

A DFT Study of Ethylene Epoxidation on AgO And Ag₂O Slab Surfaces

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Introduction

Partial oxidation of ethylene to ethylene oxide (EO) is an important industrial process. Although selectivity has been increased considerably during the last decade, a molecular level understanding has not been fully achieved yet. Starting from late 80's, with the advances in Density Functional Theory (DFT) software and computers, a considerable amount of theoretical studies have been carried out to understand the mechanism and kinetics of the formation of EO on silver catalysts. Among those, surface oxametallacycle (OME or OMME) [1,2] formation is the commonly supported idea for the clean Ag(111) surface. Furthermore, more recent studies carried out on so called trilayer silver oxide surfaces with Ag_{1.83}O or Ag₂O stoichiometries [3,4] also supported the idea of EO formation from OME intermediate. Although the idea of using a catalyst with high oxygen concentration was offered and supported during the late 80's [5-7] there has not been any research study encountered in the common literature considering highly oxidized Ag surfaces except for the works of surface oxides mentioned above. Recent surface science studies [8] have indicated diffusion of oxygen into the silver layers, thereby showing the existence of sub-surface oxygen or oxygen layers. In this work, AgO and Ag₂O slab surfaces are investigated for ethylene epoxidation and compared with silver surface with low oxygen coverage.

Materials and Methods

The calculations whose results are presented here are carried out using VASP [9] code, which uses periodic plane wave basis sets. The many-body systems are described with PAW [10,11], and GGA [12] for the exchange and the correlation energy proposed by Perdew and Wang (PW91) [13]. Except for the molecules and atoms in the gas phase, dipole corrections are included for the asymmetric slab calculations. The cut-off energies and k-points (Monkhorst Pack) used are; 500 eV and (4x4x1) for 4 layer p(2x2) AgO(001) and Ag₂O(001)slabs ; and 400 eV and (2x2x1) for 3 layer p(3x3) Ag(111) slab..

Results and Discussion

The intermediates and acetaldehyde, OME/OMME and EO that are formerly identified and studied on silver and silver surface oxides are also observed on the AgO(001) and Ag₂O(001) surfaces of this study. Another observed species in this study is the vinyl type intermediates with C₂H₃O or C₂H₃OH stoichiometry. However, unlike the previous studies, OME/OMME intermediate does not seem to be responsible for EO formation. In other words, direct oxidation of ethylene to EO is observed on both AgO and Ag₂O surfaces without facing any barriers. The only energy requirement arises during desorption of EO formed on the surface. In preliminary studies, OME and OMME intermediates are observed to be responsible for the combustion products by activating the C-H bond instead of C=C double bond. The

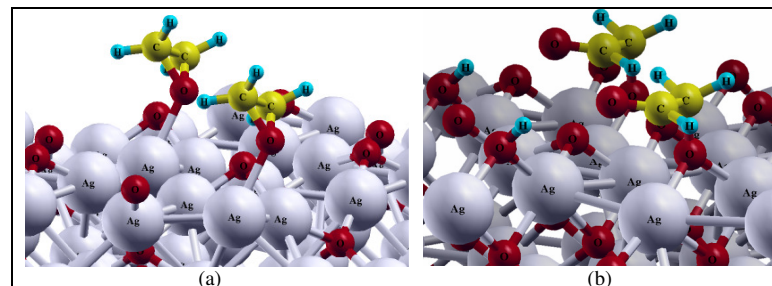


Figure 1. (a) EO formed on Ag₂O(001) surface, (b) Vinyl type intermediate formed as a result of C-H activation on AgO(001) surface.

product of CH activation is vinyl or aldehyde, which is a probable intermediate for complete oxidation of ethylene to CO₂ and H₂O.

Significance

The partial oxidation of ethylene to ethylene oxide, as well as intermediates for complete combustion, is studied using AgO(001) and Ag₂O(001) surfaces. Although OME/OMME intermediates are found to be forming exothermically on the surfaces, preliminary studies have shown that these species are responsible for combustion products and not for ethylene oxide. The surfaces studied in this work form EO without a barrier, but approx. 1eV energy is required for desorption.

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