Resolving Precursor Deligation, Surface Species Evolution, and Nanoparticle Nucleation during Palladium Atomic Layer Deposition

Yu Lei,† Junling Lu,† Haiyan Zhao,‡ Bin Liu,§ Ke-Bin Low,‖ Tianpin Wu,‡ Joseph A. Libera,‡ Jeffrey P. Greeley,‡ Peter J. Chupas,‡ Jeffrey T. Miller,§ and Jeffrey W. Elam*,⊥

†Energy Systems Division, Argonne National Laboratory, Lemont, Illinois 60439, United States
‡X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois 60439, United States
§Center for Nanoscale Materials, Argonne National Laboratory, Lemont, Illinois 60439, United States
‖Research Resources Center, University of Illinois at Chicago, Chicago, Illinois 60607, United States
¶School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, United States
#Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, Illinois 60439, United States

Supporting Information

ABSTRACT: The synthesis of highly dispersed palladium nanoparticles on TiO₂ surfaces from palladium hexafluoroacetylacetone (Pd(hfac)₂) was investigated using in situ infrared (IR) spectroscopy, in situ X-ray absorption spectroscopy (XAS), and in situ pair distribution function (PDF) measurements under practical atomic layer deposition conditions. Residual surface chlorine was found to directly participate in the transformation of organometallic compounds to nanoparticles. Deligation of the Pd(hfac)₂, evolution of the surface species, and nucleation of the Pd nanoparticles were precisely resolved. This knowledge can help direct the future design of advanced heterogeneous catalysts from organometallic compounds.

INTRODUCTION

Controlling the dispersion and structure of noble metal nanoparticles of uniform size has been critical to achieving efficient catalysts.¹⁻⁸ Atomic layer deposition (ALD) enables conformal coatings of thin films and highly dispersed nanoparticles on high aspect ratio surfaces under sequential, self-limiting surface reactions.⁹⁻¹⁴ ALD allows the nanoparticle size and composition to be controlled precisely by adjusting the number and sequence of ALD cycles. This unique feature is attractive for synthesizing heterogeneous catalysts comprised of highly dispersed catalytic materials on high surface area, mesoporous supports. By combining the ALD for metal oxides with noble metal ALD, it is possible to engineer nanocatalysts with unique structures and properties. As a result, ALD has emerged as a promising method to prepare advanced, nanostructured materials.²⁻⁷ The detailed evolution of the Pd surface species during the individual half-reactions, as well as the subsequent nucleation and growth of palladium nanoparticles, is still not clear.

Transformation of organometallics to supported precious metal nanoparticles has been intensively studied on both planar supports under ultrahigh-vacuum conditions²⁵⁻²⁸ and high surface area supports as heterogeneous catalysts.²⁹⁻³¹ The combination of in situ characterization techniques and density function theory (DFT) calculations provides a powerful means to determine the atomic arrangements in nanostructured materials and elucidate the surface reaction mechanisms.³²⁻³⁵ For instance, in situ Fourier transform infrared spectroscopy (FT-IR) is useful for identifying the surface species formed during each ALD half-reaction.³⁶⁻³⁷ X-ray absorption spectroscopy (XAS) allows one to probe the evolution of surface species under practical ALD operation conditions in real time.³⁸ It provides crucial information about nearest neighbors, bond distances, and coordination numbers. In addition to XAS, total scattering and pair distribution function (PDF) provide quantitative structural information on both short- and long-range order, making it a powerful tool to probe nanoparticle nucleation and growth.³⁹⁻⁴⁰ Here we combine in situ FT-IR,
XAS, and PDF along with DFT calculations to compose a detailed picture of Pd ALD on TiO$_2$.

