

Supplementary Information to

What leads to direct epoxidation? An exhaustive DFT investigation of electrophilic oxygen mediated epoxidation of ethylene on Ag(100)

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In the study, some optimized configurations were excluded from the main text and provided as additional information. Fig.1, Fig.2 and Fig.3 represents the configurations at 0.11 ML, 0.22 ML, and 0.33ML coverages respectively.

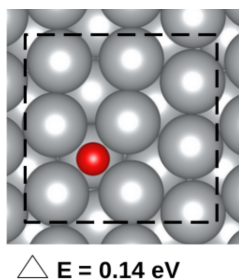


Figure 1: Configurations depicting Ag-O interaction on surface with 0.11 ML oxygen coverage. The oxygen adsorbs at a 4FH site which has been included in the study.

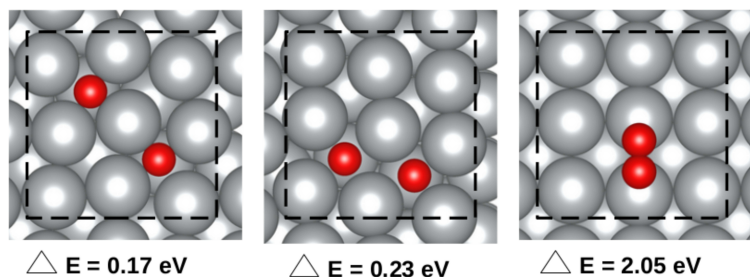


Figure 2: Optimized configurations for 0.22 ML system involving atomically and molecularly adsorbed oxygen sites. The configuration with $\Delta E = 2.05 \text{ eV}$ is excluded from the study due to high energy difference.

