

Quantum Chemical Investigation of the Catalytic Oxidation of Hydrocarbons

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The formation of ethylene oxide (C_2H_4O) over silver catalysts is an extremely important industrial process. This importance stems from the fact that the ethylene oxide structure (Figure 1), with its single bond and highly strained ring, is such that the addition of other molecules to the ring proceeds with relatively little resistance. As such, ethylene oxide is a very useful intermediate from which other chemicals, such as polymers, may be derived.

For more than half a century it has been known that silver has the unique ability of forming ethylene oxide from ethylene in a manner that is highly active and selective. Most other transition metal catalysts form acetaldehyde when ethylene is introduced. Although the mechanism of the reaction to form ethylene oxide on silver has been studied for many decades, it remains elusive. This mechanism is the key for improvements in the catalyst to proceed in a systematic way. To learn more about the mechanism, we have studied the interaction of ethylene oxide and acetaldehyde with silver by employing quantum chemistry.

One of the most basic and necessary pieces of information regarding the reaction mechanism is the

state of chemisorbed oxygen on silver. A number of experiments seem to suggest that adsorbed molecular oxygen (O_2) reacts with ethylene to form ethylene oxide,

while other experiments show that the active oxidant is adsorbed atomic oxygen (O). We have computed the potential energy for the adsorption of O_2 , the adsorption of O atoms, and the energy necessary to break the O_2 bond when it is adsorbed to the [111] face of the silver surface. We find (Figure 2) that the dissociation of O_2 has an activation energy of $24.2 - 20.4 = 3.8$ kcal/mol, but the dissociated atomic product is 33 kcal/mol more tightly bound than the molecular adsorbed state. This suggests that there will be a temperature below which very little O_2 will dissociate. However above this temperature, the chemisorbed atomic state may be accessed.

We also studied the effect of adsorbed cesium (a rate and selectivity promoter in the formation of ethylene oxide) on the computed energy barrier to break the adsorbed O_2 bond. We found that the barrier to dissociate O_2 on silver has a cesium coverage

dependence: for low coverages of cesium, dissociation of O_2 is highly favored, but as the coverage of cesium increases the probability of dissociation decreases.

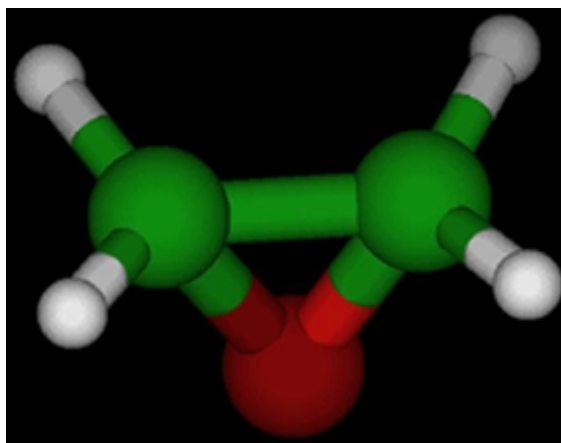


Figure 1: Ethylene oxide.

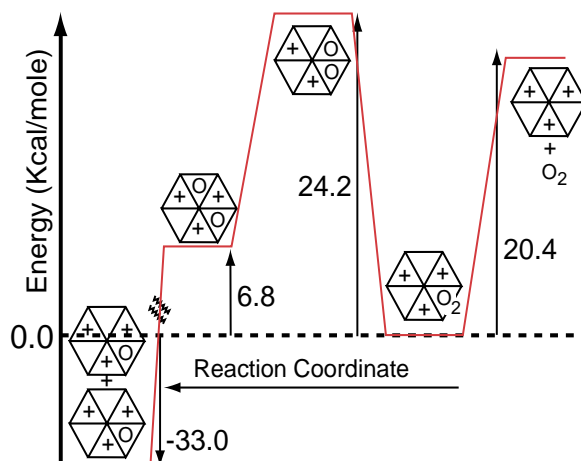


Figure 2: Potential energy diagram for O_2 dissociation on an unpromoted silver cluster.

When the calculations were repeated for another face of silver (the [110] face), a very similar cesium coverage dependence on O₂ dissociation was found. This suggests that the chemisorbed state of oxygen that is reacting with ethylene to form ethylene oxide is independent of the face of the silver surface, but will have a cesium coverage dependence. Both of these conclusions are consistent with experimental observations.

Another unresolved issue of the epoxidation reaction is if the chemisorbed oxygen species attacks ethylene via nucleophilic (nucleus seeking) or electrophilic (electron seeking) means. We found that adsorbed O atoms extract electrons from the silver surface and attack the electron-deficient C atoms of ethylene rather than the C-C double bond. Thus, our calculations suggest that epoxidation proceeds via a nucleophilic attack of adsorbed O atoms.

We have also investigated what has been postulated as the adsorbed ethylene-O species that is present before the actual reaction occurs. These species are called oxymetalloxy and it is unknown whether they are intermediates for the formation of ethylene oxide or the undesired product, acetaldehyde. Our calculations show that an adsorbed O atom is able to chemically bind to one of the carbons of ethylene with little or no barrier, thus forming the stable oxymetalloxy. The role of cesium in the formation of these oxymetalloxy has remained unknown. Our calculations show that cesium does not take part in the formation of the oxymetalloxy and is, instead, an electron donor to the silver surface, which in turn donates more electron density to the adsorbed species. These calculations have direct bearing on the unique ability (aldehyde vs. epoxide) of silver to catalyze ethylene epoxidation.

In further calculations, we have explored the energy requirements for the adsorbed oxymetalloxy to form ethylene oxide and acetaldehyde on both clean

and cesium-promoted silver surfaces. These calculations reveal that the energy barrier to form ethylene oxide is lower than the barrier to form acetaldehyde. This is not surprising since it is known experimentally that ethylene oxide is the preferred product. The question we are attempting to answer is: what makes silver a unique surface when reactions on other transition metals produce acetaldehyde as the dominant product? The calculated transition state structure for the formation of acetaldehyde on the [111] surface of silver is shown in Figure 3. As seen in this figure, the transition state involves an energy consuming H atom transfer. We speculate that this structure (and similar ones on other transition metals) will

prove to be the doorway into understanding the unique role of silver for the epoxidation of ethylene.

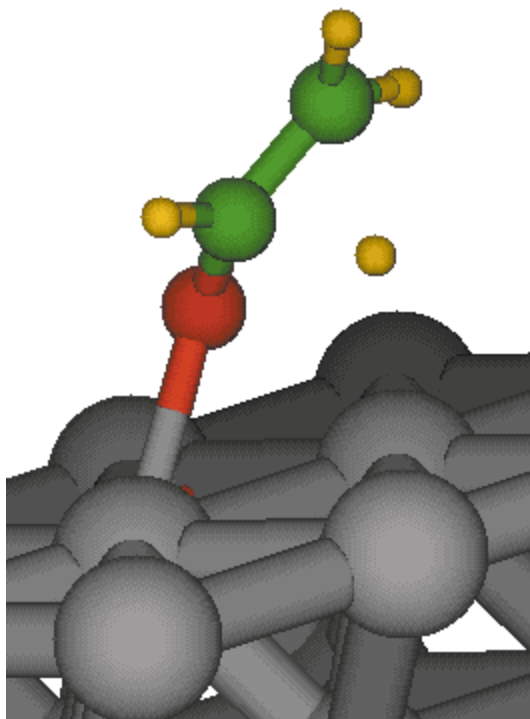


Figure 3: Transition state structure for the H atom transfer reaction to form acetaldehyde.

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