**MATERIALS AND METHODS**

**ALD Pd/TiO$_2$/SiO$_2$ Synthesis.** The ALD samples for ex situ characterization were synthesized in a hot-walled viscostory flow reactor that has been described in detail elsewhere.$^{41}$ The high surface area support used in this work was Silicycle S10040 M silica gel with $\sim$100 m$^2$/g surface area. For each batch, 0.5 g of SiO$_2$ gel was used for TiO$_2$ ALD. The SiO$_2$ gel surface was modified using five ALD cycles of TiO$_2$ with a timing sequence (100$^\circ$C $\rightarrow$ 200$^\circ$C $\rightarrow$ 120$^\circ$C $\rightarrow$ 200$^\circ$C). The TiO$_2$ ALD used alternating exposures to TiCl$_4$ (Sigma-Aldrich, 99.9%) and deionized water at 150 $^\circ$C. Five TiCl$_4$–H$_2$O ALD cycles yielded $\sim$8 wt % TiO$_2$ over SiO$_2$. The thickness of TiO$_2$ is equivalent to $\sim$2 Å with density of 4.23 g/cm$^3$ and a growth rate of six cycles of TiCl$_4$ silica gel with surface area support used in this work was Silicycle S10040 M.

Pd ALD used alternating exposures to palladium hexafluoroacetylacetonate (Pd(hfac)$_2$, Sigma-Aldrich, 99.9%) and formalin (Sigma-Aldrich, HCHO 37 wt % in H$_2$O with methanol added to limit the formation of paraformaldehyde) at 200 $^\circ$C. Pd/TiO$_2$/SiO$_2$ catalysts were prepared using one Pd ALD cycle on the ALD TiO$_2$-coated SiO$_2$. For each preparation, 0.5 g of TiO$_2$/SiO$_2$ was used as support for Pd ALD (300$^\circ$C $\rightarrow$ 300$^\circ$C $\rightarrow$ 300$^\circ$C). The Pd loading after one Pd ALD cycle is typically about $\sim$1 wt %.

The 2 wt % Pd/SiO$_2$ samples were prepared to serve as a reference for the XAS measurements. The substrate used for this synthesis was Davisl silica gel (Sigma-Aldrich, 35$-$60 mesh), and incipient wet impregnation (IWI) was the method of synthesis and Pd(NH$_3$)$_4$(NO$_3$)$_2$ was used as the precursor.

**In Situ FT-IR Experiments.** Fourier transform infrared spectroscopy (FT-IR) experiments were conducted in a specially designed in situ ALD reaction cell, using a substrate comprised of zirconia nanopowder pressed into a metal grid. The FT-IR data were recorded using a Thermo Scientific Nicolet 6700 FT-IR spectrometer. A liquid nitrogen cooled IR detector was housed in a metal box purged with ultrahigh-purity N$_2$. In situ FT-IR spectroscopy (FT-IR) experiments were conducted in a temperature-controlled X-ray beamline (10-BM) of the Materials Research Collaborative Access Team (MR-CAT) at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). XAS data were collected in the transmission mode.

**XAS and PDF along with DFT calculations to compose a detailed picture of Pd ALD on TiO$_2$.

Pd ALD was performed in a stainless steel continuous-flow reactor (1 in. o.d., 10 in. length) attached to a portable ALD system at the beamline. Kapton foil was used as the X-ray window material. All gas lines were 1/4 in. stainless steel tubes and heated accordingly. A vacuum pump was used to keep a base pressure at $\sim$3 Torr with 50 sccm ultrahigh-purity N$_2$ flow.

The high surface area support used for the in situ XAS experiment was five ALD cycles of TiO$_2$-coated SiO$_2$ gel (5c TiO$_2$/SiO$_2$). The as-prepared TiO$_2$-coated SiO$_2$ gel was pressed as a pellet in a cylindrical stainless steel sample holder (8 mm i.d.) for the in situ XAS experiment.

Two Pd ALD cycles were conducted for the in situ XAS study. Each cycle was comprised of four steps: (1) Pd(hfac)$_2$ exposure at 100 $^\circ$C for 60 min, (2) purge with ultrahigh-purity N$_2$ at 100 $^\circ$C for 10 min, (3) reduction with formalin vapor at increasing temperature from 100 to 225 $^\circ$C at every 25 $^\circ$C, (4) purge with N$_2$ and cooldown to 100 $^\circ$C. XANES and EXAFS spectra were taken in real time.

