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Transmetalation Process as a Route for Preparation of Zinc-Oxide-Supported Copper Nanoparticles

Hsuan Kung, Yichen Duan, Mackenzie G. Williams, and Andrew V. Teplyakov*

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United States

Abstract

Supported nanoparticulate materials have a variety of uses, from energy storage to catalysis. In preparing such materials, precision control can often be achieved by applying chemical deposition methods. However, ligand removal following the initial deposition presents a substantial challenge because of potential surface contamination. Traditional approaches normally include multistep processing and require a substantial thermal budget. Using transmetalation chemistry, it is possible to circumvent both disadvantages and prepare chemically reactive copper nanoparticles supported on a commercially available ZnO powder material by metal-organic vapor copper deposition followed by very mild annealing to 350 K. The self-limiting copper deposition reaction is used to demonstrate the utility of this approach for hexafluoroacetylacetonate-copper-vinyltrimethylsilane, Cu(hfac)VTMS, reacting with ZnO. The low-temperature transmetalation is confirmed by a combination of spectroscopic studies. Model density functional theory calculations are consistent with a thermodynamic driving force for the process.

Graphical abstract

1. Introduction

Supported nanoparticles play a prominent role in a variety of practical applications. Among these materials, supported metallic nanoparticles are especially important in catalysis.^{1,2}

*Corresponding Author: Tel.: 302-831-1969. Fax: 302-831-6335. andrewt@udel.edu.

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Summary of the computational cluster model structures and complete ref 37 (PDF)

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New methods to prepare supported nanoparticles are being developed constantly, with higher precision, low waste, and desired distribution and metal oxidation state.^{3–5} As the catalyst design approaches molecular-level precision, the preparation methods based on chemical deposition become more and more important, because this approach yields the opportunity to prepare catalysts and other materials in a straightforward way, relatively cheaply, and with high conformal filling, which is often required for thermal and photocatalysis.⁶ The chemical deposition methods are often followed by post-treatment procedures to remove the unwanted chemical ligands still bound to the materials deposited, which can cause surface contamination, and this is where the most difficult and costly preparation steps may be required. In addition to requiring a substantial thermal budget, these approaches do not guarantee that the nanoparticles deposited will retain the original size distribution and other properties. Thus, simple methods with a limited thermal budget are required for modern chemically deposited catalyst design.

Although it is very difficult to encompass all the possible deposition precursor ligands and all the possible metals used for catalytic applications, understanding the chemistry of β -diketonates and the removal of corresponding diketones is a very interesting and practically important problem. β -Diketonate ligands are commonly utilized to design Cu(I), Cu(II), Pd(II), and Pt(II) precursors for metal deposition on various substrates via chemical vapor deposition (CVD) or atomic layer deposition (ALD) processes. A number of reports explicitly address chemical vapor deposition and atomic layer deposition of transition metal catalysts on oxide materials,^{7–10} where decomposition reactions of β -diketonates are complex and can cause carbon, oxygen, or fluorine contamination on the surface at elevated temperatures. The chemistry of β -diketonates has also been explored as a means to be used in etching processes.^{11–14} Thus, following the deposition, it is always important to understand and quantify the behavior of these surface-bound ligands, including their effect on surface contamination and on the reactivity of the metal layers or nanoparticles they were used to deliver.

One of the interesting and practically relevant systems that use this approach for catalyst preparation is copper nanoparticles supported on ZnO powder. This Cu/ZnO catalyst can be used in methanol synthesis and hydrogen production processes.^{15–17} Recent studies report that the oxidation state of copper is extremely important for the catalyst properties.^{18,19} Copper nanoparticles have been shown to form on flat substrates and on ZnO powder in a self-limiting surface process conceptually similar to ALD.^{9,20,21} Common copper deposition precursors based on β -diketonate ligands were used for the deposition. The surface reactions of these precursors are limited by the delivery of the reducing agent *from the underlying surface* to remove β -diketonate ligands and thus the quantity of copper deposited on a surface is controlled by the surface concentration of chemical groups capable of delivering such a reducing agent. For example, amino groups²² and hydroxyl groups⁹ can be used as sources of hydrogen to deposit copper nanoparticles on solid supports. This room-temperature method to deposit copper nanoparticles and to control copper oxidation state would have been even more valuable if not for the presence of the remaining surface-bound ligands following the deposition process.

In order to remove the remaining surface-bound β -diketonate ligands, chemical displacement, thermal annealing, surface postoxidation, and electron-induced reactions can be utilized. However, chemical displacement of β -diketonates on ZnO was shown to be extremely inefficient thermodynamically,²³ and high-temperature thermal annealing²⁴ (in addition to having a very substantial thermal budget) led to ligand decomposition rather than its removal from the surface. Surface postoxidation intrinsically requires additional processing steps.^{25,26} A recent example of electron beam induced deposition (EBID) successfully deposited such metals as Pt, Pd, and Cu from corresponding β -diketonates, and the chemical state of the metal was shown to be approaching metallic, but these metals were encapsulated in an oxygen-containing carbonaceous matrix that had to be removed by additional steps including oxidation with atomic oxygen and then reduction with atomic hydrogen.²⁷ Coupled with a necessity of line-of-sight electron beam that is most useful for flat substrates, the EBID has a number of practical limitations. Of course, other approaches and combinations thereof can be used for ligand removal; however, all of them require multiple processing steps and a high thermal budget.

