Mechanistic Studies of Palladium(II) hexafluoroacetylacetonate Reactions on TiO$_2$(110) and Preparation of Palladium Nanoparticles by Atomic Layer Deposition

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Introduction
Atomic layer deposition (ALD) recently attracted significant attention due to potential applications in catalysis, semiconductors and photocatalysis. ALD is a self-limiting process for the deposition of thin films by sequential exposures to gaseous precursors. It also can be used to deposit isolated metal nanoparticles on different oxide supports for heterogeneous catalysis applications.

We report here the decomposition pathways of palladium (II) hexafluoroacetylacetonate (Pd(hfac)$_2$) on the single crystal TiO$_2$(110) surface as elucidated by X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM).

Materials and Methods
Experiments were carried out in two separate ultra high vacuum (UHV) systems. Sample cleaning, precursor deposition and sample characterization by XPS were performed on the Omicron Multi-Technique Surface Analysis Cluster Tool. STM experiments were carried out on a custom-made SPM1000/AFM100 system (RHK Technology). Pd deposition was performed by exposure of a TiO$_2$(110) crystal to Pd(hfac)$_2$ (Aldrich, 99.9%) at room temperature. The hydrogenation of ethylene was used as a test reaction in a reaction cell attached to the SPM1000 system and the products analyzed by gas chromatography.

Results and Discussion

Based on XPS data, Pd(hfac)$_2$ dissociatively adsorbs on the TiO$_2$(110) surface at room temperature as one of the hfac ligands transfers to the titania surface. The adsorbed Pd(hfac)* species does not decompose up to 250°C. Metallic Pd was detected by XPS at 300°C and was accompanied by total decomposition of the hfac ligands. This was confirmed by the disappearance of the C1s peak at 292.0 eV and the F1s peak at 688 eV which are the fingerprints of the hfac group. The resulting Pd coverage was 0.09 ML after the first deposition cycle at room temperature as estimated by XPS.

According to the STM data, the Pd(hfac)* species and the adsorbed hfac species form agglomerates with a narrow height distribution of 0.72±0.06 nm, diameter of 2.2±0.1 nm and coverage of 0.6 ML (Figure 1 (b)). The agglomerate height matches the reported value for the Pd (hfac) height, which consistent with a perpendicular orientation of Pd(hfac)* to the surface.

hfac fragments desorb from the surface at 600°C leaving on the surface Pd nanoparticles with average height of 1.45±0.07 nm and lateral diameter of 3.3±0.1 nm (Figure 1 (c)).

A cartoon of the Pd(hfac)$_2$ decomposition mechanism on the TiO$_2$(110) surface is shown in the top panel of Figure 1. The Pd(hfac)* species is assumed to bind to the surface in a bidentate fashion to the 5-fold coordinated Ti. The bridging oxygen atoms on TiO$_2$ surface are the basic sites which are favorable for absorption of the Pd(hfac)* species. This species and its fragments desorbed at 600°C in UHV. The Pd nanoparticles and carbon species remain on the surface. The residual carbon can be removed by O$_2$ DC plasma treatment following annealing at 600°C in UHV.

The hydrogenation of ethylene was performed on above sample at a total pressure of 760 Torr in the temperature range of 25 to 80°C. Apparent activation energy of 7.8±0.4 kcal/mol was observed for the Pd/TiO$_2$ sample, which is consistent with the observed activation energy for Pd foil of 8.7±0.7 kcal/mol.

Significance
Atomic layer deposition was used to prepare Pd nanoparticles with narrow size distribution on TiO$_2$(110). The reaction mechanism for Pd(hfac)$_2$, precursor decomposition was proposed.

![Schematic mechanism of the reaction of Pd(hfac)$_2$ with TiO$_2$ surface. STM images of Pd(hfac)$_2$/TiO$_2$(110): (a) clean TiO$_2$(110); (b) Pd nanoparticles on TiO$_2$ after deposition at room temperature; (c) Pd/TiO$_2$ after annealing to 600°C (75nm x75 nm, U$_i$=2.0 V, I$_t$=0.6 nA).](image-url)