The final Pd loading on the 5c TiO$_2$/SiO$_2$ was determined using XRF. The absolute amounts of Pd species during the Pd ALD process were back-calculated by multiplying the Pd fraction and the final Pd loading.

**XAS Data Analysis.** The Pd surface species fraction was calculated by conducting Pd XANES linear combination fittings using Athena in the IFEFFIT (version 1.2.11) package. PdO, Pd(hfac)$_2$, Na$_2$PdCl$_4$, and Pd nanoparticles (Pd$_0$) were considered as references and measured at the beamline. Appropriate XANES references were used for different reaction regimes. Pd XANES linear combination fittings at each data point were also cross-checked by EXAFS data fittings.

EXAFS data fittings were performed using WinXAS (version 3.1). Reference phase and amplitude files for Pd–Pd were obtained from the Pd foil EXAFS spectrum. Reference phase and amplitude files for Pd–O and Pd–C were both taken from PdO EXAFS spectra. Reference phase and amplitude files for Pd–Cl were obtained from Na$_2$PdCl$_4$. A single shell model fit of the forward and inverse $k^2$-weighted EXAFS data was obtained between $k = 2.9$–$11.7$ Å$^{-1}$ and $r = 1.3$–$2.8$ Å, respectively. Data quality was checked by performing $k^1$- and $k^3$-weighted EXAFS fittings with the same parameters.

**In Situ Pair Distribution Function Measurements.** After Pd(hfac)$_2$ was dosed to 5c TiO$_2$/SiO$_2$ at 100 $^\circ$C in the first half cycle of Pd ALD, the sample was carefully removed from the ALD chamber and transferred to the X-ray beamline for in situ pair distribution function (PDF) measurements. This sample was loaded in a Kapton capillary as a flow cell which allows flow of reactant gas during the in situ PDF measurements.$^{35}$ Temperature was precisely controlled by an Oxford Cryosystems unit. PDF data was collected: (1) in He flow at room temperature (RT); (2) elevating temperature at heating rate of 6 $^\circ$C/min from RT to 227 $^\circ$C in 20 sccm 3.5% H$_2$; (3) in He at RT.

Scattering data for PDF were collected at beamline 11-ID-B at the APS at ANL. High-energy X-rays (58 keV, $\lambda = 0.2127$ Å) were used in combination with a large amorphous silicon-based area detector. The 2-D images were transformed to 1-D scattering intensity data using software Fit2D. The structure function $S(Q)$ was obtained within software PDFgetX2. Direct Fourier transform of the reduced structure function $F(Q) = Q[S(Q) - 1]$ led to the pair distribution function $G(r)$. Contributions from support 5c TiO$_2$/SiO$_2$ were measured and subtracted to get differential PDFs. The resulting PDFs showed contributions only from Pd-atom correlations.
**Ex Situ Characterization.** Scanning transmission electron microscopy (STEM) and atomic number contrast high angle annular dark field (HAADF) imaging were performed using a probe aberration corrected 200 kV JEOL JEM-ARM200CF STEM/TEM with a resolution of less than 0.08 nm at Research Resources Center at University of Illinois at Chicago. 0.8 Å probe with 20 and 30 μm aperture was used for low- and high-magnification STEM images, respectively. The histogram of particle size distribution was generated from the STEM images using software ImageJ. Care was taken to count and measure only those particles that appeared in focus. Multiple images were taken, and more than 400 particles were measured to obtain reasonable statistics. Pd metal loadings were determined by X-ray fluorescence spectroscopy (XRF, Oxford ED2000) and inductively coupled plasma (ICP, Varian VISTA-MPX instrument). The composition of the as-prepared TiO2-coated SiO2 was analyzed with an X-ray photoemission spectroscopy (XPS, Kratos AXIS-165) system using a monochromatic Al Kα (1486.6 eV) X-ray source operating at 15 kV and 10 mA.