In this work, as opposed to annealing at high temperatures normally approaching calcination conditions, it is shown that the surface of copper nanoparticles deposited on ZnO powder in a self-limiting room temperature process from Cu(hfac)-VTMS could be cleared up of the remaining ligands by transmetalation with the surface of the support material. The process of transmetalation is closely coupled to ligand migration, and ligand migration from a single Pd deposition precursor molecule adsorbed on a surface to an underlying single crystalline TiO₂ surface has been reported previously by Gharachorlou et al.¹⁰ However, in that system, the migration of a single hfac ligand onto the oxide surface led to partial decomposition at room temperature and only high-temperature annealing could stimulate the linear growth of Pd on the TiO₂(110) surface. Nevertheless, if a similar approach can be used for nanoparticles, it will bring the catalysts prepared by related methods much closer to practical applications.

In the work reported here, by briefly annealing the copper nanoparticles prepared by the self-limiting reaction of Cu-(hfac)VTMS with commercially available ZnO powder to 350 K (a very modest thermal budget), the hfac ligands transfer from the surface of the copper nanoparticles to the ZnO substrate *without decomposition*, thus leaving these copper nanoparticles without any chemical protection. Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) are used to identify the surface chemical species. XPS is also used to identify the oxidation states of key transition metals. However, these techniques do not allow for the firm establishment of whether the remaining surface ligands are bound to copper or to ZnO surface. That is why time-of-flight secondary-ion mass spectrometry (ToF-SIMS) is used to make this identification. Density functional theory (DFT) computations are used to explain the feasibility of the transmetalation process in this system.

2. Experimental Section

2.1. Powder Sample Preparation and FT-IR Characterization

All ZnO powder samples were prepared as described earlier.⁹ A sample of approximately 30 mg of ZnO powder (99.99% purity, Alfa Aesar) was pressed onto a tungsten mesh under a pressure of ~4 tons using a hydraulic press. This assembly was mounted onto copper leads used for resistive heating, and a k-type thermocouple was spot-welded directly to the mesh to monitor the temperature.²⁸ The samples were then loaded into a custom-made infrared chamber and pumped down to $\sim 1 \times 10^{-6}$ Torr. ZnO samples were initially annealed to 850 K to remove surface contamination and the dosing of appropriate compounds was performed at room temperature following this preparation step. This procedure had been used previously to reduce surface defects and impurities and to reproducibly react with organic compounds.^{23,29} To promote the surface hydroxylation of the powder ZnO sample, following the original annealing preparation procedure, the powder was exposed to 1 Torr H₂O (Milli-Qwater, 18 M Ω cm, Millipore Corporation) at room temperature. Before reacting with the copper deposition precursor, the ZnO sample was briefly annealed to 450 K to remove molecularly adsorbed water.³⁰ Finally, the ZnO sample was exposed to the Cu(hfac)VTMS precursor at room temperature and further spectroscopic studies were performed. Cu(hfac)VTMS (hfac = hexafluoroacetylacetonate, VTMS = vinyltrimethylsilane) (97%, CupraSelect, Air Products) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH) (98+%, Alfa Aesar) were used in this study. These compounds were first treated with several freeze–pump–thaw cycles and then dosed into the vacuum chamber via a leak valve. For Cu(hfac)VTMS, the exposure of 2×10^{-2} Torr for 10 min was used at room temperature after the background infrared spectrum of ZnO powder was recorded. At this pressure and dosing time, the ZnO surface is fully reacted with the copper precursor, and no changes were observed spectroscopically if the reaction time was further increased. During the hfacH dose, the pressure of 1 Torr was maintained for 2 min to have full saturation of the surface as confirmed by previously recorded exposure profiles.²³

The samples prepared as described above were investigated by transmission infrared spectroscopy at room temperature. For temperature-profiles described below, a brief annealing to a desired temperature was followed by cooling down back to the room temperature before the spectrum was recorded. The entire heat/quench protocol required only a few minutes, and the power supply was switched off once the desired temperature was reached. The purity of the compounds including Cu(hfac)VTMS and hfacH were verified by mass spectrometry (SRS mass spectrometer) performed in a different ultrahigh vacuum chamber and then confirmed in situ by collecting infrared spectra in the gas phase at 1 Torr.

FT-IR experiments were performed using a Nicolet Magna 560 spectrometer with a nitrogen-cooled MCT detector to collect the infrared spectra in a transmission mode. The entire optical path of the infrared beam was purged by water- and CO₂-free air. All spectra were collected with a resolution of 4.0 cm⁻¹ and 512 scans per spectrum. An ion gauge was used for low pressure measurements in high-vacuum and a Baratron gauge (MKS

Instruments) was utilized for high pressure exposures. All quantitative analysis of infrared spectra was performed using Origin 9.1 software.

2.2. X-ray Photoelectron Spectroscopy (XPS)

All XPS spectra were recorded following a very brief exposure to ambient conditions during sample transfer on a K-Alpha⁺ X-ray photoelectron spectrometer (Thermo Scientific) equipped with a monochromatic aluminum K α (1486.6 eV) X-ray source. A pass energy of 58.7 eV was used to collect all spectra with 0.25 eV/step resolution. All peak positions were calibrated by C 1s peak at 284.6 eV using CasaXPS 2.3.14 software.

