Atomic Layer Deposition—Sequential Self-limiting Surface Reactions for Advanced Catalyst “bottom-up” Synthesis

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Abstract:

Catalyst synthesis with precise control over the structure of catalytic active sites at the atomic level is of essential importance for the scientific understanding of reaction mechanisms and for rational design of advanced catalysts with high performance. Such precise control is achievable using atomic layer deposition (ALD). ALD is similar to chemical vapor deposition (CVD), except that the deposition is split into a sequence of two self-limiting surface reactions between gaseous precursor molecules and a substrate. The unique self-limiting feature of ALD allows conformal deposition of catalytic materials on a high surface area catalyst support at the atomic level. The deposited catalytic materials can be precisely constructed on the support by varying the number and type of ALD cycles. As an alternative to the wet-chemistry based conventional methods, ALD provides a cycle-by-cycle “bottom-up” approach for nanostructuring supported catalysts with near atomic precision.

In this review, we summarize recent attempts to synthesize supported catalysts with ALD. Nucleation and growth of metals by ALD on oxides and carbon materials for precise synthesis of supported monometallic catalyst are reviewed. The capability of achieving precise control over the particle size of monometallic nanoparticles by ALD is emphasized. The resulting metal catalysts with high dispersions and uniformity often show comparable or remarkably higher activity than those prepared by conventional methods. For supported bimetallic catalyst synthesis, we summarize the strategies for controlling the deposition of the secondary metal selectively on the primary metal nanoparticle but not on the support to exclude monometallic formation. As a review of the surface chemistry and growth behavior of metal ALD on metal surfaces, we demonstrate the ways to precisely tune size, composition and structure of bimetallic metal nanoparticles. The cycle-by-cycle “bottom up” construction of bimetallic (or multiple components) nanoparticles with near atomic precision on supports by ALD is illustrated. Applying metal oxide ALD over metal nanoparticles can be used to precisely synthesize nanostructured metal catalysts. In this part, the surface chemistry of Al_2O_3 ALD on metals is specifically reviewed. Next, we discuss the methods of tailoring the catalytic performance of metal catalysts including activity, selectivity and stability, through selective blocking of the low-coordination sites of metal nanoparticles, the confinement effect, and the formation of new metal-oxide interfaces. Synthesis of supported metal oxide catalysts with high dispersions and “bottom up” nanostructured photocatalytic architectures are also included. Therein, the surface chemistry and morphology of oxide ALD on oxides and carbon materials as well as their catalytic performance are summarized.

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1 Introduction

1.1 A brief introduction to atomic layer deposition (ALD)

ALD is a thin film deposition technique, originally developed by Dr. Tuomo Suntola and co-workers in the mid-1970s with the motivation for the need to produce high quality thin films in electroluminescent (TFEL) flat panel displays [1, 2]. ALD shows the capability of conformal coating on complex substrates with high aspect ratio and/or high surface areas where other thin film techniques, such as physical vapor deposition, chemical vapor deposition, pulsed laser deposition etc. often fail. Moreover, the film thickness can be precisely controlled at the atomic level by varying the number of ALD cycles [3-5]. Consequently, ALD has attracted tremendous attention and applications have extended far beyond microelectronics into fields such as catalysis [5-13], photovoltaics [14-18], batteries [19], fuel cells [11, 20], and polymers [21-23].

ALD was originally named “atomic layer epitaxy (ALE)” by Dr. Tuomo Suntola and co-workers [24]. It was changed to the term of ALD in near 2000, because the ALD-grown materials are mostly found to be amorphous, without showing any epitaxial structure to the underlying substrates [25]. ALD is similar to **chemical vapor deposition (CVD)**, except that the deposition is performed in cycles each of which is a sequence of two self-limiting surface reactions between gaseous precursor molecules and a substrate [5, 21, 24, 26]. After each surface reaction step, inert gas purging is performed to remove any unreacted precursor and volatile reaction products, as shown in the schematic model in Fig. 1. The principle of sequential binary surface reactions in ALD was originally demonstrated as “molecular layering (ML)” in the early 1960s by Professors Aleskovskii and Koltsov of the USSR Academy of Sciences for controlled catalyst synthesis; wherein silica gel with high surface area was alternatively exposed to TiCl_4 and water [27-29]. These early studies are the origin of ALD as applied to catalyst synthesis, even though they were overlooked by researchers from outside the Soviet Union since they were published only in Russian.

Fig. 1. A schematic model of general ALD binary reaction sequence. Precursor **A** and **B** are sequentially introduced to a substrate surface with inert gas purging in between. Reprinted

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During ALD, each surface reaction step is self-limiting, thus the thickness of deposited film can be precisely tuned at the atomic level by varying the number of ALD cycles. The self-limiting feature of ALD allows conformal deposition on high aspect ratio structures. Thus, it meets the challenging requirements in fabricating high-k dielectric gate materials in MOSFET, trench capacitors for DRAM and other devices [3, 30, 31]. The success of ALD in the microelectronics industry for the down-scaling of device dimensions has driven a tremendous growth in ALD processes, applications and commercially available ALD equipment. Today, more than 1000 ALD processes have been developed to include a majority of elements in the periodic table in the formation of oxides, nitrides, sulfides, and metals etc. (Fig. 2) [26].

Fig. 2. Overview of elements used for ALD materials. Reprinted with permission from [26].

1.2 Motivation of ALD in catalysis

Catalysis is an essential technology for petroleum refining, chemical upgrading, automobile exhaust treatment, Fischer–Tropsch synthesis and fuel cells [32]. Heterogeneous catalysts with the catalytic active materials dispersed on a high surface area solid material is the preferred form in most industrial processes, since the catalyst can be easily separated from reaction products. The conventional methods for synthesis of heterogeneous catalyst are wet-chemistry-based ion exchange, impregnation, and precipitation [33, 34]. In the 20th

century, tremendous efforts were made to improve catalytic activities, and remarkable progresses were achieved for many catalytic processes. Nonetheless, in many cases, the resulting catalytic materials show poor uniformity of catalytic active site dispersion, which leads to a low selectivity to desired products. From the scientific point of view, the heterogeneity of catalytic active sites makes it extremely difficult to link the catalytic properties with the specific active site structure. Improving catalyst selectivity to desired products is an essential goal in the 21st century for sustainable environment. To achieve this goal, methods of advanced catalyst synthesis with precise control over the catalytic active site structure at the atomic level are required. Moreover, such atomically-precisely controlled synthesis would facilitate the scientific understanding of reaction mechanisms and development of structure-activity relationships. Colloidal synthesis shows great opportunities to control over the size, composition, and morphology of metal nanoparticles/nanocrystals in liquid phase [35-37]. The shape and composition of the resulting metal nanoparticles is possible to be further finely tuned via atomic addition and subtraction through oxidative etching [38]. However, depositing colloidal nanoparticles to a catalyst support along with the capping agents removal is a crucial step to prepare a stable and active heterogeneous metal catalyst [39]; therein it remains challenges to maintain the size and shape of metal nanoparticles after removing the capping agents [34].

Under severe reaction conditions, catalyst deactivation is the major issue [40]. Sintering of supported metal catalysts to form larger metal particles can occur during high temperature reactions [40-42], and such metal catalyst deactivation may only be partially reversible in certain cases [43, 44]. Coke formation is also a major route to catalyst deactivation in hydrocarbon reactions, by blocking the catalytic active sites via carbon deposition [45-47]. In harsh liquid-phase reactions, the leaching of active sites from the support is also a common route to catalyst deactivation [48]. In many cases, sintering, coking, and leaching of active sites occur simultaneously. The deactivated catalyst has to be replaced or regenerated. This process is costly since reaction processes have to be interrupted. Moreover, during the deactivation process there will be a loss in catalyst uniformity and hence the potential for decreased selectivity. An effective method is required to simultaneously inhibit these deactivation routes, while preserving the catalytic function. Systematic modification of the structure and composition of catalytic active sites and their chemical surroundings at the atomic level is one viable strategy both to improve catalyst stability and to better understand the materials properties that improve stability. Encapsulation of metal nanoparticles with an oxide protecting layer using techniques such as CVD and sol-gel chemistry provides an

effective way to improve the stability of metal nanoparticles [49-53]. However, the thick protective layer (usually tens of nanometers thick) often results in a large decrease in catalytic activity due to mass transfer resistance. A method of atomically precise control over the thickness and composition of protective layers is highly desirable to preserve catalytic activity to the greatest extent while improving the stability.

In the mid-1990s, Lakomaa and Suntola at Microchemistry Ltd., carried out the pioneering studies of ALD in catalysis, wherein the capability to uniformly depositing catalytic materials (metal oxides and metals) onto high surface area porous substrates using ALD were demonstrated [4, 54-58]. Indeed, when catalytic materials are deposited on a high surface support using ALD, the catalytic species can be precisely constructed on the support surface step-by-step as increasing ALD cycles. As an alternative to the wet-chemistry based conventional methods, ALD provides a “bottom-up” approach for synthesis of supported catalysts with near atomic precision, which addresses the essential need for achieving the goals related with an atomic-level understanding of reaction mechanisms and rational design of advanced catalysts with high performance.

1.3 Outline of this review

Following the introduction, Section 2 first gives a brief summary of the general growth behaviors of ALD to get an overall picture of this approach. It includes the general characteristics of ALD, temperature effects, and the type of ALD.

Metal ALD on oxides and carbon materials for precise synthesis of supported monometallic catalysts is reviewed in Section 3. Synthesis of supported metal catalysts using ALD is often carried out using only a few cycles of ALD [5, 13], thus we mainly focus on the nucleation and growth of metal ALD on these substrates. In most cases, deposited metal atoms aggregate to form metal clusters or nanoparticles on these supports, and the metal particle size varies with the number of ALD cycles. It is challenging to synthesize single-atom metal catalyst using ALD at elevated temperatures due to the accelerated metal atom aggregation. However, the preparation of single-atom metal catalysts can be achieved using ALD through careful control over the type and density of nucleation sites [59, 60]. The catalytic performance of the resulting supported metal catalysts by ALD is also reviewed.

Section 4 describes the synthesis of supported bimetallic catalysts using ALD. The challenge of combining two metal ALD processes to form bimetallic nanoparticles synthesis is first addressed. Next, the strategies developed for selective metal-on-metal ALD for precise synthesis of supported bimetallic catalysts while excluding monometallic formation are

particularly highlighted. We describe strategies used to precisely tune structure, composition, and size of bimetallic metal nanoparticles. The surface chemistry and growth behavior of metal ALD on metal surfaces is also discussed for several cases to illustrate our understanding of the growth mechanism and the resulting bimetallic structures.

Section 5 reviews oxide ALD on metals for precise synthesis of nanostructured metal catalysts. This section includes the surface chemistry of Al_2O_3 ALD on metals. We also discuss the methods for tailoring the catalytic activity, selectivity and stability of metal catalysts, through selectively blocking the low-coordination sites of metal nanoparticles, the confinement effect, and the resulting new metal-oxide interfaces.

Synthesizing supported metal oxide catalysts with high dispersions and “bottom-up” nanostructured photocatalytic architectures are discussed in Section 6. In this case, the surface chemistry and morphology of oxide ALD on oxide and carbon materials are reviewed, followed by the catalytic performance. A summary and outlook are provided in a concluding section.

2 General surface chemistry of ALD

2.1 General characteristics of ALD

In case of CVD, gaseous precursor reactants are co-introduced into a heated reaction chamber. Therein, homogeneous reactions in the gas phase and heterogeneous reactions on and near the hot surfaces take place simultaneously, resulting in a film deposition on the substrate surface [61]. The principle of ALD is similar to CVD, except that precursors are sequentially introduced into the reaction chamber with inert gas purge in between, and the deposition is achieved through sequential surface reactions. Such “isolated” exposures of precursors effectively inhibit the homogeneous gas phase reactions between precursors, making the deposition in a more controlled manner [5, 21, 24, 26]. Each ALD cycle consists of four characteristic four steps (Fig. 1): First, introduce precursor A to the reactor, and a reaction between precursor A and reactive sites on a substrate starts taking place. The saturation of precursor A on the substrate surface is reached once all available reactive sites are consumed. Second, remove all unreacted precursor and volatile by-products from the substrate by inert gas purging. Third, precursor B is introduced to the substrate to conduct the second surface reaction and convert the surface back to the starting surface with the same reactive sites. Fourth, remove the unreacted precursors and byproducts through a second inert gas purge. These four steps can be repeated to produce more ALD cycles.

Most ALD processes are based on the binary reaction sequence described above, which is

called AB-type ALD, while other variations have also emerged. For example, a new ABC-type ALD process was recently developed for noble metal depositions at lower temperatures, where ALD is carried out based on a sequence of chemisorption, combustion and reduction steps [62–66]. The steps in each ALD cycle can be automatically under computer control. When the ALD conditions for different materials are similar, the ALD processes of these components can be easily combined together in a controlled sequence to construct a variety of structures. An example is the nanolaminate (Fig. 3) [21, 67, 68]. This flexibility in ALD sequences makes it an attractive method in catalyst synthesis. This will be shown in the synthesis of supported bimetallic catalysts discussed in Section 3 and oxide architectures for photocatalysis discussed in Section 6 [69].

Fig. 3. A schematic, on the left hand side, that illustrates the materials design of an Al_2O_3 - ZnO nanolaminate. The right hand side shows a cross-sectional transmission electron micrograph of an Al_2O_3 - ZnO nanolaminate where the layer thickness is about 30 nanometers. Reprinted with permission from [67].

Two factors have been identified as responsible for the saturation of two half-reaction cycles during ALD: the number of reactive surface sites and steric hindrance of precursor ligands [26]. The number of reactive sites provides an upper limit on the amount of chemisorbed precursor. When the density of reactive sites is too high and the size of precursor ligands too large, steric constraints imposed by the precursor ligands governs the saturation. Three models have been developed for analyzing the growth rate based on the steric hindrance effect, as shown in Fig. 4 [26]. The saturation density can be estimated based on the size of ML_n reactant (Fig. 4a) [70, 71], the size and geometry of the adsorbed ML_z species (Fig. 4b) [72], and the size and number of adsorbed ligands L (Fig. 4c) [73–75]. Obviously, the deposited ALD material in each cycle is less than a monolayer, although it is called atomic layer deposition. For instance, the growth rate of Al_2O_3 ALD is about 1.1–1.3 Å/cycle, much less than the estimated monolayer thickness of 3.8 Å [21, 76]. As a

consequence, the thickness of deposited film can be precisely controlled down to submonolayer coverage, which is essentially important for synthesis of supported catalysts with near atomic precision.

Fig. 4. Schematic illustration for analyzing sterically hindered chemisorption on the basis of the size of the ML_n reactant (a), the size and geometry of the chemisorbed ML_z species (b), and the size and number of ligands L (c). Reprinted with permission from [26].

2.2 Temperature effect

The ALD growth rate usually varies with reaction temperature. the temperature dependence is induced by several factors: (i) a change in the number and type of reactive sites present on the substrate surface with temperature. (ii) the effect of temperature on the reaction mechanism. For instance, the ligand to metal (L/M) ratio in the chemisorbed ML_z species (Fig. 4b) changes with increasing the reaction temperature. (iii) uncontrolled growth via condensation of precursors on the substrate at low temperatures. (iv) uncontrolled growth via precursors thermal decomposition at high temperatures. A schematic representation of ALD growth rate with growth temperature is shown in Fig. 5. For each ALD process, there is usually a temperature regime within which self-limiting growth can be achieved. This temperature regime is often called the “ALD process window” [5, 21, 24, 26]. **Uncontrolled** growth via either condensation or thermal decomposition of precursors has to be avoided in order to achieve conformal deposition on substrates, especially in the case of catalyst synthesis, where longer precursors dose times are required to achieve saturation on high

surface area substrates [5, 7, 13, 77].

The growth temperature can also have a significant impact on the crystallinity and surface roughness of deposited films. For example, TiO_2 ALD films formed using TiCl_4 and water are amorphous at a deposition temperature of 100–165 °C. The structure changes to anatase phase in films grown at 165–350 °C; while rutile dominates in the films obtained at temperatures above 350 °C [78]. Surface roughness can also increase due to crystallization. Indeed, using atomic force microscopy (AFM), King et al. showed that TiO_2 films grown at different temperatures yielded a root-mean-square (RMS) roughness of 0.2 nm at 100 °C, 2.1 nm at 300 °C, and 9.6 nm at 600 °C [79]. In the case of supported metal catalyst synthesis, the growth temperature has a large impact on the nucleation and dispersion of metal nanoparticles, which will be discussed in Section 3.

Fig. 5. Schematic of ALD process with temperature. Reprinted with permission from Picosun.

2.3 Type of ALD

In general, there are three types of ALD processes: Thermal ALD, catalytic ALD, and plasma-enhanced ALD (PE-ALD). In case of thermal ALD, the two precursor reactions are driven by forming thermodynamically favored surface species and volatile byproducts [21]. For instance, Al_2O_3 ALD using trimethylaluminum (TMA) and water is a highly exothermic

process with an extremely high reaction enthalpy of $\Delta H = -376$ kcal for the overall reaction [80]. ALD reactions are similar to the formation of Al_2O_3 , with negative heats of reaction. Thermal ALD systems includes deposition of noble metals such as Pt, Pd, Ag, Ru, Re, Rh, metal oxides such as Al_2O_3 , TiO_2 , ZnO , ZrO_2 , Nb_2O_5 , Ta_2O_5 , metal nitrides such as TiN , TaN , W_2N , and sulfides such as ZnS , CdS , Cu_2S (also seen in the review paper elsewhere by Puurunen [26] and the references therein). Up to now, the application of ALD in catalyst synthesis has been carried out using thermal ALD [5, 13].

Fig. 6. Proposed mechanism for Lewis base catalysis of SiO_2 ALD during (a) the SiCl_4 reaction and (b) the H_2O reaction. Reprinted with permission from [81]. Copyright © 1997, The American Association for the Advancement of Science.

Catalytic ALD is a less common process; therein, a catalyst reagent vapor is introduced to the reaction via cofeeding with ALD precursors to facilitate surface reactions at low temperatures. One of the most investigated ALD systems is SiO_2 ALD using SiCl_4 and H_2O . For the thermal ALD process, the ALD surface reactions are very slow and only occur at a high temperature above 300°C after very large SiCl_4 and H_2O exposures [82]. When pyridine or ammonia was used as a Lewis base catalyst, the growth temperature was lowered to room temperature with a growth rate of $2.1 \text{ \AA/cycle}$; the reactant flux required for complete reaction was also significantly reduced from $\sim 10^9$ to $\sim 10^4$ Langmuirs. The catalytic

mechanism was proposed to be activation of the OH bond via hydrogen bonding between the Lewis base and either the SiOH* surface species during the SiCl₄ reaction or the H₂O reactant during the H₂O reaction (Fig. 6) [81, 83]. Additional studies have shown that Lewis bases can also catalyze SiO₂ ALD using other silicon precursors such as tetraethoxysilane (TEOS) [84] and tris(tert-pentoxo)silanol [85]. Low temperature ALD is important for deposition on thermally fragile substrates such as electronic circuits, polymers and biological samples.

PE-ALD (or Radical-enhanced ALD) is an important process for the deposition of single-element ALD materials, such as metals and semiconductors, since these materials are very difficult to deposit using thermal ALD processes [21, 86, 87]. Typical plasmas used during PE-ALD are those generated in O₂, H₂, N₂ and NH₃ reactant gases or combinations thereof. Such plasmas can be employed to deposit metal oxides, metal nitrides and metal films. The radicals or other energetic species in the plasma help to induce reactions that are not possible using thermal energy. A schematic diagram of hydrogen radical-enhanced ALD is shown in Fig. 7 [21]. As a consequence, PE-ALD has several benefits over conventional thermal ALD, such as a reduced process temperature, improved film qualities, and an increased scope of reactions [87]. Nevertheless, radical recombination could cause non-conformal coating on substrates with complex structures [88]. Indeed, on a trenched sample with a high aspect ratio of 40:1, a Ta film produced by PE-ALD was not conformal in the trenches [89]. The Ta film was considerably thicker on the top of trench than on the bottom due to hydrogen radical recombination on the walls of the trench. Therefore, the application of PE-ALD in catalyst synthesis might be challenging, since catalyst supports often contain a large pore volume in order to achieve high surface area. In this review, we consider only thermal ALD processes.

Fig. 7. Schematic diagram of hydrogen radical-enhanced ALD using a metal reactant and hydrogen radicals. Reprinted with permission from [21]. Copyright © 2010, American Chemical Society.

3 Metal ALD on oxides and carbon materials: precise synthesis of supported monometallic catalysts

Transition-metal nanoparticles supported on oxides or carbon-based materials are objects of great interest in heterogeneous catalysis due to their unique chemical and physical properties. They are widely used in automobile exhaust treatment [32, 90], Fischer-Tropsch synthesis [91, 92], biomass conversions [93, 94], electrocatalysis [95, 96], and many other processes [35, 97, 98]. Catalytic performance depends strongly on the size, composition, and morphology of the metal nanoparticles [96, 99-101]. As a consequence, substantial efforts to optimize the synthesis procedure and explore new synthesis methods have been devoted to improving control over these factors to obtain metal particles high uniformity that are expected to exhibit higher activity and selectivity [102-104].

Metal ALD on various oxides and carbon-based materials has been widely investigated. Metal nanoparticles, instead of uniform metal films, are often formed due to the considerably higher surface energies of metals compared to oxides (or carbon) and the ALD conditions at elevated temperatures, which promote surface metal particle nucleation and growth. Interestingly, it was found that metal particle size varies almost linearly with the number of ALD cycles, while preserving a narrow particle size distribution. Such behavior is detrimental to the preparation of thin-film electroluminescent devices and microelectronics, but it sparks a new application in catalysis [5, 13]. Precise control over the size and composition of metal nanoparticles is expected due to the molecular reaction character of ALD, thus ALD provides an alternative method for catalyst synthesis that complements conventional methods based on wet chemistry.

