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Synthesis and characterization of rhodium nanoclusters on $TiO_2(110)$ surface using organometallic compounds

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ABSTRACT

The adsorption of hexarhodium hexadecylcarbonyl ($[Rh_6(CO)_{16}]$) and rhodium dicarbonyl acetylacetonate ($[Rh(CO)_2(acac)]$) and the nucleation of Rh nanoclusters on $TiO_2(110)$ single crystal substrate were examined using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. When $[Rh_6(CO)_{16}]$ was deposited on the $TiO_2(110)$ surface at 323 K, aggregated particles with wide size distribution were formed, which resulted in Rh_6 frame destruction and rhodium aggregation after decarbonylation. In contrast, deposition of $[Rh(CO)_2(acac)]$ at 373 K in presence of CO at 10^{-7} mbar resulted in formation of site-isolated multinuclear organometallic species ($[Rh_x(CO)_y]$) with narrow size distribution, which showed minimal perturbation to $[Rh_6(CO)_{16}]$ structure and led to formation of uniform nanoparticles after decarbonylation. Subsequent annealing showed that $[Rh_x(CO)_y]$ species deposited on the surface from $[Rh_6(CO)_{16}]$ precursor formed large agglomerated particles with wide size distribution upon annealing to 573 K while $[Rh_x(CO)_y]$ prepared through surface synthesis of $[Rh(CO)_2(acac)]$ on $TiO_2(110)$ surface following CO exposure at 373 K resulted in clusters that were relatively stable up to 573 K and only underwent agglomeration beyond this temperature.

1. Introduction

Industrial heterogeneous catalysts are quite complex and highly non-uniform materials; hence, their investigation at the atomic level faces great challenges. However, such atomic level analyses are essential to understand the structural—reactivity relationship of the catalyst, as this paves the way to catalyst optimization. One way to overcome this limitation relies on the creation of well-defined model catalysts with significantly reduced heterogeneity [1]. Model catalysts consisting of metal particles supported on a thin film or single crystal metal oxide substrate were examined extensively for several decades by the surface science community, e.g., Henry [2], Campbell [3], Freund [4], Street et al. [5]., Heiz and Schneider [6]. The advantage of such models is that they provide access to the atomic level studies. Although significant progress in the understanding of catalysis has been made through such studies, these model catalysts are generally prepared by physical vapor deposition of metals, which is not a scalable synthesis method.

Alternatively, small metal clusters were synthesized on support surfaces from organometallic precursors [7–13]. Since the 1970 s, ligated metal complexes (typically metal carbonyls) including $[Rh_6(CO)_{16}]$ [14] and $[Rh(CO)_2(acac)]$ [15,16] were used to create small metal clusters with narrow size distribution and unique reactivity [17–20]. This synthesizing method provides accurate control over the cluster size and can be used to create small supported clusters.

Formation of supported metal clusters containing about 10 atoms or less via organometallic precursors give us a potentially exciting opportunity for new class of nanocatalysts [21]. However, the routes to synthesize these clusters are not well understood on a molecular level. Many researchers undertook surface science approaches to examine controlled cluster synthesis via organometallic precursors. For example, Purnell et al. studied the adsorption, reaction and decarbonylation of $[Re_2(CO)_{10}]$ and $[HRe(CO)_5]$ on ultrathin MgO(111)/Mo(110) [19,20], Lei et al. examined the deposition of $[Rh(CO)_2(acac)]$ on $Al_2O_3/Ni_3Al(111)$ [22], Khosravian et al. investigated the adsorption of $[Rh(CO)_2(acac)]$ and nucleation of rhodium nanoclusters on $TiO_2(110)$ surface [15]. As hydroxyl groups are necessary for decarbonylation and cluster assembly, Prunell et al. did not create metallic clusters with desired size range of 1–10 atoms in their work due to the absence of hydroxyl groups on MgO(111)/Mo(110) [19,20]. Similarly, Lei et al. did not produce small metal clusters in the size range of 1–10 atoms as $Al_2O_3/Ni_3Al(111)$ surface may not be hydroxylated under ultrahigh vacuum (UHV) condition. In the same context, Khosravian et al. performed decarbonylation on $TiO_2(110)$ surface, which could be hydroxylated under the experimental condition, and they created small metal clusters with diameters of 1.0–2.5 nm and a height of 0.1–0.3 nm (i.e., monolayer height). However, they did not show whether a multinuclear organometallic precursor can be used to create small uniform rhodium nanocluster on the hydroxylated rutile $TiO_2(110)$ surface. In another study, Lei et al investigated the formation of palladium nanoparticles

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on $TiO_2(110)$ from [Pd(hfac)$_2$] but they did not observe any preferential nucleation site on $TiO_2(110)$ surface for this precursor [23].