2.3. Time-of-Flight Secondary-Ion Mass Spectrometry (ToF-SIMS)

All the ToF-SIMS experiments were performed following a very brief exposure to ambient conditions during sample transfer at ToF-SIMS IV (ION-TOF, Münster, Germany) to obtain static negative and positive spectra using a 25 keV monoisotopic bismuth ion beam. The spectra were collected with mass resolution of $m/m = 9000$, and image resolution of 128×128 pixels; the analysis area was $100 \times 100 \mu\text{m}^2$ over 50 scans. All primary bismuth ion fluencies were below the threshold of 1×10^{13} ions/cm² for static SIMS. Both positive- and negative-ion spectra were collected, but only negative-ion spectra that show the most informative results are presented. All spectra were calibrated to H⁻, H₂⁻, C⁻, CH⁻, CH₂⁻, CH₃⁻, C₂⁻, C₂H⁻, C₃⁻, C₄⁻, C₅⁻, C₆⁻, and C₇⁻. Spectra containing the hfac ligand were further calibrated to the hfac fragment (C₅F₆O₂H⁻) and Zn(hfac) fragment (ZnC₅F₆O₂H⁻).

2.4. Density Functional Theory (DFT) Calculations

All the DFT calculations were carried out using the B3LYP functional^{31–33} and LANL2DZ basis set^{34–36} as implemented in Gaussian 09 suite of programs.³⁷ A Zn₂₀O₂₀ cluster model was based on mixed-terminated ZnO(10 $\bar{1}$ 0) surface to simulate the most common surface of ZnO powder.³⁸ The atoms in the first layer together with the adsorbed molecules were fully relaxed and the rest of the atoms in the cluster were fixed at their bulk position to prevent unrealistic distortion of the model structures.⁹ Relative energies (E) reported here are the energy differences between the optimized models with adsorbates and molecular structures and clusters calculated separately.

3. Results And Discussion

3.1. Spectroscopic FT-IR Signatures for Self-Limiting Copper Deposition from Cu(hfac)VTMS on Water-Predosed ZnO Powder and hfach Reaction with the Same Support Material

Previous investigations have established that the surface of ZnO powder prepared as described above in subsection 2.1 yields the surface covered with nanoparticles formed immediately while dosing the Cu(hfac)VTMS compound at room temperature.⁹ VTMS ligands were removed immediately upon adsorption and did not pose any problems with contamination; however, hfac ligands remained on the surface following the deposition. The room-temperature deposition has been studied in detail for several different copper precursor molecules^{20,21} and for a wide number of prefunctionalized surfaces, including NH_x-Si(100), H-Si(100), H-Si(111), and OH/silica.²² The formation of the nanoparticles at room

temperature has been confirmed spectroscopically and microscopically and the oxidation state of the deposited copper has been shown to depend on a number of factors. For the purposes of the current study, it is important to note that according to the spectroscopic investigations, the nanoparticles formed by Cu(hfac)VTMS contained Cu(0) and surface Cu(I) species.⁹

In order to study the transmetalation process involving copper and ZnO, it is first imperative to confirm that the hfac ligands are intact following the initial deposition.

In order to confirm the integrity of the hfac ligands following copper deposition onto a commercially available ZnO powder at room temperature, infrared spectroscopic studies summarized in Figure 1 have been performed. A comparison of the surface prepared by dosing Cu(hfac)VTMS onto a clean and well-prepared ZnO powder in Figure 1a yields an absorption signature that is nearly identical to that obtained following a Cu(hfac)VTMS dose onto the same support material predosed with water as described above to increase surface concentration of hydroxyl groups and thus the amount of copper deposited in Figure 1b. These observed absorption bands correspond to the C=O/C=C and C–F vibrations of the hfac ligand, as has been described in detail previously.⁹ Predosing ZnO with water increases the concentration of hydroxyl groups on the ZnO surface and thus leads to a more efficient deposition process and higher intensity of the infrared absorption corresponding to hfac ligands.⁹ On the other hand, the hfacH adsorption on ZnO shown in Figure 1c²³ yields a spectrum that is essentially identical to those obtained following the Cu(hfac)VTMS dose, suggesting that the surface analyzed in spectrum 1c represents an excellent model of diketonate formation on the ZnO surface. However, this comparison also implies that vibrational signatures may not be sufficient to distinguish different binding of hfac ligands on copper as opposed to a ZnO surface. Nevertheless, in all the cases considered, these vibrational signatures are fully consistent with the presence of intact hfac ligands on a surface at room temperature.

