Scanning Tunneling Microscopy of Mass-Selected Ag Clusters on Titania



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Abstract

The catalytic activity of metal nanoparticles on oxide supports has inspired many studies which attempt to shed light on the source of the unique reactivity of these systems. The particular system of interest here, Ag nanoparticles on titania, has been reported to catalyze the epoxidation of propylene.¹ Since nanoparticle size is a critical parameter for these active catalyst systems, studies which allow the controlled deposition of particular size clusters may provide insight into the underlying properties governing catalytic behavior.² Mass-selected cluster deposition from the gas phase at room temperature is reported form clusters 5A - 7A in height, and 30A - 45A in diameter. Clusters landed with ~175 eV appear much smaller, 1A - 3A in height and 10A - 30A in diameter. Upon annealing, the smaller hard-landed clusters to become larger in size, and the total atomic coverage increases, likely due to Ag diffusion from the bulk.



A pulsed Yttrium-Aluminum-Garnet laser is used to ablate a rotating silver wire in the cluster source chamber. Immediately following the laser pulse, a burst of argon gas enters the source, causing the resulting silver plasma to nucleate into gas phase Ag_n^* clusters. The clusters are then accelerated from the source to the magnet, passing through several focusing and steering lenses en route. In the magnet the clusters are size selected and sent first to a movable detector for current optimization, and then to the sample in the surface science chamber for deposition. The clusters can then be either "soft-landed" by applying a repelling voltage to the sample, or "hard-landed" by raducing or eliminating this voltage. Once the clusters have been deposited, the sample is shuttled into the STM chamber on a cryogenic manipulator and imaged. The sample can then be heated in situ.

Room Temperature Deposition of Size-Selected Clusters

The cluster source is capable of producing ions of several Ag atoms, as seen in the mass scan below (left), where the ion current on the movable detector is plotted as a function of mass. Maximum current is obtained for monomers, dimers, and trimers, which we explore here. An example energy distribution of the monomer is shown below (right). Here the ion current was measured on the movable detector as a function of applied voltage.





Energy Spread of the Monomer

STDDEV = 1 eV

Experimental Values



The STM images above depict the soft-landing of monomers, dimers, and trimers. A clean titania surface was exposed to a cluster beam current of ~0.1 nA for a specific length of time to produce an equal atomic coverage in each case. Large clusters on the order of 40 atoms in size are apparent in all images, indicating that the clusters sinter at room temperature. The table given above indicates that monomers and dimers are fairly similar in size, while the trimers seem to be somewhat smaller. In addition, the number of large clusters appears to decrease in the case of the trimer. A closer examination of the trimer deposition reveals small clusters (circled in the above image) on the order of 1 Å in height and 12 Å in width, giving rise to an apparent bimodal distribution in cluster size.

Hard-Landed Clusters

Depicted in the image below (left) is an example of the hard-landing of clusters with ~175 eV of energy. Here large sintered clusters are not observed, contrary to the case of the soft-landing experiments. The inset shows the presence o small clusters about 2Å high and 20Å wide. These types of images have beer btained for monomers, dimers, and trimers. Slight differences in the measured its and widths occur in each case (see table below), however, due to the small size of the clusters this data cannot be interpreted as a geometrica comparison, but should be thought to represent an electronic picture. In many cases these small clusters appear as bright features asymmetrically located about the titanium rows, with part of the feature overlapping a bridging O row After annealing the titania substrate to ~300°C for 15 seconds in the case of the dimer, large clusters appear on the surface on the order of 8A in height and 55A in diameter (center image). Sintering is observed after annealing in the monome deposition as well, however the clusters did not become as large due to difference in the annealing conditions. High resolution images (example far right lso show the presence of small clusters after annealing in the case of the dimer



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| Hard-landing Statistics (before and after annealing)* | | | | | | | | |
| Cluster Size | Measured Height, A | | Measured Diameter, A | | Cluster Density, clusters/Å ² | | Coverage, %ML | |
| Monomer | 1.7±0.45 | 3.1±0.79 | 17±3.1 | 38±5.6 | 1.8 x 10-4 | 6.1 x 10-5 | .09 | 0.23 |
| Dimer | 2.3±0.55 | 8.6±1.2** | 22.6±5.8 | 55.3±5.6** | 2.4 x 10-4 | 1.2 x 10-4 | 0.25 | 0.71 |
| | | 4.0±4.2** | | 23±5.8** | | | | |
| Trimer | 1.5±0.26 | | 12±2.6 | | 2.3 x 10 ⁻³ | | 0.64 | |
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Conclusions

At room temperature under soft-landing conditions, monomers, dimers, and trimers nucleate on the surface, forming clusters on the order of 40 atoms in size. In the case of the trimer, the clusters are smaller, and clusters a fow adoms in size are also apparent on the surface. Perhaps this is due to a decrease in the mobility of the trimers relative to the monomers and dimers. In the case of the hard-landing experiments, sintering does not occur at room temperature, and small clusters are observed on the surface. After heating the substrate, some of the clusters sinter, while some remain small. The small clusters appear to bind about the titanium rows, likely to a defect site formed upon impact. Interestingly, the coverage increases after annealing, likely due to the diffusion of impacted Ag clusters from below the surface. The trend of increasing apparent coverage from monomer to trimer may be due to the fact that monomers penetrate the surface more easily than dimers and trimers.

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