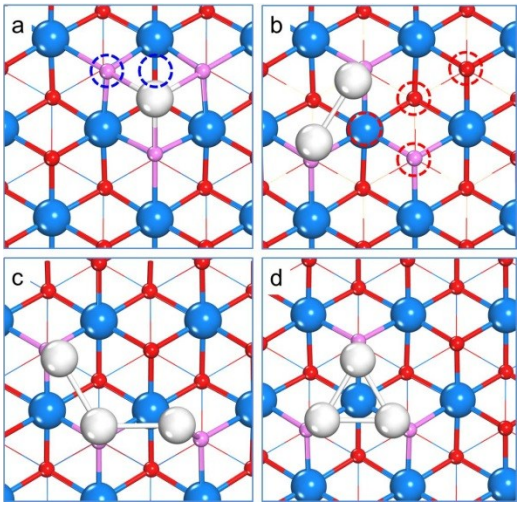

Figure S1 All attempt initial position of Ag atoms during Ag_nCeO_2 (n=1, 2 and 3) catalysts optimization. (a: Stable $AgCeO_2$ and initial location of Ag (blue dash circle), b: Stable Ag_2CeO_2 and all initial location combinations of Ag atoms (red dash circle), c: Liner structure of Ag_3CeO_2 catalyst (unstable), d: Triangle structure of Ag_3CeO_2 catalyst (stable)).

For Ag_1CeO_2 catalyst, the initial gauss location of Ag have been illustrated in Figure S1a (blue dash circle (on top and bridge site) and white ball (hollow site)), no matter where the Ag placed at initial, only one stable structure can be reached in the final as shown in Figure S1a (white ball position). For Ag_2CeO_2 catalyst, the initial gauss locations of Ag atoms are somewhat complicated. All the on-top, bridge and hollow site combinations in the catalyst optimization process have been considered. The most stable structure is shown in Figure S1b (white balls position). For Ag_3CeO_2 catalyst, two cases are considered in the calculation process, namely a linear structure (Figure S1c) and a triangular structure (Figure S1d). The calculation results show that the linear structure is unstable and it is easy to convert to a triangular configuration. For $Ag_{10}CeO_2$ catalyst, at initial, a pre-optimized Ag_{10} cluster is placed on the CeO_2 carrier, after the optimization the Ag_{10} cluster structure does not change much.