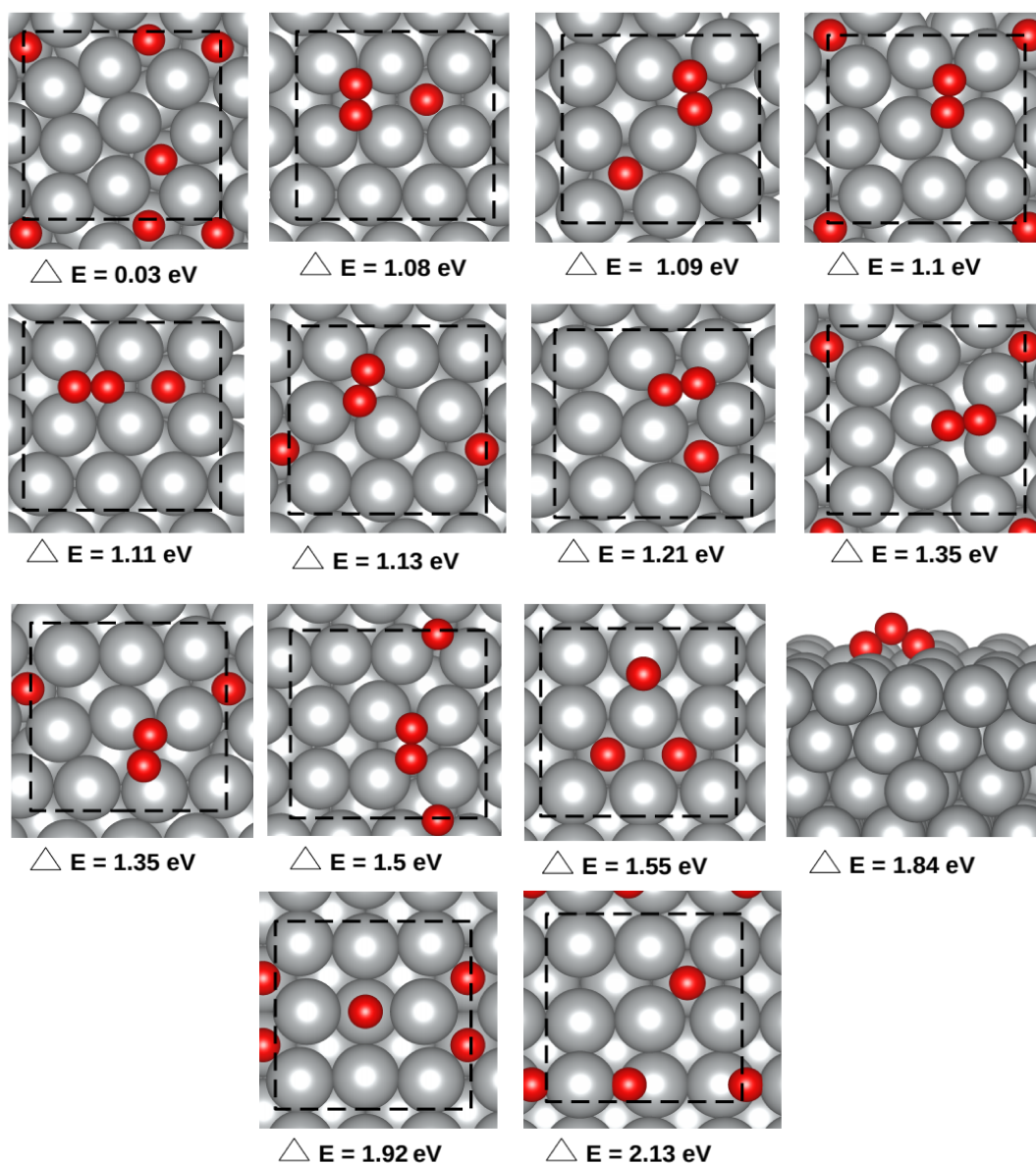


Figure 3: Optimized configurations for 0.33 ML system. The configurations include both atomically and molecularly adsorbed sites.

These configurations were not significantly different from the ones included in the main text, based on the site of oxygen adsorption. In other words, they were found to be analogous or indistinguishable. Additionally, configurations that had a high energy difference from the most stable structure per monolayer concentration were also excluded. This was done to streamline the presentation of the results and focus on the most relevant and significant findings. The excluded configurations were still examined and analyzed, but their results were not included in the main text.

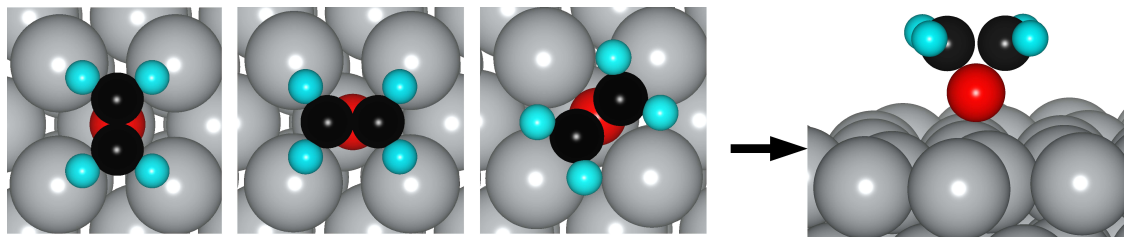


Figure 4: Arrangement of ethylene above oxygen at 4FH site. All the orientations favor EtO formation.

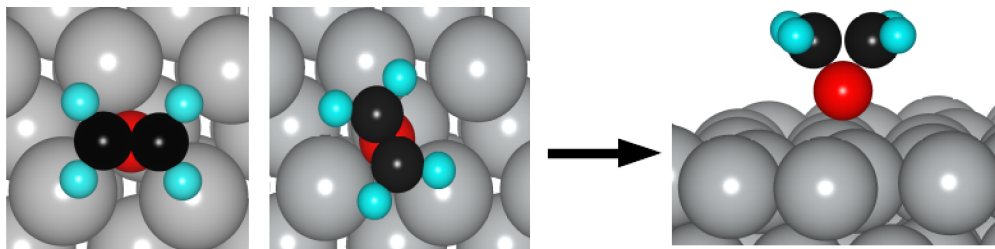


Figure 5: Arrangement of ethylene in 2 different orientations above oxygens at 3FH position in 0.11ML, 0.22ML and 0.33ML system is noted. These orientations typically generate EtO as product.

In Fig.4 and Fig.5 ethylene is positioned above oxygen species at the 4FH, 3FH, and 5FH sites. When the surface coverage is at 0.22 ML, EtO formation occurs above all oxygen variants. However, at a higher coverage of 0.33 ML, the oxygen at the 5FH site does not interact with ethylene. The oxygen at 5FH moves closer to the subsurface as the concentration increases, causing the lack of interactivity. Nevertheless, at 0.33 ML coverage, EtO is generated above the oxygen species at the 4FH and 3FH sites.