**Density Functional Theory Calculation.** Periodic density functional theory (DFT) calculations were carried out using the Vienna Ab Initio Simulation Package (VASP). The electronic exchange and correlation contributions were calculated using the generalized gradient PBE functional. The projector augmented wave (PAW) method was used to treat the explicit valence electrons and the ionic cores, and a plane-wave kinetic energy cutoff of 400 eV was used.

The stoichiometric rutile TiO2(110) surface was modeled using a four-layer slab, which has a dimension of 11.76 Å along the [001] direction and 13.06 Å, along the [110] directions, respectively. A vacuum space of ~50 Å was used between successive slabs in the periodic cell. The lattice parameters used for this work are a = 4.62 Å and c = 2.94 Å, respectively, from the relaxation of the bulk rutile TiO2 structure, and are in good agreement with the experimental values, where a = 4.594 Å and c = 2.959 Å, as reported by Baur. The top two layers were relaxed. The optimizations of the slab and the surface intermediates were performed using the conjugate gradient algorithm until the force on each atom is converged within 0.05 eV/Å. The Brillouin zone was sampled using a 2×2×2 k-point grid based on the Monkhorst–Pack scheme.

### RESULTS AND DISCUSSION

TiO2 is a one of the most frequently used support materials in catalysis. Commercial TiO2 is normally synthesized by the hydrolysis of titanium tetrachloride (TiCl4) and typically contains chlorine impurities (e.g., 0.3% HCl for Degussa P25). Residual chlorine could inhibit the reduction and lead to agglomeration of the precious metal. To model the chlorine containing TiO2 five ALD cycles of TiCl4 and H2O were used to coat a SiO2 template to serve as the substrate for Pd ALD. We measured a chlorine concentration in the ALD TiO2 of ~2 wt% using X-ray photoelectron spectroscopy, in agreement with previous reports. As shown in Figure 1a, one ALD Pd cycle on the TiO2-coated SiO2 yielded highly dispersed Pd nanoparticles with a diameter of 1.0 ± 0.3 nm. The atomic resolution aberration-corrected HAADF-STEM image revealed (Figure 1b) crystalline Pd nanoparticles with 0.22 nm fringes.

**In Situ FT-IR.** Figure 2 shows FT-IR spectra recorded during the first Pd ALD cycle on the ALD TiO2 surface at 100 °C (peak assignments are given in Table S1). Upon Pd(hfac)2 adsorption, two types of hfac ligands are seen: Pd(hfac)2 species (1605 cm−1) and Ti(hfac)2 species (1652 cm−1). This suggests that some of the hfac ligands elminated from the Pd(hfac)2 precursor adsorbed on the TiO2 surface. The initial 10 s formalin exposure at 100 °C completely eliminated the Pd(hfac)2* species and slightly increased the Ti(hfac)2* species (Figure S1). As the HCHO exposure temperature was increased, the Ti(hfac)2* species slowly disappeared, but it took more than 10 min of HCHO exposure at 225 °C to completely remove the Ti(hfac)2* species. Meanwhile, some of the Ti(hfac)2* species decomposed to Ti(COCF3)2* species and Ti(CF3)2* as demonstrated by the new features that appeared at 1376 and 1205 cm−1 assigned to C–C and CF3 stretching vibrations. Under identical conditions, Pd ALD was also performed on non-chlorine containing TiO2. The non-chlorine containing TiO2 was prepared by 12 ALD cycles of titanium isopropanoxide (TTIP) and H2O at 150 °C over ZrO2 surface. IR features corresponding to both Ti(hfac)2* and Pd(hfac)2* features were observed. This indicates that free hfac ligands deligated from Pd(hfac)2 indeed tend to bind to the TiO2 surface regardless of the presence of chlorine. However, without surface chlorine, the hfac ligands were only completely removed from Pd(hfac)2* by exposure to formalin at 150 °C, 50 °C higher than the surface chlorine. Since Pd nucleation is most likely after the deligation of Pd(hfac)2*, this suggests that the presence of surface chlorine accelerates Pd agglomeration, which is consistent with a previous report. The role of surface chlorine in Pd ALD is further studied by in situ EXAFS and density functional theory calculations.