3.1 Pt ALD

Thermal Pt ALD is one of the most extensively investigated metal ALD processes. It is usually performed using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe_3) as the Pt precursor and molecular oxygen as the nonmetal precursor at a relatively high temperature between 200 and 300 °C [105-109]; The growth rate is about 0.3 and 0.5 Å/cycle at 200 and 300 °C, respectively [106]. By quantitative analysis of *in situ* infrared spectroscopy, mass spectroscopy and ellipsometry measurements, Kessels et al, [107] proposed that MeCpPtMe_3 reacts with surface oxygen on the previously formed Pt film to form MeCpPtMe_2^* surface species and CO_2 , CH_4 , and H_2O gaseous products (Equation 1); next, molecular oxygen burns away the remaining Pt precursor ligand to form CO_2 and H_2O while oxidizing the Pt surface

(Equation 2). The produced O* surface species during oxygen exposure provide new reactive sites for the subsequent ALD cycles.

Considering the catalytic nature of Pt film, they further proposed that the formation of CH₄ during MeCpPtMe₃ exposure can be attributed to the hydrogenation of methyl surface species by hydrogen atoms released from dehydrogenation of the precursor ligands. This suggests that the surface chemistry during Pt ALD includes reactions and species not indicated in Equations 1-2. See, for example, Fig. 8 [110].

Fig. 8. Schematic representation of the surface reactions during Pt ALD. (a) At the start of the MeCpPtMe₃ half-reaction when the surface is covered with O atoms, the MeCpPtMe₃ molecules undergo combustion and dehydrogenation reactions upon adsorption, resulting predominantly in CO₂ and H₂O reaction products. The reactions continue when O becomes depleted with dehydrogenation and incomplete oxidation, which leads to H₂, CO, and CH₄ and additional hydrogenation products. (b) During the O₂ pulse, the carbonaceous layer formed in the MeCpPtMe₃ pulse is combusted, and O₂ dissociatively chemisorbs at the surface providing surface-bound oxygen for the next ALD cycle. Reprinted with permission from [110]. Copyright © 2012, American Chemical Society.

3.1.1 Nucleation and growth of Pt ALD on oxides

When Pt ALD is performed on oxide surfaces, a nucleation period was frequently observed in the initial ALD cycles before reaching a stable linear growth, where Pt ALD grows on a

continuous Pt film (Fig. 9) [109, 111-113]. It is generally believed that surface hydroxyl groups on oxide surfaces are the nucleation sites for Pt ALD [114, 115]. The strong dependence of the Pt nucleation on oxide compositions might be attributed to the reactivity of hydroxyls with the Pt precursor and to the interaction between the resulting Pt nanoparticles and the oxide support [109]. Using in-situ X-ray absorption spectroscopy (XAS), Marshall and co-workers investigated the initial stage of Pt nanoparticle formation during Pt ALD on a γ - Al_2O_3 support [114]. They demonstrated that the temperature, precursor exposure time, treatment gas, and number of ALD cycles influence the Pt particle size and density. The results suggest that MeCpPtMe_3 reacts with surface hydroxyls on the γ - Al_2O_3 support and to form MeCpPtMe_2^* surface species upon exposure of MeCpPtMe_3 . At 300 °C, reaction of MeCpPtMe_2^* with air leads to PtO. In subsequent ALD cycles, MeCpPtMe_3 reduces the PtO to metallic Pt with a stoichiometry of one precursor molecule per PtO. In addition, H_2 treatment of the MeCpPtMe_2^* surface species also removed the ligands and formed Pt nanoparticles, even though Pt ALD is not normally performed using H_2 as the second reagent. In line with this observation, Medlin et al. also demonstrated that using H_2 as the second reagent during Pt ALD leads to smaller Pt particle sizes than O_2 on alumina supports [115]. Surprisingly, using in-situ Fourier transform infrared spectroscopy (FTIR), they found that the OH group concentration did not show any discernible changes during Pt ALD using MeCpPtMe_3 - O_2 . They proposed that the Pt ALD with O_2 serves to (re)oxidize the surface to form a nearly constant level of surface hydroxyls.

Fig. 9. QCM measurements of Pt ALD on ZrO_2 , Al_2O_3 and TiO_2 surfaces at 300°C. Reprinted with permission from [109]. Copyright 2003, The Electrochemical Society.

Fig. 10. ALD Pt nanoparticle diameter versus number of Pt ALD cycles deposited on Al_2O_3 nanospheres at 300 °C and measured using TEM (blue symbols), and deposited on SrTiO_3 nanocubes and measured using X-ray diffraction (red symbols). Reprinted with permission from [5]. Copyright © 2013, American Chemical Society.

In the application to catalysis, the main focus has been on the nucleation in the first several cycles. As shown in Fig. 10, the Pt nanoparticle size is directly proportional to the number of ALD cycles and can be controlled with a precision of ~ 0.5 nm [5]. Moreover, the particle size is not strongly influenced by the substrate as evidenced by the similarity between depositions on the Al_2O_3 and SrTiO_3 surfaces. It is noteworthy that such digitally precise control over the metal particle size is an advantage for ALD in the application to catalysis. For the water-gas-shift (WGS) reaction, Marshall et al. pointed out that the ALD Pt catalysts exhibit excellent catalytic activity and stable WGS reaction rates that are comparable to those of catalysts prepared by conventional incipient wetness impregnation [114, 116].

3.1.2 Temperature effect

At the standard deposition temperature of 300 °C, 1-cycle Pt ALD on oxide supports often results in the formation of highly dispersed Pt nanoparticles with ~ 1 nm size, as shown in Fig. 10. To prepare Pt nanoparticles in the sub-nanometer range, one convenient method is to decrease the deposition temperature so that sintering of Pt nanoparticles during the ALD process can be limited. In this case, a stronger oxidizing reagent such as O_3 , instead of O_2 has to be employed to effectively combust the Pt precursor ligands. For instance, the Pt particle size remained at ~ 1 nm even after 12 cycles of Pt ALD on an Al_2O_3 support using

MeCpPtMe₃ and O₃ at 150 °C [69].

We recently developed a strategy of low-temperature ABC-type metal ALD for synthesizing subnanometer metal clusters with high loadings, as depicted in Fig. 11 [117, 118]. This procedure combines the deposition of catalytic metal at low temperatures (50-150 °C), the **A**-reaction, with deposition of new support material, the **B**- and **C**-reactions. Here the newly created support not only provides additional nucleation sites for metal deposition (Fig. 11d,e) but also retards agglomeration during the activation step (Fig. 11f). As a consequence, ultrafine uniform metal clusters, such as Pd, Pt and Ag supported on alumina and titania have been achieved. Fig. 12 shows a Pt/TiO₂ catalyst with an average particle size of 0.5 nm at a loading of 1.2 wt % synthesized using the A/B/C sequence: MeCpPtMe₃–titanium isopropoxide (TTIP)–H₂O.

Fig. 11. A schematic illustration of ABC-type ALD: (a) An initial support with nucleation sites; (b) A volatile metal precursor **A** is introduced to the surface to form metal nanoparticles with part of ligands retained (red curves); The reagent **B** and **C** is then introduced to the surface sequentially to form a new support surface (c) and (d) ; (e) New support and metal nanoparticles protected by ligands are formed on the initial support surface after a plurality of ABC cycles; (f) The protective ligands are removed to activate metal nanoparticles. Reprinted with permission from [118]. Copyright © 2010 WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 12. Morphology (a-b) and size distribution (c) histogram of subnanometer Pt clusters synthesized by 4-cycle ABC-type Pt ALD on a high surface area 20-cycle TiO₂ coated silica gel support at 50 °C. Reprinted with permission from [118]. Copyright © 2010 WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim.

3.1.3 Nucleation of Pt ALD on carbon-based materials

Carbon-based materials, such as carbon nanotubes (CNTs), graphene, and active carbon are another common class of catalyst support, especially in electrocatalysis application due to their high surface areas, good thermal and electrical conductivity, as well as mechanical and chemical stability. Pt is the well-known bench-mark metal [95, 119, 120]. Improving the atom efficiency to reduce cost while retaining the high catalytic activity of Pt remains a challenge. The advantage of precise control over the metal particle size by ALD has attracted a lot attention for design of high performance electrode materials. A number of studies of Pt ALD on carbon-based materials have been reported [11, 121-124]; therein conformal Pt deposition on carbon supports with high surface area was demonstrated, and higher Pt utilization efficiency was achieved by precisely controlling the Pt particle size and loadings through the numbers of ALD cycles. For instance, Bent et al, reported that Pt nanoparticles deposited on carbon aerogels by ALD exhibited high catalytic activity for the oxidation of CO even at loading levels as low as ~ 0.05 mg Pt/cm² with a conversion efficiency of nearly 100% in the 150–250 °C temperature range [11].

Regarding the nucleation and growth of Pt ALD on carbon-based materials at the initial stage, it was found that ALD does not grow on the surface of pristine graphene, carbon

nanotubes, carbon cloth [60, 122, 123, 125] due to the chemically inert nature of high quality graphitic carbon, since the initiation of ALD growth requires the presence of functional surface groups or defects that act as nucleation sites for the ALD precursors. Functionalization of the carbon surface is required prior to the deposition (also seen in the review paper elsewhere by Pinna et al. [126] and the references therein). Kim and co-workers reported that Pt nanoparticles were predominantly deposited on graphene's grain boundaries, folds and cracks due to the enhanced chemical reactivity of these line defect [125]. In order to facilitate the nucleation of ALD on carbon, chemical treatment of carbon based on mineral acids, such as HNO_3 , H_2SO_4 , or strong oxidizing agent, such as O_3 are commonly carried out to generate oxygen containing groups at the surface [127-129]. The resulting oxygen containing functional groups, such as $-\text{COH}$ and $-\text{COOH}$ acts as the nucleation sites for ALD growth. On nitric acid treated CNTs, Qin et al. observed an uniform dispersion of subnanometer Pt clusters up to 10 cycles of Pt ALD at 300 °C using O_3 as oxidant, even though the Pt loading was as high as 2.3%. The subnanometer Pt clusters showed high activity in styrene hydrogenation reaction [130].

Fig. 13. Schematic illustrations of Pt ALD mechanism on graphene nanosheets. (a) oxygen containing function group on graphene nanosheets; (b) Reaction of MeCpPtMe₃ with oxygen containing function group during the MeCpPtM₃ exposure step; (c) the subsequent oxygen combust the remained ligand while forming a new adsorbed oxygen layer on the Pt surface; (d) Pt deposition is precisely controlled by tuning the number of ALD cycles. Here, ‘*’ represents an active surface species, and Pt-O* represents oxygen molecules (or dissociated oxygen ions) that are adsorbed on the Pt surface. Reprinted with permission from [60]. Copyright © 2013, Rights Managed by Nature Publishing Group.

Fig. 14. HAADF-STEM images of a Pt/GNS sample synthesized by Pt ALD at 250 C for 50 cycles, the inset in (a) shows the corresponding histogram of Pt on GNS. Reprinted with permission from [60]. Copyright © 2013, Rights Managed by Nature Publishing Group.

Sun et al. [60] proposed a general schematic model for Pt ALD on oxygen functionalized graphene support as shown in Fig. 13, MeCpPtMe₃ reacts with surface oxygen species to form MeCpPtMe₂* by releasing CO₂ and water during the MeCpPtMe₃ exposure step (Fig. 13b); next, oxygen combusts off the remained ligands, and forms PtO (Fig. 13c). However, the detailed reaction mechanism during each step in the first ALD cycle is still unclear, and questions remain regarding how the isolated oxygen-containing functional group reacts with MeCpPtMe₃ to produce CO₂ and H₂O. Nevertheless, this was the first observation that a large fraction of isolated Pt atoms along with Pt nanoparticles were formed on the reduced graphene nanosheet (GNS) after 50 cycles of Pt ALD at 250 °C as shown in Fig. 14. The disagreement between the presence of isolated Pt atoms even after 50 Pt ALD cycles with the schematic model in Fig. 13, seems to be very likely due to the unsaturated exposure in each cycle, since the exposure time for MeCpPtMe₃ was only about 1 sec in their work, much

shorter than the exposure time typically required for ALD on high surface area supports (tens to hundreds of seconds are typical). In the application to direct methanol fuel cells (DMFC), the authors further demonstrated that this single-atom catalyst exhibits significantly improved catalytic activity (up to 10 times) over the state-of-the-art commercial Pt/C catalyst. X-ray absorption fine structure (XAFS) analyses revealed that a low-coordination and partially unoccupied densities of states in the Pt 5d orbital that might be responsible for the excellent performance.

3.2 Pd ALD

Thermal Pd ALD is another well-investigated metal ALD process. Unlike Pt ALD where the second reagent is O₂ used to combust the ligands, Pd ALD was successfully achieved through a hydrogenation reaction, by alternatively exposing palladium(II)hexafluoroacetylacetonate (Pd(hfac)₂) and formalin (or H₂) as a reducing agent at 200 °C [131]. Even though O₂-based combustion reaction processes for Pd ALD process was later developed using Pd(thd)₂-O₂ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato) at 180 °C [132], Pd(thd)₂-O₃ at 130–160 °C [63], Pd(thd)₂-O₃-H₂ at 130–160 °C [63], or Pd(keim₂)₂-O₂ (keim₂ = CF₃C(O)CH-C(CF₃)NBuⁿ) at 250–275 °C [106]. Detailed studies of these processes are limited. Therefore, we only discuss the Pd ALD process using Pd(hfac)₂-formalin (or H₂) here.

With the sequence Pd(hfac)₂-formalin, Elam et al. reported that the growth rate is about 0.22 Å/cycle at 200 °C [131]. Based on the QCM measurements, a reaction mechanism was proposed in Equations (3,4):

In each step, one hfac ligand of Pd(hfac)₂ precursor is released in the form of Hhfac. In fact, HCHO can be replaced by molecular H₂, once Pd ALD is growing on the Pd film itself as shown in Equation (5).

3.2.1 Nucleation and growth of Pd ALD on oxides

When Pd ALD is conducted on oxide surfaces, the Pd growth rate is initially low and then gradually increases to reach a steady state growth rate of 0.22 Å/cycle, similar to Pt ALD on oxides shown in Fig. 9. Surface hydroxyl groups were proposed as the nucleation sites [131, 133]. For instance, on alumina, Pd(hfac)₂ reacts with hydroxyl groups to form Al-O-Pdhfac*

surface species and Hhfac (Equation 6). This mechanism is supported by evidence of a reduced Pd loading, ~24%, caused by a decrease in hydroxyl density via thermal treatment at 600 °C [134]. Using angle-dependent X-ray photoelectron spectroscopy (XPS) measurements, Elam et al. showed that the Hhfac product remains on the alumina surface as a poison, producing an extended nucleation period for Pd ALD [131].

Fig. 15. (a) FTIR spectra in the O–H stretching vibration region showing the spectra for the initial hydroxylated Al₂O₃ ALD surface at 200 °C and the surface after a saturation Pd(hfac)₂ exposure at 200 °C. (b) FTIR spectra in the O–H stretching vibration region showing the spectra for the initial hydroxylated Al₂O₃ ALD surface at 200 °C and the surface after a saturation Hhfac exposure at 200 °C. Reprinted with permission from [135]. Copyright © 2011 Elsevier B.V. All rights reserved.

George et al. further investigated the nucleation of Pd ALD on alumina using *in situ* FTIR [135]. They found that the adsorption of Pd(hfac)₂ to hydroxylated alumina produced only a slight loss of hydroxyls in sharp contrast with exposure to Hhfac as shown in Fig. 15. They

suggest that $\text{Pd}(\text{hfac})_2$ adsorbs primarily through dissociative adsorption without hydroxyl group reaction (Equation 7). The slight loss of hydroxyl groups may be due to the readsorption of the Hhfac product according to the Equation 8. Indeed, Alhfac surface species were identified as a poison.

Next, when the surface decorated by Pdhfac^* and Alhfac^* is exposed to formalin, Pdhfac^* species are reduced and Pd nanoparticles are formed, while Alhfac^* remains on the surface. The Pd nanoparticles will be new nucleation sites for the next $\text{Pd}(\text{hfac})_2$ exposure in the subsequent ALD cycles, thus the size of Pd nanoparticles is precisely tuned with increasing ALD cycles (Fig. 16) [133]. Applying in situ FTIR, in situ XAS, and in situ pair distribution function (PDF) measurements under practical ALD conditions, Elam et al. followed the process of the $\text{Pd}(\text{hfac})_2$ deligation, evolution of the surface species, and formation of Pd nanoparticles [136]. It should be noted that hfac ligands may also decompose to form CF_3^* species during the Pd ALD process. Therefore, an extent of surface contamination by carbon and fluorine is expected, when a Pd catalyst is synthesized using Pd ALD with the sequence $\text{Pd}(\text{hfac})_2$ and formalin [135].

Fig. 16. STEM images of Pd ALD samples synthesized by Pd ALD on 10-cycle Al_2O_3 coated silica gel at 200 °C with different cycles: (a) 1-cycle Pd, (b) 4-cycle Pd; (c) 10-cycle Pd, (d) 25-cycle Pd. The insert shows the increase of Pd particle size as the number of Pd ALD cycles. Reprinted with permission from ref [133]. Copyright © 2010, American Chemical Society.

The nucleation rate of Pd also depends on the type of oxide substrate. For instance, the nucleation of Pd ALD on TiO₂ is obviously faster than on Al₂O₃, and Pd does not grow on silica [133], in contrast with Pt ALD, where a significantly faster nucleation rate was observed on Al₂O₃ than on TiO₂ (Fig. 9) [109]. Elam et al. [7] evaluated the catalytic performance of ALD resulting Pd/Al₂O₃ catalysts in the methanol decomposition reaction and found that the specific activity (based on the amount of metal) of Pd nanoparticles with a particle size of 1 to 2 nm was higher than the majority of Pd catalysts synthesized by other methods. Higher activity was attributed to the ultrauniform dispersion and small particle size obtained by the ALD method. Indeed, they further illustrated that large Pd particles (> 2 nm) were a factor of 2 less active than the smaller Pd particles in their following studies [134].

Fig. 17. STEM images of as-prepared Pd clusters on high surface area 10-cycle Al₂O₃ coated silica gel support by different cycles of ABC-type Pd ALD using Pd(hfac)₂–TMA–H₂O at 80 °C: (a) 1 cycle; (b) 4 cycles (c) 15 cycles. (d) Size distribution histogram of Pd clusters on the as-prepared sample with 15 cycles. (e) Pd content by weight percentage for different Pd ALD cycles. Reprinted with permission from ref [118]. Copyright © 2010 WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim.

3.2.1.1 Synthesis of ultrafine Pd clusters using low-temperature ABC-type ALD

Using low-temperature ABC-type Pd ALD as depicted in Fig. 11, the size of Pd nanoparticles can be further downsized to about 1 nm with extremely high uniformity, while varying the Pd loadings over a wide range (Fig. 17) [118]. In this case, treatment with

formalin at 200 °C was used to remove the capping hfac ligands leaving the metal particles accessible for chemisorption and catalytic function. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements of chemisorbed CO, performed after each step in the ABC process, support the capping, ligand removal, and accessibility of the metal particles depicted in Fig. 11. STEM measurements on the active Pd catalysts suggest that ultrafine Pd clusters are stable after removing the capping hfac ligands by formalin, which is most likely a consequence of the surrounding oxide formed during the BC-portion of the ABC cycles.

3.2.2 Nucleation of Pd ALD on carbon materials.

When Pd ALD is performed on carbon-based materials, it was generally found that the increase of average Pd nanoparticle size as a function of ALD cycles is significantly faster than on oxide surfaces. Elam et al. reported that the Pd nanoparticle size was about 2.6, 5.5, and 8 nm following 1, 3 and 10 ALD cycles of Pd on porous carbon, as shown in Fig. 18 [137]. By comparison, Feng et al. reported that the Pd particle size was about 8.4, 11.4 and 11.8 nm for 1, 2, and 3 cycles of Pd ALD on activated carbon (AC) (Fig. 19) [138]. On the contrary, 1 ALD cycle of Pd on alumina under similar conditions, yields Pd nanoparticles with a diameter of ~1 nm and 25 ALD cycles of Pd only increased the nanoparticle size to 2.9 ± 0.9 nm (Fig. 16) [133]. In addition, it should be noted that the metal oxide surfaces yield a higher density of Pd nanoparticles compared to the porous carbon. These results suggest that there are fewer nucleation sites for the Pd ALD on carbon supports as compared to metal oxides, and that Pd diffuses more rapidly on the carbon, yielding a smaller density Pd particles with a larger size [137].

Feng et al. investigated acid and thermal pretreatment effects on the nucleation of Pd ALD [138]. They found that pretreatment of AC using nitric acid produces a significant amount of surface oxygen-containing functional groups ($-\text{OH}$, $-\text{COC}-$, and $-\text{COOH}$), which facilitated the nucleation and promoted the dispersion of Pd nanoparticles. On an AC support which was oxidized in HNO_3 followed by annealing at 650 °C in an inert atmosphere, the average Pd sizes were 2.5, 4.6 and 5.1 nm after 1, 2 and 3 cycles of Pd ALD, considerably smaller than the ones obtained on untreated AC (Fig. 19). They pointed out that the surface functional groups play different roles at the different stages of Pd ALD: they promote dispersion of Pd species during the metal precursor exposure; on the other hand, instability of $-\text{COOH}$ will facilitate agglomeration of metal nanoparticles during the formalin reduction step. Therefore,

modifying the type and concentration of surface functional groups on the AC support will provide a measure of control over the Pd particle size. Highly dispersed Pd nanoparticles can be produced on the AC support with a low concentration of $-\text{COOH}$ but with a fair concentration of surface $-\text{OH}$ groups.