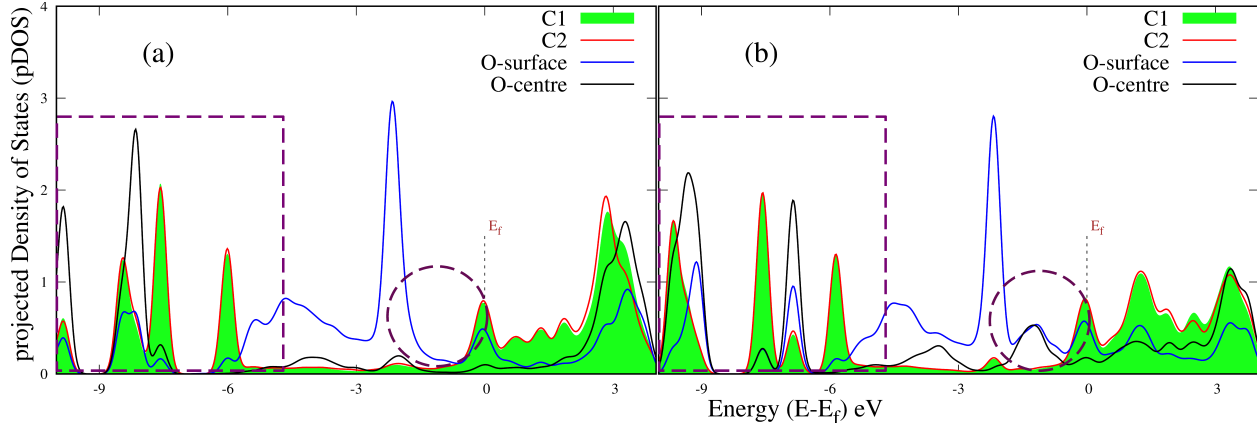


Figure 6: pDOS plot for ethylene interaction with O_3 is represented. Case (a) depicts pDOS for interaction where ethylene orients perpendicular to O_3 motif resulting in EtO formation and (b) where ethylene orients parallel to O_3 leading to repulsion.

From pDOS plots depicted in Fig.6 we observe that irrespective of symmetric overlap for case (a) and (c) the pDOS peaks show some differences. The pDOS peaks for both carbons of ethylene overlap each other in case (a) and (b) however, The peaks between (-9 to -6 eV) for case (b) are evidently different compared to that of case (a) depicting their variation in environment. Similarly, in the range of -2 to 0 eV the surface oxygen has small peak in the case where ethylene is placed parallel to O_3 indicating additional interaction in case and is absent for case where EtO forms (a). The positive IpCOOP values for carbon and surface oxygen support this observation (0.013,0.014). For case (a) the effective charge is $0.16 e^-$ while for case (c) it is $-0.02 e^-$ showcasing comparatively stronger interaction with the oxygen in the first case in presence of ethylene resulting in EtO formation.

O_2 -dis at the 3FH system has two distinct oxygen species; one lies between two Ag atoms O(1), and the other is attached to a single Ag atom O(2). For the oxygen moiety attached to a single Ag atom, we positioned the ethylene molecule in two ways such that they partially overlap with this oxygen. Each case results in two different products. The interaction results in OMC formation for case-I, while a similar setup in case-II gives EtO as the final product.

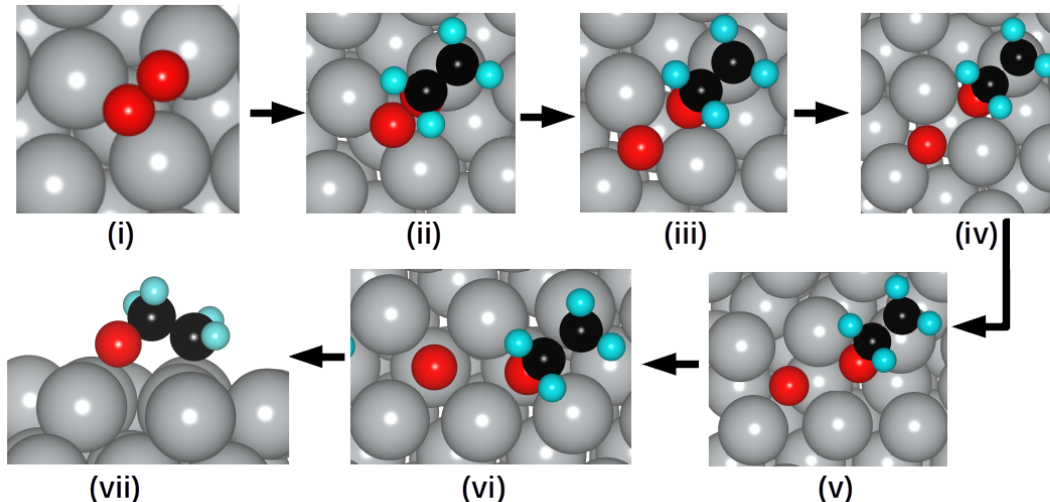


Figure 7: Case-I: Stepwise analysis of how the orientation of ethylene above O(2) of O₂-dis results in OMC as a final product is depicted in steps i-vii.

