Supporting information

Effect of Cu/Au for Propylene Epoxidation over $Ag_2O(111)$ Surface: A DFT Study

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1. AIMD simulations

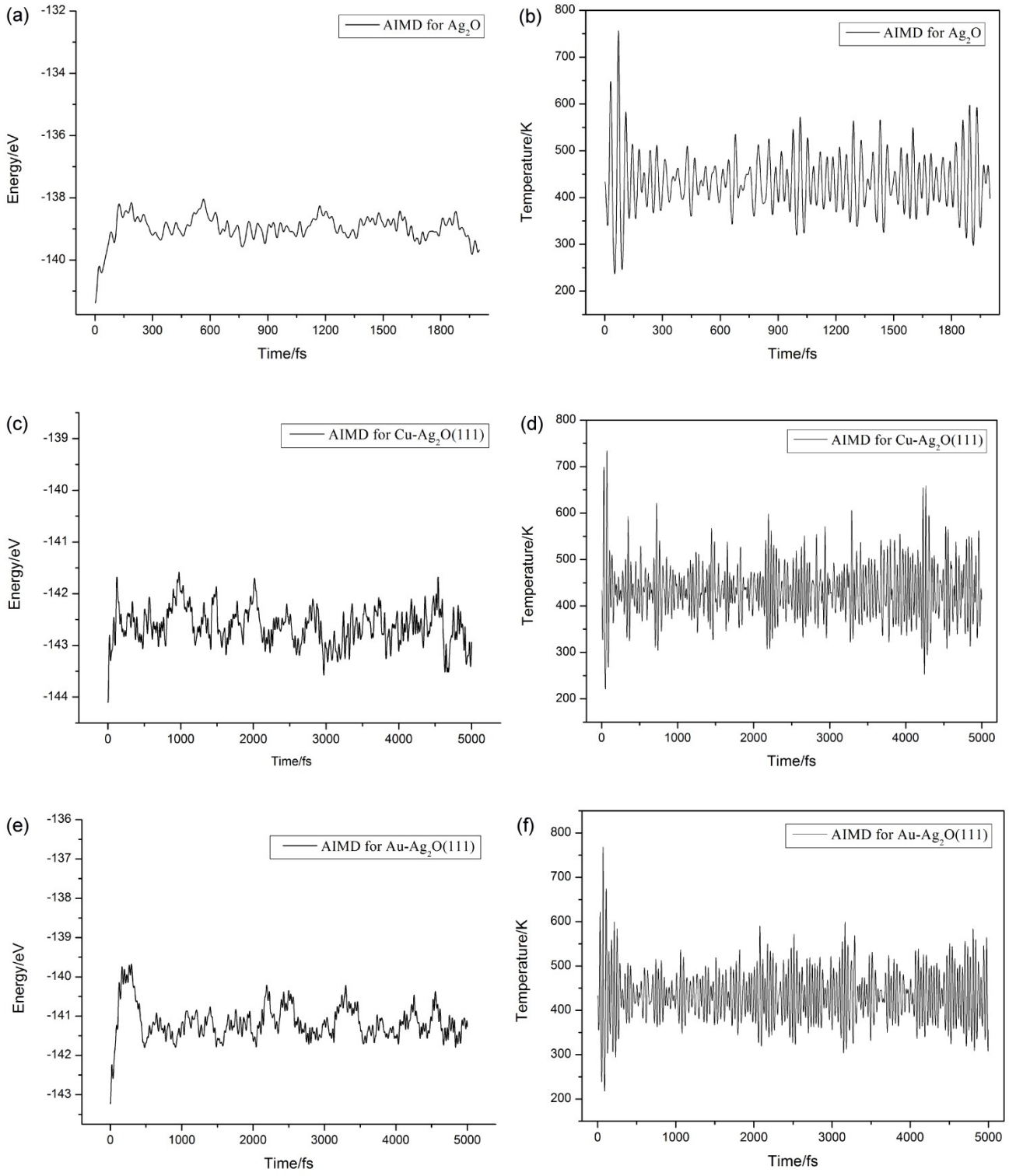

Figure S1. AIMD simulation of $Ag_2O(111)$ (a) (b), Cu−$Ag_2O(111)$ (c) (d) and Au−$Ag_2O(111)$ (e) (f) facets

