

Control of Ethylene Epoxidation Selectivity by Surface Oxametallacycles

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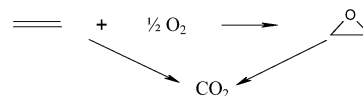
Advances in the integration of surface science with robust density functional theory (DFT) methods have produced several recent examples in which a rational approach to heterogeneous catalyst design was successfully implemented. Norskov and co-workers have reported the development from first principles of new bimetallic ammonia synthesis¹ and steam reforming catalysts². In these two examples, the catalyst design was driven by the need for more active and long-lived catalysts. Such successes motivate the application of first principles approaches to the understanding and rational design of catalysts and processes for which other considerations, for example, selectivity, are dominant.

We show here how surface science experiments, DFT calculations, and kinetic isotope effect data can be utilized to understand the elementary steps that govern the selectivity of silver catalysts for the selective oxidation of ethylene to produce ethylene oxide (EO). Understanding these steps is crucial to the rational design of more selective epoxidation catalysts. Direct epoxidation of ethylene is carried out commercially over α - Al_2O_3 -supported Ag catalysts.³ Unpromoted Ag catalysts are reported to attain EO selectivities up to ~50% with respect to ethylene converted, while promoted catalysts (Cs and Cl are among the main promoters) have been reported to generate selectivities over 80%.³ Even though this process is over 60 years old, the detailed mechanism of the reaction remains unknown.

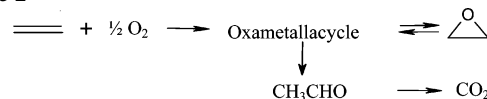
The minimum reaction network necessary to describe the process is usually depicted as a triangular or series-parallel network shown in Scheme 1.^{4,5} While virtually all partial oxidation processes involve sequential reactions, parallel paths for reactant combustion are included to explain less-than-perfect selectivity at differential conversion. Understanding the surface intermediates involved permits one to construct a mechanism of elementary steps, rather than relying on such generic reaction networks.

We have recently demonstrated the existence of a surface oxametallacycle on silver that generates ethylene oxide⁶ and have developed a reaction coordinate and microkinetic model for ethylene epoxidation centered around this species.⁷ The chemistry of oxametallacycles may be sufficient to understand and even predict the selectivity of silver epoxidation catalysis. For example, if there exists a competing reaction pathway leading to complete combustion that branches off from the selective reaction pathway at the oxametallacycle, the selectivity versus conversion behavior would be similar to that of the conventional series-parallel network. In other words, the parallel combustion step could branch off at the reactant or any intermediate. One such possibility is illustrated in Scheme 2. The idea of a common surface intermediate for selective and unselective paths was previously suggested from catalysis⁸ and surface science^{9,10} experiments; however, its identity was unknown. Scheme 2 is consistent with experimental evidence demonstrating that acetaldehyde is easily oxidized on silver to form surface acetates that are readily oxidized to form CO_2 .^{5,11}

Scheme 1



Scheme 2



We have used DFT to search for an energetically feasible, first-order transition state that would lead from the oxametallacycle intermediate to acetaldehyde. We use a combination of cluster/periodic plane wave calculations.^{12–16} Geometry optimization and transition state-searching algorithms as implemented by ADF (Amsterdam density functional) code are employed on Ag_{15} clusters to obtain the structure of the relevant transition state. The structure optimized on an Ag_{15} cluster is then used as a starting structure in the geometry optimization of the transition state in periodic plane wave calculations on a $p(3 \times 3)$ unit cell, corresponding to a coverage of 0.11 monolayers, in accord with the low coverage expected for the catalytic process. Periodic plane wave calculations are expected to be superior to cluster calculations in their ability to capture electronic properties of extended surfaces. The reported electronic energies are calculated using the periodic plane wave approach, while zero-point-energies and entropies are calculated from vibrational spectra calculated on an Ag_{15} cluster.

The calculated structure of the transition state for acetaldehyde formation is shown, along with the oxametallacycle and the transition state for EO formation, in Figure 1. The reaction coordinate for acetaldehyde formation can be described as a 1,2-hydrogen shift from the central to the terminal carbon. In the transition state, the bond between the central carbon and hydrogen is elongated from 1.1 to 1.25 Å.

If the selectivity of ethylene epoxidation is determined by the two reaction pathways from the oxametallacycle in Figure 1, then it can be estimated directly from DFT calculations. The selectivity to EO will depend only on the difference in Gibbs free energies of activation. This difference is calculated to be 0.3 kcal/mol in favor of the formation of acetaldehyde versus EO from the surface oxametallacycle. This indicates that the selectivity to EO on unpromoted Ag will be 41–43% at 400–500 K. These values represent the maximum selectivity achievable at low conversion; at higher conversions and higher temperatures, sequential reactions of the EO product may reduce selectivity, counteracting the very modest increase of selectivity with temperature that the above difference in activation barriers would predict. The calculated selectivities are in agreement with typical selectivities reported on unpromoted Ag ranging from 25 to 50%, depending on reaction conditions and reactant partial pressures.^{3,17}