In Fig.7 and Fig.8, we have demonstrated explicitly the steps involved in the collusion for case-I and II, respectively. In case-I, step (ii) depicts the orientation of ethylene over O(2) of O₂-dis. In steps (iii-iv), we can see that in the presence of ethylene, the oxygen atoms move apart from each other, occupying a tri-coordinated Ag site. Further, in steps (v-vi), we can see that both O(1) and O(2) shift to a nearby 4FH site as a consequence of reconstruction in the surface. During this translation towards a higher coordination site, O(2) does not encounter the other carbon of ethylene. At this point, it prefers to form OMC intermediate at an energetically favourable 4FH site than form EtO.

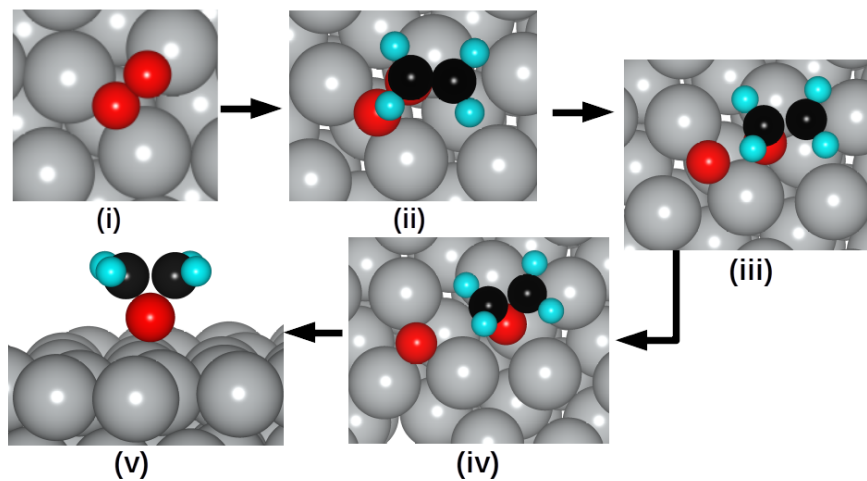


Figure 8: Case-II: Stepwise analysis of how the orientation of ethylene above O(2) of O₂-dis results in EtO as the final product is depicted in steps i-v.

In contrast, we explain the steps involved in case-II, where EtO forms as the final product due to slight variation in initial orientation. In step (ii), we set ethylene above O₂ in a different orientation than the one mentioned for case-I. As stated above, the oxygens tend to move away from each other and occupy energetically favourable 4FH sites adjacent to it, as seen from steps (iii-iv). During this translation from the 3FH site to the 4FH site they come in contact with other carbon of ethylene molecule. This triggers the formation of EtO instantaneously above the Ag surface.

Table 1: C-C bondlength, coordination number, Ag-O bond lengths and dihedral angles are tabulated. 1 and 2 refer to oxygen atom numbers 1 and 2, respectively.

System	C-C bondlength (Å)	CN	Ag-O(1) bondlength(Å)	Ag-O(2) bondlength(Å)	dihedral angle (degrees)
Eclipsed DMC	1.59	2 2	2.18 2.18	2.18 2.18	0.1 0.1
Staggered DMC	1.53	3 2	2.22 2.24 2.44	2.21 2.32	55.2 58.0

Table 1 summarizes the physical properties of the staggered and eclipsed DMC intermediate structures. Upon approaching oxygen, the C-C bond of ethylene elongates from approximately 1.34Å to 1.5Å, indicating a weaker interaction between the carbons, promoting a non-selective pathway of epoxidation. Moreover, analyzing the Ag-O bondlengths in both intermediates shows that Ag-O interactions are relatively stronger for the near-eclipsed DMC than the near-staggered DMC. The dihedral angles in both intermediates differ, and regardless of their differences, they will hinder epoxidation.