2. Adsorption properties

2.1 Propylene. Three stable configurations of absorbed propylene were considered on the $Ag_2O(111)$ surface (see Figure S2a), which can create different reaction pathways. For the first configuration (I), propylene adsorbs on the Ag_{cus} site via π type with the adsorption energy of – 1.63 eV, where the distance of C_1–Ag_{cus} is 2.29 Å and the length of C_2–Ag_{cus} is 2.38 Å. In this configuration, the methyl group of propylene aims at a nearby O_{suf}, and this absorbed configuration prefers to participate in the AHS pathway. For the second configuration (II), propylene also adsorbs on the Ag_{cus} site with π type and the C_1 atom tends to a nearby O_{suf}, where the distance of C_1–Ag_{cus} is 2.29 Å and the length of C_2–Ag_{cus} is 2.42 Å. This absorbed configuration has the adsorption energy of – 1.59 eV and inclines to the $OMMP_1$ pathway. For the third configuration (III), propylene adsorbs on the Ag_{cus} site with π type as well, different with the former absorptions, the C_2 atom approaches to a nearby O_{suf} and this absorbed configuration tends to the $OMMP_2$ pathway. In this situation, the distance of C_1–Ag_{cus} is 2.31 Å and the length of C_2–Ag_{cus} is 2.40 Å, and the adsorption energy is – 1.57 eV. Above studies indicate that the first adsorption configuration is the most stable on the $Ag_2O(111)$ surface.

On the Cu−$Ag_2O(111)$ surface, propylene employed three different adsorbed types for different reaction pathways (see Figure S2b). For the first type (I), tending to the AHS pathway, propylene prefers to the Cu site with π type, where the length of C_1–Cu is 2.02 Å and the distance of C_2–Cu is 2.09 Å. The methyl group of propylene in this type approaches to a nearby O_{suf}, and this type has the adsorption energy of – 2.46 eV. For the second type (II), propylene adsorbs on the Cu site for π type with the adsorption energy of – 2.31 eV, in which the length of C_1–Cu is 2.02 Å and the distance of C_2–Cu is 2.08 Å, and the C_1 atom is inclined to a neighboring O_{suf}. For the third type (III), propylene adsorbs on the Cu site with π type as well, in which the length of C_1–Cu is 2.01 Å and the distance of C_2–Cu is 2.09 Å. In this absorbed type, the C_2 atom towards a neighboring O_{suf}, and the adsorption energy is – 2.29 eV. Both type (II) and type (III) prefer the OMMP pathway, the calculations exhibit that the first adsorption type is the most stable on the Cu−$Ag_2O(111)$ surface.

On the Au−$Ag_2O(111)$ surface, three adsorbed configurations of propylene were discussed for different pathways (see Figure S2c). For the first configuration (I), propylene prefers to the Au site with π type, where the length of C_1–Au is 2.15 Å and the distance of C_2–Au is 2.20 Å. The methyl group approaches to a nearby O_{suf}, and this type has the adsorption energy of – 2.61 eV, which tends to the AHS pathway. For the second configuration (II), propylene adsorbs on the Au site for π type

with the adsorption energy of – 2.43 eV, where the length of C_1–Au is 2.15 Å and the distance of C_2–Au is 2.20 Å, and the C_1 atom is inclined to a neighboring O_{suf}. For the third configuration (III), propylene adsorbs on the Au site with π type, where the length of C_1–Au is 2.14 Å and the distance of C_2–Au is 2.19 Å, the C_2 atom towards a neighboring O_{suf}, and the adsorption energy is – 2.43 eV. Both configuration (II) and configuration (III) tend to the OMMP pathway, the calculations show that the first adsorption configuration is the most stable on the Au−Ag_2O(111) surface.

2.2 Allyl. The adsorption of allyl on the Ag_2O(111) surface with and without Cu or Au doping has been calculated, it can be found that the stable adsorbent configuration prefers top site, where the terminal C atom binds to surface Ag_{cus}/Cu/Au atom. On the Ag_2O(111) surface, the distance of C−Ag_{cus} is about 2.20 Å, and the adsorption energy is –1.85 eV (Figure S2a). On the Cu−Ag_2O(111) surface, the length of C−Cu is 1.99 Å, and the adsorption energy is –2.67 eV (Figure S2b). On the Au−Ag_2O(111) surface, the distance of C−Au is 2.08 Å, and the adsorption energy is –2.78 eV (Figure S2c).

