Selective Propene Oxidation to Propylene Oxide or Acrolein on Immobilized Au_{6-10} Clusters: The Effect of Hydrogen and Water on Selectivity and Activity

Stefan Vajda[1, 2, ¶], Sungsik Lee[1], Michael J. Pellin[3], Jeffrey W. Elam[4], Byeongdu Lee[5], Sönke Seifert[5], Randall E. Winans[5], Luis Molina[6], Julio A. Alonso[6], Maria López[6], Bjørk Hammer[7]

[1]*Chemical Sciences and Engineering Division,*[2]*Center for Nanoscale Materials,* [3]*Materials Science Division,* [4]*Energy Systems Division,* [5] *X-ray Sciences Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA*

[6]*Departamento de Física Teórica, Atómica y Óptica, Universidad Valladolid, Spain*

[7]*iNano and Department of Physics and Astronomy, University of Aarhus, Denmark*

[¶]*Department of Chemical Engineering, School of Engineering & Applied Science, Yale University, 9 Hillhouse Avenue, New Haven, CT 06520, USA*

Introduction

Propylene oxide is an important intermediate industrial chemical and is commercially produced using either the chlorohydrin or the hydroperoxide routes, each with its own problems[1], such as the production of undesirable byproducts or need for expensive. A possible new route for propylene oxide production was shown in the experiments of Haruta et al, using gold nanocatalysts.[2] These new catalysts, convert up to 10% propene with very high selectivity. However, although those results make the use of gold nanoparticles very promising, several issues still need to be improved in order to employ it in practical applications. First, the selectivity is extremely sensitive to the nanoparticle size and shape, with particles smaller than ~2.0 nm mainly producing propane, and particles larger than ~4 nm mainly burning propene. Second, it is desirable to lower or to suppress hydrogen consumption for economical reasons. Finally, the stability of the catalysts needs to be improved as well.

In this paper, we present the results of a novel joint experimental and theoretical study of the catalytic activity of soft-landed sub-nanometer gold clusters Au_6-Au_{10} for selective propene oxidation.

Materials and Methods

The fabrication of the gold model nanocatalysts involved several steps. First, a thin alumina film was grown by atomic layer deposition (ALD)[3] on top of naturally oxidized silicon wafers, providing a rough and amorphous base support. Second, a distribution of gold clusters in the range Au_6^+-Au_{10}^+ was soft-landed[4] while keeping surface coverages below 3% ML. Third, in order to suppress cluster sintering, an additional ALD alumina layer was grown on top, leaving the clusters in wells on the support. Catalyst tests were performed in a reactor by feeding various gas mixtures (C_3H_6/O_2, $C_3H_6/O_2/H_2$ and $C_3H_6/O_2/H_2O$ in helium) by monitoring reaction products with a mass spectrometer. Simultaneous X-ray scattering was used to monitor the size of the Au clusters. No change in cluster size was observed during hours of experiments, thus confirming that the immobilized Au clusters were sintering-resistant.

Results and Discussion

Propene oxide and acrolein co-product formation at various compositions of the gas mixture, both as a function of temperature (30- 200 ºC) and reaction time (at constant 200 ºC). By plotting the temperature-dependent ratio of propene oxide vs. acrolein (Figure 1), we obtain an estimation of the catalyst selectivity.[5] With no additives,the production of acrolein is preferred; with H_2, we obtain ratios around 1:1. The most spectacular results are found for water, where up the formation of acrolein is almost completely suppressed at 200 °C. Thus, by turning the feed of water vapor on or off, the gold catalyst will preferentially produce propylene oxide or acrolein. DFT calculations reveal the reaction mechanism, identify the cluster-support interface where the reaction intermediate (metallacycle) is formed, describes the important role of surface OH-groups at the healing of oxygen vacancies.

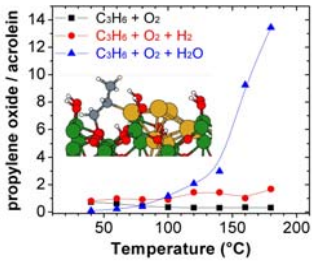

Figure 1. Propylene-oxide to acrolein ratio as a function of temperature and additives.

Significance

In summary, the results from the joint experimental and theoretical study are unexpected and surprising in several ways. First, we demonstrate in the present work that our model catalysts fabricated of sub-nanometer gold clusters are active for the partial oxidation of propene. Our work thus complements existing reports on similar activity of larger gold nanoparticles[1-2]. Second, to our knowledge, this is the first catalytic system which uses alumina as support, instead of the commonly applied titania considered to be essential for the production of -OH/-OOH radicals, which are believed to be needed for the promotion of the partial oxidation step on gold/titania. Third, and more important, for Al_2O_3-supported gold sub-nanometer clusters the expensive and dangerous hydrogen can be replaced by abundant and safe water vapor. It will be a challenging task to scale up the production of size-selected clusters by conventional chemical routes, but there are encouraging studies suggesting that this will be feasible.[6]

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