To investigate the formation of site-isolated Rh_6 on titania powder from a multinuclear organometallic compound, Goellner and Gates used [Rh(CO)$_2$(acac)] and [$Rh_6(CO)_{16}$] as their mononuclear and multinuclear organometallic precursors [18]. They characterized the cluster preparation and its subsequent decarbonylation on titania powder through a combination of EXAFS (extended X-ray absorption fine structure) and DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy). They have shown that deposition from a solution of [$Rh_6(CO)_{16}$] leads to formation of aggregated particles, which consequently resulted in the destruction of Rh_6 frame and rhodium aggregation after decarbonylation [18]. However, they showed that site-isolated [$Rh_6(CO)_{16}$] clusters could be generated in situ from [Rh(CO)$_2$(acac)] on P25 TiO_2 after exposure to CO at 373 K [18]. Once site-isolated [$Rh_6(CO)_{16}$] species were formed, further exposure of the catalyst to H_2 at 373 K resulted in complete deligation and formation of [Rh_6H_x] clusters. By using EXAFS spectroscopy, Goellner and Gates confirmed that the first shell Rh–Rh coordination number is 4.4 ± 0.4, which is consistent with octahedral Rh_6 [18]. Although these results enhance our understanding of chemistry of the cluster formation on supports, the molecular level mechanisms by which the clusters are created, the exact nucleation sites on the support and the effects of nonuniformity of the powder support remained unknown.

In our earlier work, we established the conditions to form small rhodium nanoparticles from [Rh(CO)$_2$(acac)] and we showed that rhodium nanoclusters with narrow size distribution can be fabricated on the $TiO_2(110)$ surface under mild condition [15]. Using DFT calculation, we also showed that formation of multinuclear organometallic compound (i.e. [$Rh_6(CO)_{12}$]) is a thermodynamically favorable phenomenon on the hydroxylated rutile surface [15]. However, our primary focus was on the mononuclear organometallic compound, [Rh(CO)$_2$(acac)], and how it can be used as a building block to create rhodium metal nanoclusters on the $TiO_2(110)$ surface and we did not identify the formation of rhodium clusters via a multinuclear organometallic precursor. Such knowledge is critical to ensure accurate control over the cluster size and to enhance our ability in creating small supported clusters.

Accordingly, in the present work, scanning tunneling microscopy (STM) and density functional theory (DFT) calculations were used to investigate the adsorption of [$Rh_6(CO)_{16}$] precursor on $TiO_2(110)$ surface. [$Rh_6(CO)_{16}$] was chosen because the adsorption and preparation of this compound on other supports was already established [24,25]. In this work, the conditions to prepare this multinuclear organometallic precursor by two different methods are studied: (1) by using a mononuclear, [Rh(CO)$_2$(acac)], organometallic precursor; (2) through chemical vapor deposition of a multinuclear, [$Rh_6(CO)_{16}$], organometallic precursor. The adsorption of [$Rh_x(CO)_y$] (i.e., CO covered Rh nanoparticles) on planar substrate rutile $TiO_2(110)$ and the nucleation of rhodium metal clusters after decarbonylation under mild conditions on $TiO_2(110)$ substrate are examined. Finally, the stability of created [$Rh_x(CO)_y$] species on $TiO_2(110)$ surface under temperatures up to 573 K is reported.

2. Experimental section

All experiments were carried out in a system under ultrahigh vacuum (UHV) condition. The base pressure of the UHV chamber was approximately about 1×10^{-10} mbar and it was equipped with a Variable Temperature Scanning Tunneling Microscope (VT-STM, Omicron) chamber, and a separate preparation chamber, which includes an ion sputter gun for sample cleaning, a LEED (Low Energy Electron Diffraction) system, and a directional gas doser.