2.3 Acrolein(C_3H_4O). The adsorption of acrolein has been calculated on these surfaces (Figure S2), it can be found that the adsorption of acrolein prefers top site through O. The distance between O in acrolein and Ag_{cus} is 2.21 Å on Ag_2O(111) surface, and the adsorption energy is –1.05 eV. On the Cu−Ag_2O(111) surface, the length of Cu−O is about 1.83 Å, and the adsorption energy is about – 1.97 eV. On the Au−Ag_2O(111) surface, the distance of Au−O is 2.05 Å, and the adsorption energy is–1.68 eV.

2.4 OMMP. Propylene oxametallacycle intermediates are important for the OMMP pathway, and two different configuration intermediates can be formed by the interaction between propylene and the surface, named $OMMP_1$ and $OMMP_2$. One intermediate is $OMMP_1$, adopting 1,2–di–σ type, where the C_1 atom connects to a O_{suf} and the C_2 atom binds to a nearby Ag_{cus}/Cu/Au, the other intermediate is $OMMP_2$, also adopting 1,2–di–σ type, where the C_2 atom connects to a O_{suf} and the C_1 atom binds to a neighboring Ag_{cus}/Cu/Au. On clean surface, the distance of C_1–O_{suf} is 1.48 Å and the length of C_2–Ag_{cus} is 2.16 Å in $OMMP_1$ and the adsorption energy of $OMMP_1$ is – 1.29 eV. The distance of C_2–O_{suf} is 1.48 Å and the length of C_1–Ag_{cus} is 2.15 Å in $OMMP_2$ and the adsorption energy of $OMMP_2$ is – 1.59 eV. On the Cu–doped surface, the distance of C_1–O_{suf} is 1.48 Å and the bond length of C_2–Cu is 1.95 Å in $OMMP_1$ and the adsorption energy is – 1.94 eV, the distance of C_2–O_{suf} is 1.49 Å and the bond length of C_1–Cu is 1.94 Å in $OMMP_2$ and the adsorption energy is – 2.18 eV.

On the Au–Ag_2O(111) surface, the distance of C_1–O_{suf} is 1.46 Å and the bond length of C_2–Cu is 2.08 Å in $OMMP_1$ and the adsorption energy is –2.61 eV, the distance of C_2–O_{suf} is 1.47 Å and the bond length of C_1–Cu is 2.06 Å in $OMMP_2$ and the adsorption energy is – 2.83 eV.

2.5 PO, Propanal, and Acetone. The adsorption properties of products in the OMMP pathway have been discussed, it can be found that all products adsorption prefer top type, where the oxygen atom among product binds to a surface Ag_{cus}/Cu/Au. On clean surface, the distances between Ag_{cus} and oxygen atom among PO, propanal, and acetone are 2.24, 2.22, and 2.17 Å, and the corresponding adsorption energies are – 1.16 eV, – 1.22 eV, and – 1.12 eV, respectively. On the Cu–Ag_2O(111) surface, the corresponding distances of PO, propanal, and acetone are 1.89, 1.84 and 1.84 Å, and the adsorption energies are – 1.88 eV, – 2.03 eV, and – 2.07 eV, respectively. On the Au–Ag_2O(111) surface, the corresponding lengths of PO, propanal, and acetone are 2.10, 2.05 and 2.05 Å, and the adsorption energies are – 1.64 eV, – 1.81 eV, and – 1.81 eV, respectively.