Fig. 18. STEM images of (a) 1c-Pd/C, (b) 3c-Pd/C, and (c) 10c-Pd/C. (d) HRTEM of a Pd nanoparticle ~ 5.5 nm in diameter prepared by ALD supported over carbon. (e) Pd particle size as a function of ALD cycles. Reprinted with permission from [137]. Copyright © 2013, American Chemical Society.

Fig. 19. Particle size distributions of ALD Pd/AC catalysts: 1, 2, and 3 cycles of Pd ALD on untreated AC (designated as AC Pd ALD *xc*); 1, 2, and 3 cycles of Pd ALD on pretreated AC where AC was treated in HNO₃ followed by annealing at 650 °C in an inert atmosphere (designated as AC-HNO₃-650 Pd ALD *xc*); and 1 cycle of Pd ALD on pretreated AC where AC was treated in HNO₃ followed by annealing at 800 °C in an inert atmosphere (designated as AC-HNO₃-650 Pd ALD *xc*). Reprinted with permission from [138]. Copyright © 2015, American Chemical Society.

3.2.2.1 *Synthesis of a single-atom Pd₁/graphene catalyst and its performance*

Atomically dispersed noble metal catalysts have attracted rapidly increasing attention due to their unique catalytic properties and maximal atom efficiency for low-cost [139-148]. The synthesis of single-atom metal catalysts via gas phase deposition is a grand challenge, since it is usually carried out at elevated temperatures, which would significantly accelerate metal atom aggregation during synthesis. Indeed, Sun et al. observed the formation of a mixture of atoms, clusters and nanoparticles with Pt ALD on graphene (Fig. 14) [60]. Botton et al. also reported the formation of a mixture of Pt atoms and clusters on a N-doped graphene support using Pt ALD [149].

Very recently, we successfully demonstrated that atomically dispersed Pd on graphene can be achieved using ALD by a careful control over the oxygen-containing functional groups on the graphene surface (Fig. 20). Therein, by combining XPS, aberration-corrected HADDF STEM, and XAS measurements, isolated phenol groups were identified to be the active sites for anchoring the Pd(hfac)₂ precursor, by forming –O–Pd-hfac* surface species and gaseous Hhfac product, similar to the reaction between Pd(hfac)₂ and hydroxyls on oxide surfaces [131]. Isolated Pd single atoms are formed after removing the remaining hfac ligand by formalin exposure [131]. On the other hand, other oxygen-containing functional groups such as –COOH should cause the Pd nanoparticle formation, in line with the previous results that instability of –COOH facilitates agglomeration of Pd nanoparticles [138]. It should be noted that Pd ALD does not grow on pristine graphene or over reduced graphene, even though a large number of edges and defects sites are present. This appears to be different from Pt and alumina ALD, where the nucleation of Pt and alumina both can take place at the edges and defects of graphene [125, 150].

When the resulting single-atom Pd₁/graphene catalyst was evaluated in selective hydrogenation of 1,3-butadiene, it revealed superior catalytic performance, with 100% selectivity to butenes, and the highest ever 1-butene selectivity of ~70% at a conversion of 95%

under mild reaction temperature of ca. 50 °C (Fig. 21a,b). In the presence of an excess of propene, the propene stream was effectively unreacted with a conversion limited to only 0.1% at a 1,3-butadiene conversion of 98% (Fig. 21c). The effect of temperature on the butene selectivity was minor. We speculate that the mono- π -adsorption mode of 1,3-butadiene and the enhanced steric effect induced by 1,3-butadiene adsorption on isolated Pd atoms both play important roles in the improvement of butene selectivity (Fig. 21e). More importantly, Pd₁/graphene showed excellent durability against deactivation via either metal atom aggregation or coking during 100 h on stream. This work suggests that single-atom metal catalyst can open up new opportunities in hydrogenation reactions for improved selectivity and durability in addition to water-gas shift (WGS) and oxidation reactions [139].

Fig. 20. (a) A schematic illustration of single-atom Pd₁/graphene catalyst synthesis via a process of anchor sites creation and selection and Pd ALD on pristine graphene. Representative HAADF-STEM images of Pd₁/graphene at low (b-c) and high (d) magnifications. Atomically dispersed Pd atoms in image (d) are highlighted by the white circles. Reprinted with permission from [59]. Copyright © 2015, American Chemical Society.

Fig. 21. Catalytic performances of Pd₁/graphene, Pd-NPs/graphene, Pd-NPs/graphene-500C, and Pd/carbon samples in selective hydrogenation of 1,3-butadiene. (a) Butenes selectivity as a function of conversion by changing the reaction temperatures; (b) the distribution of butenes at 95% conversion. Propene conversion (c) and the distribution of butenes (d) at 98% 1,3-butadiene conversion in hydrogenation of 1,3-butadiene in the presence of propene. (e) Schematic illustration of improvement of butenes selectivity on single-atom Pd₁/graphene catalyst. Note: the figure legend in (b) also applies to (d). Reprinted with permission from [59]. Copyright © 2015, American Chemical Society.

3.3 Ir ALD

Conventional thermal Ir ALD has been carried out using a sequential combustion-type surface reactions using molecular oxygen as the oxidant at temperatures above 220 °C. The frequently used Ir precursors are iridium(III)acetylacetonate (Ir(acac)₃) [151-155], (ethylcyclopentadienyl)(1,3-cyclohexadiene)iridium (Ir(EtCp)(CHD)) [64, 156], and (ethylcyclopentadienyl)(1,5-cyclooctadiene)iridium (EtCpIr(COD)) [157-159]. Ir(acac)₃ has a lower vapor pressure than the latter two precursors, which necessitates heating to at least 150 °C to get a reasonable vapor pressure for the ALD process [65]. Nevertheless, we mainly focus on Ir(acac)₃-based Ir ALD process, since this precursor has been employed for the

synthesis of supported Ir catalysts.

The growth rate of metallic Ir film using $\text{Ir}(\text{acac})_3\text{-O}_2$ depends on the deposition temperature [155]. It is about 0.2 Å/cycle at 225 °C and gradually increases with temperature. The maximum growth rate is about 0.4 Å/cycle at 375 °C and slightly decreases at 400 °C. Using ozone as the oxidant, the deposition temperature can be further decreased to 165 °C with a growth rate of about 0.2 Å/cycle. However, IrO_2 films, in this case, are formed rather than metallic Ir [152].

When the deposition temperature is higher than 225 °C, in situ QMS measurements showed that $(14 \pm 2) \%$ CO_2 and $(57 \pm 2)\%$ H_2O released during each ALD cycle are produced by the $\text{Ir}(\text{acac})_3$ exposures, indicating that a fraction of the acac ligands react with surface oxygen at this temperature [160]. During the following oxygen exposure, the remaining acac ligands are combusted releasing the balance of the CO_2 and H_2O and regenerating the surface oxygen. No other gaseous reaction byproducts (e.g. Hacac) were detected. In contrast, the $\text{Ir}(\text{acac})_3\text{-O}_3$ process releases CO_2 and H_2O only during the O_3 exposures at temperature below 200 °C. The authors suggested that $\text{Ir}(\text{acac})_3$ adsorbs molecularly on the IrO_2 surface in this case, different from the dissociative chemisorption observed at higher temperatures [160].

Besides the conventional AB-type Ir ALD described above, Hämäläinen and coworkers first reported that adding an additional reduction step to each IrO_2 ALD cycle in an ABC-type process ($\text{Ir}(\text{acac})_3\text{-O}_3\text{-H}_2$) can produce metallic Ir films at temperatures as low as 165 °C [62]. It is worth noting that this ABC-type ALD process using ozone and molecular hydrogen as co-reactants was later successfully extended to three additional noble metals: Rh, Pt and Pd [63, 64].

3.3.1 Nucleation and growth of Ir ALD on oxides

Several mechanisms have been proposed or identified for bonding of the general class of metal β -diketonate molecules on oxide supports [151]: (i) ligand exchange reactions where the metal β -diketonate molecule reacts with surface hydroxyls to release 1-2 Hacac into gas phase, (ii) dissociative adsorption, where the molecule splits onto coordinatively unsaturated sites or oxygen bridges leaving both parts bound to the surface, (iii) saturating associative adsorption where the molecule remains intact and either the center metal atom or the ligands interact with surface sites. The amount of metal adsorbed on the support surface in a self-limiting gas-solid reaction with β -diketonates is primarily controlled by the number of reactive sites on the support surface and by the size of the β -diketonate ligands. On oxide

supports the reactive sites are considered to consist of OH groups, coordinatively unsaturated sites and oxygen bridges [161, 162]. On alumina, the primary reactive sites for metal β -diketonates are the basic OH groups, and on silica they are the isolated OH groups [163]. In the case of $\text{Ir}(\text{acac})_3$, it has been found that ligand exchange reaction takes places on alumina, alumina-silica, silica, and β -zeolite, according to elemental analysis and IR measurements [151, 164]. Moreover, partially blocking the reactive sites with Hacac provides additional way to tune the Ir loading on these supports. Vuori et al. pointed out that ALD can be beneficial in preparing highly active iridium catalysts with a small metal particle size (ca. 1-3 nm) compared with conventional impregnation methods [165].

3.4 Ag ALD

Unlike other noble metal ALD, Ag ALD has been challenging due to the lack of stable and volatile Ag precursors. The PE-ALD of Ag thin films has been demonstrated using $\text{Ag}(\text{fod})(\text{PEt}_3)$ (fod = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dionato, and PEt_3 = triethyl-phosphine) and a hydrogen plasma [166]. Very recently, Stair et al. reported a thermal Ag ALD process using trimethylphosphine-(hexafluoroacetylacetonato)silver(I) ($(\text{hfac})\text{Ag}(\text{PMe}_3)$) as the metal precursor, and formalin as the reducing reagent in a relatively narrow temperature range between 170 and 200 °C [167]. The silver growth rate is low, about only 0.07 Å/cycle at 200 °C. The following reaction mechanism was proposed: During the $(\text{hfac})\text{Ag}(\text{PMe}_3)$ exposure step, $(\text{hfac})\text{Ag}(\text{PMe}_3)$ dissociatively chemisorbs on the Ag surface by forming $\text{Ag}(\text{hfac})$ surface species while releasing the PMe_3 ligand; next, HCHO removes the remained hfac ligand.

Fig. 22. HAADF STEM image (a) and the size distribution histogram (b) of as-prepared 10 cycles of Ag ALD nanoparticles on alumina-coated silica gel at 200 °C. Reprinted with permission from [167]. Copyright © 2014, American Chemical Society

On oxide surfaces such as alumina, a nucleation period was observed in the initial Ag ALD cycles. The nucleation sites for (hfac)Ag(PMe₃) were suggested to be surface oxygen, where the surface reactions in each exposure step is in a similar manor with the ones of Ag ALD on Ag surface in the linear growth region. On a high surface area alumina-coated silica gel, this process generated Ag nanoparticles with diameter of 1.8 ± 0.4 nm after 10 cycles of Ag ALD, as shown in Fig. 22.

3.5 Cu ALD

Cu ALD has attracted much attention due to the variety of industrial applications, including replacing aluminum in microelectronic interconnections because of its higher electrical conductivity and superior resistance to electromigration [168]. Such broad applications have boosted tremendous efforts to develop a large number of thermal Cu ALD processes: CuCl–H₂ at 360–410 °C [169, 170], Cu(thd)₂–H₂ at 150–350 °C [171–173], Cu(acac)₂–H₂ at about 250 °C [174], Cu(dialkylacetamidinate)₂/H₂ at 180–300 °C [175, 176], Cu(dmap)₂–ZnEt₂, (damp = methylamino-2-propoxide) at 100–120 °C [177], Cu(pirim)₂–ZnEt₂ (pyrim = *N*-ethyl-2-pyrrolylaldiminate) at 120–150 °C [178], Cu(dmamb)₂–HCOOH–N₂H₄ (dmamb = dimethylamino-2-methyl-2-butoxide) at 100–170 °C [179], Cu(dmap)₂–HCOOH–BH₃NHMe₂ at 130–160 °C [180], and Cu(hfac)₂–isopropanol at about 260 °C [181].

Among these precursors, copper acetamidinates are one of the most promising precursor families due to their relative resistance to reactions with air and their reasonable vapor pressure [175, 176, 182, 183]. For instance, copper(I) *N,N'*-di-sec-butylacetamidinate ((Cu(^sBu-amd))₂) developed by Gordon et al, has a vapor pressure of 0.1 Torr at 85 °C [184]. Using (Cu(^sBu-amd))₂ as the metal precursor and molecular hydrogen as the reducing agent, Cu ALD was achieved in a relative low temperature range of 150–190 °C [176]. The growth rate varied from 1.5–2 Å/cycle on SiO₂ or Si₃N₄, but was only 0.1–0.5 Å/cycle on metallic Ru, Cu, and Co surfaces. On oxide surfaces, the (Cu(^sBu-amd))₂–H₂ process forms isolated copper crystallites that merge into rough polycrystalline films after more deposition cycles. On Ru and Co metal surfaces, the ALD Cu nucleates densely, forming smooth and strongly adherent films that are continuous even for only 4 atomic layers [176].

Using in situ FTIR measurements and DFT calculations, Chabal et al. investigated the initial surface chemistry and growth mechanisms of Cu ALD on SiO₂ surfaces using (Cu(^sBu-amd))₂ and molecular hydrogen [185]. They showed that the initial surface reaction of (Cu(^sBu-amd))₂ with hydroxylated SiO₂ takes place by displacement of one of the sec-butylacetamidinate ligands at a surface -OH site, thus forming a Si-O-Cu-(sBu-amd)* surface

species (as shown in the schematic model in Fig. 23a,b). During the subsequent molecular hydrogen exposure, hydrogen reacts with most of the sec-butylacetamidinate ligands bound to Cu by releasing free amidine vapor product, leaving Cu atoms free to agglomerate on the surface (Fig. 23c-e); meanwhile, more reactive sites becomes available for the next $(\text{Cu}^{\text{sBu-amd}})_2$ pulse. When the ALD temperature was above 220 °C, the thermally activated ligand rearrangement from bidentate- to monodentate- binding of the sec-butylacetamidinate ligand occurred through hydrogenation of the ligand by surface hydroxyl groups, accompanied by releasing a Cu atom.

Fig. 23. Schematic model of the reactions of $(\text{Cu}^{\text{sBu-amd}})_2$ (a, b) and H_2 (c, d) on the SiO_2 surface. A free amidinate in panel (d) represents a gas-phase byproduct after ligand removal by H_2 . Panel (d) shows a possible intermediate Cu–H bond, which is not observed experimentally (possibly due to its very short lifetime at 185 °C). Panel (e) shows agglomeration of Cu atoms in a schematic way. Reprinted with permission from [185]. Copyright © 2010, American Chemical Society.

Zaera et al. studied the detailed surface reactions of $(\text{Cu}^{\text{sBu-amd}})_2$ on $\text{Cu}(100)$ surfaces using temperature programmed desorption (TPD) and XPS under ultrahigh vacuum to establish the Cu ALD process on Cu surfaces [186]. As shown in Fig. 24, they discovered that adsorption of the copper acetamidinate dimer from the gas phase leads to its partial dissociation on the surface at 90 K. Molecular desorption was first seen at below 300 K.

Additional amidinate desorption was seen at 480 K, indicating a relatively high thermal stability for the amidinate intermediate. With increasing temperature, the amidinate decomposed as evidenced by the formation of butane, butene, and hydrogen, at temperatures slightly below 500 K.

Fig. 24. Survey TPD data from 10.0 L of $(\text{Cu}^{\text{s-Bu-amd}})_2$ dosed on Cu(110) at 90 K. Traces are shown for the desorption of the main products detected in the gas phase, namely (from top to bottom): hydrogen, butene, butane, the original $(\text{Cu}^{\text{s-Bu-amd}})_2$, and amidinate. The signals for 2, 56, 58, 170 and 114 amu were used to follow these products, respectively. Reprinted with permission from [186]. Rights managed by AIP Publishing LLC.

In the application of Cu ALD for catalysis, Chen et al, has performed extensive studies of the catalytic activity of Cu/SiO₂ catalysts in the reverse water-gas-shift (RWGS) [172] reaction, and the WGS [187, 188] reactions, where ALD Cu/SiO₂ catalysts were prepared using Cu ALD with Cu(thd)₂ at 160 °C (ALE-Cu/SiO₂). The activity of the ALE-Cu/SiO₂ catalyst was compared with a Cu/SiO₂ catalyst synthesized using impregnation method (IM-Cu/SiO₂) and commercial Cu/ZnO/Al₂O₃, Pd/SiO₂ and Pt/SiO₂ catalysts. It was found that the ALE-Cu/SiO₂ provided a higher TOF than the IM-Cu/SiO₂ within 12 h by a factor of about 14-24, and was comparable to the Pt and Pd catalysts in the RWGS reaction (Fig. 25A,B) [172]. According to the CO TPD spectra, they showed that the ALE-Cu/SiO₂

catalyst exhibited a very different behavior compared to typical Cu-based catalysts. The ALE-Cu/SiO₂ catalyst showed two CO desorption peaks at approximately 343–353 and 443–463 K (Fig. 25C), whereas CO generally desorbs from Cu surfaces below room temperature. The authors suggested that the smaller Cu particle sizes (Fig. 26) produced by ALD might strongly bind the CO, leading to a high catalytic activity in RWGS. Later, they showed that this ALE-Cu/SiO₂ catalyst is also very active in the WGS reaction [187, 188]. Two major active sites were identified on the copper surface, namely defect sites on small Cu particles or isolated Cu atoms by using DRIFTS CO chemisorption measurements. In brief, their work provides a good example, illustrating the advantages of the ALD method for catalyst synthesis.

Fig. 25. (A and B) The dependence of CO₂ conversion on reaction time for H₂/CO₂ with 1:1 ratio and 100 ml/min over catalysts at 773 K. (C) TPD spectra of CO from 2.4% ALE-Cu/SiO₂ with various dosing amounts of CO. The adsorption of CO was carried out in a CO stream with 30 ml/min flow rate. Reprinted with permission from [172]. Copyright © 2006, American Chemical Society.

Fig. 26. TEM image of ALE-Cu/SiO₂ after calcinations and reduction. Reprinted with permission from [172]. Copyright © 2006, American Chemical Society.

3.6 Ni ALD

Unlike the ALD of noble metals (e.g. Pt, Rh, and Ru), the ALD of Ni (a transition metal) using O₂ or O₃ as the co-reactant yields NiO instead of metallic Ni at 143–300 °C [174, 189–191]. Using water as the co-reactant also produced NiO films [192–197]. The ALD of metallic Ni has been achieved by a hydrogenation-reaction surface chemistry using either H₂ or NH₃ as the reductant, similar to Pd ALD [131]. So far, the successful Ni ALD processes are: Ni(iPro-AMD)₂–H₂ (iPr-AMD = N,N'-diisopropylacetamidinato) at 250 °C [175], Ni(dmamb)₂–H₂ at 200–250 °C [198], (dmamb = dimethylamino-2-methyl-2-butoxo), and Ni(dmamb)₂–NH₃ at 300 °C [199]. Other processes such as Ni(acac)₂–H₂ at 250 °C [174] and Ni(Cp)₂–H₂ at 300 °C (Cp = cyclopentadienyl) [200] were have been reported, but these studies did not include measurements of self-limiting chemistry, linearity, and film uniformity. In the Ni(dmamb)₂–H₂ process, significant carbon contamination was observed [198]. However, by replacing molecular H₂ with NH₃, Kim deposited high purity Ni films with only a small amount of oxygen and negligible amounts of nitrogen and carbon, and the Ni growth rate was 0.64 Å/cycle [199]. In addition to the processes described above, metallic Ni films have been prepared first depositing ALD NiO, and subsequently converting this to Ni using a post-deposition reduction step [174, 201].

The synthesis of supported Ni catalysts with high dispersions via Ni ALD has been investigated by several groups. For instance, Medlin, et al. synthesized ALD Ni/Al₂O₃ catalysts using Ni(Cp)₂–H₂ at 300 °C. By varying the number of ALD Ni cycles from 1 to 15, the average Ni particle size was precisely tuned from 2.4 ± 0.1 to 3.3 ± 0.1 nm, and the Ni loading was adjusted between 4.7–16.7 wt.% [200]. The ALD Ni/Al₂O₃ catalysts had a higher activity in the hydrogenolysis reaction compared to comparable Ni catalysts prepared by incipient wetness impregnation (IWI), and this was attributed to a larger fraction of defect sites (steps and kinks) on the Ni surface of the ALD catalyst compared to the IWI catalyst. On a SiO₂ support, Liang et al, recently reported a Ni particle size of ~2.4 nm after 1 cycle Ni ALD and only a slight increase to 2.6 nm after 15 cycles [202]. The ALD Ni/SiO₂ catalyst with high dispersion could activate hydrazine hydrate as a reducing agent in the transfer hydrogenation of aryl nitro compounds into the corresponding amines with high selectivity and high yield.