The rutile $TiO_2(110)$ single crystal (PKEM) utilized in this study was polished on both sides and it was mounted on a standard tantalum plate from Omicron with an 8-mm hole on its back side to facilitate electron bombardment heating. The cleaning process of rutile $TiO_2(110)$ surface and the deposition of rhodium(I) dicarbonylacetylacetonate, [Rh(CO)$_2$(acac)], (Strem, 99%) was explained in more detail elsewhere [15]. This study utilized the following two procedures to form [$Rh_x(CO)_y$] on rutile $TiO_2(110)$ surface:

Procedure 1: [Rh(CO)$_2$(acac)] was deposited on rutile $TiO_2(110)$ single crystal at a coverage of $4.0 \times 10^{11}/cm^2$ by using a homemade organic compound doser. Organic compounds were vaporized and delivered to preparation chamber via a leak valve and a directional gas doser, which contained a stainless-steel tube with a 1 cm inner diameter. To enhance the dosing efficiency with the least amount of background exposure, the distance between the opening of the stainless-steel tube and the sample surface was set to 1 mm. After deposition process, the sample was exposed to 3.3×10^{-7} mbar of CO at 373 K for 10 min. The process aimed at synthesizing the multi nuclear organometallic compound, [$Rh_x(CO)_y$], from mononuclear precursor, [Rh(CO)$_2$(acac)], following the approach presented by Goellner and Gates [18].

Procedure 2: [$Rh_6(CO)_{16}$] was deposited on rutile $TiO_2(110)$ single crystal at room temperature by means of chemical vapor deposition using the same organic compound doser described above. Having low vapor pressure at room temperature, [$Rh_6(CO)_{16}$] powder (Strem) was heated slowly up to 323 K over the course of 20 min to transfer adequate quantity of it into the vapor phase.

All STM images were collected at room temperature by using electrochemically etched W homemade tips with a sample bias of 1 V and a constant tunneling current of 0.1 nA. All the post annealing images were generally acquired 2 h after the experiment so that the sample had returned to room temperature. To ensure that the images shown here are consistent across the crystal face, for any given surface condition, images were collected at multiple locations (usually 4 or 5) on the surface. Particle size distributions were based on images of 200 nm × 200 nm. Heights and diameters were measured by using the WSxM 5.0 software [26] via line scans of each particle in the image. In many cases the particles were not perfectly hemispherical; therefore, the heights and diameters were chosen based upon the largest height and diameter measured. Features below 0.5 nm in diameter and below 0.1 nm in height were excluded.

3. Results and discussion

Controlled synthesis of rhodium nanoparticles from [Rh(CO)$_2$(acac)] was established in our earlier study [15]. Following the same approach, [Rh(CO)$_2$(acac)] was first deposited on the rutile $TiO_2(110)$ surface under UHV condition and characterized with STM to confirm the agreement with previous published data [15]. To study the assembly of site isolated Rh_6 nanoclusters on rutile $TiO_2(110)$ surface and to confirm the necessity of using mononuclear species to generate deligated metal clusters on this surface, two synthesis methods described in experimental section were undertaken to generate multinuclear metal complex, [$Rh_x(CO)_y$], in situ. The characterization of produced multinuclear metal complexes from these two methods, their size distribution after decarbonylation, and their thermal stability are compared.

3.1. Synthesis and characterization of [$Rh_x(CO)_y$]/$TiO_2(110)$

Goellner and Gates used Infrared spectroscopy and EXAFS spectroscopy to study the deposition of [$Rh_6(CO)_{16}$] from solution on TiO_2 powder (calcined at 200 or 400 °C) [18]. They showed that the only cluster-support interaction for these samples are through short Rh–O bonds. They also reported that [$Rh_6(CO)_{16}$] aggregated and formed three-dimensional aggregates on $TiO_{2,400}$ and raft-like aggregates on $TiO_{2,200}$ [18]. In this study, the chemistry of [$Rh_x(CO)_y$] formation on a well-characterized $TiO_2(110)$ single crystal substrate was investigated by imaging the surface species using STM to gain understanding of the molecular level cluster formation. It was found that deposition of [$Rh_6(CO)_{16}$] on a well-characterized planar substrate (rutile $TiO_2(110)$) gave disc-type aggregates. In contrast, site-isolated [$Rh_x(CO)_y$] particles