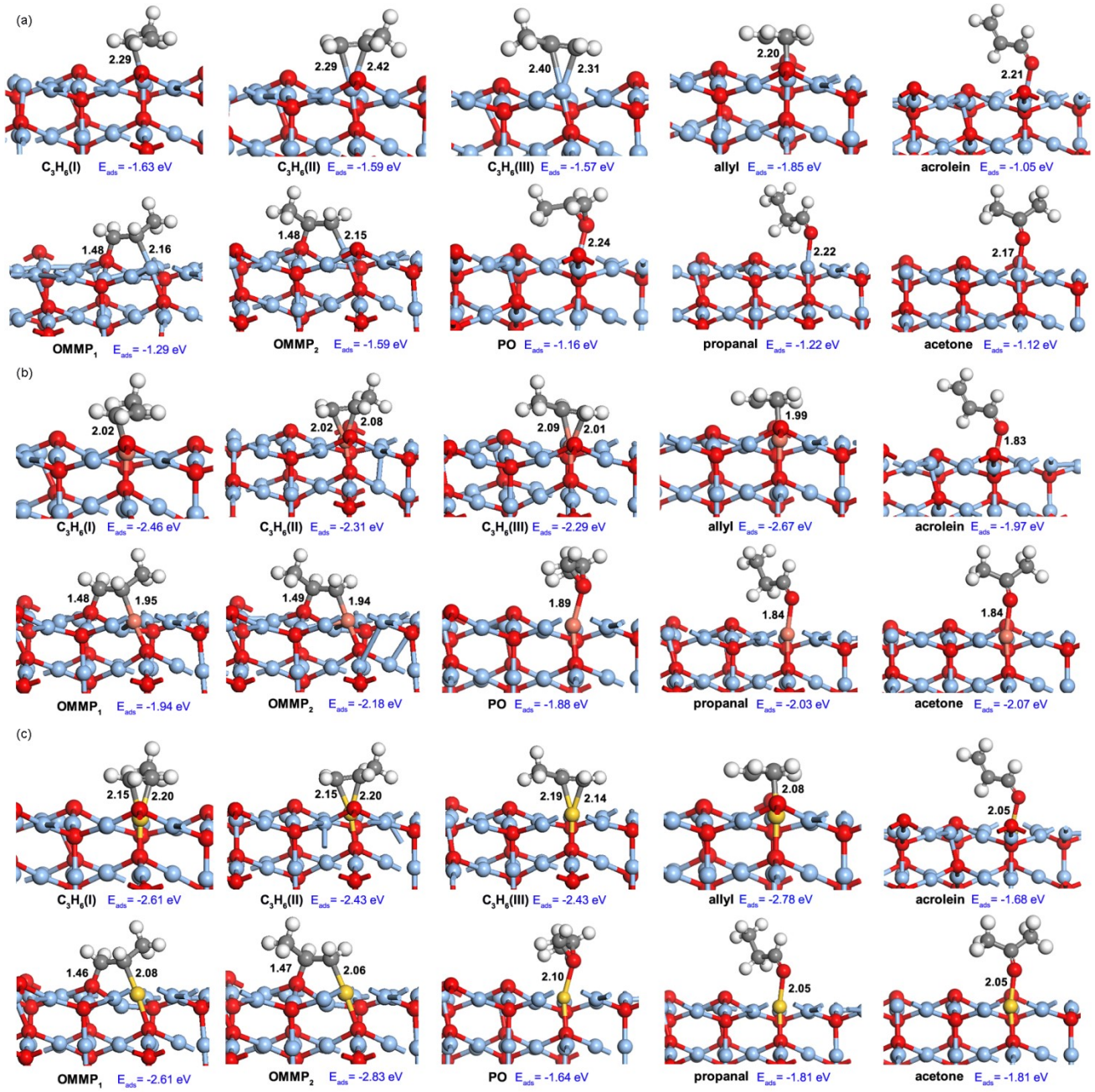

Figure S2. Optimized geometries and corresponding adsorption energies for key species for propylene epoxidation on the $Ag_2O(111)$ (a) , $Cu-Ag_2O(111)$ (b), and $Au-Ag_2O(111)$ (c) surfaces (unit: Å).