Qin, et al. recently reported a general approach to synthesize multiply confined Ni/Al₂O₃ catalyst by first growing NiO nanoparticles on carbon nanocoils as sacrificial templates using NiO ALD through a Ni(Cp)₂–O₃ process at 200 °C [203]. Next, Al₂O₃ ALD was

carried out to coat the entire surface. Finally, calcination and reduction at 550 °C yielded Ni nanoparticles confined within the ALD Al_2O_3 nanotubes and embedded in the inner Al_2O_3 wall (Ni-in-ANTs). The Ni nanoparticles were about 4.8, 6.1 and 7.5 nm in diameter for 50, 150 and 300 NiO ALD cycles, respectively. They further demonstrated that the multiply confined Ni/ Al_2O_3 catalyst has significantly higher activities in cinnamaldehyde and nitrobenzene hydrogenation reactions with improved stability, compared with the same ALD Ni catalyst where the Ni was supported on the outer surfaces of the Al_2O_3 nanotubes (Ni-out-ANTs). This enhanced performance was attributed to the rich Ni– Al_2O_3 interfacial sites (Fig. 27).

In summary, highly dispersed Ni catalysts can be obtained through either directly metallic Ni ALD with molecular H_2 (or NH_3) as the reductant or using NiO ALD followed by high temperature reduction. In both cases, a slow increase in Ni particle size as the number of ALD cycles was observed.

Fig. 27. A) The evolution of cinnamaldehyde conversion with reaction time and B) the recycling results for the catalysts in the hydrogenation of cinnamaldehyde. TEM images of Ni-in-ANTs, on which 150 NiO ALD cycles was performed, C) after reaction for 10 min and D) after the fourth run; and of Ni-out-ANTs, on which 150 NiO ALD cycles was performed, E) after reaction for 10 min and F) after the fourth run. Reprinted with permission from [203].

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3.7 Other metals ALD

In addition to the metals described above, the ALD of other metals, including Ru [204-213], Rh [63, 214-216], Co [175, 217, 218], Fe [175], Mo [219], and W [220-223], have been reported. However, the application of these metals to catalysis has thus far been limited. Both Rh and Ru have been prepared by ALD using either O₂ or O₃ as the oxidant at temperatures above 200 °C, very similar to the cases of Pt and Ir ALD. Rh(acac)₃ is the commonly used precursor for Rh ALD [63, 214-216]. A wide variety of ALD Ru precursors have been explored including metallocenes, β -diketonates, and their derivatives [204-212]. Among these, the most widely studied and applied Ru ALD precursors are metallocenes and their derivatives, for instance, bis(ethylcyclopentadienyl)ruthenium (Ru(EtCp)₂) [206, 208, 209, 213].

Fig. 28. Schematic illustration of low temperature ABC-type Ru ALD using Ru(EtCp)₂–O₂–H₂. Reprinted with permission from [66]. Copyright © 2015, American Chemical Society.

As pointed out previously, this oxygen-based, combustion-type noble metal ALD typically requires temperatures above 200 °C (~ 300 °C in most cases), to burn off the organic ligands [65, 106, 204-211, 224]. In order to reduce the growth temperature for broader applications, Hämäläinen and coworkers demonstrated that Ir, Rh, Pt and Pd ALD can be performed at a significantly lower temperature by using ozone and molecular hydrogen as co-reactants in an ABC-type ALD process (also seen in the review paper [65] and the references therein) [63, 64]. Very recently, we demonstrated that Ru ALD can be performed at as low as 150 °C by using O₂ and H₂ as the co-reactants. In situ QCM and QMS measurements both indicated that this ABC-type ALD occurs through sequential steps of *dissociative chemisorption*, *combustion*, and *reduction* for the Ru(EtCp)₂, oxygen and hydrogen, respectively [66]. Therein, the Ru(EtCp)₂ undergoes dissociative chemisorption on the existing Ru metal surface to form Ru(EtCp)* and EtCp* surface species during the Ru(EtCp)₂ exposure. Next, the O₂ combusts the EtCp* surface species releasing CO₂ and H₂O gaseous products, and forms Ru oxide. Finally, the H₂ reduces the Ru oxide to Ru metal releasing H₂O vapor, and regenerating new chemisorption sites for the next Ru(EtCp)₂ exposure (Fig. 28). This

molecular O₂ and H₂ based ABC-type ALD could be exploited for the ALD of other noble metals to lower the deposition temperature and reduce oxygen impurities.

Gordon introduced a new family of homoleptic *N,N'*-dialkylacetamidinato metal compounds as ALD precursors for depositing transition metals including Cu, Ni, Co, and Fe using molecular hydrogen gas as the co-reactant [175]. The surface reactions using these compounds were found to be complementary and self-limiting, and yielded highly uniform and conformal coatings. NH₃ was later shown to be an efficient reductant for these *N,N'*-dialkylacetamidinato metal compounds. For instance, Kim et al. showed that ALD Co films with excellent conformality and nanoscale thickness controllability can be produced using Co(*i*Pr-amd)₂-NH₃ at 350 °C [217]. In the cases of both ALD Co and Ni, the NH₃ reductant provided significantly lower carbon, oxygen and nitrogen impurities compared to H₂ [199, 217].

W and Mo are catalytically relevant metals that have both been deposited by ALD, but using a much different strategy than the metals discussed above. The W and Mo ALD use volatile metal fluorides in combination with silane precursors, such as SiH₄ and Si₂H₆ [220-223, 225], and the overall equations for the W and Mo ALD were determined to be:

These reactions are highly exothermic and have heats of reaction of $\Delta H = -331$ and -221 kcal, for Equations (9) and (10), respectively [219]. The driving force for these reactions is the formation of the very stable Si-F bonds in the volatile fluorosilane products. W ALD can be performed over a wide temperature range of 30–325 °C [220, 221]. The W ALD growth rates typically range from 4.0–6.0 Å/cycle depending on the growth temperature [221]. The lower temperatures in this range are sufficiently mild to permit W ALD on polymer substrates [226, 227]. Mo ALD can also be performed at relatively low temperatures of 90-150 °C with a growth rate of 6.0-7.0 Å/cycle [219]. Despite the favorable attributes for these ALD processes, there have been no reports describing their use in supported metal catalysts except as model systems [228, 229].

4 Selective metal ALD on metals: precise synthesis of supported bimetallic catalysts

Supported bimetallic catalysts often show superior catalytic properties compared to those of their parent monometallic counterparts due to the synergistic effect [230-245], which may originate from the ensemble effect (specific metal atoms arrangements that are required for facilitating a particular catalytic process) or the electronic effect (modification of electronic

states resulting from hetero-nuclear metal-metal bond formation). Therefore, achieving atomically precise control over the size, structure, and composition of bimetallic nanoparticles are the essential goal for synthesis of supported bimetallic catalysts.

Traditional methods for bimetallic nanoparticle synthesis such as successive impregnation or co-impregnation often fail to provide precise control over composition and structure, yielding a mixture of monometallic and bimetallic particles with various compositions [233, 240, 246-249]. Other strategic routes have been reported that provide better control, such as electroless deposition [250] anion coordination protocol [251], sacrificial hydrogen method [252], surface-specific reductants [253], redox transmetalation reactions [254], and controlled simultaneous reduction [255]. Nevertheless, a facile method for bimetallic nanoparticle synthesis with atomically-precise control is still missing.

4.1 Challenges of synthesis of supported bimetallic catalysts using ALD

Due to the self-limiting feature, ALD can (in principle) achieve independent control over the size, composition, and structure of the bimetallic nanoparticles with near atomic precision: The size of the bimetallic particles is determined by the total number of ALD cycles performed; the composition is dictated by the relative number of ALD cycles used for each component; and the structure of the bimetallic nanoparticles is controlled by the order in which the individual cycles are executed [5, 69]. Nonetheless, it has turned out that synthesis of supported bimetallic catalysts using ALD remains as a challenge, even though ALD has shown success in synthesis of supported monometallic catalysts as discussed in Section 3. The major reasons are that the two metals do not share a common ALD temperature window and the surface chemistries might be incompatible. For instance, Pd ALD is often carried out at 200 °C based on a hydrogenation surface chemistry [131], while Pt ALD is usually performed at about 300 °C based on a combustion surface chemistry [105-109]. As a consequence, there have been only few reports describing the synthesis of supported bimetallic nanoparticles by ALD [9, 256-259]. Besides the above issues, it is challenging to restrict the secondary metal growth to be only on the primary metal nanoparticle but not on the support, especially given the natural tendency for ALD materials to grow uniformly on all surfaces.

4.2 Strategies for selective metal ALD

Up to now, three strategies have been developed for controlling the deposition of the

secondary metal selectively on the primary metal nanoparticle but not on the support, thereby excluding monometallic formation:

(1) Reduce the oxygen partial pressure. For Pt ALD using $\text{MeCpPtMe}_3\text{-O}_2$ at 300 °C, Kessels et al. reported that Pt ALD on Al_2O_3 surface can be inhibited by decreasing the O_2 partial pressure to ~ 7.5 mTorr [112, 260, 261]. As shown in Fig. 29d, no Pt growth was observed on Al_2O_3 , even after 600 Pt ALD cycles [260]. On the other hand, the Pt grew immediately on a Pd substrate at a rate of ~ 0.45 Å/cycle. The Pt ALD process at an O_2 pressure of 7.5 mTorr was considered as selective toward Pd versus Al_2O_3 . Indeed, they deposited Pt shells on Pd particles supported on planar substrates using the low oxygen pressure at 300 °C, where the Pd core was prepared by Pd PEALD at 100 °C using a H_2 plasma as the reducing agent. The selective deposition was indicated by an increase in the average particle size while the nanoparticle number density remained constant (Fig. 29e,f). Aberration-corrected HAADF STEM imaging further showed the presence of the Pt shell. However, the need to perform the growth of the two metals at different temperatures is inconvenient, and makes the growth of bimetallic alloy nanoparticles, where the two ALD metal processes must be frequently alternated, practically impossible.

Fig. 29. (a) Thickness evolution of Pd during ALD using the $\text{Pd}(\text{hfac})_2$ and a H_2 plasma on Al_2O_3 at 100 °C, obtained from *in situ* spectroscopic ellipsometry (SE). (b) HAADF-STEM image of Pd nanoparticles obtained by applying 200 cycles of plasma-assisted ALD of Pd on an Al_2O_3 covered Si_3N_4 TEM window. (c) Particle size distribution extracted from part b. (d) Thickness evolution of Pt during Pt ALD on Pd and Al_2O_3 surfaces from MeCpPtMe_3 and O_2 gas at a pressure of 7.5 mTorr at

300 °C. The data was obtained from *in situ* SE. (e) HAADF-STEM image of Pd/Pt nanoparticles supported on an Al₂O₃ covered Si₃N₄ TEM window. The nanoparticles were obtained by applying 200 cycles of plasma-assisted ALD of Pd and subsequently 50 cycles of ALD of Pt. (f) Particle size distribution extracted from part e. Reprinted with permission from [260]. Copyright © 2012, American Chemical Society.

Fig. 30. Schematic illustration for fabricating the core shell nanoparticles through AS-ALD on ODTS modified substrate. Reprinted with permission from [262]. Copyright © 2015, Rights Managed by Nature Publishing Group.

Fig. 31. Cross-sectional compositional line profile on a single Pd/Pt core shell NP, (b) bright field HRTEM image of the Pd/Pt core shell NP and corresponding Fourier transform pattern. Reprinted with permission from [262]. Copyright © 2015, Rights Managed by Nature Publishing Group.

(2) Use self-assembled monolayers (SAMs). Chen et al. demonstrated that octadecyltrichlorosilane (ODTS) SAMs can be utilized to modify a substrate surface to achieve area-selective ALD [262]. Therein, pinholes in the unsaturated ODTS SAMs layer were utilized as active sites for the initial ALD nucleation of the primary metal cores (Fig. 30). Next, the closely packed ODTS layer enables selective growth of the secondary metal onto the primary metal formed in the pinholes to form uniformly distributed core-shell nanoparticles, while prohibiting monometallic nanoparticle formation. In this case, the core-shell nanoparticles were obtained using typical ALD recipes for the two metals without special adjustment. For instance, Pd@Pt core-shell nanoparticles were synthesized by first selectively depositing the Pd core into the pinholes at 200 °C using Pd(hfac)₂–formalin, followed by Pt ALD at 300 °C using MeCpPtMe₃–O₂. Formation of the core-shell structure was confirmed by high resolution TEM as shown in Fig. 31. They further showed that annealing in an ambient environment at 400 °C for 1 h removed the ODTS SAMs from the substrate while preserving the core-shell structure.

(3) Use a lower deposition temperature and a proper co-reactant. As discussed in Section 3, the ALD of metals on oxide surfaces typically exhibits a nucleation period during the initial cycles characterized by an apparent lower growth rate compared to the steady-state (Fig. 9) [109, 111-113, 131, 133]. We demonstrated that at sufficiently low deposition temperatures the nucleation period for metal ALD on oxide surfaces can be extended indefinitely while the growth on metal surfaces persists. For instance, at 150 °C the ALD of Pd, Pt and Ru were essentially zero on oxide surfaces (TiO₂, Al₂O₃ and ZrO₂), but on metal surfaces the metal ALD was linear as demonstrated by in situ QCM measurements in Fig. 32 [69]. It is worthwhile to note that an ABC-type strategy was adopted for Ru ALD using the exposure sequence Ru(EtCp)₂–O₂–H₂ for the low temperature growth [66]. The higher initial Ru growth rates observed on the Pd and Pt surfaces at 150 °C suggest that these metals facilitate the Ru nucleation (Fig. 32c) [69]. In line with our observations, Johansson et al reported that Ru ALD does not proceed on alumina surfaces below 250 °C [263].

More recently, we performed Pd ALD on a high surface area silica support using Pd(hfac)₂–H₂ at 150 °C and measured no Pd using inductively coupled plasma atomic emission spectroscopy (ICP-AES) even after 8 Pd ALD cycles [264]. In contrast, the Pd loadings increased considerably on an Au/SiO₂ catalyst with the

number of Pd ALD cycles. Evidently, the Pd grows selectively on the Au nanoparticles but not on the SiO_2 support and exclusively forms AuPd bimetallic nanoparticles without any monometallic Pd nanoparticles.

Fig. 32. In situ QCM measurements of metal ALD on metal and oxides surfaces. (a) Pd ALD on Pt, Ru, Al_2O_3 , TiO_2 , and ZrO_2 using $\text{Pd}(\text{hfac})_2$ and H_2 at 150 °C. (b) Pt ALD on Pd, Ru, Al_2O_3 , TiO_2 , and ZrO_2 using MeCpPtMe_3 and O_2 at 150 °C. (c) ABC-type Ru ALD on Pd and Pt at 150 and 200 °C, and on Al_2O_3 , TiO_2 , and ZrO_2 at 200 °C using $\text{Ru}(\text{EtCp})_2$, O_2 , and H_2 . Reprinted with permission from ref [69]. Copyright © 2014, Rights Managed by Nature Publishing Group.

The selective deposition of Cu on Pd and Pt metal surfaces using $\text{Cu}(\text{thd})_2\text{-H}_2$, was also reported [173, 265, 266]. It was found that the temperature window for selective Cu growth is 190–260 °C. At higher temperatures, the selectivity was lost, and nucleation was independent of substrate material. Selective growth was explained by the different reaction mechanisms on hydroxylated oxide surfaces and on metals [173]. On the hydroxyl-terminated oxide surface, $\text{Cu}(\text{thd})_2$ reacts with the hydroxyl group and one of the ligands is then removed as a volatile $\text{H}(\text{thd})$ molecule. The second ligand cannot be removed at the low temperatures, thus the deposition process stops. However, $\text{Cu}(\text{thd})_2$ might dissociate on metal surfaces. Upon hydrogen adsorption, electrons are supplied to the substrate and the ligands can be completely removed as $\text{H}(\text{thd})$ through reaction with the dissociated surface hydrogen. As a consequence, selective deposition of Cu on Pd and Pt metal surfaces but not on oxides supports was achieved. Taken together, the above results from several independent research groups suggest that the catalytic nature of noble metals compared with oxides plays the essential role in facilitating the selective ALD on metals at lower temperatures.

Along with reducing the deposition temperature, the choice of co-reactant can also facilitate selective metal ALD. For instance, using H_2 instead of HCHO as the co-reactant for Pd ALD effectively suppresses Pd ALD on oxide surfaces, while maintaining Pd growth on metal surfaces at 150 °C [69]. Similarly, no Pt ALD is observed on oxide surfaces at 150 °C using $\text{MeCpPtMe}_3\text{-O}_2$. However, when the O_2 is replaced with O_3 , Pt ALD proceeds on oxide surfaces. More importantly, the ALD of well-mixed bimetallic alloy nanoparticles can be conveniently accomplished by alternating between the ALD processes for the individual metals, since these noble metal ALD processes can be performed at the same temperature of 150 °C. We will discuss this point in a later subsection.

4.3 *Precise synthesis of bimetallic catalysts with core-shell structure*

The selective ALD of metals on metal surfaces but not on oxide supports leads exclusively to bimetallic nanoparticles without forming monometallic nanoparticles of the primary or the secondary metal. Using the methods described above, bimetallic core-shell nanoparticles can in principle be formed on oxide surfaces with precise control over the shell thickness by adjusting the number of ALD cycles for the secondary metal. Next, the surface chemistry and morphology of metal ALD on metal surfaces will be discussed in the following subsections.

4.3.1 Pd ALD on Pt.

Using the three strategies for selective metal ALD presented above, Pt@Pd core-shell nanoparticles have been synthesized with great precision [69, 260, 262]. Using Pd(hfac)₂-H₂ at 150 °C, in situ QCM measurements showed that Pd ALD on Pt exhibited linear growth without any nucleation delay, indicating a layer-by-layer growth mode (Fig. 32a). Using CO as a probe molecule, in situ FTIR was employed to map the atomic-scale evolution of the surface composition and thereby infer the nanoparticle structure after each ALD cycle during the bimetallic nanoparticle synthesis (e.g. core-shell vs. well-mixed alloy). As shown in Fig. 33, the IR spectrum taken after 1 Pd cycle on a Pt/Al₂O₃ sample (1c-Pd) revealed the disappearance of a broad shoulder at 2010 cm⁻¹, indicating that Pd preferentially nucleated at the low-coordination Pt surface sites. This finding is in excellent agreement with the theoretical prediction by Fortunelli, et al. that Pd mainly decorates at the steps and corners of Pt in multi-shell PdPt alloy nanoparticles [267]. Meanwhile, we assigned the new peak at 1900 cm⁻¹ to bridge-bonded CO on the PdPt mixture [268]. With increasing Pd ALD cycles, the linear CO on Pt continuously decreased in intensity and red shifted, implying that the number of surface Pt atoms diminished. Surprisingly, the 1900 cm⁻¹ peak remained and the characteristic bridge CO peak at 1931 cm⁻¹ for pure Pd surfaces was not observed even after 30 Pd cycles (~3.5 ML Pd). This finding suggests that Pt atoms diffused to the surface during the Pd shell growth, thus resulting in a Pd-rich PdPt shell under current ALD conditions. Such structure was further confirmed by aberration-corrected HAADF-STEM measurement along with the energy-dispersive spectroscopy (EDS).

Fig. 33. In situ CO chemisorption FTIR measurements during ALD of Pd shell on an ALD Pt/Al₂O₃ sample at 150 °C. Scale bar, 3%, scale bar for the inset, 1%. Reprinted with

Fig. 34. Aberration-corrected HAADF-STEM images of different bimetallic catalysts at low and high magnifications: (a) and (e) Au@3Pd/SiO₂; (b) and (f) Au@8Pd/SiO₂; (c) and (g) Au@20Pd/SiO₂. (d) The growth of Au@Pd particle size as a function of Pd ALD cycles. (h) The Pd shell thickness as a function of Pd ALD cycles. (i) A lower magnification HAADF-STEM image of Au@8Pd/SiO₂, and corresponding EDX mapping images: (j) Au L α 1 and (k) Pd L α 1 signals, and (l) the reconstructed Au-Pd bimetallic composition image. Reprinted with permission from [264]. Copyright © 2015 Elsevier Inc. All rights reserved.

4.3.2 Pd ALD on Au

AuPd bimetallic catalysts have showed superior catalytic performance in many reactions including CO oxidation [269, 270], direct synthesis of hydrogen peroxide [271, 272], direct synthesis of vinyl acetate [273], formic acid decomposition [274, 275], and alcohol oxidation [276-287]. Recently, we synthesized SiO₂ supported Au@Pd core-shell catalysts with precisely controlled Pd shell thickness using a combination of wet-chemistry and ALD: An Au/SiO₂ catalyst was first synthesized using the deposition-precipitation method, and then Pd was selectively deposited on the surface of Au nanoparticles but not on the SiO₂ support using Pd ALD to form uniform Au@Pd core-shell nanoparticles. Using Pd(hfac)₂-H₂ at 150 °C, a linear growth of the Pd shell at ~ 0.08 nm/cycle was observed on the Au nanoparticles, as indicated by both an increase in mean particle size and an increase in the Pd shell thickness in aberration-corrected HAADF-STEM images (Fig. 34) [264]. Note that Pd appears darker than Au in these images due to Z-contrast. DRIFTS CO chemisorption measurements further revealed the gradual evolution of Pd species on the Au nanoparticle surfaces with increasing Pd ALD cycles: from isolated Pd adatoms or very small aggregates to larger ensembles, and to continuous islands or films according to the development of linear- and bridge-bonded CO (Fig. 35) [288, 289]. XPS further illustrated that the thinner the Pd shell, the more negative the shift in Pd 3d_{5/2} binding energy, which strongly indicates that the modification of Pd electronic properties by Au depends tightly on the Pd shell thickness. In solvent-free aerobic oxidation of benzyl alcohol, the Au@Pd core-shell bimetallic catalysts showed a clear volcano-like trend as a function of the Pd shell thickness, wherein the Au@Pd core-shell catalyst with a Pd shell thickness of 0.6~0.8 nm showed a maximum TOF of 27600 h⁻¹ (or a specific activity of 9800 h⁻¹). Combining the results of DRIFTS CO chemisorption, UV-Vis, and XPS, the catalytic activity enhancement was suggested to be a synergistic effect combining both ensemble and electronic promotion.

