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 catalysts, 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 here. Monomers, dimers, and trimers landed with ~175 eV of energy nucleate to form clusters 5Å – 7Å in height, and 36Å – 45Å in diameter. Clusters landed with ~175 eV appear much smaller, 1Å – 3Å in height and 10Å – 30Å in diameter. Upon annealing, the smaller hard-landed clusters sinter to become larger in size, and the total atomic coverage increases, likely due to Ag diffusion from the bulk.

Experimental

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+ 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 reducing or eliminating this voltage. Since the clusters have been deposited, the sample is shrunk 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 choose 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. The sample can be positively biased in order to decelerate the incoming ions, allowing those ions with energy greater than or equal to the bias voltage to reach the sample. This is “soft-landing.” When the sample is not biased, the entire distribution is allowed to reach the surface (“hard-landing”). The distribution gives us the energy spread of the incoming ions in both cases (see cartoon left).

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 of small clusters about 2Å high and 20Å wide. These types of images have been obtained for monomers, dimers, and trimers. Slight differences in the measured heights and widths occur in each case (see table below), however, due to the small size of the clusters these data cannot be interpreted as a geometrical 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.

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 trimers, the clusters are smaller, and clusters a few atoms 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 sample temperatures, 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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References