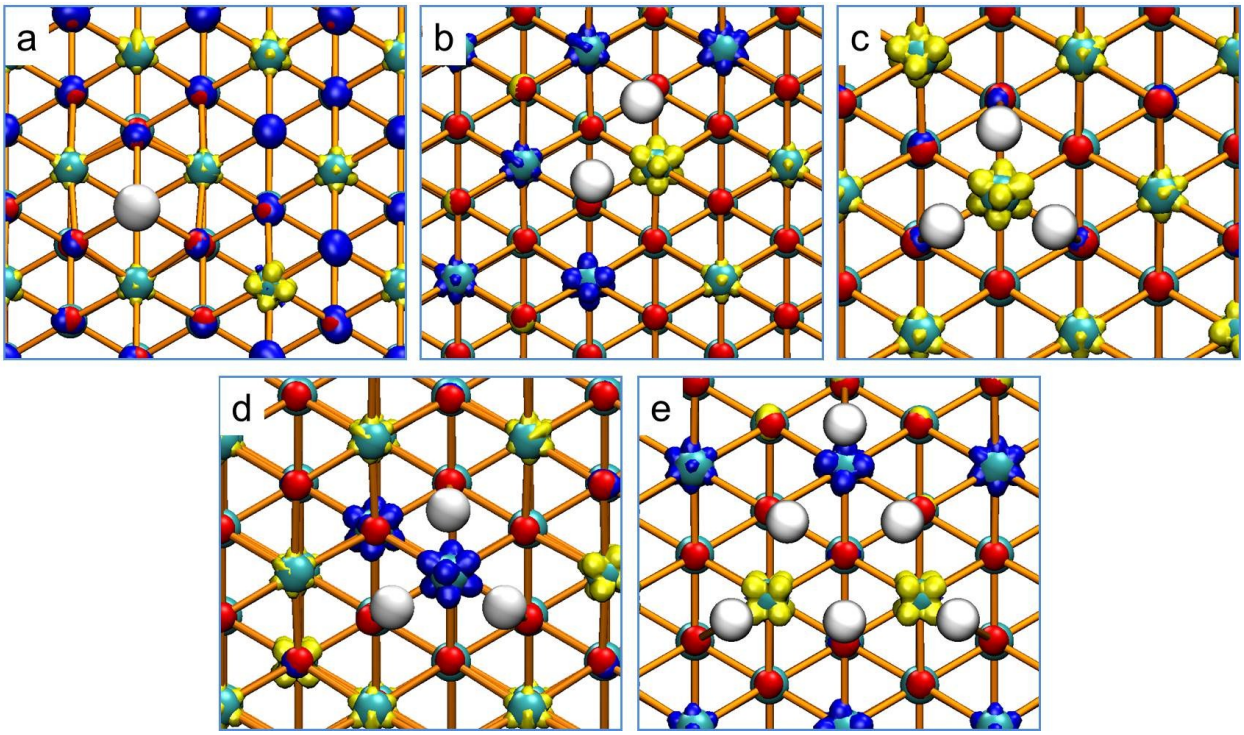

Figure S2 Spin density of Ag_nCeO_2 (n=1, 2, 3, 4 and 10). (a: Ag_1CeO_2, b: Ag_2CeO_2, c: Ag_3CeO_2, d: Ag_4CeO_2, e: $Ag_{10}CeO_2$, yellow isosurface: up spin, blue isosurface: up spin)