3.2. Thermal Stability of Copper Species Prepared on ZnO Powder Following Cu(hfac)VTMS Exposure Determined by FT-IR

the previous investigations of thermal stability of hfac species prepared on ZnO powder by hfacH dissociation²⁴ have explored high-temperature annealing and suggested that at elevated temperatures the hfac species decomposed on this material to form ketene-like species. The set of temperature-dependent infrared spectra shown in Figure 2 for the Cu(hfac)VTMS dose is very similar to that obtained previously for hfacH adsorbed on a ZnO powder surface.²⁴ Here a decrease of the intensity of a peak at 1250 cm⁻¹ indicates the decomposition of the C–CF₃ bond. As described in detail earlier,²⁴ this decomposition led to the formation of ketene-like structures with vibrational signatures between 1900–2100 cm⁻¹. The ketene species on the copper-containing ZnO powder surface shown in Figure 2 appear at a lower temperature (~600 K) than the ketene species in the previous hfacH work.²⁴ This observation suggests that the formation of these species may be catalytic in the present study. However, a detailed mechanistic investigation of the high-temperature chemistry of Cu(hfac)VTMS is outside the scope of this work. From the previously published work by Girolami et al.,³⁹ the ketene-like structure from the decomposition of hfac on a Cu(100)

single crystalline surface was reported to be present at temperatures above 375 K. A recent paper by Anderson et al.⁸ followed the Pt deposition on a TiO₂ surface starting with a Pt^{II} β -diketonate (Pt(hfac)₂). That work suggested that the absorption bands within the 2000–2200 cm⁻¹ spectral region are indicative of the CO on platinum. It was consistent with the observation of these bands following the reaction for the platinum precursor but not for the hfacH dosed onto the same surface at the same temperature. However, it is likely that some of the observed absorption bands actually correspond to ketene-like structures as well and the reaction on platinum sites corresponds to the Pt-catalyzed process, similarly to the work described here. In our case, if the majority of the hfac ligands are expected to be located on copper surface sites, the formation of ketenes during annealing should also be observed at temperatures much lower than those established for a similar reaction on an unmodified ZnO powder, below 600 K. In the studies presented in Figure 2, the formation of ketenes is only observed above 500 K. The main result of this observation is that annealing this material to temperatures below this point should keep the hfac ligands intact. However, again, these spectroscopic studies cannot be used to definitively determine if the remaining hfac ligands are bound to copper or to the ZnO surface directly. In order to determine this point conclusively, the ToF-SIMS was utilized, as described below.

3.3. Surface Chemical Changes upon Annealing, As Investigated by ToF-SIMS

The ToF-SIMS signature of Cu(hfac)VTMS on water-predosed ZnO is very complex because of a mixture of the isotopes for copper, zinc, oxygen and carbon atoms. These mixtures are overlapped with each other and may yield misleading interpretations for specific surface species. For example, the possible species for m/z from 134.8 to 135.1 are ^{65.926}ZnCF₃⁻, ^{63.929}ZnCF₃H₂⁻, ^{63.929}Zn^{13.003}CF₃H⁻, ^{64.927}CuCF₃H⁻, ^{64.927}Cu^{13.003}C F₃⁻, and ^{62.929}Cu^{13.003}CF₃H₂⁻. However, as shown in Figure 3, the signatures of the hfac ligand bound to Cu/ZnO are qualitatively different from the signature of this same ligand bound to a ZnO surface. Based on the infrared results described above, hfac is formed following hfacH dissociation on ZnO powder. Thus, the most straightforward way to determine if the hfac ligands are bonded to copper or to ZnO is to compare the ToF-SIMS signature of the ZnO material exposed to hfacH with that of the ZnO powder exposed to Cu(hfac)VTMS. The representative m/z 240 to 280 region shown in Figure 3 covers the signatures of most relevant ^{63.929}Zn(hfac) (m/z 270.917) and ^{62.929}Cu(hfac) (m/z 269.917) fragments. It is clear that the room temperature mass spectral patterns of hfac groups on a copper-containing sample (Figure 3a) and on a ZnO surface (Figure 3c) are absolutely different.

However, very brief annealing of the copper-containing sample to a mere 350 K changes the observed mass spectrum (Figure 3b) to a spectrum that is nearly identical with the signature of hfac on ZnO (Figure 3c). The same figure also reports on the ToF-SIMS spectrum of the ZnO powder surface itself in spectrum (d), which is markedly different from any of the spectra discussed above. The temperature of 350 K is not sufficient to start the decomposition of the hfac ligands, as suggested above by the infrared spectroscopy studies and also confirmed below with XPS. Therefore, any changes in the ToF-SIMS spectra can only be explained by the migration of the *intact* hfac moieties.

The zoom-in view of a portion of the representative m/z range from Figure 3 is presented in Figure 4. It should be emphasized that it is extremely difficult to make all the assignments correctly because the possible representative ions are spaced so closely. Nevertheless, several comparisons can be made. The fragments that are only observed for hfac reacted on ZnO can be detected for hfac/ZnO in Figure 4c but not following the copper deposition at room temperature (Figure 4b). However, brief annealing to 350 K (Figure 4a) yields the surface that is very similar to that. At the same time, Figure 4b clearly shows the peaks associated with the hfac attached to copper. Finally, following the mild annealing a number of fragments containing copper, ZnO, and hfac parts can be identified. In other words, the qualitative information obtained from Figure 3 can be expanded to provide a more specific set of observed fragments. Again, it should be mentioned that the assignment is still preliminary and is greatly complicated by the complexity of the surface-bound species. For example, the definitive difference in peaks around $m/z = 275$ in Figure 4a–c is interpreted as corresponding to the hfac migration from copper atom to zinc atom on a surface. However, the attempt to assign and quantify all the possible species corresponding to this m/z would require fitting at least 30 different fragments with various isotopes for a single m/z ratio, which is beyond this work. This observation also means that the fragments indicated explicitly in this figure comprise only a small fraction of all the possibilities and thus the expected isotopic ratios for identical Zn-containing fragments with different zinc isotopes cannot be quantified, as this would require a complete fitting of the contribution of all possible fragments.