4.3.3 Pt ALD on Pd

The selective ALD of Pt on Pd using MeCpPtMe₃-O₂ can be accomplished by reducing the oxygen partial pressure [260] or by decreasing the deposition temperature to 150 °C [69], and yields a linear growth at ~ 0.4 Å/cycle. When selective low-temperature Pt ALD was executed on a Pd/Al₂O₃ catalyst to grow Pd@Pt core-shell nanoparticles at 150 °C, in situ FTIR CO chemisorption performed after each Pt ALD cycle clearly demonstrated a progressive change in surface composition [69]. The gradual decrease of bridge-bonded CO

on Pd (1917 cm^{-1}), and simultaneous increase of the linear CO on Pt (at between $2054\text{--}2075\text{ cm}^{-1}$), provide direct evidence for the continuous deposition of Pt on the Pd nanoparticle surface with increasing Pt ALD cycles (Fig. 36). Completion of a continuous Pt shell on the Pd nanoparticle core occurred after ~ 10 Pt ALD cycles ($\sim 1.5\text{ ML}$), as indicated by the disappearance of the bridge-bonded CO peak on Pd, in contrast with the Pt@Pd growth where Pt diffusion to the surface was observed (Fig. 33). Consequently, the Pt shell thickness on Pd nanoparticles can be precisely tuned by increments of $\sim 0.15\text{ ML}$ per cycle. The formation of Pd@Pt core-shell nanoparticles was further confirmed by aberration-corrected HAADF-STEM measurements along with EDS line profile analysis.

Fig. 35. DRIFT spectra of CO chemisorption at 298 K on various $\text{Au}@x\text{Pd}/\text{SiO}_2$ catalysts at the CO saturation coverage. Here x denotes the number of Pd ALD cycles. Reprinted with permission from [264]. Copyright © 2015 Elsevier Inc. All rights reserved.

Fig. 36. In situ CO chemisorption FTIR measurements during ALD of Pt shell on an ALD $\text{Pd}/\text{Al}_2\text{O}_3$ sample at $150\text{ }^\circ\text{C}$. Scale bar, 1%, scale bar for the inset, 0.5%. Reprinted with

4.3.4 Ru ALD on Pt.

Ru ALD on Pt surfaces using $\text{Ru}(\text{EtCp})_2\text{-O}_2\text{-H}_2$ exhibited linear growth at a rate of ~ 0.21 Å/cycle (22.4 ng/cm^2 per cycle) at 200°C (Fig. 32c). At 150°C , a higher initial Ru growth rate observed on Pt surface, suggesting that Pt accelerates the Ru nucleation at low temperatures [69]. In situ CO chemisorption FTIR studies of Ru ALD on a Pt/ Al_2O_3 sample at 200°C demonstrated a gradual increase in Ru surface coverage with increasing Ru ALD cycles (Fig. 37), as evidenced by the decrease of linear CO on Pt (2069 cm^{-1}) and the growth of a new peak at 2010 cm^{-1} in intensity, assigned to linear CO on Ru [290]. The peak of linear CO on Pt persisted even after 35 Ru ALD cycles (~ 3 Ru ML), suggesting diffusion of Pt to the surface during Ru ALD. EDS line profile analysis further confirmed the presence of Pt atoms on the surface of a Pt-core Ru-shell sample.

Fig. 37. In situ CO chemisorption FTIR measurements during ALD of Ru shell on an ALD Pt/ Al_2O_3 sample at 200°C . Scale bar, 2%. Reprinted with permission from [69]. Copyright © 2014, Rights Managed by Nature Publishing Group.

Shim et al. investigated Ru ALD on sputtered Pt columns using high resolution TEM. The Ru ALD was conducted using $\text{Ru}(\text{EtCp})_2\text{-O}_2$ at 320°C . They discovered “island growth” of Ru ALD on the Pt, which they attributed to lack of appropriate functional groups on the Pt surface for Ru nucleation, and the higher surface energy of Ru (3.9 J/m^2), compared to Pt (2.7 J/m^2) (Fig. 38) [291, 292]. The formation of Ru clusters would be thermodynamically favored as this would lower the surface energy. In line with this observation, Johansson et al. also reported “island growth” of Ru ALD on Pt nanoparticles which were supported on nitrogen-

doped multi-walled carbon nanotubes [263]. When the sputtered Pt anode coated with 100 cycles of Ru ALD film was employed in DMFCs, the performance was improved by more than 1 order of magnitude in terms of power output. XPS measurements revealed that increasing the Ru coverage results in a dramatic reduction in the amount of surface-bound CO that would otherwise passivate the Pt anode [291].

Fig. 38. (a–c) HRTEM cross-sectional images of a sputtered Pt anode surface after 400 cycles of Ru ALD using $\text{Ru}(\text{EtCp})_2\text{--O}_2$ at 320 °C. (c) The presence of deposited Ru is indicated in yellow. (d) and (e) show the corresponding diffraction patterns for Pt and Ru at the points marked in (c). (f–h) HRTEM cross-sectional image of the Pt/Ru ALD 400 anode surface with EDS composition analysis. Reprinted with permission from [291]. Copyright © 2015, American Chemical Society.

4.3.5 Cu ALD on Ni

Employing surface-science characterization techniques under UHV conditions, Zaera, et al. investigated the surface chemistry for Cu ALD on Ni(110) using $(\text{Cu}^{\text{sBu-amd}})_2\text{--H}_2$ [184, 293]. They found that $(\text{Cu}^{\text{sBu-amd}})_2$ dissociatively adsorbed on the nickel surface above 300 K, indicated by the observation of metallic copper according to the Cu $2p_{3/2}$ XPS peak at 932.5 eV (Fig. 39). The optimum deposition temperature was identified to be ~350 K, where self-limiting adsorption was achieved (Fig. 39b). The Cu film growth rate was about 0.75 Å/cycle. Above 400 K, Cu multilayer deposition and even decomposition was observed. Very interestingly, they reported no detectable changes in deposition rate or surface chemistry upon presaturation of the nickel substrate with hydrogen (Fig. 39b). They attributed this to the early desorption of hydrogen from the nickel surface at temperatures below those required

for the Cu ALD. They pointed out that significant H surface coverages could be maintained under H₂ pressures above $\sim 10^{-6}$ bar, which is the case in typical ALD processing conditions. In addition, their work suggests that the organic intermediates may form on the surface upon thermal activation of adsorbed copper acetamidinate, which needs to be stable at the temperatures used in ALD in order to be available for hydrogenation and removal from the surface in the second half-cycle. Otherwise, these organic intermediates are likely to dehydrogenate and form irreversible adsorbates, thus ultimately incorporate carbon and/or nitrogen impurities into the grown films.

Fig. 39. (a) Cu 2p_{3/2} XPS uptake for (Cu(sBu-amd))₂ on Ni(110) at 350 (left), 400 (center) and 460 (right) K. All peaks are centered at 932.5 eV, a value typical for metallic copper. (b) Copper uptake estimated from Cu 2p_{3/2} XPS experiments shown in (a) for (Cu(sBu-amd))₂ on clean (open symbols) and hydrogen presaturated (150 L H₂ at 90 K; filled symbols) Ni(110) as a function of surface temperature. No significant differences are observed between the surfaces with versus without preadsorbed hydrogen. Reprinted with permission from [184]. Copyright © 2010, American Chemical Society.

4.3.6 Cu ALD on Pt and Pd

With the sequence Cu(thd)₂–H₂, selective Cu ALD on Pd and Pt surfaces but not on SiO₂ was achieved in the temperature range 190–260 °C [173, 265, 266]. It was suggested that Cu(thd)₂ dissociatively chemisorbs on the Pd and Pt surfaces, similar to the case of copper acetamidinate on Ni [184, 293]. Upon hydrogen adsorption, the thd ligands are completely removed as H(thd) through reaction with the dissociated surface hydrogen. Using auger electron spectroscopy (AES), glancing incidence x-ray diffraction (GIXRD) and XPS, Willis et al, revealed a significant Pd surface segregation to form a CuPd alloy, where a Cu film was deposited onto a Pd seed layer (XPS results are shown in Fig. 40). Based on the in-situ real-

time spectroscopic ellipsometry measurements, they proposed that precursor adsorption is reversible, and dissociatively adsorbed hydrogen is the stable surface intermediates between growth cycles; therein, strong H^* binding to Pd is responsible for the continuous diffusion of Pd from the underlying seed layer into the deposited Cu film. Less intermixing occurs at lower growth temperatures and shorter cycle times as a consequence of the reduced Cu/Pd inter-diffusion [265]. In contrast, Cu ALD on the Pt seed layers showed a clear Cu-Pt interface without any Pt surface segregation [266]. In line with these results, Winter et al. observed a more pronounced Cu/Pd inter-diffusion than Cu/Pt when Cu metal films were grown on Pd and Pt using an ABC-type Cu ALD with a sequence of $Cu(OCHMeCH_2NMe_2)_2$ –formic acid– $BH_3(NHMe_2)$ at 135–165 °C [180].

Fig. 40. XPS depth profile of a sample of Pd seed layer on silicon wafer after 600 cycles of Cu ALD at 235 °C. Here the layers of the film are removed with an argon ion sputter gun. Reprinted with permission from [266]. Rights managed by AIP Publishing LLC.

4.4 Precise synthesis of well-mixed alloy bimetallic catalysts

Bimetallic alloy ALD can be accomplished by alternating between the ALD processes for the individual metals; therein, the composition is tuned by the relative number of ALD cycles used for each component [5, 69, 294]. When the ALD processes of two metals share the same deposition temperature and mutually compatible surface chemistries, these two ALD processes can be directly combined together [153, 294, 295]. For instance, Pt and Ir ALD are both carried out at 300 °C based on a combustion-like surface chemistry, using $MeCpPtMe_3-O_2$ and $Ir(acac)_3-O_2$, respectively [105, 107]. Elam et al. demonstrated that the QCM step ratios and QMS product distributions did not change for the Pt and Ir ALD cycles in the 1:1 mixed metal film, compared to the corresponding signals for the pure metals (Fig. 41). These

results indicate that the growth mechanisms for the Pt and Ir were not perturbed by the presence of the other metal [153].

Fig. 41. In situ QCM and QMS data for (a) Pt ALD, (b) Ir ALD, and (c) Ir-Pt mixed-metal ALD using a 1:1 Ir(acac)₃:MeCpPtMe₃ cycles ratio at 300 °C. The QCM thickness trace for Pt in (a) shows an increase during Pt(MeCp)Me₃ adsorption (Δm_0) and a smaller decrease from the O₂ dose to yield a net Pt thickness increase (denoted as Δm_1). In panel (c), the QCM thickness trace yields the net thickness increases from individual Ir ALD cycles (Δm_{Ir}) and Pt ALD cycles (Δm_{Pt}), which enable determination of the film composition. The middle section shows the reaction byproducts of $m/z=15$ for CH₄ and $m/z=44$ for CO₂ from in situ QMS data. The bottom sections of the graphs show the precursor valve operation, where a value of 1 indicates that the respective precursor dosing valve is open. Reprinted with permission from [153]. Copyright © 2010, American Chemical Society.

When the ALD processes of two metals do *not* share a common deposition temperature, or the surface chemistries are incompatible, this can make the alloy film growth extremely challenging or impractical. Fortunately, low-temperature selective metal ALD seems to satisfy these strict requirements for many bimetallic systems [69]. The incompatibility between ALD processes can be rectified by adding a H₂-reduction step at the end of combustion-reaction based ALD and an O₂-oxidation step at the end of hydrogenation-reaction based ALD in each alloy ALD cycle (Fig. 42). For instance, Pd ALD is a hydrogenation reaction process where surface H* are the active sites [131, 296]; while Pt ALD is a combustion reaction process, where surface O* are the active sites [105, 107]. The

direct combination of AB type Pd ALD ($\text{Pd}(\text{hfac})_2\text{-H}_2$) with AB type Pt ALD ($\text{MeCpPtMe}_3\text{-O}_2$) caused decomposition of the hfac ligands on the O-terminated surface, which contaminates the surface with carbon and fluorine according to in situ QMS and suppress further Pd growth according to in situ QCM [69]. On the other hand, an O_2 exposure added after the H_2 exposure in each Pd ALD cycle will oxidize and O-terminate the Pd surface in preparation for the MeCpPtMe_3 adsorption in the subsequent Pt cycle. Similarly, a H_2 exposure added after the O_2 exposure in each Pt ALD cycle can reduce and H-terminate the surface for the $\text{Pd}(\text{hfac})_2$ adsorption in the subsequent Pd ALD cycle. Implementing this ABC strategy can satisfy the surface chemistries of both ALD process and facilitate the growth of the two components. Indeed, the growth rate of PtPd alloy ALD is 136.4 ng/cm^2 per alloy cycle using $\text{MeCpPtMe}_3\text{-O}_2\text{-H}_2\text{-Pd}(\text{hfac})_2\text{-H}_2\text{-O}_2$, much greater than using $\text{MeCpPtMe}_3\text{-O}_2\text{-Pd}(\text{hfac})_2\text{-H}_2$ (90.9 ng/cm^2 per cycle).

In the following subsections, we discuss the synthesis, structure, and catalytic activities of several ALD alloy catalysts.

Fig. 42. In situ QCM studies of low temperature metal alloy ALD at 150 °C. (a) Linear growth of PtPd, RuPd, and RuPt alloys by alternating between the ALD processes for the two metals. PtPd alloy ALD sequence: $\text{MeCpPtMe}_3\text{-O}_2\text{-H}_2\text{-Pd}(\text{hfac})_2\text{-H}_2\text{-O}_2$; RuPd alloy sequence: $\text{Ru}(\text{EtCp})_2\text{-O}_2\text{-H}_2\text{-Pd}(\text{hfac})_2\text{-H}_2$; RuPt alloy sequence: $\text{Ru}(\text{EtCp})_2\text{-O}_2\text{-H}_2\text{-}$

MeCpPtMe₃-O₂-H₂. (b) Detailed mass changes during two PtPd alloy supercycles. (c) Detailed mass changes during two RuPd alloy supercycles. (d) Detailed mass changes during two RuPt alloy supercycles. The mole ratios of these metals in the alloy ALD are indicated. The sequential exposure steps of each reactant are shown as columns in color at the bottom of each figure, nitrogen purge step is in between the columns. Reprinted with permission from [69]. Copyright © 2014, Rights Managed by Nature Publishing Group.

Fig. 43. TEM images of ALD RuPt bimetallic nanoparticles on Al₂O₃ synthesized using 2 cycles Ru ALD, 1 cycle Pt ALD and 1 cycle Ru ALD at 300 °C. The mean particle diameter is 1.2 nm with a distribution width of 0.3 nm. (b) High-resolution TEM image showing lattice fringes for the Al₂O₃ and the Ru–Pt nanoparticles. (c) X-ray absorption spectra at Ru K-edge for ALD Ru–Pt/Al₂O₃ and a reference 3% Ru/SiO₂. For the ALD catalysts, the Ru K-edge is shifted 3 eV higher and has a distinctly different line profile compared to the Ru reference. (d) Fourier transforms of the absorption spectra where the solid line shows the magnitude and the broken line shows the imaginary part. Peaks at 2 and 2.5 Å are smaller for the ALD catalyst when compared to the Ru reference. Reprinted with permission from [9]. Copyright © 2010, American Chemical Society.

4.4.1 RuPt alloy ALD

Ru and Pt ALD share the same deposition temperature of 300 °C and the compatible combustion-like surface chemistry. Elam et al. observed that the growth rates for Ru and Pt in the RuPt alloy ALD at 300 °C were very similar to the growth rates for the corresponding pure metal, in a similar fashion as Ir–Pt ALD alloy, indicating little perturbation of the growth chemistries upon transitioning between materials [9]. A bimetallic RuPt/Al₂O₃ catalyst was synthesized on high surface area Al₂O₃ powder using RuPt alloy ALD with the following scheme: 2 cycles Ru ALD, 1 cycle Pt ALD, and 1 cycle Ru ALD. High resolution TEM revealed that the Ru–Pt deposited as discrete nanoparticles with a diameter of 1.2 ± 0.3 nm on the alumina support, and EXAFS measurements confirmed that the Ru–Pt nanoparticles were bimetallic (Fig. 43). In the CH₃OH decomposition reaction, the resulting bimetallic RuPt/Al₂O₃ catalyst yielded a considerably higher catalytic activity compared to a physical mixture of Ru/Al₂O₃ and Pt/Al₂O₃ catalysts.

When Ru and Pt ALD were used to grow RuPt alloy nanoparticles on N-doped multi-walled carbon nanotubes at 250 °C, Johansson et al, [294] also observed a linear correlation between the Ru:Pt content ratio and the Ru:Pt ALD cycle ratio. Consequently, the composition was easily tuned by varying the relative number of ALD cycles. The ALD RuPt alloy catalysts were tested toward the CO oxidation and methanol oxidation reaction (MOR) in a three-electrode electrochemical set-up. They found that the catalysts with a Ru content of 29 at.% exhibited the highest catalytic activity and attributed this to a bifunctional mechanism [295].

4.4.2 PdCu alloy ALD

Molenbroek et al. synthesized PdCu alloy nanoparticles on SiO₂ and Al₂O₃ supports using 1 cycle Cu ALD followed by 1 cycle Pd ALD with Cu(thd)₂, Pd(thd)₂ and O₂ as reactants. The deposition temperature was 170 °C for the metal precursor exposure step and 450 °C for the O₂ oxidation step. TEM showed that the resulting PdCu particles had a high dispersion and particle sizes of 2.5–7.0 nm on SiO₂ and 2.0–6.0 nm on Al₂O₃. Interestingly, their EXAFS measurements showed that the type of alloying in the PdCu system depended on the support. Surface segregation of Cu was observed for the alumina-supported samples, but random alloying was seen for the silica-supported samples [256].

4.4.3 PdPt alloy ALD

As discussed previously, Pd and Pt ALD have dissimilar surface chemistries. Direct combination of the conventional AB type Pd ALD ($\text{Pd}(\text{hfac})_2\text{-H}_2$) with Pt ALD ($\text{MeCpPtMe}_3\text{-O}_2$) would cause decomposition of the hfac ligands on the O-terminated surface, producing carbon and fluorine contamination and also suppressing the Pd growth [69]. On the other hand, adding an O_2 oxidation step at the end of each Pd ALD cycle, and a H_2 reduction step at the end of each Pt ALD cycle can satisfy the surface chemistries of each ALD process and thus facilitate the growth of the two components. Using the ABC sequences of $\text{MeCpPtMe}_3\text{-O}_2\text{-H}_2$ and $\text{Pd}(\text{hfac})_2\text{-H}_2\text{-O}_2$ to alternatively deposit Pt and Pd, PdPt alloy nanoparticles can in principle be formed. In situ CO chemisorption FTIR provided solid evidence for the formation of a well-mixed PdPt alloy using ABC sequences for the Pt and Pd ALD. As illustrated in Fig. 44a, the linear CO peak on Pt (2067 cm^{-1}) was suppressed while the 1931 cm^{-1} peak (bridge-bonded CO on Pd) increased after each Pd ALD step, clearly demonstrating that the Pd covered a fraction of the surface Pt atoms. Similarly, each Pt ALD step reversed these trends, indicating that Pt covered some of the surface Pd atoms. These reversible changes in the spectral features persisted over multiple PtPd alloy supercycles, indicating the formation of a well-mixed PdPt alloy. High resolution HAADF-STEM along with elemental line profile analysis further confirmed the well-mixed PtPd alloy structure (Fig. 44b).

Fig. 44. (a) In situ CO chemisorption FTIR measurements during PtPd alloy ALD on an ALD Pt/ Al_2O_3 sample at $150\text{ }^\circ\text{C}$. “Supercycles” of the PdPt alloy ALD were performed comprising 3c-Pd ALD followed by 2c-Pt ALD, and CO chemisorption was performed after each 3c-Pd and each 2c-Pt to probe the surface composition. Scale bar, 10%. (b) Representative aberration-corrected HAADF-STEM images and corresponding EDS line profiles of PtPd alloy bimetallic nanoparticles on spherical alumina support. Reprinted with permission from [69]. Copyright © 2014, Rights Managed by Nature Publishing Group.

4.5 Summary

Due to the unique self-limiting character, ALD provides a promising way to precisely synthesize supported bimetallic nanoparticles on the atomic level. The major challenge is to ensure that the ALD processes for two metals share a common deposition temperature and compatible surface chemistries. The temperature requirement is less important for bimetallic nanoparticles with core-shell structure, since the temperature need only be changed once when commencing growth of the shell metal.

An essential goal in catalysis science is to establish catalyst structure-activity relationships. Selective metal ALD on metal surfaces but not on supports to exclude any monometallic nanoparticle formation is a powerful means to achieve this goal. ALD enables the atomically-precise synthesis of supported bimetallic nanoparticles by digitally tailoring the ALD pulse sequences. The bimetallic particle size is determined by the total number of ALD cycles performed, the composition is dictated by the relative number of ALD cycles used for each component, and the structure of the bimetallic nanoparticles is controlled by the order in which the individual cycles are executed. Such cycle-by-cycle “bottom up” construction of bimetallic (or **multimetallic**) nanoparticles on supports shows obvious advantages over conventional methods such as successive impregnation. For example, the thickness of Pt shell on Pd@Pt core-shell nanoparticles can be precisely tuned by ~0.15 ML per cycle (Fig. 36) [69]. Such controlled supported bimetallic catalysts synthesis facilitates the establishment of the correlation between the bimetallic nanoparticles structures and their catalytic performance, thus providing insights for understanding the reaction mechanism and the rational design of improved catalysts. Nevertheless, we have shown that interdiffusion or surface segregation of metal atoms can occur during bimetallic nanoparticle synthesis, resulting in a different structure than intended. In such cases, depositing the metals at a lower temperature might suppress the metal atom interdiffusion or surface segregation.