3. The reaction mechanism of propylene epoxidation on the $Ag_2O(111)$ surface

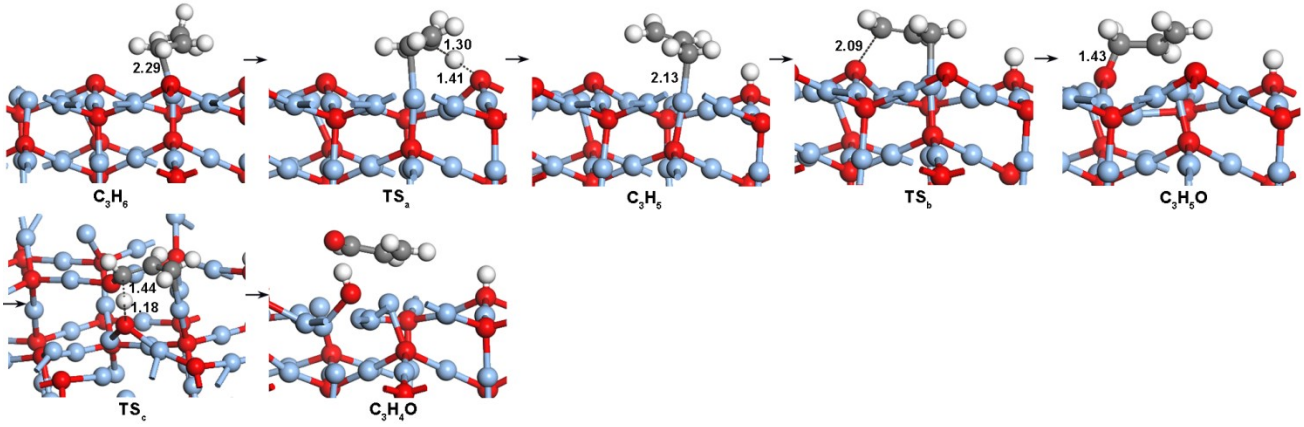

Figure S3. Optimized geometries along the AHS pathway of propylene on $Ag_2O(111)$ surface (unit: Å).