Interesting parallels can be drawn between this observation and the previously reported transmetalation reactions involving hfac ligands on metal surfaces. For example, hfac ligands of bis(hexafluoroacetylacetonato) palladium(II) ($\text{Pd}(\text{hfac})_2$) were found to transfer to a copper substrate via a redox transmetalation reaction below 120 K.⁴⁰ The overall reaction can be written as

In this reaction, the Pd^{2+} of the $\text{Pd}(\text{hfac})_2$ molecule is reduced to Pd^0 by surface copper and the copper substrate is etched by forming the volatile byproduct $\text{Cu}(\text{hfac})_2$. Gharachorlou et al.¹⁰ have reported thermal decomposition of $\text{Pd}(\text{hfac})_2$ on a TiO_2 surface. At room temperature, the precursor dissociated into $\text{Pd}(\text{hfac})$ and hfac adsorbed on the TiO_2 surface. The hfac decomposed upon heating. In these studies,^{39–41} the transmetalation was specifically observed for a single organometallic precursor molecule following its adsorption on a surface. In contrast, the study presented here suggests that the transmetalation process is much more general, it can involve an entire nanoparticle and it can be more similar to the traditional spillover processes where a very complex species, hfac, is transferred from the nanoparticle surface to the ZnO support material. It is especially interesting that very mild annealing was sufficient to transfer the ligand to the metal oxide surface. The activation energy of this thermal diffusion reaction can be approximately estimated to be 84.8 kJ/mol based on the Redhead method,⁴² assuming the reaction to occur at approximately 325 K with the pre-exponential factor of $1.0 \times 10^{13} \text{ s}^{-1}$ for the first order process. Since this work

was performed in a high vacuum system with high exposure of the copper precursor followed by ex situ surface characterization, it is possible that ambient oxygen could play a role in determining the final state of copper on a surface (as detailed in the following section); however, the diffusion of intact hfac ligands from copper surface sites onto ZnO surface sites is unambiguous.

3.4. Copper Oxidation State and Decomposition of hfac ligands Determined by XPS

Since the detailed investigation of the copper nanoparticles formation at room temperature has been presented previously,⁹ only a brief summary of selected results will be provided in this section, targeting specifically the changes in hfac ligand and copper signatures. A summary of temperature-dependent changes in the F 1s region determined by XPS is shown in Figure 5. The F 1s signal at ~684 eV represents Zn–F or Cu–F species⁴³ and starts to appear above 400 K, following the decomposition of the hfac groups. A single peak present at approximately 688.4 eV at room temperature and 350 K indicates that hfac groups adsorbed on the surface are intact at this point.⁹ Figure 6a shows that copper species are indeed deposited on the surface as confirmed by the Cu 2p spectral region. Based on the comparison with the Auger spectral region (not shown) and on the previous detailed investigations of copper deposition from Cu(hfac)VTMS, results, the dominant oxidation state of copper is determined to be Cu⁺. This oxidation state can be confirmed by the XPS Cu 2p region to differentiate Cu⁺ and Cu²⁺ and by the Cu L₃M₄₅M₄₅ Auger region to differentiate Cu⁰ and Cu⁺.^{44,45}

As the mild annealing to 350 K transfers the protecting hfac ligands from copper to ZnO, copper shakeup satellite peaks appear at a higher binding energy following brief exposure to ambient conditions, indicating the formation of Cu²⁺, as would be expected for the unprotected copper surface shown in Figure 6b. This observation is fully consistent with the enhanced reactivity of unprotected copper. The overall surface process involving migration of hfac ligands driven by mild annealing on this Cu/ZnO catalyst is summarized in Figure 7.

3.5. Intactness of Copper Nanoparticles Confirmed by SEM

One additional point that has to be addressed to justify the transmetalation-driven preparation of copper structures on ZnO powder is the identity of the copper-deposited structures. It has been determined previously that copper nanoparticles can be formed successfully by the self-limiting reaction of Cu(hfac)VTMS at room temperature on flat functionalized substrates^{20,21} or on ZnO powder.⁹ The total amount of copper deposited depends on surface functionalization but at room temperature does not exceed one monolayer equivalent. The nanoparticles deposited using such an approach onto a flat functionalized single crystalline silicon surface survived annealing to 600 °C.²⁰ The question though is if these structures survive transmetalation on a ZnO powder surface at elevated temperature. As shown in the SEM images presented in Figure 8a, the clean ZnO powder surface used in this study is free of any nanostructures or nanoparticles at room temperature. The image in Figure 8b clearly shows a change in surface morphology, and the nanoparticles formed remain on the surface following annealing to 350 K, as shown in the image in Figure 8c. These results deserve additional explanation. The SEM investigation only follows the formation of the largest structures observed. The fraction of the

