

Propylene oxidation on silver: A density functional and ONIOM study

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Introduction

There is a long history of experimental research for ethylene oxide formation due to its industrial importance. Considerable experimental effort has been devoted to understanding the mechanism of silver-catalyzed ethylene epoxidation as outlined in reviews [1-3]. The issues most often addressed have been the roles of oxygen and the promoters in the reaction. Grant and Lambert [4] carried out fundamental studies using primarily Ag 111 and Ag 110 single crystals which provided evidence for the key role of atomic rather than molecular oxygen in both the epoxidation and combustion reactions. As part of a continuing effort to understand the mechanism of olefin epoxidation, Barteau and co-workers [5, 6] used density functional theory (DFT) calculations to demonstrate that surface oxametallacycles are moderately stable with respect to the corresponding gas-phase monoolefin epoxides. Linic and Barteau [7, 8] used DFT calculations to investigate a possible reaction coordinate for the epoxidation of ethylene on silver and concluded that reactions of surface oxametallacycles control the selectivity of ethylene epoxidation on silver catalysts at moderate conversions. They obtained various surface intermediates and transition states along the reaction coordinate with structures, binding energies, and vibrational frequencies that were in good agreement with experimental results. DFT calculations indicated that ethylene reacts with adsorbed oxygen to form a surface intermediate, identified as a surface oxametallacycle. This intermediate reacts through a transition state to form gas-phase ethylene oxide. Kobayashi and Shimodaira [9] carried out DFT calculations to investigate the reaction mechanisms for propylene oxide formation on Ag and Au catalysts. The reaction profiles were calculated repeatedly using neutral, cationic and anionic clusters.

Materials and Methods

Preliminary calculations of atomic and molecular oxygen adsorption followed by reaction with propylene from the gas phase on a 22 Ag atom ONIOM cluster which simulates Ag (111) surface were carried out using DFT/B3LYP method with basis sets composed of Los Alamos LANL2DZ effective core pseudo-potentials (ECP) for silver and 3-21G** for carbon, oxygen and hydrogen as implemented in Gaussian 2003. A 22 Ag atom 2 layer ONIOM method is used to simulate Ag (111) surface where 4 Ag atoms are in high layer DFT region and the rest of the cluster (18 Ag atoms) is in low layer molecular mechanics region utilizing universal force field (UFF). Relative energy profiles as functions of a chosen reaction coordinate were calculated and two distinct pathways, one directly leading to propylene oxide, and the other forming a Π -allyl radical were identified. Equilibrium geometry calculations were in general performed.

Results and Discussion

Oxygen was both molecularly and atomically adsorbed onto the Ag cluster and optimized equilibrium geometries and relative energies of adsorption were calculated. The heat

of adsorption values obtained in our study show reasonable agreement with the experimental values under low surface oxygen coverage conditions: -12.42 vs -9.2 kcal/mole for molecular and -51.15 vs -40.8 kcal/mole for atomic adsorption, respectively. Since it is generally accepted that atomic oxygen, rather than molecularly adsorbed oxygen reacts with ethylene [4], the calculations involving propylene adsorption and reaction were carried out involving an oxygen atom adsorbed on silver cluster. The next step along the reaction coordinate is the adsorption of propylene onto the oxygen-covered Ag surface. The final optimized equilibrium propylene oxide formation is found at a relative energy value of -11.70 kcal/mole and its geometry is illustrated in Figure 1. Approximate transition state energy barriers indicated a more favorable route for the case of Π -allyl radical formation (5.03 kcal/mole) as opposed to propylene oxide formation (14.99 kcal/mole).

Significance

DFT calculations indicate that Π -allyl radical formation is a more favorable route as opposed to direct propylene epoxidation on Ag (111) surface. Since Π -allyl radical leads to combustion products which lower propylene oxide selectivity, this mechanistic result explains why Ag (111) surface is not a good catalyst surface for this reaction in line with experimental observations.

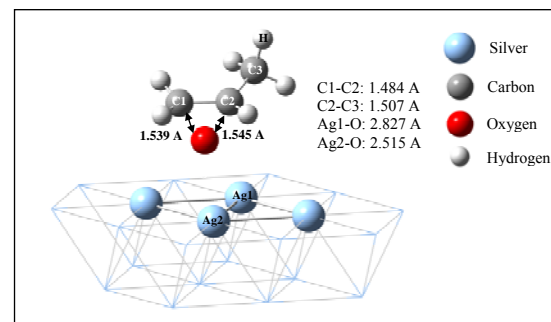


Figure 1. Equilibrium geometry of propylene oxidation on oxygen atom adsorbed 22 atom silver cluster. (DFT region represented by ball-bond view, Molecular Mechanics region represented by wireframe view)

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