**In Situ XAS.** In analogy with Pd ALD on hydroxylated Al2O3, we might expect Ti–O–Pd(hfac)2 to be the product of the first half-reaction. As we show below, however, in situ
XAS measurements revealed that residual chlorine on the TiO$_2$ surface completely changes the nature of the Pd(hfac)$_2$ adsorption. To facilitate interpretation of the in situ XAS measurements, XAS reference spectra were recorded for PdO, Pd(hfac)$_2$, Na$_2$PdCl$_4$, and Pd NPs as shown in Figure 3. The neighbors, with a bond distance of $\sim 2.05$ Å. Similarly, a monometallic organometallic compound, Pd(hfac)$_2$ is also surrounded by four oxygen atoms as nearest-neighbors with a slightly shorter bond distance of 2.00 Å. The Pd–Cl bond distance of 2.31 Å has been obtained in Na$_2$PdCl$_4$, close to that observed in $D_{4h}$ symmetry [PdCl$_4$]$^{2-}$ and octahedral symmetry [PdCl$_6$]$^{2-}$. A H$_2$ reduced 2 wt% Pd/SiO$_2$ sample prepared by incipient wet impregnation was used as reference Pd NPs where the bond distance of 2.75 Å was obtained.

The Pd K-edge Fourier transform for the as-deposited Pd species (Figure 3b) shows two peaks in the 1–2 Å regime. This clearly indicates a second scatterer in the first shell. A structure of Pd coordinating with two oxygen and two chloride atoms was obtained from quantitative EXAFS fitting (see Figure S2 and Table 2). Thus, Pd(hfac)$_2$ adsorbs on the TiO$_2$ during the first half-reaction through surface chlorine to form Pd(hfac)–Cl$_2$. In agreement with this interpretation, DFT calculations found that formation of Pd(hfac)Cl$_2$ is more favorable than Pd(hfac)O$_2$ on TiO$_2$ in the presence of surface chlorine. Shown in Figure 4, gas phase Pd(hfac)$_2$ two clean TiO$_2$ (110) surfaces, and two adsorbed Cl atoms are used as the reference state. The numbers in the parentheses represent the calculated potential energies based on the reference. Instead of the O sites on the TiO$_2$(110) surface, Pd(hfac)$_2$ binds much stronger with surface Cl species by forming Pd(hfac)Cl$_2$ species. The stable Pd(hfac)Cl$_2$ species as an intermediate indicates this reaction is a surface self-limiting reaction. A recent DFT study also showed that surface species, including H, OH, and residual Cl, can mobilize to supported Pt nanoclusters and stabilize them on the Al$_2$O$_3$ surface.

In accord with the FT-IR measurements, XAS showed that the Pd easily deligated at the lowest HCHO exposure temperature of 100 °C, leaving the Pd bound to nearby surface chlorine and oxygen. During the subsequent HCHO exposures at higher temperatures, EXAFS (Table 2) and DFT calculations (Figure 4) suggested that Pd(II) tended to bind to surface Cl if available. DFT calculations also show that on the TiO$_2$(110) surface Pd is able to bind one additional Cl atom forming PdOCl$_4$* species, which is slightly more stable than PdO$_2$Cl$_2$*, species, consistent with the EXAFS data fitting. Figure 3b and Table 2 show that Pd–O bond cleavage started as low as 100 °C and was complete at 150 °C, as CN$_{Pd-O}$ decreased to null. Subsequently, Pd–Cl bond cleavage began at 150 °C and completed at 200 °C. With the loss of Pd–Cl bonding, Pd atoms became mobile and formed small nanoparticles, leading to the appearance of Pd–Pd bonding at $\sim 2.5$ Å (uncorrected distance) at 150 °C.