nanoparticles observed by SEM can be correlated with the fraction of the particles observed on flat functionalized surfaces following similar deposition procedures. For example, the nanoparticles of the sizes observed in Figure 8 constitute only a few percent of all the nanoparticles observed with different microscopic techniques, such as atomic force microscopy on flat substrates reported in the previous studies.²⁰ To elaborate this point, a set of atomic force microscopy studies of OH-terminated Si(100) model surface is presented in Figure S1 in the Supporting Information. Here, a small number of relatively large nanoparticles (only a few per square micron) is contrasted with a much larger number of small nanoparticles, below 2 nm in height. Of course, the SEM images in Figure 8 only provide information about those larger nanoparticles. Nevertheless, although the exact size distribution is beyond the capability of the instrument used in this work, it is most important that no changes are recorded for these nanoparticles following their brief annealing to 350 K. No morphological changes are observed for the nanoparticles following the annealing procedure to remove the hfac ligands from copper onto the ZnO substrate material. It can be noted that annealing to 600 K does show noticeable morphological changes, consistent with the previously described thermal processes for hfac on ZnO powder surface.²⁰

3.6. Computational Description of Thermodynamics of Transmetalation Process for hfac Species on Cu/ZnO Surface

In order to determine thermal stability of hfac species on the Cu/ZnO surface, a hydrogenated form of hfac (hfacH) is used as an adsorbate to produce the hfac moiety on Cu/ZnO cluster via DFT calculations. A similar calculation and experimental description of hexafluoroacetylacetone (hfacH) adsorption on ZnO surface has been reported previously.²³ For Cu/ZnO, three possibilities of adsorption sites and their relative adsorption energies are summarized in Figure 9. These results reveal that the stability of hfac ligands on the ZnO surface is substantially higher compared to that on small copper islands on the same ZnO surface. This implies the thermodynamic driving force for the observed transmetalation process. The thermal energy obtained from the Redhead method (subsection 3.3) is consistent with this result. One may also question if adsorption of hfac ligands at the interface between copper and ZnO may lead to a very stable species, thus hindering the transmetalation process, similarly to the site-blocking effect proposed for platinum ALD on metal oxides by Anderson et al.⁸ However, as shown in Figure 9, an example of such interfacial adsorption yields an adsorption energy that is higher than that for hfac on copper but still lower than that for hfac attached to the ZnO surface. This simple computational exploration obviously does not cover all the possible surface structures and only covers a selected ZnO surface (albeit representative of this system, as discussed in detail previously^{9,29}) but it does provide the roadmap for estimation of the reaction rates and also supports the thermodynamic driving force for the transmetalation processes. The detailed ball-and-stick computational cluster models used are provided in the Supporting Information.

4. Conclusions

The work described in this publication offers a novel opportunity for creating and activating supported nanoparticles that can be used in thermal and photocatalysis, sensing applications, and many other fields.

Despite a variety of methods available to make these materials, the proposed approach is based purely on the self-limiting chemical interaction of a CVD precursor with commercially available oxide powder material and requires a very modest thermal budget to selectively migrate the remaining ligands following the deposition process from the deposited copper nanoparticles onto a surface of the ZnO support material.

Spectroscopic methods together with the microscopic studies suggest that this transmetalation process requires very mild thermal annealing at 350 K and at this temperature, the ligands are intact. Computational investigation suggests that this process is driven thermodynamically and the formation of the interfacial organic species between the copper structures and underlying ZnO substrate material does not hinder transmetalation.

This approach can be expanded further to include other metals, especially for β -diketonate-based precursors and other support materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Henry CR. Surface Studies of Supported Model Catalysts. *Surf Sci Rep.* 1998; 31:231–325.
2. Stakheev AY, Kustov LM. Effects of the Support on the Morphology and Electronic Properties of Supported Metal Clusters: Modern Concepts and Progress in 1990s. *Appl Catal, A.* 1999; 188:3–35.
3. George SM. Atomic Layer Deposition: An Overview. *Chem Rev.* 2010; 110:111–131. [PubMed: 19947596]
4. Cuenya BR. Synthesis and Catalytic Properties of Metal Nanoparticles: Size, Shape, Support, Composition, and Oxidation State Effects. *Thin Solid Films.* 2010; 518:3127–3150.
5. Campelo JM, Luna D, Luque R, Marinas JM, Romero AA. Sustainable Preparation of Supported Metal Nanoparticles and Their Applications in Catalysis. *ChemSusChem.* 2009; 2:18–45. [PubMed: 19142903]
6. Serp P, Kalck P, Feurer R. Chemical Vapor Deposition Methods for the Controlled Preparation of Supported Catalytic Materials. *Chem Rev.* 2002; 102:3085–3128. [PubMed: 12222983]
7. Okumura M, Nakamura S, Tsubota S, Nakamura T, Azuma M, Haruta M. Chemical Vapor Deposition of Gold on Al₂O₃, SiO₂, and TiO₂ for the Oxidation of CO and of H₂. *Catal Lett.* 1998; 51:53–58.

