

Adsorption and Reaction of $\text{Rh}(\text{CO})_2(\text{acac})$ on $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(111)$

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Introduction

Organometallic precursors have been used to create supported cluster catalysts with unique reactivity. Through careful experimentation, it has been shown that precursors such as $\text{Rh}(\text{CO})_2(\text{acac})$ (acac is acetylacetonate) can be decarbonylated by heating in helium (or H_2), and intact metal cluster catalysts can be created. One of the key advantages of this method for synthesizing clusters is the precise degree of size control available while using a method that lends itself to high-surface-area supports. Although not every metal at every cluster size is possible, these metal carbonyl precursors can also be used to generate larger clusters (containing tens of atoms) by heating in hydrogen to induce mild sintering. Gates *et al.* have shown in a number of instances the size dependent reaction behavior exhibited by supported metal clusters created from organometallic precursors [1]. There is significant evidence that hydroxyl groups play an important role in the synthesis and activation of these clusters. However, the interaction of these precursors with supports is currently still largely unknown.

Materials and Methods

Thin Al_2O_3 films were grown on the $\text{Ni}_3\text{Al}(111)$ single crystal by exposure to 10^{-7} mbar at 1000 K for 5 min. The $\text{Rh}(\text{CO})_2(\text{acac})$ precursor was then dosed onto the thin film at room temperature by gently heating the precursor to obtain sufficient vapor pressure for dosing. All scanning tunneling microscopy images were taken at room temperature. Density functional theory based calculations were performed using the program VASP[2] with a plane wave basis set and ultrasoft pseudopotentials with periodic supercells.

Results and Discussion

Currently STM studies confirm that we can dose the $\text{Rh}(\text{CO})_2(\text{acac})$ precursor in vacuum and image it effectively. Figure 2 shows an STM image of the rhodium dicarbonyl acac on a thin alumina film grown on the $\text{Ni}_3\text{Al}(111)$ single crystal. This film is known to possess a periodic structure which gives rise to preferential nucleation points when metal clusters are deposited on the film [3]. After heating the substrate to 473 K in vacuum, the precursor still retains its size and shape. However, after heating to 573 K, the surface shows the presence of features in the size range of 2 nm in diameter (6 Å in height). Images also indicate some clustering of the precursor at step edges.

Density functional theory calculations have been performed in an effort to understand both the nucleation process and to examine the effect of hydroxyl groups on the chemistry of the supported organometallic precursor [4]. We have found that the ability of the

cluster to be hydrogenated by surface hydroxyls varies greatly depending upon the identity of the support. On zeolite substrates, reverse hydrogen spillover is a highly exothermic process (-1.2 eV/H atom on LTA for example). However, on other substrates such as $\alpha\text{-Al}_2\text{O}_3(0001)$, this process is thermoneutral. Therefore, in order to activate the organometallic, it may be necessary to support the organometallic on substrates which can readily donate protons.

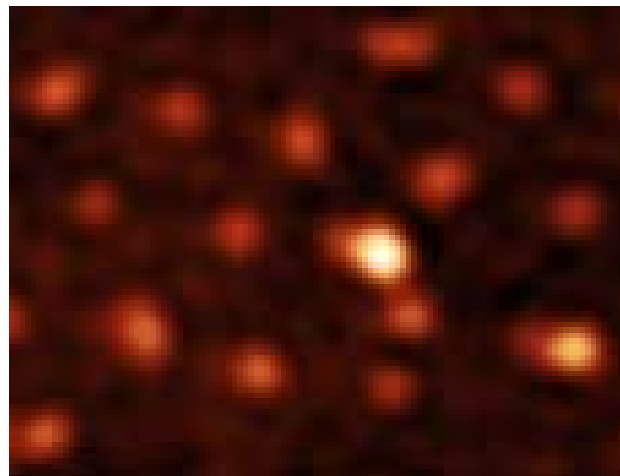


Figure 1. STM image of $\text{Rh}(\text{CO})_2(\text{acac})$ deposited at room temperature on $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(111)$ ($150 \times 200 \text{ Å}^2$). Notice that Rh species adsorbs at well defined points on the film that are nearly equally spaced by 4 nm.

Significance

Surface science studies of organometallic precursors on model supports are critical to an understanding of how to synthesize clusters on the order of 10 atoms, paving the way toward a new class of catalytic materials. We have demonstrated that we can follow the decomposition and sintering process of Rh carbonyl acac on a model alumina support using scanning tunneling microscopy. Calculations aid in improving our understanding of the support dependent chemistry of these clusters. Through this work, we hope to expand the use of organometallic surface chemistry for the preparation of supported metal clusters with unique activity and selectivity.

References

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