A QM/MM Study of Potential Steps in Direct Propylene Epoxidation Using H_2 and O_2 on Au/TS-1 Catalysts

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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 H_2O_2/TS-1 based route to PO appears imminent,[1] due to handling problems and cost associated with H_2O_2, researchers have also focused on direct gas-phase propylene oxidation using H_2 and O_2 over Au/Ti catalysts.[2-4] The assumption that such catalysts operate by (1) H_2O_2 formation on Au and (2) propylene epoxidation on Ti using that H_2O_2 is supported by recent literature.[5,6]

Materials and Methods

Since studies of Au/TS-1[7,8] 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 Au_3 adsorbed[9] on them and investigated OOH/H_2O_2 formation pathways.[10]

Results and Discussion

Consistent with experiments on Au/SiO_2,[11] we found that O_2 pre-adsorbed on Au_3 enhanced the dissociative adsorption of H_2 to form stable OOH species (ΔE_{act} = 7.7 kcal/mol, Au_3/Ti-non-defect). We speculate that an H_2O_2 formation pathway similar to that found on gas-phase Au clusters[12,13] is likely to operate on Au_3/Ti-non-defect sites—see Figure 2.. H_2O_2 formed on these sites can then migrate to PO-producing sites via diffusion along the pore walls. Assuming such availability of H_2O_2, we modeled three different sites for propylene epoxidation: (1) Si-defect, (2) Ti-defect, and (3) Au_3-Ti-defect.[10] We found that formation of Si-OOH species due to reaction of H_2O_2 with a metal-vacancy Si-defect sites is both kinetically (ΔE_{act} = 33.2 kcal/mol) and thermodynamically unfavorable (ΔE = +2.8 kcal/mol). However, it is much easier (ΔE_{act} = 16.8 kcal/mol) to form Ti-OOH species (and water) by attacking the Ti-defect site with H_2O_2 (ΔE = -8.0 kcal/mol). Propylene reacts with these Ti-OOH species to form propylene oxide with ΔE_{act} = 15.8 kcal/mol and ΔE = -51.3 kcal/mol. Interestingly, we predict that the activation barrier to form Ti-OOH species on Au_3/Ti-defect sites is significantly higher (ΔE_{act} = 28.1 kcal/mol) than that for the Ti-defect site without Au_3 and that OOH species formed on Au_3 in an Au_3/Ti-defect site are likely to decompose rapidly to form water (ΔE_{act} = 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 Au_3/Ti-defect site but is favorable with a combination of Au_3/Ti-non-defect and Ti-defect sites.

Significance

The commercialization of a gas-phase heterogenous catalyst for production of propylene oxide would lead to more environmentally friendly processes in what is a $9+ billion per year industry. Understanding the underlining mechanisms for these systems is an important step for improving catalytic properties.

Figure 1

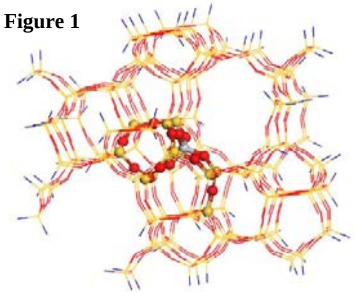

Figure 2

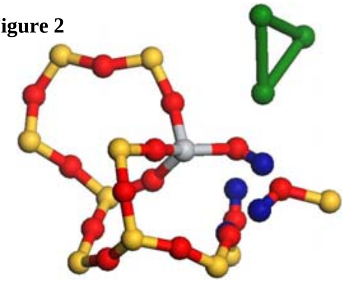

Figure 1. QM/MM molecular model of a Ti/Si-vacancy site in the TS-1 lattice.
Figure 2. Au_3 cluster anchored near a Si-vacancy site (defect) adjacent to Ti in TS-1 lattice.

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