5 Oxide ALD on metals: precise synthesis of nanostructured metal catalysts

The sintering of supported metal catalysts, especially under severe reaction conditions, is one major technical issue in applied catalysis. Improving the stability of metal particles against sintering under reaction conditions has drawn tremendous attentions [40-42]. Encapsulation of metal nanoparticles with porous oxide layers is the most commonly used methods. The protective oxide layer is often grown using the techniques including CVD and sol-gel chemistry to form core-shell structures. With an oxide protective layer, such as mesoporous silica [49, 53], tin oxide [297], zirconia [298], or ceria [50, 299], the

encapsulated metal nanoparticles sometimes show good sintering resistance up to 800 °C. However, in most cases there is a large decrease in catalytic activity due to mass transfer resistance associated with the thick protective shell (usually tens of nm's thick). Atomically-precise control over the thickness of protective layers can be critical to achieve an optimal balance between sintering resistance and high catalytic activity.

Motivated by the atomically-precise thickness and composition control afforded by ALD, a large number of studies have been performed to improve the stability of metal nanoparticles against sintering and leaching using ALD oxide overcoats, where conformal ultrathin ALD metal oxide layers are deposited on metal nanoparticles as well as the support [8, 12, 300-303]. The ability to form ultrathin ALD coatings on metal particles illustrates the potential to minimize the mass transfer resistance.

In an effort to maintain high catalytic activity, several methods for generating and controlling the porosity of ALD oxide overcoats have been developed, including self-inhibited growth [304], high-temperature treatment [12, 305], organic porogens [301], and selective growth [306]. These methods were discussed in previous reviews [5, 13]. Here we will mainly focus on the surface chemistry of oxide ALD on metals and the catalytic performance of the resulting overcoated metal catalysts in this section. In particular, the selective blocking of low-coordination sites of metal nanoparticles, the confinement effect, and the creation of new metal-oxide interfaces will be discussed.

5.1 Al_2O_3 ALD on Pd

5.1.1 Surface chemistry

Al_2O_3 ALD performed using TMA and water is one of the most successful ALD procedures, and has been extensively investigated [26, 307-310]. The mechanism for Al_2O_3 ALD on oxide surfaces is well understood: first, TMA reacts with hydroxyl groups on the starting surface forming $Al(CH_3)_x^*$ ($x = 1-2$) surface species and CH_4 gaseous product; next, exposure to H_2O transforms the $Al(CH_3)_x^*$ terminated surface to an $Al(OH)_x^*$ ($x = 1-2$) terminated surface and again releases CH_4 [26, 309, 310]. The ratio of the total mass gain in one ALD cycle (Δm_0) to the mass gain after the TMA exposure (Δm_1) is about 1.1 according to in situ QCM measurements [26, 309, 311].

However, the growth mechanism for Al_2O_3 ALD on metal surfaces can be quite different. For instance, we observed a significantly higher mass ratio of $\Delta m_0/\Delta m_1 = 1.6$ in the first Al_2O_3 ALD cycle on Pd using in situ QCM measurements (Fig. 45a) [304, 312]. Furthermore,

in situ QMS measurements detected C₂H₆ during the first TMA exposure and H₂ during the first H₂O exposure along with the dominant CH₄ product (Fig. 45b). DFT calculations performed on Pd(111) and Pd(211) revealed that TMA adsorbs most strongly on the 3-fold (hcp) site, and quickly dissociates to Al(CH₃)^{*} (also with a slight preference for hcp adsorption) and CH₃^{*} surface species (Equations 11,12). The formation of Al(CH₃)^{*} surface species was further confirmed by scanning tunnelling microscopy (STM), which showed locally-ordered species with a height of about 0.15 nm and a separation distance of ~0.43 nm [312]. Some Al(CH₃)^{*} might further dissociate into Al^{*} and CH₃^{*} on step edges (Equation 13). Zemlyanov et al. later reported the formation of a Pd-Al alloy phase after TMA exposure on Pd as evidenced by a Pd 3d higher binding energy shift of 0.6 eV from the metallic phase using XPS, in line with our results [313]. The ethane observed by QMS likely forms through the coupling of two adjacent CH₃^{*} species according to Equation 15, which further support the existence of a large concentration of CH₃^{*} on the Pd surface from TMA dissociation. More interestingly, the DFT results demonstrate that the step sites are much more thermodynamically favorable for TMA dissociative adsorption than the Pd(111) terraces by about 0.81 eV.

In the water exposure, the transformation of Al(CH₃)^{*} into Al(OH)^{*} accompanied by methane release is represented by Equation 16. This reaction is highly exothermic, and has a free energy change of ~1.3 eV, on both the Pd(111) and Pd(211) surfaces. Additional reaction with water to form Al(OH)₂^{*} and Al(OH)₃^{*} (Equations 17-20), was found to be thermodynamically favorable on both Pd(111) and Pd(211) surfaces. In fact, Al(OH)₃^{*} was the most thermodynamically stable intermediate on the Pd surfaces following H₂O exposure. These H^{*} can react with either CH₃^{*} species to release methane, (Equation 14), or combine

with an additional H^* to form molecular hydrogen (Equation 21), consistent with the observation of both methane and hydrogen by QMS during the initial water exposures (Fig. 45b).

Fig. 45. (a) In situ QCM measurements of Al_2O_3 ALD on a Pd surface at 200 °C during the first 4 cycles. (b) In situ QMS measurements of Al_2O_3 ALD on the Pd surface at 200 °C during the first 7 cycles. Continuously produced CH_4 in each TMA micropulse is from the cracking pattern of TMA during ionization. The H_2 and C_2H_6 QMS signals were multiplied by 10. The TMA and water exposures are indicated at the top of each figure. Reprinted with permission from [312]. Copyright © 2014, American Chemical Society.

A high concentration of CH_3^* species formed on Pd surface could inhibit the Al_2O_3 ALD by blocking the potential TMA adsorption sites. This site blocking is expected to be only temporary, since the CH_3^* species are released as CH_4 during the following water dose, thereby “cleaning” the Pd for TMA adsorption. This self-poisoning, self-cleaning process continues for ~ 7 cycles, as demonstrated by the persistent but gradually decreasing H_2 production [304]. This mechanism will allow the continuous nucleation of new Al_2O_3 islands

on the exposed Pd sites as well as the growth of existing Al_2O_3 patches in three dimensions. As a consequence, the Al_2O_3 grows as a discontinuous film rather than a continuous, pinhole-free coating typical for ALD, which was further confirmed by the STM measurements (Fig. 46a). More interestingly, once the ALD alumina film was annealed at 500 °C in UHV for 1h, the density of clusters significantly decreased on the terraces and the step edges were decorated with strips of alumina clusters (Fig. 46b), providing direct evidence for the preferential decoration of low-coordination Pd sites with ALD Al_2O_3 layers, especially after high temperature treatment [8, 12]. This observation is also consistent with the DFT calculations.

Fig. 46. STM images of 4-cycle ALD alumina films prepared at 200 °C on Pd (111) (a) as-deposited, and after annealing at 500 °C in UHV for one hour (b). The scanning parameters for (a) and (b) are $V = 1$ V, $I = 0.1$ nA and $V = -2$ V, $I = 0.2$ nA, respectively. Reprinted with permission from [312]. Copyright © 2014, American Chemical Society.

5.1.2 Structures of $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts with ALD alumina overcoat

When Al_2O_3 ALD was performed on a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst, the thickness of ALD Al_2O_3 overcoats was found to grow linearly with the number of ALD cycles at a growth rate of 0.16 nm/cycle (Fig. 47). This value is consistent with ALD of Al_2O_3 on boron nitride and ZrO_2 high surface area powders reported in the literature [305, 314], but slightly higher than the growth rate on planar surfaces, possibly due to some CVD during the long precursor exposure times. Even though the presence of porosity within ALD Al_2O_3 overcoats was suggested by in situ QMS and STM [304, 312], directly imaging porosity within the amorphous Al_2O_3 overcoats by high resolution TEM has proved challenging. Nevertheless, the porosity of ALD Al_2O_3 overcoats can be verified by nitrogen BET measurements. On a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst with 20 cycles of ALD alumina overcoat, we observed a micropore size of ~ 1 nm in diameter. Once this sample was calcined at 350 °C in 10% O_2 for 1 h, larger pores

with a size between 2–4 nm were formed (Fig. 48) [77]. Similarly, we observed that micropores of ~2 nm were formed within an 8 nm thick ALD alumina overcoat after calcination at 700 °C for two hours in 10% oxygen in helium [12]. We proposed that the pores are formed as a result of structural changes in the amorphous Al₂O₃ over-coating layer (e.g. densification) caused by dehydration [305], and the removal of carbon residues from the ALD process, and dewetting of the Al₂O₃ overcoats from the Pd nanoparticle surface [12].

Fig. 47. TEM images of spherical alumina supported Pd catalysts with different numbers of Al₂O₃ ALD overcoating cycles (insets show higher magnification images). (a) 0 cycle Al₂O₃; (b) 5 cycles Al₂O₃; (c) 10 cycles Al₂O₃; (d) 15 cycles Al₂O₃; (e) 20 cycles Al₂O₃; (f) thickness of Al₂O₃ overcoats versus ALD cycles. Reprinted with permission from [304]. Copyright © 2012, American Chemical Society.

Fig. 48. Pore size distributions calculated based on the DFT model from the N₂ adsorption isotherms of the as-prepared 20Al/Pd/Al₂O₃-WI and 20Al/Pd/Al₂O₃-WI-350C samples. Here the 20Al/Pd/Al₂O₃-WI-350C sample was obtained by calcining the 20Al/Pd/Al₂O₃-WI sample at 350 °C in 10% O₂ in Ar for 1 h followed by reduction at 150 °C in 10% H₂ in Ar for another 1 h. Reprinted with permission from [77]. Copyright © 2015, American Chemical Society.

Fig. 49. DRIFTS spectra of CO chemisorption at saturation coverage on fresh and used Pd catalysts with different numbers of ALD Al₂O₃ over-coating cycles (0c, 1c, 8c, 16c, and 24c-Al₂O₃). Spectra for fresh and used 16c and 20c-Al₂O₃ samples were enlarged by x20. Spectra for fresh and used 24c-Al₂O₃ samples were enlarged by 100. Reprinted with permission from [8]. Copyright © 2011, Springer Science+Business Media, LLC.

Using CO as a probe molecule, DRIFTS measurements clearly revealed that the embedded Pd nanoparticles within the ALD alumina overcoats remained accessible [8]. More interestingly, we found that the first ALD Al₂O₃ cycle preferentially nucleates at Pd edge and corner sites, revealed by a more pronounced decrease in the CO peaks at 2095 and 1978 cm⁻¹, compared with the peak at 1933 cm⁻¹, which are assigned to linear CO on the Pd corner atoms, μ_2 bridge-bonded CO on the step and edge sites of Pd NPs, and μ_2 bridge-bonded CO on Pd(111) facets, respectively (Fig. 49) [8, 315, 316]. Preferential nucleation of ALD Al₂O₃ at the low-coordination Pd sites agrees very well with our STM measurements and DFT calculations [304, 312]. With increasing ALD Al₂O₃ overcoat cycles, the Pd gradually becomes encapsulated such that no chemisorbed CO is observed by DRIFTS for the 24c-Al₂O₃ overcoated Pd sample.

5.1.3 Catalytic performance of Pd/Al₂O₃ catalysts tailored by ALD alumina overcoats

On the Pd/Al₂O₃ catalysts with ALD alumina overcoats, the catalytic performance including selectivity, activity and stability might be significantly altered by either selective blocking of the low-coordination sites of Pd nanoparticles or the confinement effect induced by the micropores within the overlayer. A study of methanol decomposition on a Pd/Al₂O₃ catalyst with and without alumina overcoats demonstrates the effect on both catalytic activity and stability [8]. Surprisingly, a single ALD Al₂O₃ cycle (~0.1 nm) was sufficient to suppress sintering of Pd nanoparticles during methanol decomposition at 270 °C for 6 hours, while considerable sintering occurred on the uncoated sample. The catalytic activity was nearly identical for the Pd samples with 1 to 16 cycles of alumina overcoats, which were all slightly higher than the uncoated Pd sample. Beyond 16 ALD cycles, the catalytic activity decreased (Fig. 50). The slightly enhanced activity for the Pd samples with 1 to 16 cycles of alumina overcoats is attributed to the selective blockage of the low-coordination sites of Pd nanoparticles, since the low-coordination Pd sites contribute little to the dehydrogenation reaction pathway for methanol decomposition [317]. On the contrary, the uncoated Pd nanoparticles lost a large number of active sites due to sintering, resulting in lower activity. This study demonstrates a good example showing the importance of precise control over the oxide overcoat thickness.

Fig. 50. Methanol conversion for Pd catalysts with 0 to 32 cycles of ALD Al₂O₃ over-coating in the methanol decomposition reaction carried out at 270 °C. Reprinted with permission from [8]. Copyright © 2011, Springer Science+Business Media, LLC.

In oxidative dehydrogenation of ethane (ODHE) at 675 °C, an 8 nm thick ALD alumina overcoat (45 ALD cycles) is necessary in order to achieve long term stability of Pd

nanoparticles against sintering [12]. In this reaction, the initial ethane conversion on the uncoated Pd/Al₂O₃ catalyst was 55% with CO and CO₂ as the major products, while the yield of the desired ethylene product was only 1.9% (Fig. 51). This Pd catalyst completely deactivated in less than 30 minutes due to heavy coke formation and severe sintering, in line with the literature [318]. In contrast, Pd nanoparticles with ~8 nm ALD Al₂O₃ overcoat exhibited excellent thermal stability against sintering and resistance to coke formation over two days of reaction testing at 675 °C, and produced an ethylene yield of 23%. Meanwhile, the yields of undesired products, CO, CO₂ and CH₄, were remarkably suppressed and stable at 5.1%, 3.9%, and 0.9%, respectively. In this study, we discovered that the edge and corner Pd atoms played a central role for sintering, coking and undesired reactions from C-C bond breaking [319]. As a consequence, exceptional resistance to sintering and coking in high temperature catalytic reactions, along with significantly enhanced selectivity, were simultaneously achieved because the edge and corner atoms were selectively blocked and stabilized by the ALD Al₂O₃ overcoats.

Fig. 51. Products yield on the Pd/Al₂O₃ samples with and without ALD Al₂O₃ over-coat during the ODHE reaction as a function of reaction time at 675 °C under the identical reaction conditions. Diamonds with dash line: product yields on the uncoated Pd/Al₂O₃ sample; circles with solid line: product yields on the 45Al/Pd/Al₂O₃ sample. Reprinted with permission from [12]. Copyright © 2012, The American Association for the Advancement of Science.

Marshall and co-workers investigated ALD alumina overcoated Pd catalysts in the selective hydrogenation of furfural, a biomass platform molecule. Along with a decrease in the activity with the number of ALD cycles, they found that the selectivity to furan increased

with increasing the ratio of terrace to edge sites. DFT calculations revealed that the furfural hydrogenation to furfuryl alcohol on step sites is more thermodynamically favorable than on terrace sites, whereas the furfural hydrogenation to furan on step sites is less favorable than on terrace sites [320].

Besides the selective blocking of low-coordinated Pd sites, the confinement effect induced by the micropores within the overlayer can be also utilized to tailor the catalytic performance of Pd catalysts. In selective hydrogenation of 1,3-butadiene, we recently demonstrated that at high conversions, the selectivity to all butenes increased remarkably with ALD alumina overcoat thickness [77]. On a Pd/Al₂O₃ catalyst with 30 cycles of ALD alumina overcoat (30Al/Pd/Al₂O₃), the selectivity to all butenes was 99% at a conversion of 95%, comparable to Au catalyst [321, 322]. On the contrary, it was only 46% at the same conversion on the uncoated Pd/Al₂O₃ catalyst (Fig. 52a). Compared to trans-2-butene and cis-2-butene, the improvement of 1-butene selectivity with increasing overcoat thickness was most pronounced at a conversion of 95% (Fig. 52b). It should be noted that high temperature pretreatment of ALD alumina coated Pd samples caused a large decrease in butenes selectivity due to the formation of larger pores (greater than 2 nm in diameter as shown in Fig. 48). Therefore, the remarkable increase in butenes selectivity is attributed to the confinement effect within the ~1 nm micropores in the overcoat according to the N₂ physisorption measurements (Fig. 48). The Pd surfaces exposed by the micropores would consist of small Pd ensembles on which the adsorbed 1,3-butadiene might favor selective hydrogenation due to steric effect. Meanwhile, the isomerization of 1-butene to trans-2-butene and cis-2-butene was retarded by the confinement effect [323]. In addition, long term durability against progressive deactivation was achieved on the Al₂O₃ coated Pd catalysts during 124 h on stream without any visible activity decline or selectivity changes.

Fig. 52. Catalytic performance of Pd/Al₂O₃ samples with and without ALD alumina overcoats in selective hydrogenation of 1,3-butadiene. (a) The selectivity to all butenes as a

function of 1,3-butadiene conversion. (b) The detailed selectivities to 1-butene, trans-2-butene and cis-2-butene at a conversion of 95%. The feed gas was 1.9% 1,3-butadiene and 4.7% H₂ with Ar as the balance gas at a total flow rate of 25 ml/min. Reprinted with permission from [77]. Copyright © 2015, American Chemical Society.

5.2 Al₂O₃ ALD on Pt

Similar to Al₂O₃ ALD on Pd discussed above (Fig. 45), in situ QCM and QMS measurements for Al₂O₃ ALD on Pt also showed a significantly higher $\Delta m_0/\Delta m_1$ mass ratio and the production of C₂H₆ and H₂ during the first ALD alumina cycle [312]. DFT calculations revealed that TMA undergoes dissociative chemisorption to form Al(CH₃)^{*} on Pd and Pt, and then transform into Al(OH)₃^{*} during the subsequent water exposure (Fig. 53), analogous to Al₂O₃ ALD on Pd. On Pt(211), Al(CH₃)^{*} could also dissociate to form Al^{*} and CH₃^{*} (Fig. 53a). In general, TMA decomposition is more exothermic on Pt than on Pd. However, we discovered that the difference in free energy change for alumina ALD on the (111) and (211) facets of Pd (0.81 eV for TMA and 0.39 eV for water) are much greater than the corresponding free energy changes on Pt (0.35 and 0.22 eV). These differences explain the preferential decoration of step edges on Pd but not on Pt observed by STM after high temperature treatment. Moreover, On Pd, C₂H₆ is likely produced at the low-coordinated sites through direct CH₃^{*}-CH₃^{*} coupling with a barrier of 1.02 eV [304], while on Pt, C^{*} and CH₃^{*} coupling appears to be a more plausible route, since the decomposition of CH₃^{*} to form C^{*} is thermodynamically more favorable on Pt compared to Pd, and this facilitates C₂H₆ production via C-C bond formation and subsequent hydrogenation [312].

5.3 Al₂O₃ ALD on Ir

Similar to our findings on Pd and Pt, DFT calculations showed that TMA dissociation on Ir is highly exothermic. However, the difference in free energy changes for TMA dissociation on the Ir terrace and step sites (2.19 eV) is much higher than the Pd and Pt [312]. On Ir, CH₃^{*} species from TMA dissociation can easily decompose into CH^{*} and H^{*}, where the energy barriers for C-H bond breaking are 0.44 and 0.04 eV, respectively in the sequential decomposition steps on Ir(111): CH₃^{*} + ^{*} → CH₂^{*} + H^{*} and CH₂^{*} + ^{*} → CH^{*} + H^{*}. The considerably lower energy barrier for C-H bond cleavage in the first decomposition step compared to both Pd(111) (0.77 eV) and Pt(111) (0.73 eV), results in abundant H^{*} species on Ir. Thus, H₂ production via the recombination of two H^{*} is more facile on Ir compared to Pd and Pt. Indeed, H₂ was observed during the first TMA exposure by in situ QMS

measurements along with the main CH_4 product. During the subsequent hydration steps, the hydroxylation of $\text{Al}(\text{CH}_3)^*$ to $\text{Al}(\text{OH})_3^*$ is more thermodynamically favorable on Ir(111) compared to Pd and Pt. While on Ir(211), $\text{O-Al}(\text{OH})_2^*$ was found to be the most stable intermediate, which is about 0.28 eV lower than the $\text{Al}(\text{OH})_3^*$ intermediate.

Fig. 53. Free energy diagrams (at 200 °C and 1 atm) for (a) TMA exposure; and (b) water exposure on Pt (111) (solid blue line) and Pt (211) (dashed blue line), Pd(111) (solid magenta line) and Pd (211) (dashed magenta line), respectively. The gas phase TMA, clean surface, and a pre-adsorbed H atom are used as the reference state (the black bar at 0 eV in panel a). Schematic representations of surface species are also presented. Numerical values in parentheses are the free energies corresponding to each intermediate state. The initial states for water exposure assume the desorption of one molecule of methane, i.e. $\text{CH}_3^* + \text{H}^* \rightarrow$

CH₄ (g). Reprinted with permission from [312]. Copyright © 2014, American Chemical Society.

Fig. 54. Plots of growth rate and QCM step ratio vs Al₂O₃ ALD cycles measured with QCM on a 50 nm Ag film at 50 °C. QCM measurements of 0–100 cycles (A), first 5 cycles (B) and the final 4 cycles (c). The shaded areas represent the time periods that the TMA and water dosing valves were open. Reprinted with permission from [324]. Copyright © 2005, American Chemical Society.

