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A mechanistic density functional study of partial oxidation of propene on supported subnanometer silver clusters JEFFERY P. GREELEY, Center for Nanoscale Materials, Argonne National Laboratory, FAISAL MEHMOOD, Materials Science Division, Argonne National Laboratory, STEFAN VAJDA, LARRY A. CURTISS, Center for Nanoscale Materials and Materials Science Division, Argonne National Laboratory — Density functional theory (DFT) calculations were carried out to investigate the fundamental chemical mechanisms underlying the selective oxidation of propene (CH_3–CH=CH_2) to propylene oxide (CH_3–CH–CH_2O) or acrolein (CH_2=CH–CHO). Silver which is a known catalyst for these reactions, is modeled as a silver trimer supported on θ-Al_2O_3 surface to investigate reaction mechanisms. Each reaction step starts with O_2 dissociation on interface of Ag_3 and alumina with an activation barrier that was found to be significantly smaller than what was reported on an Ag(111) surface. Propylene oxide formation was achieved through oxametallocyle formation with a much small barrier of 0.12 eV compared to 0.70 eV on Ag(111). We will also show how acrolein formation can be triggered by the abstraction of first H atom with essentially no apparent barrier on a Ag_3 cluster. Finally, we rationalize our results in comparison to experiments that show an enormous increase in reactivity for propylene epoxidation on subnanometer silver cluster. We will also discuss the preference of Ag trimers over tetramers for O_2 dissociation and how the microscopic understanding of such information can help better design new catalysts.

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