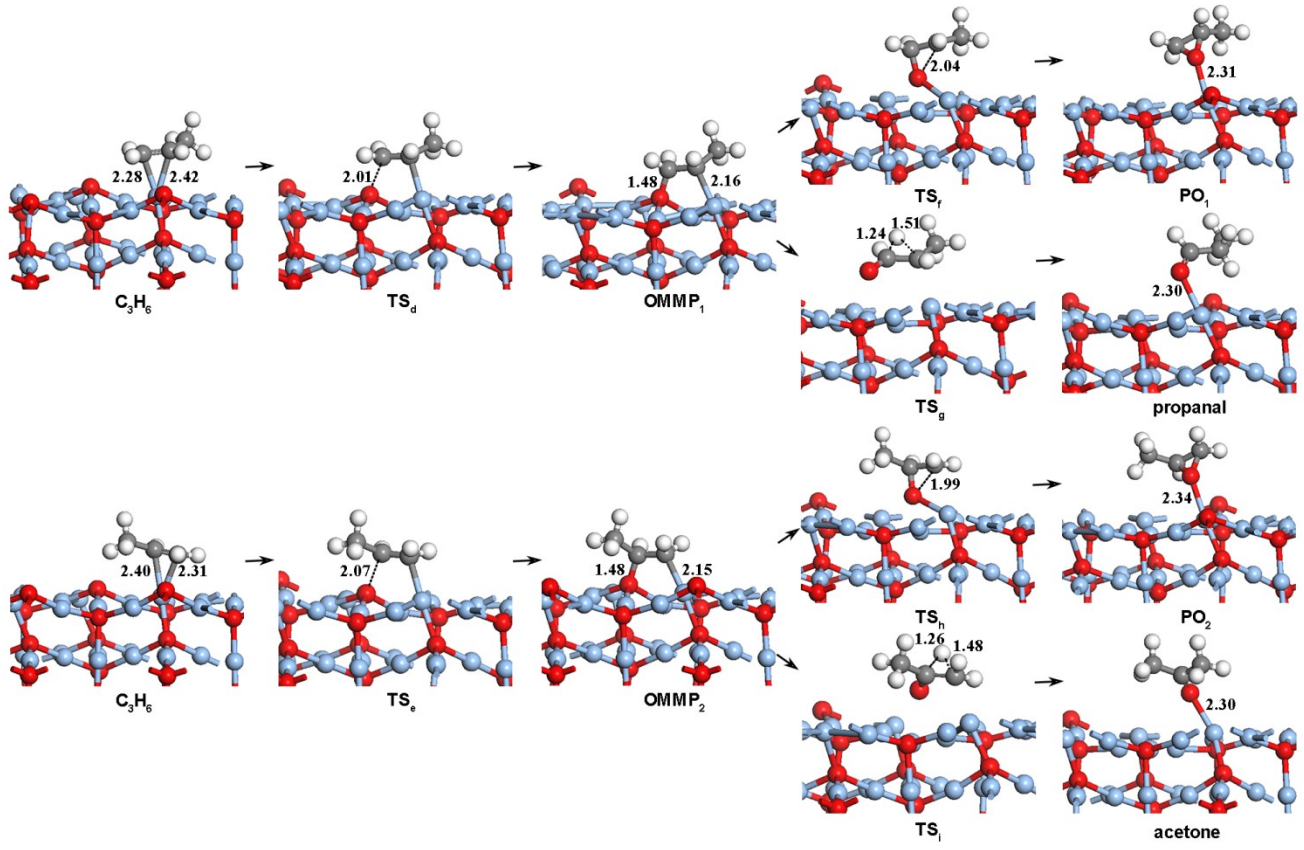

Figure S4. Optimized geometries along the OMMP pathway of propylene on $Ag_2O(111)$ surface (unit: Å).

4. The reaction mechanism of propylene epoxidation on the Au-Ag_2O(111) surface

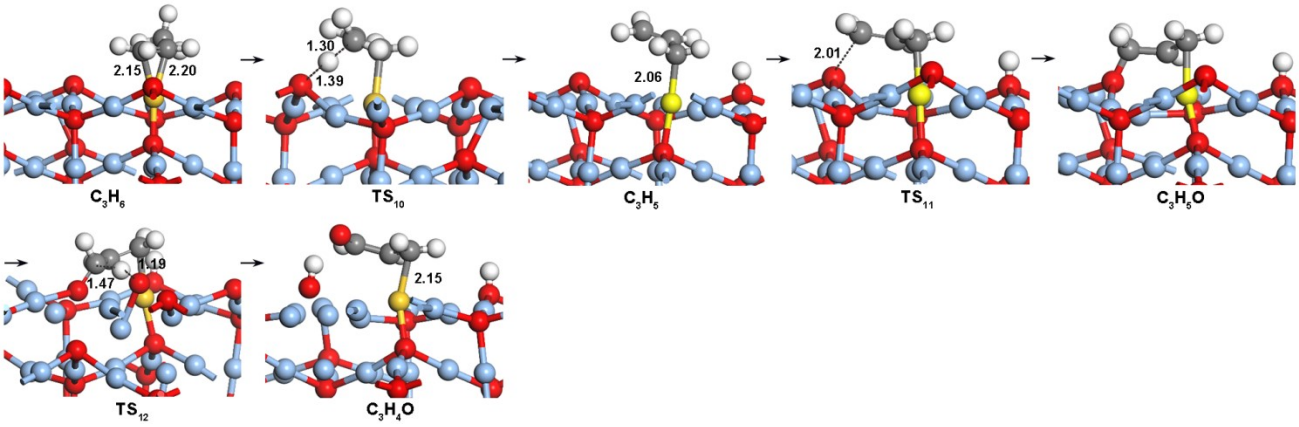

Figure S5. Optimized geometries along the AHS pathway of propylene on the Au-Ag_2O(111) surface (unit: Å).