Figure 3d shows XANES spectra recorded during the formalin exposure in the first Pd ALD cycle. A continuous narrowing of peaks accompanied by a shift of the edge to lower energy signals the gradual conversion of surface Pd species to metallic Pd. The final spectrum is similar to the XANES reference spectrum for Pd NPs shown in Figure 3c.

After complete reduction at 200 °C, the EXAFS fitting revealed a Pd–Pd bond distance of 2.78 Å, indicating lattice expansion in the Pd–Pd bond distance compared to the bulk Pd value of 2.75 Å. It is known that metal nanoparticles of a few nanometers size undergo lattice contraction to minimize under coordination. The lattice expansion of Pd in our study may result from the formation of a palladium hydride or palladium carbide. As shown in Figure 5a, XANES of the ALD Pd showed broadening at the peak of the 1s → 5p transition as compared to the XANES from metallic Pd nanoparticles synthesized from a noncarbon containing precursor. Pd K edge Fourier transforms of the ALD Pd shifted 0.13 Å to higher R in Figure 5b. Consequently, both XANES and Fourier transform suggest the formation of a Pd–C phase.

The formation of Pd–C might have resulted from the very long HCHO exposures used in this experiment. The Pd–C coordination number was determined to be 0.9 after the first Pd ALD cycle. In the second Pd ALD cycle (Figure S3), the as-deposited spectrum consisted of 1–2 Å bonds and Pd–Pd bonds at 2.49 Å (uncorrected distance), representing a mixture of both adsorbed Pd precursor and agglomerated Pd nano-

<table>
<thead>
<tr>
<th>sample</th>
<th>scatter</th>
<th>CN</th>
<th>$R$ (Å)</th>
<th>DWF $(\times 10^3)$</th>
<th>$E_0$ (eV)</th>
<th>assigned structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference PdO</td>
<td>Pd–O</td>
<td>4.0</td>
<td>2.05</td>
<td>0.0</td>
<td>−0.4</td>
<td>PdO</td>
</tr>
<tr>
<td>reference Pd(hfac)$_2$</td>
<td>Pd–O</td>
<td>4.0</td>
<td>2.00</td>
<td>0.7</td>
<td>3.4</td>
<td>Pd(hfac)$_2$</td>
</tr>
<tr>
<td>reference Na$_2$PdCl$_4$</td>
<td>Pd–Cl</td>
<td>4.0</td>
<td>2.31</td>
<td>0.3</td>
<td>0.3</td>
<td>Na$_2$PdCl$_4$</td>
</tr>
<tr>
<td>reference Pd NPs</td>
<td>Pd–Pd</td>
<td>9.0</td>
<td>2.75</td>
<td>1.5</td>
<td>2.4</td>
<td>Pd NPs</td>
</tr>
</tbody>
</table>

$^*Pd K$ edge was measured. CN is coordination numbers with error ±10%. $R$ is bond distance with error ±0.02 Å. DWF is Debye–Waller factor. $E_0$ is energy shift. A two-shell model fit of the $k^2$-weighted EXAFS data was obtained between $k = 2.9–11.7$ Å$^{-1}$ and $r = 1.3–2.8$ Å.
particles. After the second Pd ALD cycle, the CN for Pd−Pd increased only marginally from 6.1 to 6.9, implying a small increase in Pd particle size. This observation is consistent with the previous STEM results that the size of Pd nanoparticles increases only slightly after the first few Pd ALD cycles.20

XANES spectra of Pd(hfac)Cl$_2^-\text{hfac}$ and Pd/PdC$_x$ were used in linear combination fitting (LCF) to the XANES spectra during the second half-reaction. Figure 6 and Figure S4 illustrate the Pd surface species evolution for two cycles of Pd ALD. As expected, the Pd(hfac)Cl$_2^-\text{hfac}$ species decreased continuously with increasing HCHO exposure temperature. After the initial exposure to Pd(hfac)$_2$ at 100 °C, the TiO$_2$ surface was saturated with 11 μmol of Pd(hfac)Cl$_2$. Only ∼9 μmol of Pd(hfac)Cl$_2$ was deposited during the Pd(hfac)$_2$ exposure in the second cycle. The lower uptake in the second cycle may be due to active sites blocked by residues from the hfac ligands as suggested by the in situ FT-IR experiments. The surface Pd(hfac)Cl$_2^-\text{hfac}$ species were only completely reduced to Pd after the 200 °C HCHO treatment.