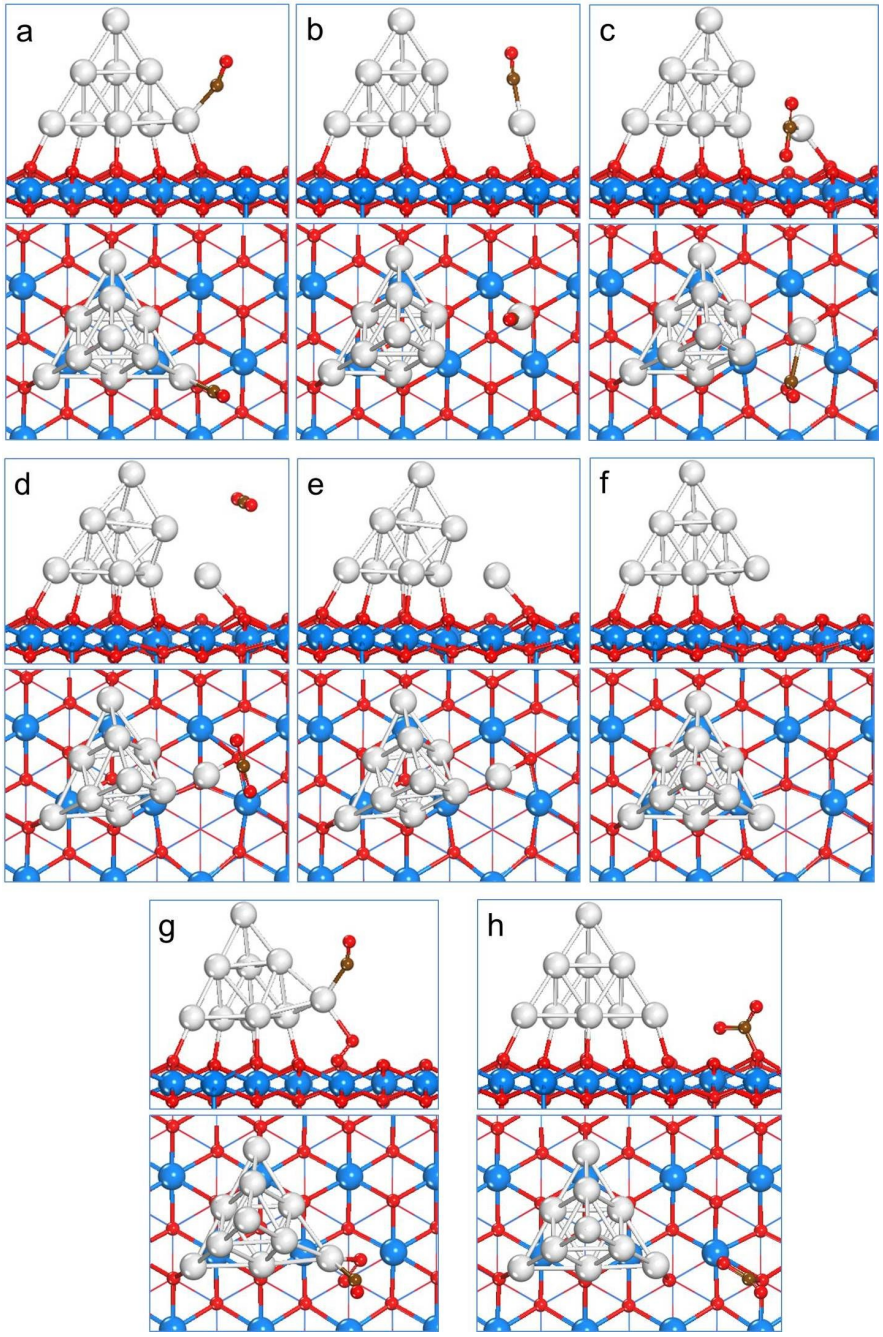

Figure S3 Stationary points involved in the CO oxidation on $Ag_{10}CeO_2$ catalyst. (a: $\{CO\}Ag_{10}CeO_2$, b: $\{CO\text{-}Ag\}Ag_9CeO_2$, c: $\{CO\text{-}O\text{-}Ag\}Ag_9CeO_2$, d: $\{CO_2\}AgAg_9CeO_2$, e: $AgAg_9CeO_2$(V), f: $Ag_{10}CeO_2$(V), g: $\{CO\text{-}O_2\}Ag_{10}CeO_2$, h: $\{CO_2\}Ag_{10}CeO_2$. a-h correspond to II-IX in Figure 3 (main text), respectively.

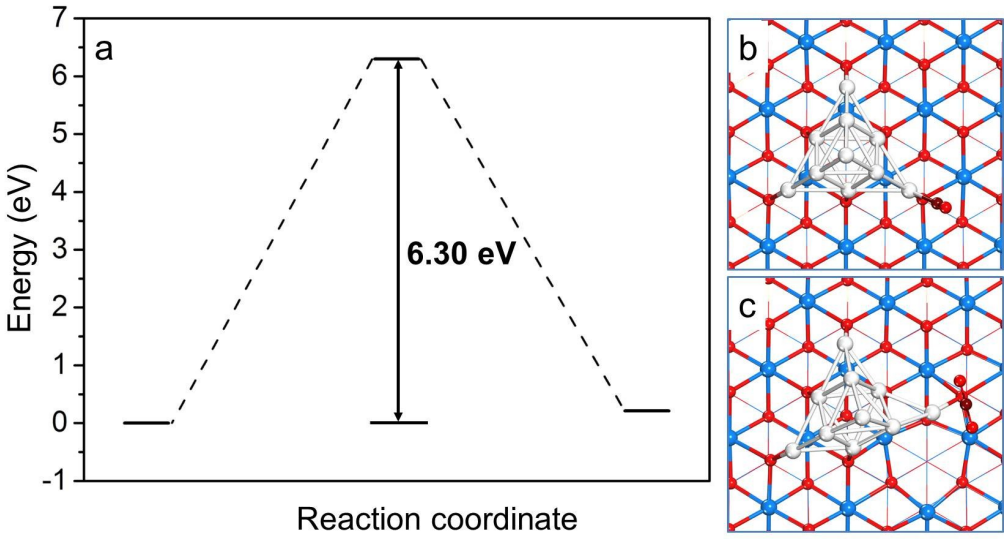

Figure S4 Activation energy needed for the direct reaction between CO and lattice oxygen.

