

Highly Selective Oxidative Dehydrogenation of Propane on Sub-Nanometer Platinum Clusters

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Introduction

In addition to studies of nm size particles, surface chemistry studies on supported atomic clusters demonstrated an extraordinary and often an atom-by-atom tunable catalytic activity of size-preselected clusters supported on single-crystal oxide surfaces. The objective of this work was to identify new catalyst composition for highly activity and selective oxidative dehydrogenation of propane by using highly monodisperse sub-nm size atomic platinum clusters. The applied combination of synthesis 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 supports¹⁻⁴.

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 clusters are exceptionally stable on thin alumina films fabricated by atomic layer deposition (ALD)⁵ These films were used to precoat the anodized aluminum oxide (AAO) membranes prior Pt-cluster deposition as well as to deposit the tin-oxide promoter after Pt-cluster deposition.

Production of narrow cluster size distributions: The clusters were produced in a continuous beam laser vaporization cluster source.^{6,7} A narrow distribution of Pt₈₋₁₀ cluster sizes was preselected isolated utilizing a quadrupole deflector operated in energy filter mode and the clusters soft-landed on one site of the AAO membranes.

Catalyst Tests: The tests of Pt₈₋₁₀/Al₂O₃/AAO and Pt₈₋₁₀/SnO/Al₂O₃/AAO were performed under atmospheric pressure in a freestanding AAO (FAAO) flow reactor at temperatures reaching 550 °C and the products formed were analyzed by on-line gas chromatography.

Results and Discussion

Selectivity towards propylene up to 85% was observed, depending temperature, presence of SnO promoter and location of the clusters in the membranes. 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 VO_x and Pt-based ODH catalysts reported in the literature. The high selectivity (only one or maximum two side-products CO, CO₂) and high activity can be explained by the very low activation energy found in experiment and in theoretical

calculations for the activation of the C-H bond on the Pt clusters.⁸ Catalytic performance did not change during the heat treatment, thus indicating highly stable Pt clusters.

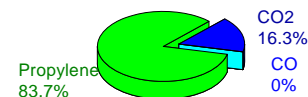


Figure 1. Selectivity of the Pt₈₋₁₀/SnO/Al₂O₃/AAO catalysts at 400 °C with Pt clusters on the exit of the membrane reactor.

Significance

In summary, highly uniform size-preselected cluster based nanocatalysts were synthesized and their performance tested under realistic reaction conditions. To our knowledge, the work reported here is the first investigation of size-preselected Pt clusters under realistic high temperature catalytic conditions. It has revealed a very high activity of subnanometer Pt-cluster based catalysts for the oxidative dehydrogenation of propane to propylene. Combined with quantum chemical studies, this work has shown that the high activity is due to the under-coordination of the Pt in the clusters and that the clusters favor the scission of C-H bonds relative to C-C or C=C bonds. Some recent work in our laboratory demonstrates that small gold clusters (Au₆₋₁₀) are highly active for propene epoxidation; thus providing further evidence for the unique catalytic properties of sub-nanometer clusters.⁹ In the future, size-selected clusters stabilized on appropriate supports with uniform surface chemistry hold great promise for design of new catalytic materials with highly bond-selective chemistry. While it will be a challenging task to scale up the production of size-selected clusters by more conventional chemical methods, but there are very encouraging efforts suggesting that this will ultimately be possible.¹⁰

The work at Argonne National Laboratory was supported by the US Department of Energy, BES-Chemical Sciences, BES-Materials Sciences, and BES-Scientific User Facilities under Contract DE-AC-02-06CH11357 with UChicago Argonne, LLC, Operator of Argonne National Laboratory. S.V. gratefully acknowledges the support by the Air Force Office of Scientific Research.

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