**In Situ PDF.** In situ XAS has been successfully employed to revolve the nucleation and growth of precious metals. However, EXAFS data require intensive data fitting which is not trivial for very small targets under a complicated chemical environment. To understand particle growth during the Pd ALD, we performed in situ PDF measurements. Quantitative differential PDF (d-PDF), where the contribution from the 5c TiO$_2$/SiO$_2$ support is precisely subtracted from the total PDF, provides only the atom−atom correlations from the supported Pd species (e.g., Pd−Pd).39,64 Figure 7 shows no obvious changes between RT and 99 °C. Pd aggregation started at 105 °C with the appearance of peaks corresponding to the Pd−Pd shells. This aggregation temperature coincides well with the Pd(hfac)-Cl$_2^-\text{hfac}$ deligation temperature seen in XAS and the loss of Pd(hfac) vibrational features observed in FT-IR. Both EXAFS data fitting and DFT calculations suggested that most Pd was

![Figure 4](dx.doi.org/10.1021/jp401196f.1)
still bound to TiO$_2$ through Pd$^{-}\text{O}$ and Pd$^{-}\text{Cl}$ bonds after HCHO reduction at 100 °C. However, some Pd aggregation already occurred once the hfac ligand detached from the Pd atoms. The peaks at 2.78, 4.83, and 7.37 Å are slightly larger than 2.75, 4.76, and 7.28 Å for the first, third, and sixth Pd$^{-}\text{Pd}$ shell of fcc bulk Pd, respectively. This is probably due to the formation of palladium hydride. The peak intensity further increased with increasing annealing temperature, suggesting an increase in the concentration of Pd nanoparticles.

### CONCLUSIONS

In summary, we systematically investigated the initial stages of Pd ALD on an ALD TiO$_2$ surface with residual chlorine using in situ FT-IR, in situ XAS, and in situ PDF. During the first half-reaction, Pd(hfac)$_2$ decomposed on the TiO$_2$ surface to form Pd(hfac)Cl$_2^*$ and Ti(hfac)$^*$. In the following HCHO exposure at 100 °C, the Pd(hfac)Cl$_2^*$ rapidly lost its remaining hfac ligand and bound to the TiO$_2$ through surface chlorine and oxygen. This transformation was accompanied by some Pd nanoparticle agglomeration. Increasing the HCHO exposure temperature caused first Pd$^{-}\text{O}$ bond cleavage followed Pd$^{-}\text{Cl}$ bond cleavage. Following the Pd$^{-}\text{Cl}$ bond cleavage, most of the Pd atoms rapidly agglomerated to form 1 nm nanoparticles. The adsorbed Pd precursors were reduced to Pd nanoparticles at 200 °C with a minor Pd$^{-}\text{C}$ phase. Repeated Pd ALD cycles nearly doubled the Pd loading without increasing the particle size. As a result, a detailed understanding of heterogeneous Pd/TiO$_2$ catalyst synthesis using Pd(hfac)$_2$ under practical ALD conditions was achieved. This knowledge can help direct the future design of advanced heterogeneous catalysts from organometallic compounds.

### ASSOCIATED CONTENT

* Supporting Information Additional details on FT-IR spectra and assignment, EXAFS spectra, and XANES linear combination fitting. This material is available free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

*Corresponding Author

*Phone 1-630-252-3520, e-mail jelam@anl.gov (J.W.E.).

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This material is based upon work supported as part of the Institute for Atom-efficient Chemical Transformations (IACT), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357. MRCAT operations are supported by the Department of Energy and the MRCAT member institutions. We gratefully acknowledge the computing resources provided on “Fusion”, a
REFERENCES


