ACS-PRF # 47369-AC5 – Nugget (2)

As demand for fossil fuel alternatives is rapidly growing in the civilized world in recent years – so is the renewed interest in catalysis with emphasis on heterogeneous catalysis. One of the outstanding problems in heterogeneous catalysis is the need to design sintering resistant catalysts that will ensure thermal stability of catalyzed reactions at high temperature.

In our previous report we have demonstrated how bi-metallic nano-clusters (Pd-Au) can be prepared on top of a model silicon oxide model support, by employing buffer layer assisted growth (BLAG). Moreover, we have shown that by small variation of the preparation procedure, one can modify overall reactivity and selectivity of a model reaction, in our case the hydrogenation and trimerization of acetylene to ethylene and benzene, respectively.

Recently we have focused our research on the development of methods that will result in thermally stabilized Pd-Au nano-clusters. This is important in order to avoid clusters mobility and sintering, thus maintaining their chemical activity at higher, industrially relevant temperature. In Figure 1, the shape of clusters before (Figs. 1a and 1b) and after defects formation (using argon ion sputter, figs. 1c and 1d))

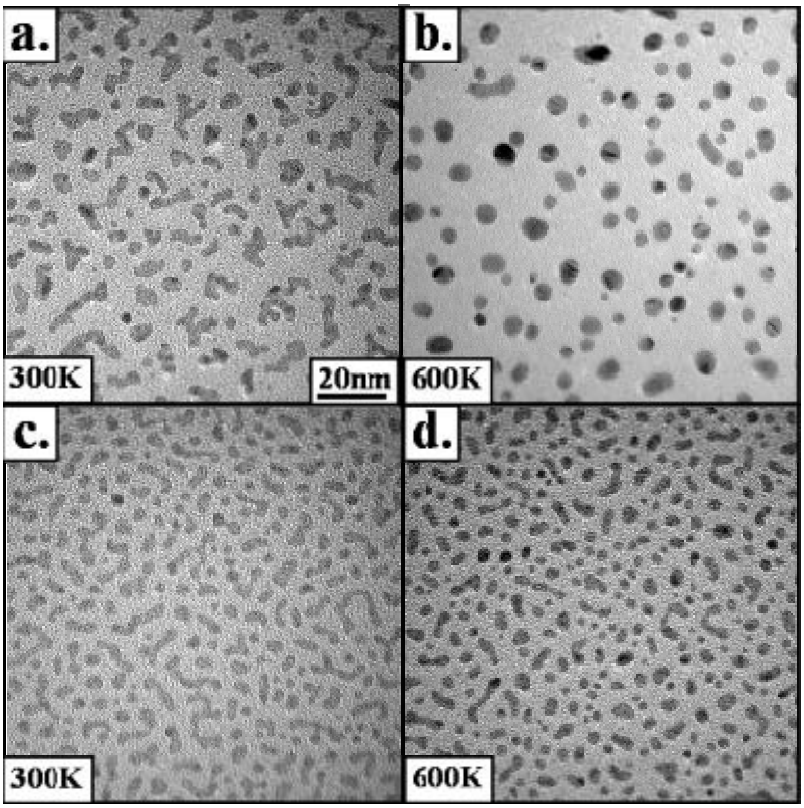

Figure 1: HR-TEM images of BLAG clusters at 300K and after annealing to 600K, the clusters were prepared on a-C substrate (Fig. 1a and 1b, respectively) and on sputtered a-C substrate (Fig. 1c and 1d, respectively). The clusters were prepared by simultaneous evaporation of 2Å Pd and 2Å Au toward 30ML H_2O adsorbed on the cold (130K) substrates, followed by annealing to 300 (1a, 1c) and 600K (1b, 1d). The HR-TEM images were taken ex-situ.

In order to better understand the important role substrate defects have on clusters reactivity, we have employ temperature programmed reaction (TPR) after pre-annealing the clusters to various temperatures. The clusters reactivity has been demonstrated via production of benzene and ethylene, comparing performance before (red line, Fig. 2a) and after (black line, Fig. 2a) defects formation.

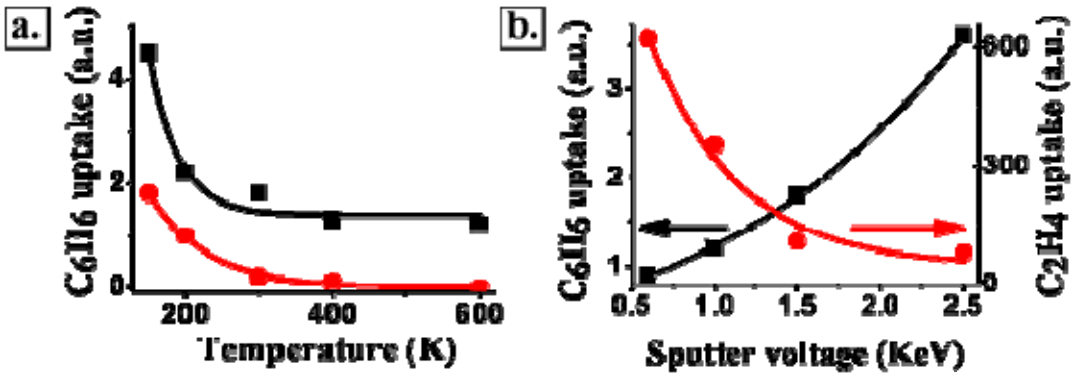

Figure 2: a. Benzene formation at the indicated substrate annealing temperatures. Benzene uptake was measured following adsorption of 3L C_2H_2 at 120K at different pre-annealing temperature, the clusters were prepared on smooth native SiO_2/Si(100) (red) and on sputtered SiO_2/Si(100) substrates (black). **b.** Benzene (black) and ethylene (red) formation as function of the sputter beam voltages.

There are two main important observations out of this study: a. Significant thermal stabilization of Pd-Au bimetallic clusters takes place as a result of argon-ion sputter at ion energies of 2.5 KeV, prevents sintering. b. Bi-metallic clusters at the defect sites restructure with surface segregation of Pd. As a result, benzene if formed at higher rates, changing the selectivity of the reaction towards benzene formation, compared with the smooth, non-sputtered silicon oxide substrate.

We believe this is a rather general and significant lesson for other metal-support interactions: It seems that the role of surface defects is in affecting not only thermal stability and thus maintaining reactivity at high temperature, but also its selectivity.