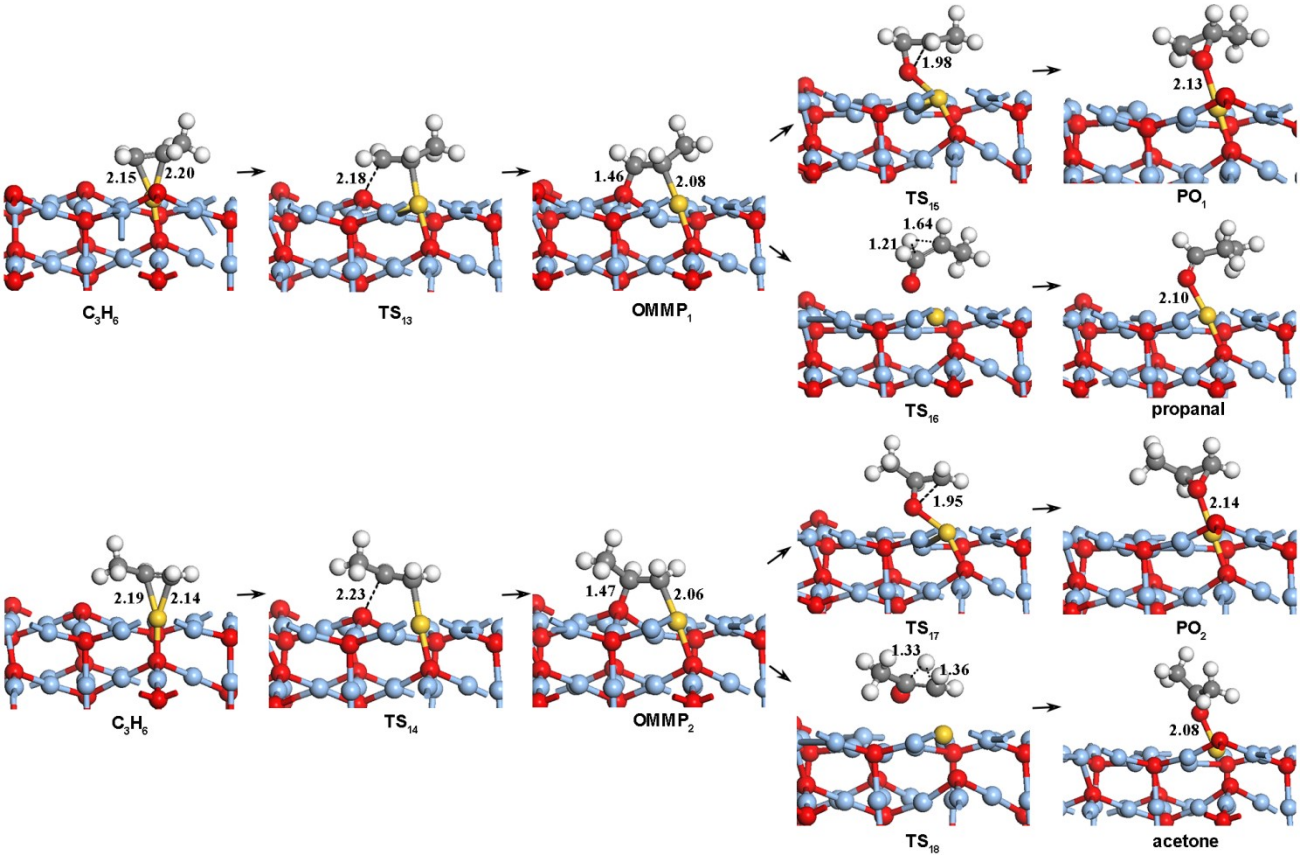

Figure S6. Optimized geometries along the OMMP pathway of propylene on the Au-Ag_2O(111) surface (unit: Å).

5. PDOS analysis

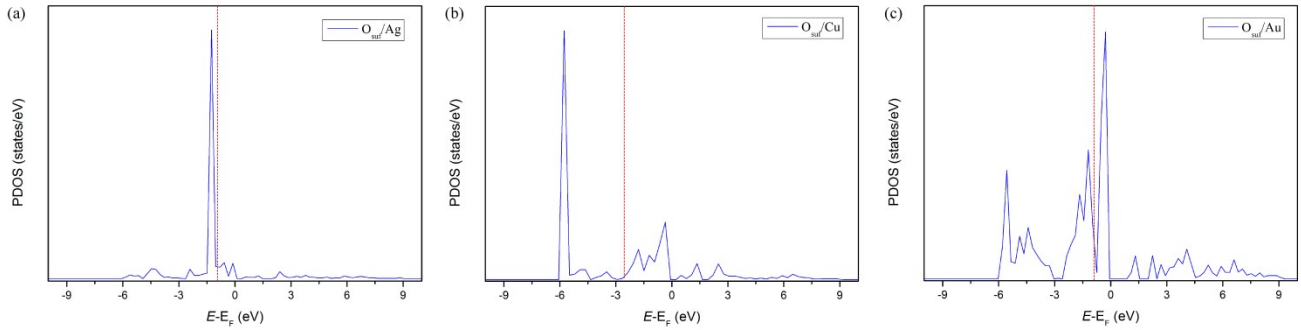

Figure S7. The PDOS of the O_{suf} 2p orbitals on the $Ag_2O(111)$ (a), Cu–$Ag_2O(111)$ (b), and Au–$Ag_2O(111)$ (c) facets.