

# Highly Selective Size-Selected Nanocatalysts:

## I. Oxidative Dehydrogenation of Propane by Pt<sub>8-10</sub> Clusters Supported on Mesoporous Anodized Aluminum Oxide Membranes and

## II. Oxidation of Alkenes on Size-Selected Silver and Gold Clusters and Nanoparticles Supported on Amorphous Alumina Films

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### Introduction

The exceptional performance of nanocatalysts has motivated intense research and many of highly dispersed nanocatalysts are widely used in commercial applications. In addition to nm size particles, surface chemistry studies on supported atomic clusters demonstrated an extraordinary and atom-by-atom tunable catalytic activity of size-selected clusters supported on single-crystal oxide surfaces. The objective of this work is to achieve high catalytic activity and selectivity in oxidative reactions by using highly monodisperse sub-nm size atomic metal clusters, as well as few nm size particles. The applied combination of techniques allows for ultimate control of both: surface composition, as well as catalytic particle size and composition – prerequisites in producing highly uniform active sites on technologically relevant supports<sup>1-4</sup>.

### Materials and Methods

**Support preparation.** Sintering of catalysts under reaction conditions can lead to the loss of highly size-dependent catalytic activity and selectivity. Our earlier studies on various oxide films showed, that small Pt and Au clusters are exceptionally stable on thin alumina films fabricated by atomic layer deposition (ALD)<sup>5-6</sup>. These films were selected to pre-coat the AAO membranes and flat silicon wafers prior to cluster and nanoparticle deposition. Using ALD, the diameter of the membrane pores was reduced to 10 nm.

**Catalyst deposition.** Size-selected metal clusters and nanoparticles were produced for deposition in a continuous laser vaporization<sup>5</sup> and an arc cluster ion source (ACIS)<sup>7</sup>.

**Pt<sub>8-10</sub>/Al<sub>2</sub>O<sub>3</sub>/AAO and Pt<sub>8-10</sub>/SnO/Al<sub>2</sub>O<sub>3</sub>/AAO Catalyst Tests.** The tests were performed under atmospheric pressure in a freestanding AAO flow reactor.

**Ag and Au Catalyst Tests.** The performance of the catalysts was tested in a unique setup at the Advanced Photon Source which, at atmospheric pressure, allows for simultaneous mass-analysis and *in situ* acquisition of grazing incidence small angle X-ray scattering (GISAXS) images. for a direct correlation of catalytic performance to particle size and shape.

### Results and Discussion

**ODH of Propane on Pt<sub>8-10</sub>/Al<sub>2</sub>O<sub>3</sub>/AAO and Pt<sub>8-10</sub>/SnO/Al<sub>2</sub>O<sub>3</sub>/AAO Catalysts.** Conversion rates of propane up to 95% and selectivity towards propylene up to 85% were

observed, depending temperature, presence of SnO promoter and location of the clusters in the membranes. The superb selectivity (only one single or maximal two side-products) can be explained by very short contact times on highly uniform dispersed catalytic particles. Catalytic performance did not change even after lengthy heat treatment, thus indicating highly stable nanocatalysts. The observed turn-over frequencies are by up to 2 orders of magnitude higher than those obtained on our reference vanadia based catalysts, as well as VOx and Pt-based catalysts reported in the literature.

**Oxidation of Ethylene and Propylene on Au and Ag Nanocatalysts.** Onset of product formation was observed between 160-200 °C. During the reaction, the smallest silver particles grew to about 3 nm size aggregates of extremely narrow size distribution, while gold clusters stabilized with a protective alumina overcoat (Figure 2) retained their size during the 7 hours long test. Evolution of activity with size and shape of size selected silver nanoparticles (between 1 and 15 nm) will be discussed, along with the observed changes in the alumina overcoat film structure.

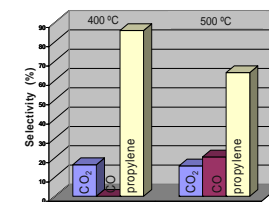
### Significance

In summary, highly uniform metal cluster based nanocatalysts were synthesized. The results clearly demonstrate that by employing spatially localized highly dispersed ultra-small Pt particles on high-surface area supports can lead to affordable new noble-metal based catalysts for highly efficient and very economic propene production, including considerably simplified separation of the olefin produced. Ag and Au clusters of optimal sizes and shapes can serve as models for oxidation catalysts of alkenes. In conclusion, model nanocatalysts systems made of size-selected particles supported on technologically relevant supports hold a great promise to enhance progress toward the oriented design and application of specific new nanocatalysts.

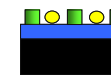
The work at Argonne National Laboratory was supported by the US Department of Energy, BES Contract DE-AC-02-06CH11357 with UChicago Argonne, LLC, Operator of Argonne National Laboratory.

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**Figure 1.** Selectivity of the Pt<sub>8-10</sub>/SnO/Al<sub>2</sub>O<sub>3</sub>/AAO catalysts with Pt clusters on the exit of the membrane reactor.



**Figure 2.** Schematic of the ~2ML selective protective alumina overcoat around supported gold clusters