

## **Sub-Nano Ge-Doped Pt<sub>n</sub>/Alumina as an Effective Dehydrogenation Catalyst With Good Resistance to Coking and Thermal Sintering.**

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Alumina supported sub-nano Pt catalysts suffer greatly from deactivation via coke formation at reaction sites and sintering during high temperature reactions such as dehydrogenation of alkanes, of interest for endothermic cooling of hypersonic vehicles. One approach towards overcoming these limitations involves the doping these sub-nano clusters with other elements. We have previously shown efficient coke suppression with boron, silicon, and tin as dopants, but here we show that Ge is an efficient dopant. With a joint experimental and computational approach, we find that the addition of Ge to size-selected sub-nano Pt catalysts on alumina dramatically improves stability and selectivity.

We prepared size-selected Pt clusters on the alumina support and selectively incorporated Ge into the clusters via an atomic-layer-deposition-like process. For small Pt<sub>n</sub>Ge<sub>x</sub>, this process adds one Ge atom *per* four Pt atoms, while for larger clusters the Pt:Ge ratio is slightly higher. The stability and dehydrogenation abilities of the PtGe clusters were probed with temperature-programmed-desorption (TPD) of ethylene and D<sub>2</sub>. Compared to the ethylene TPD of Pt clusters that deactivated after being heated just once to 750 K with an ethylene saturated surface, PtGe showed little sign of catalyst deactivation even after multiple ethylene saturated heatings to 750 K. Furthermore, ethylene dehydrogenation leading to coke precursors was substantially reduced in the Ge-containing clusters. Changes in the electronic environment and the morphology of the clusters throughout the experiments were tracked using x-ray photoelectron spectroscopy and He ion scattering spectroscopy. Interestingly, Sn alloying suppressing coking even more efficiently, but the resulting Pt<sub>n</sub>Sn<sub>z</sub> catalysts are *less stable* in multiple reaction cycles.

We explain this unique stability and selectivity through DFT calculations. Of the computed thermally accessible Pt<sub>4</sub>Ge structures, we found that only one higher-lying isomer was capable of binding ethylene in the reactive di-sigma mode. This binding mode had a lower first dehydrogenation barrier than all the other  $\pi$ -bound ethylene modes, which accounted for the small but steady D<sub>2</sub> desorption seen via TPD. Only a small population of the thermally accessible Pt<sub>4</sub>Ge clusters were capable of deeper dehydrogenation, therefore stabilizing the catalysts against coking relative to pure Pt clusters. Furthermore, we saw evidence from the DFT calculations that the formation of small amounts of coke in the Pt<sub>4</sub>Ge clusters may in fact further improve the selectivity of the system due to cluster isomerization and the resulting change in the ethylene binding modes.