

# Catalyst Sintering Kinetics and its Effect on Particle Size Distributions, with Examples for Gold Supported on TiO<sub>2</sub>

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## Introduction

Sintering is a major mode of deactivation for many catalysts, especially for late transition metal particles dispersed on oxides or other supports. These catalysts sinter or ripen with time on-stream, starting from a collection of many small, highly dispersed particles and eventually converting to their thermodynamically-preferred state: fewer, larger particles [1, 2]. Currently there is no reliable way to predict the sintering kinetics, so any newly-developed catalyst must be tested for the total duration of its required lifetime, often on the order of one year. Development of new catalyst materials could be accelerated if there were a kinetic model which could predict accurately long-term sintering based on short-term kinetic measurements.

We recently derived an improved kinetic model for sintering of supported metal nanoparticles [3]. It follows the pioneering model of Wynblatt and Gjostein (WJ) [1], but removes two assumptions that create dramatic errors in sintering rates for particles smaller than 6 nm in diameter, including: (1) use of the Gibbs-Thomson (GT) relation assuming that the surface free energy of metal particles is independent of size, and (2) neglect of all but the first-order terms in a Taylor series expansion. Recent microcalorimetry measurements have shown these assumptions to be untrue in that metal particles smaller than 6 nm have much higher surface free energies than large particles. A modified bond-additivity (MBA) model more accurately reproduces particle energy versus size [4]. This estimate was incorporated into our new kinetic model. We showed that this model can accurately predict the measured sintering kinetics of Au particles on TiO<sub>2</sub> at different loadings [3]. Here we use this model to predict sintering after long times.

## Materials and Methods

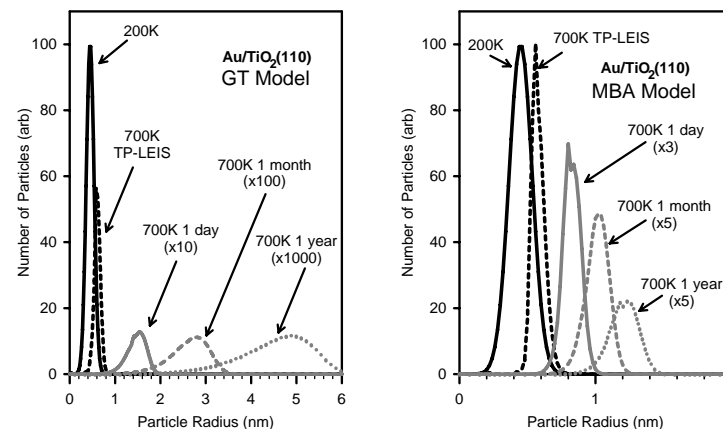
The experimental methods for preparing the Au on TiO<sub>2</sub>(110) model catalyst and monitoring its sintering kinetics in ultrahigh vacuum are described in detail elsewhere [3].

## Results and Discussion

We numerically simulated the kinetic model for sintering via the Ostwald ripening mechanism with interface control, derived in [3]. This model is based on an atomistic mechanism, and many of the kinetic parameters were already known. Those that remained were collected into a single energy parameter and prefactor. Earlier, we applied this method to simulate new experimental measurements of the sintering of gold nanoparticles supported on TiO<sub>2</sub>(110). By fitting the experimental kinetics on several different gold loadings at temperatures from 200 to 700 K, we determined these kinetic parameters [3].

Using these best-fit parameters determined from short-term kinetics, we have extended this kinetic model to make predictions regarding the long-term sintering kinetics of this catalyst under the isothermal conditions of real catalysis, as shown in Fig. 1. The new

model predicts much slower long-term sintering and much narrower particle size distributions than the same model using instead the GT relation to estimate particle energy versus size.



**Figure 1.** A comparison of the predicted sintering kinetics for Au particles on TiO<sub>2</sub>(110) based on modeling the size dependence of the particle energy with the GT relation (left) and the new MBA model (right). The parameters in both models were determined by fitting to experimental temperature-programmed low-energy ion scattering (TP-LEIS) measurements of the initial sintering while the as-deposited Au particles were heated from 200 K to 700 K at 1K/s [3].

## Significance

The resulting size distributions show that there are serious problems with a classic method for determining the sintering mechanism based on the shape of the particle size distribution, which claims that the distribution is log-normal (i.e., has a sharp leading edge and a long tail to larger sizes) if the sintering occurs by particle diffusion / coalescence whereas it has a long tail to small sizes and a sharp trailing edge when sintering occurs by Ostwald ripening [5]. This is not seen in the MBA model of Fig. 1.

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## References

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