Active Alloying of Au with Pt Nanoclusters Supported on a Thin Film of Al_2O_3/NiAl(100)

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Alloying is empirically an effective way to modify the catalytic properties of transition- metal surfaces. Supported bimetallic clusters typically exhibit superior catalytic properties relative to their single-metal counterparts; many commercial heterogeneous catalysts hence consist of multimetallic materials, but the nature of the synergistic metal-metal interactions that produce the desired catalytic properties in mixed-metal catalysts is not well understood. Knowledge about bulk alloys is not simply applicable to supported nanoscale clusters; understanding the metal-metal interactions in the supported nanoclusters becomes crucial in the design of novel catalysts or in improving the current ones. Responding to this situation, we illuminate the interactions through an investigation of the surface composition, atomic and electronic structures of bimetallic nanoclusters grown by vapor deposition on a highly ordered oxide surface under well defined ultrahigh vacuum (UHV) conditions. In such a model system, the clusters are characterized in a precisely controlled manner.

We investigated the alloying of Au-Pt nanoclusters supported on an ultra-thin film of Al_2O_3 grown on a NiAl(100) substrate. Au-Pt clusters have been studied in recent years, mainly with an objective to improve the performance of catalysts in a fuel cell of methanol oxidation. The Au and Pt deposited from vapor onto the thin-film Al_2O_3/NiAl(100) at 300 K formed bimetallic nanoclusters which exhibited in the photoelectron spectra unusually small binding energy (BE) and line width for Au 4f core-levels as compared to those from pure Au clusters, in spite of metal deposition in a reverse order and concurrent deposition of Au and Pt. This spectral contrast resulted as the Au-Pt bimetallic clusters formed with a preferential structure.

The significant BE shift indicates increased screening, attributed primarily to the increased coordination number of the alloying Au atom and secondarily to the charge transfer from Pt to Au; the narrowed spectral line reflects the structurally more ordered clusters and enhanced uniformity of the chemical environment around each Au atom. We argue accordingly that the alloying clusters incline to form either an Au core-Pt shell structure or an Au-Pt intermixed structure, but with Au in interior of the clusters. The preferred bimetallic structure became unstable above 400 K, at which the Au 4f lines shifted positively and broadened evidently, indicating presence of Au atoms at the cluster surface. This behavior conforms to earlier theoretical anticipation. Nevertheless, the measured electronic structures differ from those of either Au core-Pt shell or Pt core-Au shell nanoclusters synthesized through ligated-metal complex in solution, for which opposite charge transfer, from Au to Pt, was indicated.

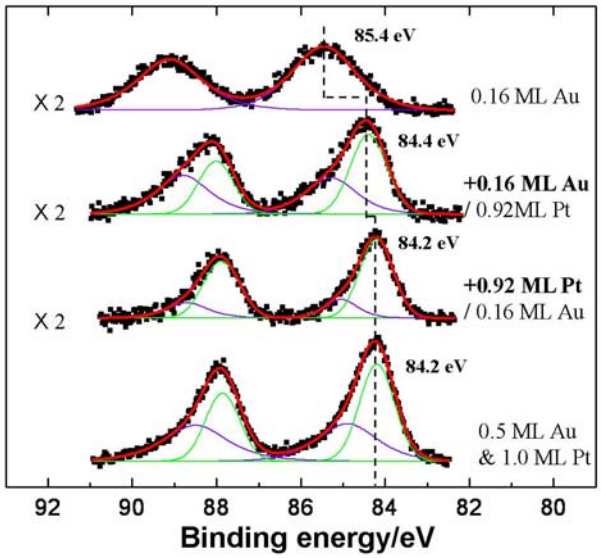

Fig. 1: Photoelectron spectra of Au 4f core-levels from 0.16 ML Au clusters (top) and Au-Pt bimetallic clusters formed on metal deposition in a varied order (the second one for first 0.92 ML Pt then 0.16 ML Au, and the third one for first 0.16 ML Au then 0.92 ML Pt) and concurrent deposition of Au and Pt (the fourth one) on the oxide thin film. The black dots denote raw spectra; green Gaussian-Lorentzian curves represent the signals from Au 4f in saturated Au-Pt bimetallic clusters; purple curves denote the signals from Au 4f in Au which does not intermix with Pt; red curves indicate the sums of fitted Gaussian-Lorentzian curves. The dashed lines indicate the variation of the Au $4f_{7/2}$ peak. The notation "0.5 ML Au & 1.0 ML Pt" serves as shorthand for concurrent deposition of 0.5 ML Au and 1.0 ML Pt.