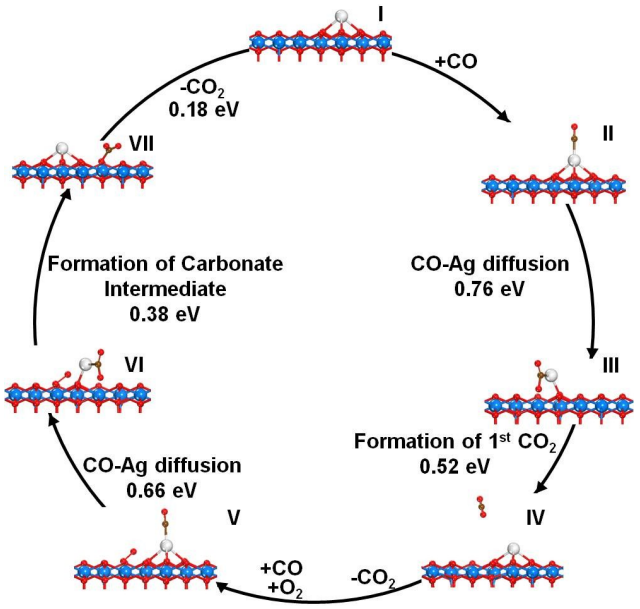

Figure S5 Reaction Mechanism of CO Oxidation on the Ag_1CeO_2 catalyst.

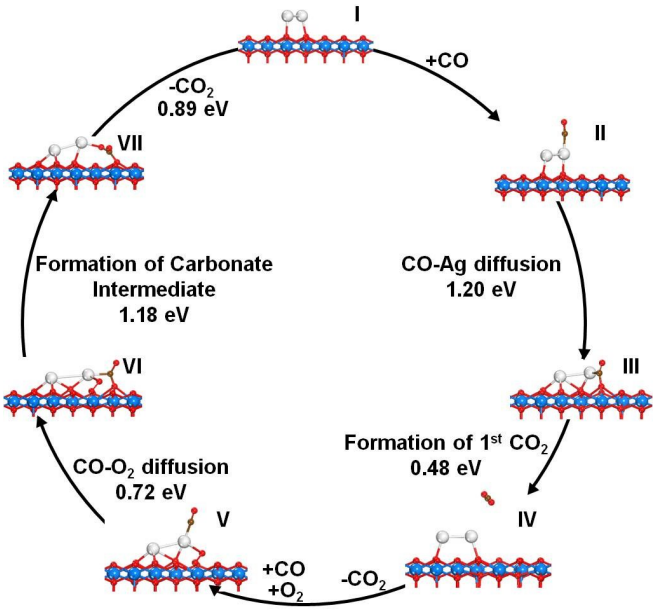

Figure S6 Reaction Mechanism of CO Oxidation on the Ag_2CeO_2 catalyst.

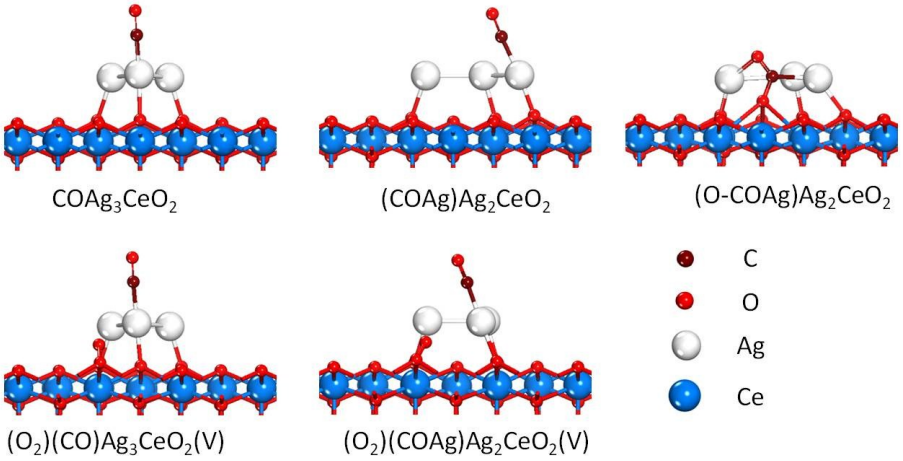

Figure S7 Optimized stationary points for the 1st CO_2 formation on the Ag_3CeO_2 catalyst.