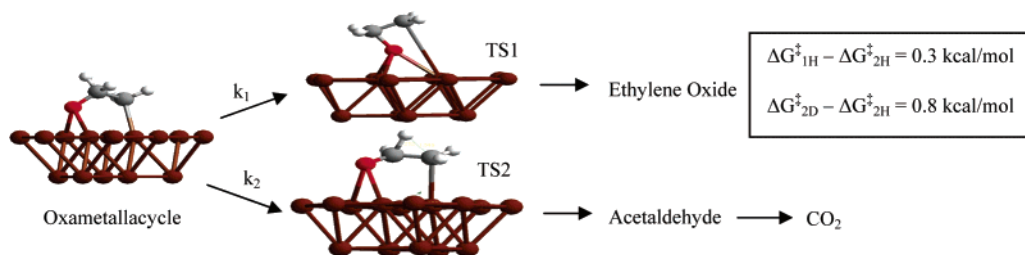


Figure 1. DFT-calculated competing reaction pathways. The inset shows the difference in Gibbs free energy of activation for the combustion versus selective pathway at $T = 500$ K and the difference for deuterated versus nonlabeled reactant at 0.1 monolayer and $T = 420$ K for the combustion pathways.

Kinetic isotope effect measurements provide a further test of this scheme. Several groups have reported results for epoxidation of C_2D_4 .^{8,18} These experiments yielded selectivities ranging from 50 to 73% for deuterated ethylene oxide depending on the reaction conditions.^{8,18} It is important to note that the selectivity change was accompanied by a significant increase in the rate of ethylene oxide production and a significant decrease in the combustion rate.⁸ These observations have been interpreted in terms of a common intermediate for selective and combustion pathways.⁸ The mechanism proposed in Figure 1 is in accord with these observations.

We have examined quantitatively the kinetic isotope effect in the context of the mechanism in Figure 1. Because step 1 (EO formation) does not involve C–H bond breaking, we assume that there is not a significant kinetic isotope effect for this step. We are interested in the changes in selectivity as the feed is switched from C_2H_4 to C_2D_4 . Selectivity can be related to the rate constants as follows:

$$k_{2H}/k_{2D} = [S_{1D}(1 - S_{1H})/S_{1H}(1 - S_{1D})]$$

Here k_2 is the rate constant for oxametallacycle isomerization to acetaldehyde, and S_1 is the selectivity to ethylene oxide. Subscripts H and D refer to nonlabeled and labeled reactants, respectively. From this expression, the selectivity to ethylene oxide, S_{1D} , with the reactant C_2D_4 can be easily determined if S_{1H} and the ratio k_{2H}/k_{2D} are known. S_{1H} is the experimentally measured selectivity to ethylene oxide with C_2H_4 as the reactant. The ratio k_{2H}/k_{2D} can be calculated from the transition state theory by using the DFT results as the necessary input.

The vibrational mode of the oxametallacycle intermediate that evolves into the reaction coordinate responsible for the formation of acetaldehyde is a C–H bending mode that appears in the vibrational spectrum at 1302 cm^{-1} (1012 cm^{-1} in the deuterated version). If we assume that all vibrational modes other than the reaction coordinate are conserved, the difference in the activation energy for this process (i.e., the zero-point-energy difference) can be determined from this frequency. The activation energy for step 2 calculated using this approach is 0.4 kcal/mol higher when C_2D_4 is the reactant. This value underestimates the kinetic isotope effects reported in the literature.^{8,18} We have therefore calculated free energies associated with deuterated and nonlabeled transition states for oxametallacycle isomerization into acetaldehyde, shown in Figure 1. The difference in the free energies of activation calculated by DFT for oxametallacycle isomerization to acetaldehyde with deuterated versus nonlabeled reactant is 0.8 kcal/mol at $T = 420$ K, where the barrier associated with C_2H_4 is energetically easier to overcome. This value exceeds the zero-point-energy difference of the C–H bending mode because the assumption of conservation of all vibrational modes other than the reaction coordinate does not hold; there is significant perturbation of the C–H stretches of the transition state. The activation energy for EO formation did not change significantly upon deuteration as corroborated by the calculated change of less than 0.05 kcal/mol .

From the difference in the free energies of activation for oxametallacycle isomerization to acetaldehyde, we calculate the ratio k_{2H}/k_{2D} to be 2.7 at $T = 420$ K. This suggests that the epoxide selectivity should increase from 49 to 73–74% at $T = 420$ K when the reactant is switched from C_2H_4 to C_2D_4 , using the selectivity of 49% for C_2H_4 epoxidation, reported in the literature.⁸ This is in excellent agreement with the experimentally measured selectivity increase to 73% at 420 K.⁸

We conclude that reactions of surface oxametallacycles control the selectivity of ethylene epoxidation on silver catalysts at moderate conversions. We have shown that the mechanism proposed in Figure 1 not only offers qualitative agreement with the experimental observations by proposing a common intermediate for the selective and unselective pathways, but it also provides a basis for quantitative prediction of selectivity in ethylene epoxidation on silver. The parallel 1,2-hydrogen shift to form acetaldehyde may be sufficient to explain the selectivity limitations traditionally ascribed to ethylene combustion. Recognizing the central role of the oxametallacycle in this process provides a platform, not only for understanding catalyst performance, but also for exploring the influence of coadsorbates (e.g., oxygen) and of catalyst promoters at the molecular level, and ultimately for rational design of selective oxidation catalysts.

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Supporting Information Available: Computational method employed and the geometries of the structures shown in Figure 1 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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