5.4 Al₂O₃ ALD on Ag

Van Duyne and co-workers investigated the growth of Al₂O₃ ALD on Ag using in situ QCM measurement, where a 50 nm Ag film was deposited directly on the QCM crystal by e-beam [324]. As shown in Fig. 54, QCM measurements demonstrated highly linear Al₂O₃ growth on Ag without any initial delay. Moreover, a large thickness change of 3–4 Å during the first TMA exposure and a slight thickness decrease following the H₂O doses and purges were observed during the early cycles (Fig. 54B), in contrast with Al₂O₃ ALD on Pd (Fig. 45a), Pt, and Ir, which showed a considerable larger mass gain during the first water exposure [312]. The authors suggested that the TMA reacts directly with the Ag, even though a small amount of surface hydroxyls bound to a thin native oxide layer on the Ag might partially contribute to the TMA adsorption. The thickness decreases during the TMA purge periods in the initial Al₂O₃ ALD cycles may result from the reaction of surface methyl groups and the subsequent desorption of methane. The decreases in thickness following the water exposures may result from the absence of OH groups on the metallic Ag surface. The SEM analysis further confirmed the layer-by-layer growth of ALD Al₂O₃ on the triangular Ag nanoparticles (Fig. 55).

The authors further demonstrated that the localized surface plasmon resonance (LSPR) nanosensor can detect Al₂O₃ film growth with atomic spatial resolution normal to the

nanoparticle surface, which is approximately 10 times greater spatial resolution than that in long-range distance-dependence study using multilayer self-assembled monolayer shells [324]. Compared to the bare Ag nanoparticles, 1.0 nm thick ALD Al_2O_3 layer improved the stability of the Ag nanoparticles against femtosecond laser exposures by a factor of 10 [325]. Moreover, after depositing a sub-1-nm alumina layer by ALD, silver film-over-nanosphere (AgFON) substrates demonstrated twice the sensitivity with 6 times shorter data acquisition time and 7 times longer temporal stability in the application of surface-enhanced Raman spectroscopy (SERS) [302].

Fig. 55. SEM images of (A) bare Ag nanoparticles ($a = 90$ nm, $b = 51$ nm) and Ag nanoparticles following (B) 100, (C) 200, (D) 400, and (E) 600 Al_2O_3 ALD cycles at 50°C . (F) Plot of in-plane width of Ag nanoparticle with ALD cycles determined from the SEM images. Reprinted with permission from [324]. Copyright © 2005, American Chemical Society.

5.5 Al_2O_3 ALD on Au

The detailed growth mechanism of Al_2O_3 ALD on Au has not yet been reported. However, Qian et al. showed that the Al_2O_3 ALD thickness increases linearly with ALD cycles on nanoporous Au surfaces with a rate of 0.15 nm/cycle based on TEM measurements (Fig. 56) [326-328]. Similarly, Biener and co-workers illustrated linear Al_2O_3 ALD on nanoporous Au using mass gain measurements [329], where they observed a growth rate of ~ 0.25 nm/cycle. They also demonstrated that nanoporous Au coated with sub-nanometer thick alumina films (2 ALD cycles) were stable up to at least 900°C , while the uncoated Au sintered severely at temperatures below 400°C . Tian et al. also demonstrated the conformal coating of Au nanoparticles with ALD Al_2O_3 , which are used as shell-isolated nanoparticles for SERS

applications [330]. In these studies however, the accessibility of the embedded Au nanoparticles for catalysis was not reported. Our recent work showed that the activity of Au/TiO₂ catalysts in CO oxidation was almost completely lost after only one ALD Al₂O₃ cycle, suggesting that the ultrathin alumina films on Au are dense.

5.6 Al₂O₃ ALD on Cu

DFT calculations show that TMA dissociation is endothermic to form Al(CH₃)* on Cu(111) surfaces with a free energy change of 0.72 eV, and only slightly exothermic on Cu(211) [312]. Consequently, Al₂O₃ ALD on clean Cu surface below 200 °C is thermodynamically more difficult than on Pd and Pt. Indeed, STM revealed no changes in surface features attributable to chemisorbed TMA after subjecting a clean Cu(111) crystal to a TMA exposure of ~3000 L (2×10^{-6} Torr for 25 min) at 200 °C (Compare Fig. 56a with b). Moreover, exposing the clean Cu surface to water (1×10^{-6} Torr for ~200 L) prior to the 3000 L TMA exposure at 200 °C did not induce TMA chemisorption (Fig. 56c). This observation is consistent with previous studies in which no observable hydroxyl formation from water dissociation on the chemically inert Cu(111) surface was reported [331, 332].

Fig. 56. STM images of (a) clean Cu (111) surface, $V = -0.5$ V, $I = 1$ nA; (b) STM image of Cu(111) surface after exposing TMA for ~ 3000 L at 200 °C, the corrugated step edges are highlighted by the black arrows, $V = -0.5$ V, $I = 1$ nA; (c) Cu(111) surface after sequentially

exposing water and TMA for 200 and 3000 L at 200 °C, respectively, $V = -1$ V, $I = 1$ nA; (d) Cu(111) surface after exposing oxygen for ~3000 L at room temperature and water for 200 L at 200 °C; $V = -2$ V, and $I = 0.2$ nA; (e) Cu(111) surface after exposing TMA to the pre-oxidized and hydrated surface for ~3000 L at 200 °C; $V = -2$ V, and $I = 0.2$ nA; (f) height profile along the solid black line in (e), illustrating the height of alumina clusters. Reprinted with permission from [312]. Copyright © 2014, American Chemical Society.

In order to facilitate Al_2O_3 ALD on Cu, it was necessary to expose the Cu to oxygen and then water (Fig. 56d), since it was reported that the chemisorbed oxygen assists the water dissociation to produce submonolayer hydroxyls thereby rendering the surface reactive towards the TMA (Fig. 56e) [333]. STM images revealed two different regions on the Cu surface after the oxygen and water treatment. Based on literature reports [334, 335], the well-ordered regions were assigned to hydroxyl-free Cu_2O , and the less ordered regions mainly near step edges or surface defects were assigned to hydroxylated Cu_2O . After exposing 3000 L TMA to the oxidized and hydroxylated Cu surface at 200 °C, STM revealed $\text{Al}(\text{CH}_3)_x^*$ ($x = 1, 2$) species preferentially at the step edges with a height of ~ 0.3 nm (Fig. 56e,f) and large “clean” patches on the terraces.

Based on XPS measurements, Zemlyanov and co-workers also found that no reaction between TMA and metallic Cu, consistent with our STM results (Fig. 56b). However, they found that TMA readily adsorbs on the $\text{Cu}_2\text{O}/\text{Cu}(111)$ surface at 200 °C, resulting in a partial reduction of the surface Cu^{1+} to metallic copper and the formation of a copper aluminate, most likely CuAlO_2 according to the XPS measurements [336]. STM demonstrated formation of two-dimensional (2D) islands of the aluminate after the first TMA half-cycle on $\text{Cu}_2\text{O}/\text{Cu}(111)$ (Fig. 57a,b). Following TMA exposure to the $\text{Cu}_2\text{O}/\text{Cu}(111)$ surface, O_2 was exposed to the resulting surface for 4500 L at 350 °C to complete one ALD cycle. STM revealed the formation of islands with an average height of 0.17 nm (marked by black arrows in Fig. 57c) and a reappearance of the well-ordered Cu_2O structure in a large portion (Fig. 57d,e). According to their STM results, the alumina island coverage seems very low. DFT calculations further revealed that adsorption and sequential dissociation of TMA on the $\text{Cu}_2\text{O}/\text{Cu}(111)$ surface is exothermic, in contrast with TMA reaction on metallic Cu (Fig. 58). TMA tends to first adsorb at the top position on O in the Cu–O ring via an Al atom with a binding energy of –0.93 eV. TMA then sequentially dissociates to form Al^* and CH_3^* surface species. A simplified stoichiometric equation for TMA reaction with $\text{Cu}_2\text{O}/\text{Cu}(111)$ is Equation 22:

It is surprising that the morphology of ALD alumina films on $\text{Cu}_2\text{O}/\text{Cu}(111)$ using TMA and O_2 is largely different from that on hydroxylated $\text{Cu}_2\text{O}/\text{Cu}(111)$ surfaces using TMA and water (Fig. 56e). Additional experimental studies, including a more detailed examination of the surface morphology and measurement of the gaseous reaction products, might explain these differences.

Fig. 57. STM images of the $\text{Cu}_2\text{O}/\text{Cu}(111)$ surface exposed to 2000 L TMA at 200 °C (a) 200 nm × 200 nm and (b) 100 nm × 100 nm. STM images after first O_2 half-cycle (4500 L O_2 at 350 °C) (c) 200 nm × 200 nm, (d) 50 nm × 50 nm, and (e) 25 nm × 25 nm. (f) Line profile along the solid white line indicated in image e. $V = -0.75$ V, $I = 1.0$ nA. Reprinted with permission from [336]. Copyright © 2015 American Chemical Society.

Dumesic and co-workers deposited ALD Al_2O_3 on $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ catalysts to improve their stability against sintering and leaching under liquid-phase conditions [48, 337, 338]. Using Solid state ^{27}Al magic-angle spinning (MAS) NMR spectroscopy, they detected that 6-, 5-, and 4-coordinate aluminum atoms in the as-prepared alumina overcoat. The presence of 5-coordinate aluminum is consistent with the amorphous nature of the overcoat before calcination; after calcination at 700 °C, the resonance corresponding to 5-coordinate

aluminum disappears, and the ratio of 6- to 4-coordinate aluminum suggests crystallization. Densification upon crystallization might generate pores in the Al_2O_3 overcoat that modify the catalytic behavior of the Cu. STM measurements on the surface of a pre-oxidized and hydrated (i.e., exposed to air and then water) Cu(111) surface after four cycles of alumina (Fig. 59a) revealed that alumina preferentially decorates the step edges and defects of the Cu(111) surface [48]. After four cycles, alumina occupied $59 \pm 3\%$ of the terrace sites and $91 \pm 1\%$ of the edge and defect sites. When this surface was heated to $500\text{ }^\circ\text{C}$ under ultra-high vacuum, the coverage of Cu(111) terraces decreased relative to that of the edges ($30 \pm 4\%$ of terraces vs. $80 \pm 3\%$ of edges and defects; Fig. 59b). These results implied that alumina preferentially binds to under-coordinated copper surface atoms (e.g., steps), leaving most terraces open after annealing. The preferential decoration of under-coordinated Cu sites was further confirmed by DRIFTS CO chemisorption, where the broad band at lower wavenumber nearly disappeared on the ALD alumina overcoated Cu/ $\gamma\text{-Al}_2\text{O}_3$ catalysts (45ALD/Cu/ $\gamma\text{-Al}_2\text{O}_3$ -973, Fig. 59e). In hydrogenation of furfural, a fully regenerable copper catalyst with excellent resistance to sintering and leaching was produced with only five ALD Al_2O_3 cycles [337].

Fig. 58. Free energy diagrams of TMA dissociation on Cu(111) and $\text{Cu}_2\text{O}/\text{Cu}(111)$. The insets are the optimized most stable structures of adsorbed TMA, dimethylaluminum (DMA), methylaluminum (MA), Al, and CH_3 , respectively. The orange, green, pink, black, red, and white spheres represent Cu of Cu(111), Cu of Cu_2O , Al, C, O, and H atoms, respectively. Reprinted with permission from [336]. Copyright © 2015 American Chemical Society.

Fig. 59. a) STM image of an oxidized and hydrated Cu(111) surface after four cycles of exposure to TMA and water. b) STM image after annealing at 500 °C in vacuum. The dashed lines highlight the step edges. c, d) Height profiles along the solid blue lines (for a and b, respectively) indicate the position of a step edge. e) IR bands for CO adsorbed on Cu/ γ -Al₂O₃ (blue solid line) and 45ALD/Cu/ γ -Al₂O₃-973 (red solid line) at -150 and 10 °C (dashed lines). The intensities are normalized by the pellet density and copper loading. Shaded regions indicate typical wavenumbers for CO adsorbed at different types of copper surface sites. Reprinted with permission from [48]. Copyright © 2013 WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim.

5.7 TiO₂ ALD on Metals.

Compared with Al₂O₃ ALD, there have been far fewer studies of TiO₂ ALD on metal surfaces. In one study, Martinson et al. reported “island growth” of TiO₂ ALD on Au using tetrakis(dimethylamido)titanium and water at 150 °C, where a lower growth rate was observed by in situ QCM measurements during the first 30 cycles [339]. They commented

that surface oxygen contamination of the nominally bare Au might have nucleated the TiO₂ ALD. Recently, we also observed that TiO₂ islands (highlighted by the black arrows) rather than uniform films formed on the corner and defect sites of Au nanocrystals after 20 TiO₂ ALD cycles using titanium tetraisopropoxide (TTIP) and H₂O at 150 °C based on high resolution TEM (Fig. 60) [340]. Preferential nucleation of TiO₂ on the low-coordinated Au sites was further confirmed by atomic force microscopy (AFM) and CO chemisorption DRIFTS measurements. Therein, the intensity of the CO peak at 2101 cm⁻¹, assigned to linear CO on low-coordination neutral Au sites [341-344], decreased dramatically with TiO₂ ALD cycles. This is not surprising since low-coordinated Au sites are expected to be more active than terrace sites for reaction with TTIP. The average growth rate of TiO₂ overcoat on Au was estimated to be ~0.3 Å/cycle based on TEM measurements. In contrast, Biener and co-workers reported that 10 cycles of TiO₂ ALD using TiCl₄ and water at 110 °C forms continuous and smooth TiO₂ coatings, which completely encapsulate the nanoporous Au, since the catalytic activity in CO oxidation disappears [329]. After annealing at 600 °C, the continuous TiO₂ film breaks into highly dispersed anatase TiO₂ nanoparticles on nanoporous Au, and exhibits an almost 3 times larger activity for CO oxidation compared to the uncoated Au. The different growth modes of TiO₂ ALD on Au might derive from variations in the nucleation for the different titanium precursors.

Fig. 60. HRTEM images of unsupported Au nanocrystals with 20 cycles of TiO₂ overcoat at low (a) and high (b) magnifications. Here TiO₂ islands formed on the Au nanocrystals are

highlighted by the black arrows. Reprinted with permission from [340]. Copyright © 2016, American Chemical Society.

“Island growth” was also observed for TiO₂ ALD on Ni using TTIP and H₂O at 180 °C [345]. The TiO₂ island density increased with increasing ALDTiO₂ cycles (Fig. 61b,c) and coalesced to form a smooth film after 180 cycles. It was noted that the Ni surface was mostly oxidized to Ni₂O₃ in their work. After 10 TiO₂ ALD cycles, the Ni₂O₃ was partly reduced to NiO, suggesting that the 180 °C deposition temperature was sufficient to reduce the surface.

When ALD TiO₂ is used to overcoat supported metal catalysts, an enhancement in catalytic activity and improved stability are frequently seen. For instance, TiO₂ coated Au/Al₂O₃ catalysts showed a remarkable catalytic enhancement for CO oxidation [340]. Furthermore, the activity as a function of TiO₂ ALD cycles showed a “volcano-like” behavior, providing direct evidence that the catalytic activities of TiO₂ overcoated Au catalysts strongly correlate with the total length of perimeter sites at the Au-TiO₂ interface. Kim et al. also reported that TiO₂ ALD not only improves the catalytic activity of Ni catalysts in the CO₂ reforming of methane, but also effectively suppresses graphitic carbon deposition on the Ni surface [345, 346]. The high activity of the TiO₂ coated Ni catalyst was maintained over 65 h at 800 °C, whereas deactivation of the bare Ni surface began within 1 h under the same conditions (Fig. 62) [346]. Recently, Huber et al. demonstrated that a Co/C catalyst with a thin-layer overcoating of ALD TiO₂ exhibited 2.5 times higher turnover frequency (TOF) compared to the uncoated Co/C catalyst in the electrochemical oxidation of water. The TOF of the TiO₂-overcoated Co/C catalyst increased from 5 to 60 with increasing ALD TiO₂ cycles [347]. Moreover, the ALD TiO₂ preserved the activity of the Co/C catalyst and inhibited leaching and sintering of cobalt in aqueous-phase hydrogenation reactions. This behavior is in sharp contrast with ALD Al₂O₃ overcoats which produced an irreducible cobalt aluminate phase without any catalytic activity [348]. A similar trend was also observed for ALD TiO₂ and Al₂O₃ overcoated copper chromite catalysts in the selective hydrogenation of furfural reaction [349].

Fig. 61. SEM images of (a) bare and (b-d) TiO_2 -covered Ni surfaces. The number of ALD cycles used for TiO_2 deposition is noted in the images. TiO_2 islands are denoted by white circles. Reprinted with permission from [345].

Fig. 62. Catalytic performance over (a) bare Ni and (b) TiO_2 -Ni catalysts at 800 °C in CO_2 reforming of methane. Accumulated amount of gas flow at the outlet of the reactor for every

25 min was described in number of moles, and change in the amount (mmol) of each gas in the reactor outlet is plotted as a function of reaction time for 65 h at 800 °C. CO₂ and CH₄ level (mmol) without sample was shown in a dashed gray line. Reprinted with permission from [346].

5.8 Summary

Al₂O₃ ALD has been extensively studied on a number of metal surfaces. The dissociative adsorption of TMA was found to be common on noble metal surfaces including Pd, Pt, and Ir, and also likely on Ag and Au. In contrast, Al₂O₃ ALD does not proceed on Cu, a transition metal, and either hydroxylated Cu oxide or Cu₂O is required to promote the TMA reaction. Beyond these examples, there have been relatively few studies of ALD oxide surface chemistry on other metal surfaces.

Precisely applying metal oxide overcoats on supported metal catalysts using ALD has drawn significant attention as a means to tailor their catalytic behavior. The self-limiting surface chemistry of ALD allows conformal deposition over high surface area supports, where the oxide overcoat thickness can be precisely controlled on the atomic level. As a consequence, the mass transfer resistance problem induced by thicker oxide overcoat is minimized. In general, it has been successfully demonstrated that ultrathin oxide ALD overcoats significantly improve the stability of supported metal catalysts under severe reaction conditions. While the activity changes by oxide overcoat depends on the overcoat material, the overcoat thickness, the embedded metal nanoparticles and the reactions. For instance, ultrathin alumina overcoats improves the activity of Pd/Al₂O₃ catalysts in the methanol decomposition reaction [8], but considerably suppresses the activity of similar Pd catalysts in the selective hydrogenation of 1,3-butadiene [323]. On the other hand, TiO₂ overcoats have shown potential to enhance the catalytic activity of metal catalysts in several reactions, such as TiO₂ overcoated Au for CO oxidation [329, 350], TiO₂ overcoated Ni catalyst for CO₂ reforming of methane [345, 346], and TiO₂ overcoated Co in electrochemical water oxidation [347]. Gorte et al. also illustrated that ZrO₂ overcoats on PdO/Al₂O₃ catalysts not only stabilizes PdO nanoparticles against sintering at high temperatures, but also enhances the methane oxidation activity [351].

It was discovered that micropores can be formed within various ALD oxides overcoat (such as Al₂O₃ [12, 48, 77, 349, 352], SiO₂ [300], TiO₂ [329, 349, 350] and ZrO₂ [351]) by high temperature treatment [5, 13], and these pores provide access to the nanoparticle surface for catalytic function. The pore size is controlled by the overcoat thickness and the

pretreatment conditions. As a consequence, the catalytic behavior of metal catalysts, especially selectivity, might be tuned through the confinement effect induced by the micropores [77]. In addition, molecular layer deposition (MLD) might provide an alternative method for tuning the porosity within oxide overcoats. In this case, porosity is generated by first depositing an organic-inorganic hybrid film using a combination of MLD and ALD, followed by high temperature calcination to remove the organic portion to leave a highly porous oxide film [301, 353-355].

One particularly interesting case of catalyst selectivity control through ALD overcoating is the selective blocking of low-coordination metal sites while only leaving terrace sites accessible. This could provide a novel strategy for discerning the individual roles played by the low-coordinated and terrace sites of metal nanoparticles in structure-sensitive reactions to gain atomic level understanding of the reaction mechanism. When undesired side reactions take place at the low-coordination metal sites, preferential blocking of these undesirable sites would produce a more selective catalytic material [12, 320]. As a consequence, porous oxide overcoatings by ALD (or MLD) provide a promising way to tailor the catalytic performance of metal catalysts at the atomic level.

6 Oxide ALD on oxide and carbon materials: synthesizing supported metal oxide catalysts and nanostructuring photocatalytic architectures at the atomic level

Metal oxides represent another important and widely employed category of solid catalysts, and are used as both active phases and supports. Due to their unique acid–base and redox properties, metal oxides have been widely used in a broad range of reactions including catalytic cracking of hydrocarbons [356], alcohol dehydration [357], alkane partial oxidation [358], oxidative dehydrogenation of alkanes [359], selective reduction of NO with NH₃ [360], biomass conversions [361], etc. Performing one or only a few ALD oxide cycles can produce an exceptionally uniform coverage of well dispersed metal oxide surface species with high catalytic activity. Upon increasing the number of ALD oxide cycles, these species coalesce to form a continuous film. Many of the ALD oxide films are in an amorphous phase (the most notable exception to this is ALD TiO₂ [78]) [25]. Consequently, post-annealing in an oxygen environment is often required to improve the crystallinity of the ALD oxide film as well as the quality of the interface between the ALD oxide layer and the substrate. Nonetheless, achieving epitaxial growth of crystalline film on single crystal substrates is possible. Deposition of photocatalytic oxide layers onto various supports or as passivation overlayers on photoelectrodes with atomic precision using ALD has drawn extensive attention in

photocatalysis. On the other hand, ultrathin oxide layers on carbon materials illustrated potential in electrocatalysis.

