

## **Pd nanoclusters supported on MgO(100): effects of cluster size on chemisorption properties**

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### **Project Summary:**

Nanometer-size Pd particles supported on oxides are active catalysts for a variety of important reactions involving small alkanes. For example, low-temperature combustion of methane allows for cleaner energy production, as it minimizes NO<sub>x</sub> pollution.

The intent of this project to study particle size effects on the adsorption and dissociation of methane, ethane, and propane on model catalysts consisting of size-controlled Pd nanoclusters supported on MgO(100). The reactions are studied by molecular beams and temperature programmed desorption at low temperatures, a regime little explored for such well-defined model catalysts. MgO(100) thin films are grown on a Mo(100) substrate. Pd is vapor deposited at low temperatures and annealed to control the size of the Pd nanoparticles. The organic molecules are deposited with a cold molecular beam to prevent direct dissociation upon impact, or at higher energies to open up direct dissociation.

We have first conducted experiments to measure the interaction of the small alkane molecules with the MgO. Their initial sticking coefficients are plotted in Figure 1. We see that the initial sticking increases with molecule size up to octane at which point the sticking coefficient is unity. The adsorption energy is derived from a measurement of the flux of desorbing molecules as the temperature of the sample is increased at a controlled rate. Figure 2 shows temperature programmed desorption spectra for these molecules from a 1.0 ML initial coverage. There is a clear trend of increasing desorption temperature with increasing alkane chain length. This represents an increase in desorption energy, which is due in part to the number of binding sites per molecule as the size of the molecule increases.

We have also measured the dissociation of methane on MgO-supported Pd nanoparticles for several Pd coverages and beam energies. Some fraction of the hydrocarbon molecules dissociate as they reach the surface, leaving behind surface C. The residual C is titrated from the surface with a molecular O<sub>2</sub> beam to calculate the dissociation rate. Preliminary analysis of the data indicates that dissociation of methane is more active on smaller Pd particles. We will look at the dissociation rates for the larger hydrocarbon molecules at various beam energies and for several Pd particle sizes. By studying the larger hydrocarbon molecules, we hope to gain more information about the ability of the Pd particles to break the C-H bonds in these molecules, which is a critical step in the dissociative adsorption of the molecules and in the combustion of methane.

Complementary non-contact atomic force microscopy (NC-AFM) measurements, which will be conducted at the UW will yield information about the morphology and number density of the Pd nanoclusters as a function of deposition temperature and coverage, under the same conditions as the TPD experiments conducted at PNNL. Together these measurements will allow a greater understanding of the catalytic activity

of this important combustion catalyst, and particle size effects in hydrocarbon catalysis in general.

### Publications, Presentations and Proposals:

“Adsorption energies of small alkane molecules on MgO (100) by temperature programmed desorption.” S. L. Tait, Jr., Z. Dohnálek, B. D. Kay, C. T. Campbell, AVS 50<sup>th</sup> International Symposium, Baltimore, Maryland, November 2003.

“Adsorption energies of small alkane molecules on MgO (100) by molecular beams and temperature programmed desorption.” S. L. Tait, Jr., Z. Dohnálek, B. D. Kay, C. T. Campbell (in preparation).

“Dissociative adsorption of CH<sub>4</sub> on MgO-supported Pd particles.” S. L. Tait, Jr., Z. Dohnálek, B. D. Kay, C. T. Campbell (in preparation).

### Funding that has resulted from this research:

None so far.

### Figures:

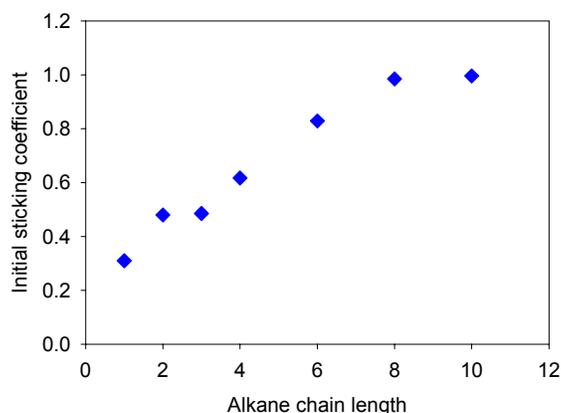


Figure 1. Initial sticking coefficient on MgO(100) versus alkane chain length for small alkane molecules (1 methane, 2 ethane, 3 propane, 4 butane, 6 hexane, 8 octane, 10 decane).

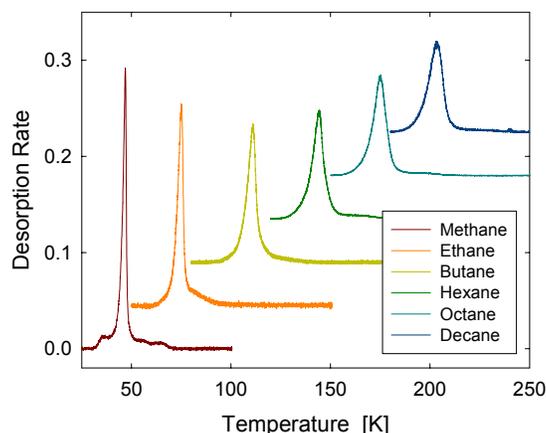


Figure 2. Temperature programmed desorption of small alkane molecules from MgO. Initial coverage of each molecule was about 1.0 ML.