8. Anderson VR, Leick N, Clancey JW, Hurst KE, Jones KM, Dillon AC, George SM. Atomic Layer Deposition of Platinum Nanoparticles on Titanium Oxide and Tungsten Oxide Using Platinum(II) Hexafluoroacetylacetonate and Formalin as the Reactants. *J Phys Chem C*. 2014; 118:8960–8970.
9. Kung H, Teplyakov AV. Formation of Copper Nanoparticles on ZnO Powder by a Surface-Limited Reaction. *J Phys Chem C*. 2014; 118:1990–1998.
10. Gharachorlou A, Detwiler MD, Nartova AV, Lei Y, Lu J, Elam JW, Delgass WN, Ribeiro FH, Zemlyanov DY. Palladium Nanoparticle Formation on TiO₂(110) by Thermal Decomposition of Palladium(II) Hexafluoroacetylacetonate. *ACS Appl Mater Interfaces*. 2014; 6:14702–14711. [PubMed: 25093626]
11. Rousseau F, Jain A, Kodas TT, Hampden-Smith M, Farr JD, Muenchausen R. Low-Temperature Dry Etching of Metal Oxides and ZnS via Formation of Volatile Metal β -diketonate Complexes. *J Mater Chem*. 1992; 2:893–894.
12. George MA, Hess DW, Beck SE, Young K, Bohling DA, Voloshin G, Lane AP. Reaction of 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (H⁺hfac) with Iron and Iron Oxide Thin films. *J Electrochem Soc*. 1996; 143:3257–3266.
13. Kytokivi A, Rautiainen A, Root A. Reaction of Acetylacetone Vapour with γ -Alumina. *J Chem Soc, Faraday Trans*. 1997; 93:4079–4084.
14. Lee Y, George SM. Atomic Layer Etching of Al₂O₃ Using Sequential, Self-Limiting Thermal Reactions with Sn(acac)₂ and Hydrogen Fluoride. *ACS Nano*. 2015; 9:2061–2070. [PubMed: 25604976]
15. Burch R, Golunski SE, Spencer MS. The Role of Copper and Zinc Oxide in Methanol Synthesis Catalysts. *J Chem Soc, Faraday Trans*. 1990; 86:2683–2691.
16. Spencer MS. The Role of Zinc Oxide in Cu/ZnO Catalysts for Methanol Synthesis and the Water–Gas Shift Reaction. *Top Catal*. 1999; 8:259–266.
17. Shishido T, Yamamoto Y, Morioka H, Takehira K. Production of Hydrogen from Methanol over Cu/ZnO and Cu/ZnO/Al₂O₃ Catalysts Prepared by Homogeneous Precipitation: Steam Reforming and Oxidative Steam Reforming. *J Mol Catal A: Chem*. 2007; 268:185–194.
18. Nakamura J, Choi Y, Fujitani T. On the Issue of the Active Site and the Role of ZnO in Cu/ZnO Methanol Synthesis Catalysts. *Top Catal*. 2003; 22:277–285.
19. Suh YW, Moon SH, Rhee HK. Active Sites in Cu/ZnO/ZrO₂ Catalysts for Methanol Synthesis from CO/H₂. *Catal Today*. 2000; 63:447–452.
20. Perrine KA, Teplyakov AV. Metallic Nanostructure Formation Limited by the Surface Hydrogen on Silicon. *Langmuir*. 2010; 26:12648–12658. [PubMed: 20608693]
21. Duan Y, Gao F, Teplyakov AV. Role of the Deposition Precursor Molecules in Defining Oxidation State of Deposited Copper in Surface Reduction Reactions on H-Terminated Si(111) Surface. *J Phys Chem C*. 2015; 119:27018–27027.
22. Perrine KA, Lin JM, Teplyakov AV. Controlling the Formation of Metallic Nanoparticles on Functionalized Silicon Surfaces. *J Phys Chem C*. 2012; 116:14431–14444.
23. Kung H, Teplyakov AV. In situ Investigation of Organic Ligand Displacement Processes on ZnO Powder Surface. *J Phys: Condens Matter*. 2015; 27:054007. [PubMed: 25414158]
24. Kung H, Teplyakov AV. Selectivity and Mechanism of Thermal Decomposition of β -diketones on ZnO Powder. *J Catal*. 2015; 330:145–153. [PubMed: 26309333]
25. Aaltonen T, Ritala M, Sajavaara T, Keinonen J, Leskelä M. Atomic Layer Deposition of Platinum Thin Films. *Chem Mater*. 2003; 15:1924–1928.
26. Hämäläinen J, Munnik F, Ritala M, Leskelä M. Atomic Layer Deposition of Platinum Oxide and Metallic Platinum Thin Films from Pt(acac)₂ and Ozone. *Chem Mater*. 2008; 20:6840–6846.
27. Rosenberg SG, Barclay M, Fairbrother DH. Electron Induced Surface Reactions of Organometallic Metal(hfac)₂ Precursors and Deposit Purification. *ACS Appl Mater Interfaces*. 2014; 6:8590–8601. [PubMed: 24784352]
28. Wingrave JA, Teplyakov AV. Infrared Spectrometer Attachment Assembly for Use with Vacuum and High-pressure Cells. *J Vac Sci Technol, A*. 2003; 21:1800–1801.
29. Gao J, Teplyakov AV. Surface Species Formed during Thermal Transformation of Ethanol on ZnO Powder. *J Catal*. 2013; 300:163–173.

