A QM/MM Study of Potential Steps in Direct Propylene Epoxidation Using H₂ and O₂ on Au/TS-1 Catalysts

Kendall T. Thomson*, Ajay Joshi, and W. Nicholas Delgass
Purdue University, School of Chemical Engineering, West Lafayette, Indiana, USA 47907
*thomsonk@ecn.purdue.edu

Introduction
Production of propylene oxide (PO) in a single step with no side products has been a long-sought industrial target. While a liquid-phase H₂O₂/TS-1 based route to PO appears imminent, due to handling problems and cost associated with H₂O₂, researchers have also focused on direct gas-phase propylene oxidation using H₂ and O₂ over Au/Ti catalysts. The assumption that such catalysts operate by (1) H₂O₂ formation on Au and (2) propylene epoxidation on Ti using that H₂O₂ is supported by recent literature.

Materials and Methods
Since studies of Au/TS-1 suggest that part of the epoxidation activity is associated with Au/Ti sites inside the zeolite channels, we have employed the hybrid quantum-mechanics/molecular-mechanics (QM/MM) approach—see Figure 1, augmented with full thermochemistry (298.15 K, 1 atm), to develop epoxidation mechanisms inside the TS-1 pores (5.5 Å). We considered both non-defect and Si-vacancy defect Ti-sites with and without Au₃ adsorbed on them and investigated OOH/H₂O₂ formation pathways.

Results and Discussion
Consistent with experiments on Au/SiO₂, we found that O₂ pre-adsorbed on Au enhanced the dissociative adsorption of H₂ to form stable OOH species (ΔEₚ = 7.7 kcal/mol, Au₃/Ti-non-defect). We speculate that an H₂O₂ formation pathway similar to that found on gas-phase Au clusters is likely to operate on Au₃/Ti-non-defect sites—see Figure 2. H₂O₂ formed on these sites can then migrate to PO-producing sites via diffusion along the pore walls. Assuming such availability of H₂O₂, we modeled three different sites for propylene epoxidation: (1) Si-defect, (2) Ti-defect, and (3) Au₃-Ti-defect. We found that formation of Si-OOH species due to reaction of H₂O₂ with a metal-vacancy Si-defect sites is both kinetically (ΔEₚ = 16.8 kcal/mol) and thermodynamically unfavorable (ΔE = +2.8 kcal/mol). However, it is much easier (ΔEₚ = 6.8 kcal/mol) to form Ti-OOH species (and water) by attacking the Ti-defect site with H₂O₂ (ΔE = -8.0 kcal/mol). Propylene reacts with these Ti-OOH species to form propylene oxide with ΔEₚ = 15.8 kcal/mol and ΔE = -51.3 kcal/mol. Interestingly, we predict that the activation barrier to form Ti-OOH species on Au₃/Ti-defect sites is significantly higher (ΔEₚ = 28.1 kcal/mol) than that for the Ti-defect site without Au₃ and that OOH species formed on Au₃ in an Au₃/Ti-defect site are likely to decompose rapidly to form water (ΔEₚ = 1.3 kcal/mol) due to strong interaction with the silanol (Si-OH) groups around the defect. Thus, we conclude that the sequential propylene epoxidation pathway is kinetically unfavorable on the Au₃/Ti-defect site but is favorable with a combination of Au₃/Ti-non-defect and Ti-defect sites.