

# Elucidating Mechanisms that Control Metal Sintering

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## Introduction

The sintering of metal particles is responsible for catalyst deactivation and the loss of catalyst lifetime for a wide range of different metal-catalyzed reactions. Despite its importance, sintering is not very understood. Theory is combined with well-defined experimental studies herein to examine the migration of Ag clusters over model  $\alpha$ - $\text{Al}_2\text{O}_3$  surfaces in order to elucidate the fundamental factors and the mechanisms that control sintering. Experimental results which follow particle growth rate indicate that Ostwald Ripening dominates over particle coalescence. The mechanism for Ostwald ripening is proposed to proceed through the detachment of small mobile Ag complexes which diffuse across the alumina surface and subsequently reattach to larger supported metal particles. First principle density functional theoretical calculations were used together with kinetic Monte Carlo simulations to model each of these steps in detail and examine the influence of the parent Ag particle size, the size and the nature of the  $\text{Ag}_x$ -Y mobile species which detaches from the particle and diffuses along the surface, and the influence of the oxide support.

## Methods

Nonlocal gradient corrected plane wave density functional theoretical methods were used to calculate the adsorption energies as well as the activation energies for metal atoms and metal clusters to detach from the parent metal particle, diffuse along the oxide support and as reattach to larger particles. The results for different size Ag clusters were used to help construct an ab initio based kinetic Monte Carlo simulation which was subsequently used to analyze the rates of Ag diffusion and particle growth on the oxide support.

## Results and Discussion

The adsorption and diffusion of Ag on the alumina support was found to be highly sensitive to the termination of the  $\alpha$ - $\text{Al}_2\text{O}_3$  surface. Silver cluster binding energies on the Al-terminated surface were found to be rather weak thus resulting in very low diffusion barriers. Locally reduced aluminum sites on the carrier surface were found to enhance the mobility of Ag. The binding energies for different Ag clusters on the oxygen-terminated surface were all found to be much stronger than those on the Al-terminated surfaces which resulted in significantly higher activation barriers for diffusion. The diffusion on such surfaces would be quite limited. [1] While the Al- and O-terminated surfaces provide valuable information, ab initio thermodynamic calculations indicate that a more realistic model of the surface under reaction conditions is one that is hydroxylated. Full and partial hydroxylated alumina surfaces were found to be thermodynamically favored at higher partial pressures of water.[1-2] Partial hydroxylation increases the interaction between Ag and support which increases the barrier for Ag diffusion as compared to the Al-terminated surface. This is consistent previous

experiments of Kelber and co-workers for a similar system for the diffusion Cu particles on  $\alpha$ - $\text{Al}_2\text{O}_3$ (0001). [3] The mobile Ag precursors are likely Ag adatoms or small Ag clusters. The simulated diffusion coefficients for different Ag clusters on  $\alpha$ - $\text{Al}_2\text{O}_3$  surface are given in Fig. 1

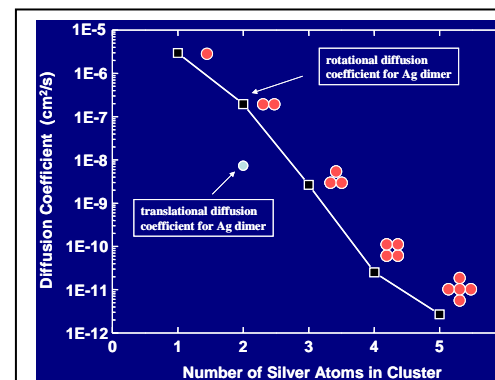
The activation barriers for the detachment of small mobile Ag complexes from larger Ag particles were found to be higher than those for surface diffusion thus indicating the detachment of Ag controls the rate of reaction. For example, the detachment of  $\text{Ag}_1$  from a  $\text{Ag}_{22}$  complex on  $\alpha$ - $\text{Al}_2\text{O}_3$  is shown in Fig. 2. The calculated barriers for detachment were found to be directly correlated with the coordination number of the metal atoms which it detaches. Smaller Ag clusters were found to show unique electronic structures which dictate their adsorption and diffusion over the  $\alpha$ - $\text{Al}_2\text{O}_3$  (0001) surface. The presence of oxygen, hydroxyl and chlorine intermediates to the mobile Ag fragments were found to enhance their detachment from the parent Ag cluster as well as their diffusion along the oxide support. The activation barriers for the diffusion of  $\text{Ag}_1$ - $\text{Ag}_3$  complexes were found to decrease in the following order  $\text{Ag-Ag} > \text{Ag-OH} > \text{Ag-Cl}$ .

## Significance

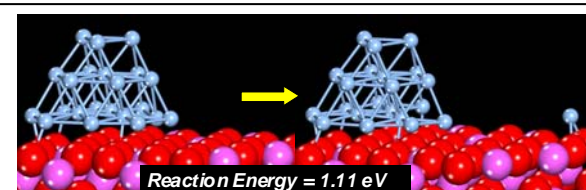
The work provides insights into the fundamental factors that control sintering which play a critical role in catalyst deactivation.

## References

1. Meyer, R., et al. *Chem. Phys. Lett.*, 449, 155-159 (2007).
2. Ge, Q., Meyer, R., Lockmeyer, J., Yeates, R., Lemanski, M. Reinalda, D. and Neurock, M. *Surf. Sci.*, 601, 134-145, 2007.
3. J. A. Kelber, C. Y. Niu, K. Shepherd, D. R. Jennison, and A. Bogicevic, *Surf Sci*, **446** (2000) 76.



**Figure 1.** Diffusion coefficients derived from ab initio based kinetic Monte Carlo simulations for different Ag clusters over  $\alpha$ - $\text{Al}_2\text{O}_3$  surface.



**Figure 2.** DFT calculated energy for the detachment of  $\text{Ag}_1$  from a  $\text{Ag}_{22}$  complex bound to the  $\alpha$ - $\text{Al}_2\text{O}_3$ (0001) surface.