30. Noei H, Qiu H, Wang Y, Loffler E, Woll C, Muhler M. The Identification of Hydroxyl groups on ZnO Nanoparticles by Infrared Spectroscopy. *Phys Chem Chem Phys*. 2008; 10:7092–7097. [PubMed: 19039343]
31. Becke AD. A New Mixing of Hartree–Fock and Local Density-Functional Theories. *J Chem Phys*. 1993; 98:1372–1377.
32. Becke AD. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J Chem Phys*. 1993; 98:5648–5652.
33. Wander A, Harrison NM. An Ab Initio Study of ZnO(1010). *Surf Sci*. 2000; 457:L342–L346.
34. Hay PJ, Wadt WR. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for the Transition Metal Atoms Sc to Hg. *J Chem Phys*. 1985; 82:270–283.
35. Hay PJ, Wadt WR. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for K to Au Including the Outermost Core Orbitals. *J Chem Phys*. 1985; 82:299–310.
36. Wadt WR, Hay PJ. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for Main Group Elements Na to Bi. *J Chem Phys*. 1985; 82:284–298.
37. Frisch, MJ.; Trucks, GW.; Schlegel, HB.; Scuseria, GE.; Robb, MA.; Cheeseman, JR.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, GA., et al. Gaussian 09. Gaussian, Inc.; Wallingford, CT: 2009. Revision D.01
38. Wöll C. The Chemistry and Physics of Zinc Oxide Surfaces. *Prog Surf Sci*. 2007; 82:55–120.
39. Girolami GS, Jeffries PM, Dubois LH. Mechanistic Studies of Copper Thin-Film Growth from Cu^I and Cu^{II} β -diketonates. *J Am Chem Soc*. 1993; 115:1015–1024.
40. Lin W, Warren TH, Nuzzo RG, Girolami GS. Surface-Selective Deposition of Palladium and Silver Films from Metal-Organic Precursors: A Novel Metal-Organic Chemical Vapor Deposition Redox Transmetalation Process. *J Am Chem Soc*. 1993; 115:11644–11645.
41. Crane EL, You Y, Nuzzo RG, Girolami GS. Mechanistic Studies of CVD Metallization Processes: Reactions of Rhodium and Platinum β -Diketonate Complexes on Copper Surfaces. *J Am Chem Soc*. 2000; 122:3422–3435.
42. Redhead PA. Thermal desorption of gases. *Vacuum*. 1962; 12:203–211.
43. Wagner, CD.; Riggs, WM.; Davis, LE.; Moulder, JF.; Muilenberg, GE. Handbook of X-Ray Photoelectron Spectroscopy; Perkin-Elmer Corporation. Physical Electronics Division; Eden Prairie, Minn: 1979.
44. Biesinger MC, Lau LWM, Gerson AR, Smart RSC. Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Sc, Ti, V, Cu and Zn. *Appl Surf Sci*. 2010; 257:887–898.
45. Kroll M, Lober T, Schott V, Woll C, Kohler U. Thermal Behavior of MOCVD-Grown Cu-Clusters on ZnO(1010). *Phys Chem Chem Phys*. 2012; 14:1654–1659. [PubMed: 22193927]

Figure 1. FT-IR spectra of Cu(hfac)VTMS reaction with the ZnO powder surface at room temperature: (a) without predosing water and (b) following predosing water. (c) hfacH adsorption on ZnO powder at room temperature.

Figure 2. Temperature-dependent infrared spectra following the transformation of the material prepared by the exposure of Cu(hfac)VTMS onto the water-predosed ZnO powder surface. All the spectra are collected at room temperature, following a very brief annealing to the temperatures indicated.

Figure 3.

Negative ion ToF-SIMS spectra of Cu(hfac)VTMS exposure on (a) water-predosed ZnO powder surface and following by (b) annealing at 350 K, (c) hfac exposure on ZnO powder and (d) ZnO powder.

Figure 4.

Zoom-in of the negative ion ToF-SIMS spectra of Cu(hfac)VTMS exposure on water-predosed ZnO powder surface before (b) and after (a) annealing at 350 K, (c) hfac exposure on ZnO powder and (d) ZnO powder. The proposed species indicated in the figure are only examples and do not represent the complete list of species with similar m/z signatures.

Figure 5. Temperature dependent F 1s XPS of water-predosed ZnO powder following Cu(hfac)VTMS deposition and brief annealing to temperatures indicated.

Figure 6. Cu 2p XPS spectra of the (a) Cu(hfac)VTMS deposited on water-predosed ZnO powder and (b) the same surface recorded following a brief annealing to 350 K.

Figure 7. hfac ligand migration (transmetalation) during copper deposition followed by a brief annealing to 350 K.

Figure 8. Summary of SEM investigations of (a) pure ZnO powder as received, (b) formation of copper nanoparticles following exposure of the water-predosed ZnO powder to Cu(hfac)VTMS at room temperature, and (c) sample in (b) briefly annealed to 350 K.

Figure 9.

Possible adsorbed forms of hfac on Cu/ZnO(10 $\bar{1}$ 0) represented by a cluster model based on dissociation of hfacH on model surfaces with corresponding energy changes. The third structure (right) is calculated without copper atoms on the ZnO cluster.