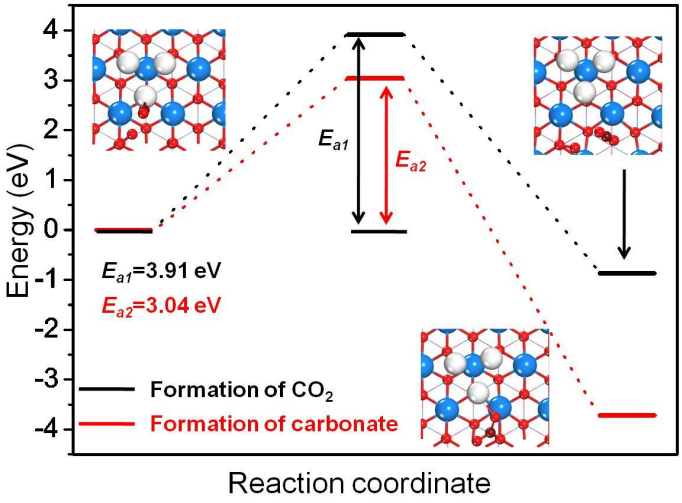

Figure S8 Reaction mechanism for the formation of 2nd CO_2 and carbonate intermediate on the Ag_3CeO_2 catalyst. (Black line: direct reaction between CO and O_2 which adsorbed in O vacancy to generate CO_2. Red line: direct reaction between CO and O_2 which adsorbed in O vacancy to generate carbonate intermediate.)

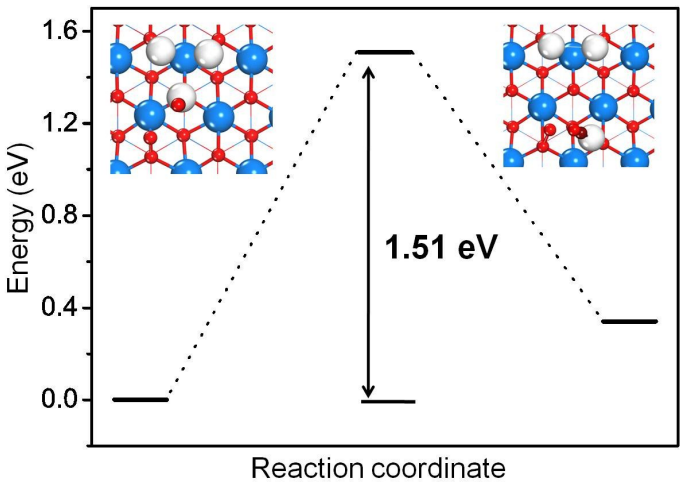

Figure S9 Reaction mechanism of "CO-Ag" structure ({CO-Ag_1}$O_2Ag_2CeO_2$(V) intermediate) formation on Ag_3CeO_2 catalyst.

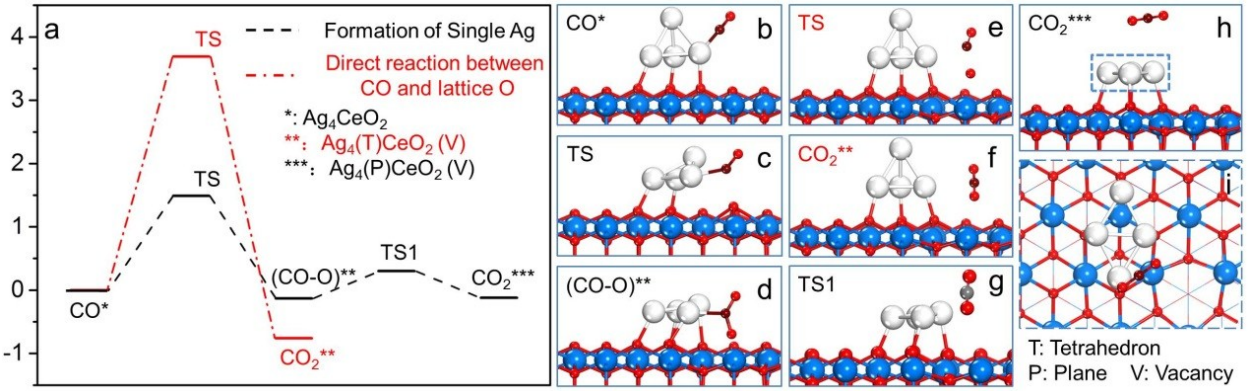

Figure S10 Reaction mechanism and related stationary points structures for the formation of 1st CO_2 on Ag_4CeO_2 catalyst. (a) Reaction mechanism, (b)-(h) Ptationary points structures for the formation of 1st CO_2 on Ag_4CeO_2 catalyst, (i) Planer structure of Ag_4 cluster.