

## High temperatures sublimation and sintering in nanoparticle catalysts

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### Introduction

While sintering or Ostwald ripening is a commonly considered effect in the reduction of catalyst activity at higher temperatures, sublimation is a less obvious deactivation mechanism. This is particularly so for catalysts like platinum which have extremely low vapor pressures in the bulk form. However, at the elevated temperatures required for processes like the hydrogen producing sulfur-iodine thermochemical cycle (e.g., 850 °C), the nanoparticle nature of supported catalysts results in non-bulk like phenomena including enhanced sublimation.

At elevated temperatures, the vapor pressure of small metal particles can be orders of magnitude higher than that of the bulk metal. While the effect of reduced dimensionality on the properties of nanoparticles, such as melting point and band gap, is well known, it has not commonly been applied to catalytic nanoparticles. At the temperatures required for the sulfur-iodine thermochemical cycle, Pt nanoparticles less than about 5 nm sublime orders of magnitude faster than expected based on bulk properties. Our work shows that the nanoparticle vapor pressures increase exponentially with the inverse of the particle diameter. This effect is not confined to Pt, but is found in other metal nanoparticles, most at substantially lower temperatures. Interestingly enough, the same sublimation enthalpy that governs the evaporation also controls sintering. The combined phenomena of sublimation and sintering can have a significant impact on catalyst deactivation.

### Computational Methods

We have studied the deactivation of supported Pt catalysts both experimentally (1) and theoretically (2). In our theoretical work, we have modeled the effect of both sublimation and sintering on the deactivation of supported Pt catalysts at 850 C. First principles, density functional theory calculations have been performed to determine the heat of vaporization of Pt atoms from nanoparticles, the adsorption energy of Pt atoms on a support (TiO<sub>2</sub>) substrate, and the diffusion activation energy for metal adatoms on the same. These results have been combined with the sintering formalism of Wynblatt and Gjostein (3) to form a combined sublimation-sintering model for this system that allows us to follow the evolution of the Pt nanoparticle size distribution as a function of time. This, in turn, gives the time dependence of the catalyst surface area which has a first order effect on the catalyst activity.

### Results and Discussion

Deactivation due to sublimation is strongly dependent upon the initial size distribution. This, in turn, is a function of the percentage of Pt in the catalyst, with lower concentrations resulting in larger relative sublimation losses. Specifically, for 1 % Pt on TiO<sub>2</sub>, we find that most of the loss of material due to sublimation is actually confined to relatively

short times. The increase in particle size due to sintering actually minimizes this sublimation loss over times on the order of a day or less.

However, the deactivation due to sintering continues over longer periods of time (e.g., days to months depending on the original conditions). The particle size distribution during sintering quickly loses its memory of the initial distribution and establishes a quasi-Gaussian distribution that gradually evolves to increasing mean particle size. This increase in size results in a decrease in the average surface to volume ratio of the particles with a corresponding loss in activity.

The interplay between sublimation and sintering is dependent on the nature of the support surface, the transition metal concentration, thermal history and reaction temperature. It can also be influenced by the chemistry of the reaction ambient.

### Significance

These deactivation mechanisms are extremely important for supported Pt metal catalysts at temperature near (and above) 850 °C, as proposed for the sulfur-iodine thermochemical cycle. In essence, they make the use of Pt catalysts for the thermochemical production of hydrogen extremely inefficient and uneconomical. These processes can occur in other high temperature applications as well, and are not limited to Pt. In fact, other less refractory metals will suffer from these phenomena at proportionally lower temperatures. (Conversely, metals with larger sublimation enthalpies, such as Ir, should be stable over significantly longer times and higher temperatures.)

Beyond the potential industrial significance of these effects, their behavior is also of fundamental interest. While sintering has long been studied as an aspect of nanoparticles, their vapor pressure has been essentially ignored despite the general acceptance of related phenomena attributable to reduced dimensionality. Further, an understanding of the interaction between sublimation and sintering opens up new insights into the dynamics of nanomaterials at elevated temperatures.

### References

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