From Sub-Nanometer to Nanometer Size Silver Catalysts: The Effect of Catalyst Size in Selective Oxidation of Propene

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Introduction

In this paper, we present the results of a study of the effect of the size of alumina-supported highly uniform silver catalysts for the direct oxidation of propene to propylene oxide. The smallest clusters studied were triatomic size-preselected clusters, the largest size-preselected silver nanoparticles measured about 25nm in diameter and 15 nm in height.

Materials and Methods

Support material: The amorphous alumina film was grown by atomic layer deposition (ALD)[1] on top of naturally oxidized silicon wafers.

Cluster deposition: The Ag_3 clusters were produced in a laser vaporization source, size-preselected in a mass filter – qudrupole deflector assembly and soft-landed on the support. The silver nanoparticles were produced in an ACIS cluster source and size-preselected using an energy filter.[3]

SEM characterization: The nanosized catalysts were imaged using high-resolution SEM before and after the catalytic tests.

Catalysts tests: In a temperature programmed reactivity tests, the reaction products were monitoring with a mass spectrometer. Simultaneous X-ray scattering was used to monitor the size of the catalyst during the reaction.

Results and Discussion

Silver cluster based catalyst tested in the size range of 8-24 nm, show increased selectivity towards propylene oxide production with increasing size; however at the expense of a decreased activity. Typical temperature-dependent reactivity data for a silver catalyst of various sizes is shown in Figure 1 below. The comparison of surface X-ray scattering data and the SEM performed before and after the catalytic tests reaching 200 °C and up to 8 hours in duration confirmed stable, sintering-resistant silver nanoparticles.

However, the highest catalytic activity and the highest selectivity towards propylene oxide formation was observed on Ag_3 clusters and 2 nm size nanoparticles assembled from Ag_3 clusters – a surprising results not expected from the tendency of the evolution of catalytic properties of particles between 5 to 25 nm in size.

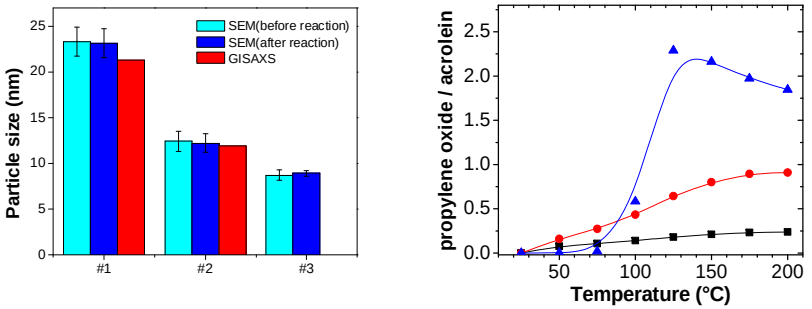

Figure 1. Left: Size of the tested nanocatalysts determined by high SEM before and after the catalytic tests and from synchrotron grazing incidence small angle X-ray scattering. Right: Selectivity for three cluster sizes as the ratio between propylene-oxide and acrolein produced by 25 nm, 13nm and 8 nm clusters (squares, circles and triangles, respectively).

DFT calculations reveal that the high activity of Ag_3 clusters towards propylene oxide formation is caused by a very low activation barrier for this reaction channel on the small clusters (Figure 2.).

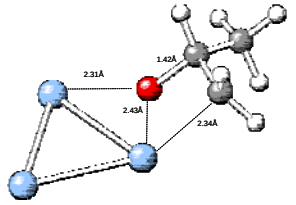

Figure 2. Structure of reaction intermediate.

Significance

Strongly size-dependent activity and selectivity of silver nanocatalysts was observed in the epoxidation of propene. The results underline the important role of undercoordinated metal atoms in the sub-nanometer silver clusters which result in unexpected high activity as well as selectivity.

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