6.1 *ALD of highly dispersed oxide species on oxide surfaces*

6.1.1 *VO_x ALD on alumina*

Supported vanadium oxide (VO_x) catalysts are widely used in heterogeneous catalysis [362, 363]. The activity and selectivity of VO_x depends strongly on its molecular structure [364, 365], since the electronic and chemical properties of the supported vanadia species change progressively from isolated monomers, to two-dimensional polymers, to three-dimensional crystals [366, 367]. Significant effort has been devoted to achieving precise control over the structures of vanadia species with high homogeneity on supports.

Stair and co-workers investigated the nucleation of ALD VO_x on anodic aluminum oxide (AAO) by alternating exposures to vanadyl triisopropoxide (VOTP) and H₂O₂ at 100 °C [10]. They found that 1-cycle ALD VO_x on AAO yielded a vanadium density of 2.8 V/nm², much less than the monolayer loading of 8 V/nm², indicating that a single ALD cycle does not completely cover the surface, due to the steric effect by the bulky ligands on the VOTP precursor. The edge energy of 1-cycle ALD VO_x sample was 3.64 eV, which corresponds to isolated, tetrahedrally coordinated VO₄ species according to the adsorption edge energy values in the reference compounds. They suggested that only V–O–Al bonds are formed in the first VOTP exposure based on the expected reaction between surface hydroxyl groups (Al–OH) and the isopropoxide ligands. Removal of the remaining isopropoxide ligands during the subsequent hydrogen peroxide exposure produces V–OH species, as indicated in Fig. 63. With additional ALD VO_x cycles, reactions between V–OH groups and VOTP result in the formation of V–O–V bonds, and progressively increase the average VO_x domain size. As a consequence, the predominant form of the supported VO_x transforms from monovanadate sites to polyvanadate domains with increasing VO_x ALD cycles, indicated by the decrease in the edge energy observed in the UV-Vis spectra. In oxidative dehydrogenation (ODH) of cyclohexane, the resulting ALD VO_x catalysts showed specific activities between 2 and 7.5 times higher than catalysts of similar loading prepared by incipient wetness impregnation (IWI). This reflects the higher dispersion of the VO_x species afforded by ALD compared to IWI.

Fig. 63. Schematic illustration of proposed molecular structures of surface vanadyl species formed by VO_x ALD using VOTP and H_2O_2 . Reprinted with permission from [10].

6.1.2 WO_x ALD on SBA-15

Peden and co-workers introduced a liquid phase ALD process to graft tungsten oxide species onto mesoporous silica (SBA-15) surfaces [368]. They used organic solvents and anhydrous conditions refluxed with N_2 to control the tungsten oxide growth onto the silica surface and to avoid the formation of WO_x oligomers prevalent in aqueous solutions at nearly neutral pH. The adsorption edge energies for the samples of ALD WO_x / SBA-15 up to a loading of 30 wt.% were between 3.0–3.8 eV higher than the reference compound $((\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$, 3.0 eV), indicating that the ALD WO_x domains are very small. Under the severe conditions of methanol dehydration reaction, the ALD WO_x /SBA-15 samples showed enhanced stability against sintering compared to comparable IWI catalyst. The differences in activity observed between the samples prepared by ALD and IWI were attributed mainly to the improved resistance toward sintering of the ALD catalyst resulting from the higher density of Si–O–W moieties. In addition, the temperature-programmed oxidation results revealed that the samples prepared by ALD have a more uniform acid strength compared with the samples prepared by conventional impregnation.

6.1.3 SiO_2 ALD on γ -alumina

Stair and co-workers recently found that SiO_2 ALD on γ -alumina selectively yields monomeric SiO_x species using the exposures to tetraethylorthosilicate (TEOS) and H_2O at 50 °C [369]. The highest loading was about 3.2 Si/nm^2 , even though multiple SiO_2 ALD cycles were performed (Fig. 64A). NH_3 DRIFTS revealed that the TEOS preferentially nucleates at strong Lewis acid sites on the γ -alumina surface. When these sites are consumed, the film growth stops. The Si 2p binding energy of the calcined $\text{SiO}_x/\text{Al}_2\text{O}_3$ is found to be

102.4 ± 0.2 eV for all Si loadings (Fig. 64B) and differs from that of bulk SiO₂ (104.1 eV). The lower Si binding energy relative to bulk silica was attributed to Si-O-M structures where M ≠ Si. Increased acidity in the silanol proton is attributable to this electronic effect. NMR further revealed that calcination enhances the Si site homogeneity and increases the density of Si-O-Al linkages, evidenced by narrowing and downfield displacement of the ²⁹Si signal (Fig. 64C). Moreover the $\delta = -81$ ppm position suggests that the major Si surface species after calcination has an Si(3Al,OH) geometry. Interestingly, they found that the ratio of Brønsted acid to Lewis acid sites is linearly correlated with the Si surface density. Finally, they showed that the ALD-derived SiO_x/Al₂O₃ catalysts exhibited higher catalytic activity than γ -Al₂O₃ sites in cyclohexanol dehydration. In contrast to stronger Brønsted acid sites in a conventional silica–alumina catalyst, no carbon loss is detected, demonstrating the benefit of a catalyst having more uniform/less acidic SiO_x sites.

Fig. 64. (A) Si surface coverage in Si/nm² as determined by ICP. (B) Si (2p) XPS spectrum of SiO_x catalysts. (C) DNP-enhanced ²⁹Si CPMAS NMR spectra before and after calcining. Spectra were obtained at 100 K using MAS rate $\nu_R = 10$ kHz, recycle delay $\tau_{RD} = 1.5$ s, contact time $\tau_{CP} = 3$ ms, number of scans NS=2048, acquisition time AT=50 min. The surface structures Si(3Al,OH), Si(Al,Si,2OH), Si(2Al,2OH), Si(2Al,Si,OH), and Si(3Al,Si) are depicted on the right. Note that Si(3Al,OH) is the principle species in the calcined sample. Reprinted with permission from [369]. © 2015 WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim.

6.2 Conformal ALD coatings on mesoporous materials for enhanced acidity

6.2.1 Al_2O_3 ALD on mesoporous zeolite

The TMA molecule has a kinetic diameter of ca. 0.55 nm [370]. Martens et al. recently reported TMA can penetrate into the ultrastable Y zeolite which has supercages with free diameters of ca. 1.2 nm and four apertures measuring 0.74 nm [371]. On the Y zeolite, ten alumina ALD cycles using TMA and water increased the Al content from 2428 to 3015 mmol/kg, corresponding to a change in the bulk Al/(Al + Si) molar ratio from 0.146 to 0.175. By measuring the Al/(Al + Si) molar ratio at the surface of the zeolite, XPS showed a modest increase from 0.167 to 0.270, which confirmed that the alumina introduced via ALD penetrated into the zeolite crystals and did not accumulate at the surface. ^{27}Al MAS NMR showed that the aluminum introduced via ALD is mostly in pentacoordinated and octahedral extra framework Al. The authors further characterized the acidity using pyridine FTIR. They found that the Al deposited into the Y zeolite increased the number of Brønsted acid sites from 488 mmol/kg to 570 mmol/kg, while the Lewis acid site content increased only slightly from 151 mmol/kg to 156 mmol/kg. In comparison, increasing the Al content of ZSM-5 from Si/Al = 49.6 to 37.1 by desilication decreased the concentration of strong Brønsted acid sites from 256 mmol/kg to 179 mmol/kg as measured using the same pyridine adsorption technique. Increasing the aluminum content through desilication improves the accessibility of the acid sites via formation of secondary porosity but reduces the acidity in contrast to the alumina ALD. More recently, Martens et al. demonstrated that five cycles of alumina ALD on a purely siliceous zeolite (-COK-14) with intersecting 10- and 12-membered rings of tetrahedral pore systems resulted in an aluminum coordination of ca. 21% tetrahedral Al, ca. 19% pentacoordinated or distorted tetrahedral Al, and 60% octahedral extra-framework Al [372]. Interestingly, this modification causes a permanent conversion of the originally interrupted framework of -COK-14 to a fully connected OKO type framework, and generates new acid sites which are catalytically active for hydrocracking of n-decane. As a consequence, the introduction of aluminum into mesoporous zeolite and hierarchical materials by ALD was suggested to be an effective way to enhance the acidity and acid catalytic activity (Fig. 65) [371, 373]. However, one should keep in mind that ALD will only be effective for zeolites having pore sizes larger than the kinetic diameter of the ALD precursors.

Fig. 65. Decane conversion over (a) Al-ALD (10 cycles) modified CBV-712, (b) parent CBV-712, (c) Al-ALD (30 cycles) modified CBV-760, (d) parent CBV-760, (e) Al-ALD (10 cycles) modified Zeotile-4 and (f) parent Zeotile-4 material. Reprinted with permission from [373]. Copyright © 2011, Royal Society of Chemistry

6.2.2 Nb_2O_5 ALD on SBA-15

Dumesic and co-workers successfully deposited conformal ALD Nb_2O_5 layers within the pores of a mesoporous silica (SBA-15) using alternating exposures to niobium(V) ethoxide ($\text{Nb}(\text{OCH}_2\text{CH}_3)_5$) and water at 200 °C (Fig. 66) [374]. Figure Fig. 66A shows a high-angle annular dark field STEM image of a sample of SBA-15 coated with 30 ALD Nb_2O_5 cycles. In this image, silica walls appear dark while the niobia layers are brighter since STEM is based on Z contrast (atomic number) and niobia has a higher average Z value compared with silica. The thin dark lines sandwiched between pairs of bright niobia layers are the open pores within the structure and highlight the excellent conformality of the ALD coating. Nitrogen adsorption measurements revealed that SBA-15 has an initial pore diameter of 6.49 nm, and that the pore diameter is progressively reduced to 5.8, 5.6, 4.75 and 3.74 nm after 1, 10, 19 and 30 cycles of Nb_2O_5 ALD, respectively; meanwhile, the surface area decreased from 930 m^2/g to 671, 326, 246 and 126 m^2/g , respectively. Raman spectroscopy of the ALD niobia-treated SBA-15 and comparison with reference spectra for bulk specimens of amorphous and crystalline niobia revealed that the ALD Nb_2O_5 was hydrated and amorphous according to the Raman bands and 650 and 886 cm^{-1} . Very interestingly, materials containing 10, 19, and 30 cycles showed remarkable hydrothermal stability, with minimal changes in porosity and structure after treatment in liquid water at 200 °C. The mesoporous niobia material produced by 19 cycles was evaluated as an acid catalyst for the gas-phase dehydration of 2-propanol,

and for the dehydration of 2-butanol in both the gas and liquid phases. It was superior to commercial niobia (HY-340) in both activity and stability.

Fig. 66. High-magnification STEM images of (A) SBA-15 coated with 30 ALD cycles of Nb_2O_5 and (B) SBA-15. Reprinted with permission from [374]. Copyright © 2011, American Chemical Society.

6.3 ALD oxide architectures for photocatalysis

The possibility of depositing photocatalytic oxide layers by ALD onto electrically conducting nanostructured supports has drawn the attention of the photocatalysis community. This application requires precise control over the composition, structure, and thickness of the photocatalytic oxide layers. For instance, Martinson and co-workers showed that ALD CoO_x deposited onto hematite photoanodes significantly enhanced the photoelectrochemical (PEC) water oxidation performance (Fig. 67) [375]. The optimal coating was found to be a single CoO_x ALD cycle, which amounts to a submonolayer of $\text{Co}(\text{OH})_2/\text{Co}_3\text{O}_4$ according to ellipsometric, XPS and X-ray absorption near-edge spectroscopy (XANES) measurements.

Fig. 67. J–E curves for 13 nm hematite photoanodes on a flat FTO–ITO substrate (black), on

an ITO-coated inverse opal scaffold (green), on an equivalent flat electrode further coated with 1 CoCp2/O3 ALD cycle (blue, dashed), and on an equivalent inverse opal scaffold further coated with 1 CoCp2/O3 ALD cycle (purple, dashed). Performance was measured at pH 13.1 under ~ 1 sun illumination. Reprinted with permission from [375]. Copyright © 2013, American Chemical Society.

Fig. 68. (a) Schematic illustration of the design principle, which involves the use of a highly conductive TiSi_2 nanonet as an effective charge collector. The electronic band structure is shown in the enlarged cross-sectional view. Efficient charge collection is achieved when the hematite thickness is smaller than the charge-diffusion distance. (b) Low-magnification TEM image showing the structural complexity of a typical hetero-nanostructure and its TiSi_2 core/hematite shell nature. (c) High-resolution (HR) TEM data. A dashed line has been added at the interface as a guide to the eyes. Insets: (left) lattice-fringe-resolved HRTEM image showing the hematite lattice spacings for (110) (0.250 nm) and $(\bar{3}\bar{3}0)$ (0.145 nm); (right) electron diffraction pattern of hematite. Reprinted with permission from [376].

ALD oxide films often grow in an amorphous phase, and in some cases post-deposition annealing in an oxygen environment is required to crystallize the ALD film and to improve the interface quality between the ALD oxide layer and the substrate. For instance, Wang et al. constructed TiSi_2 nanonet-based hematite ($\alpha\text{-Fe}_2\text{O}_3$) heterostructures by depositing Fe_2O_3 onto the TiSi_2 nanonet using $\text{Fe}_2(\text{OtBu})_6$ and H_2O at 140 °C [376]. Post-growth annealing at 500 °C in O_2 was carried out to improve the crystallinity of the hematite, as evidenced by the structural characterization in Fig. 68. Without the addition of any oxygen-evolving catalysts, the $\text{Fe}_2\text{O}_3/\text{TiSi}_2$ heterostructures (Fe_2O_3 thickness 25 nm) showed photocurrents of 1.6 and 2.7 mA/cm^2 at 1.23 and 1.53 V vs a reversible hydrogen electrode (RHE), respectively. The

high surface area, conductive TiSi_2 nanonets serve a dual role as a structural support and an efficient charge collector, allowing for maximum photon-to-charge conversion, benefited from the conformal coating $\alpha\text{-Fe}_2\text{O}_3$ and the defect-free interface between the Fe_2O_3 and the TiSi_2 . Wang et al. also devised a new method for WO_3 ALD that eliminates the corrosive byproducts associated with the more common halogenated precursors by using $(\text{tBuN})_2(\text{Me}_2\text{N})_2\text{W}$ and H_2O as the tungsten and oxygen source, respectively at temperatures of 250–350 °C [377]. WO_3 was deposited either on indium-tin oxide (ITO) or on TiSi_2 nanonets. Post-annealing at 550 °C in O_2 was carried out to improve the crystallinity of the ALD WO_3 . When coated with a novel Mn-based catalyst, the resulting WO_3 survives soaking in H_2O at pH 7 and produces oxygen by splitting H_2O under illumination.

The surface modification of semiconductor photoelectrodes with passivating overlayers has been shown to be an effective strategy to improve the charge-separation and charge-transfer processes across the semiconductor–liquid interfaces, as well as the stability of photoelectrodes [17, 378–382]. Yang et al, showed that 0.8 nm ALD TiO_2 (20 cycles) on hematite photoanodes considerably improved the PEC water oxidation performance, and reduced the overpotential by ca. 100 mV [380]. McIntyre et al. [17] demonstrated that PEC water oxidation can be sustained using an ALD TiO_2 (2 nm thick) protected silicon anode for many hours in harsh pH and oxidative environments whereas comparable silicon anodes without the TiO_2 coating quickly fail. The desirable electrochemical efficiency and corrosion resistance of these anodes was attributed to the low electron-tunneling resistance and uniform thickness of the ALD TiO_2 layer. The thickness of the TiO_2 protective layer is very critical (Fig. 69), because as the film becomes thicker, it no longer conducts holes via a tunneling mechanism and also introduces a large resistance, degrading its efficiency to low values [381]. Lewis and co-workers revealed that amorphous ALD TiO_2 is electronically defective and possibly nonstoichiometric and this allows very high ($>1 \text{ A/cm}^2$) current densities to pass through the “leaky” dielectric. The electronic defects in amorphous ALD TiO_2 films presumably arise from structural disorder in the amorphous phase and/or chemical impurities such as carbon or nitrogen residues from the ALD precursors. In contrast, crystalline TiO_2 films produced by thermal annealing create an interfacial tunneling barrier for photogenerated charge carriers. Amorphous TiO_2 films with 4 to 143 nanometer thickness are sufficiently transparent to reach the light-limited performance of protected semiconductors. The authors demonstrated that ALD TiO_2 -coated GaAs and GaP photoelectrodes exhibited photovoltages of 0.81 and 0.59 V and light-limiting photocurrent densities of 14.3 and 3.4 milliamperes per square centimeter, respectively, for water oxidation [382].

Fig. 69. (a) TEM images of of three ALD-TiO₂ films of thickness 2 nm, 5 nm, and 12 nm from left to right. (b) Water oxidation *i*-*E* curves in basic solution using Ir/*x* nm of TiO₂/SiO₂/p⁺-Si anodes. The vertical dashed line indicates the thermodynamic potential for water oxidation in base, 0.404 V, and the horizontal solid line indicates 1 mA/cm², the characteristic current density at which all overpotentials are measured. (c) Overpotentials for water oxidation at 1 mA/cm² and ferri/ferrocyanide half peak-to-peak splitting as a function of TiO₂ thickness. Reprinted with permission from [381]. Copyright © 2013, Royal Society of Chemistry.

Fig. 70. HAADF-STEM images of 200 cycles ALD-CeO₂ films grown on YSZ substrate and viewed along the CeO₂[100]/YSZ[100] zone axis. Low and high magnification HAADF Z-contrast images of as-deposited (a, b and c) and post-treated (d, e, and f) CeO₂ films,

respectively. Insets show the corresponding FFT patterns. (a and d) Arrows point to the CeO₂ layer. (c and f) High magnification Z-contrast images of the interface between ceria and the substrate of as-deposited and post-treated CeO₂ films, respectively. ALD CeO₂ films were post-treated at 900 °C, 15 min in oxygen. Arrows mark the position of misfit dislocations. Reprinted with permission from [383]. Copyright © 2012, American Chemical Society.

It is possible to deposit highly crystalline films and even achieve epitaxial growth on lattice-matched substrates at low temperatures using ALD (also seen in the review elsewhere by Puurunen et al. [25] and the references therein). For instance, Grätzel et al. recently developed a low-temperature ALD process to deposit phase-pure and crystalline α -Fe₂O₃ films at 230 °C using N-(dimethylaminomethyl)ferrocene (DMAMFc) and ozone, as the Fe and O precursors, respectively [384]. The grow rate was 0.25 ± 0.01 Å/cycle. These as-deposited α -Fe₂O₃ films were investigated as photoanodes for PEC water oxidation and found to be highly photoactive. Combined with a TiO₂ underlayer and a low-cost Ni(OH)₂ catalyst, hematite films of less than 10 nm in thickness reached photocurrent densities of 0.3 mA/cm² at 1.23 V vs RHE and a photocurrent onset potential of less than 0.9 V vs RHE. Coll et al. demonstrated highly epitaxial, ultrasmooth, and pure (001) CeO₂ ultrathin films by ALD at a low deposition temperature of 275 °C on single crystal substrates, such as Y-stabilized ZrO₂ (YSZ) (Fig. 70) [383]. The CeO₂ ALD conditions were optimized using Ce(thd)₄ and ozone as precursors, and yielded a growth per cycle of ~ 0.2 Å/cycle. The authors speculated that the extremely low growth rates for the CeO₂ ALD (~ 0.016 nm/min) along with the use of single crystal substrate, facilitates the epitaxial orientation of ceria films.

Fig. 71. (a) Schematic representation of the structure of the surface-protected Cu₂O photocathode. (b) Scanning electron micrograph showing a top view of the electrode after ALD of 5×(4 nm ZnO/0.17 nm Al₂O₃)/11 nm TiO₂ followed by electrodeposition of Pt nanoparticles. Reprinted with permission from [385]. Copyright © 2011, Rights Managed by Nature Publishing Group.

ALD is well suited for growing nanostructured thin films consisting of different oxide materials since the composition, structure, and interfaces can be precisely tailored by controlling the sequence of precursor exposures. This capability has been exploited to create nanostructured electrodes for photocatalysis [385-388]. For example, Thimsen et al. [385] demonstrated that nanolayers of ALD Al-doped ZnO and TiO₂ on Cu₂O photocathodes effectively inhibit the photocathodic decomposition of Cu₂O in aqueous electrolytes. Photocurrents up to -7.6 mA/cm² at 0 V versus RHE were achieved using electrodes protected with catalysed layers of n-type oxides with the structure 5×(4 nm ZnO/0.17 nm Al₂O₃)/11 nm TiO₂ (Fig. 71). The electrodes remained active after 1 h of testing, and the Cu₂O was found to be stable during the water reduction reaction and the Faradaic efficiency was estimated to be close to 100%. The authors investigated the roles of the different surface protection components, and they found that TiO₂ had a staggered type-II band offset, so that photogenerated electrons can flow from the Cu₂O through the protective layer to the electrolyte to promote water reduction, whereas holes flow into the Cu₂O bulk. Moreover, its conduction band is above the water reduction potential, ensuring no reductive degradation reactions at potentials in the bandgap. The 20 nm ZnO buffer layer between the Cu₂O and 10 nm TiO₂ was necessary to obtain stable electrodes. Finally, inserting monolayers of Al₂O₃ periodically into the ZnO was necessary to further improve the stability of the electrode without changing the photocurrent.

Fig. 72. (a) Synthesis of a nanocavity sieving layer onto a non-porous catalyst support using the molecular-templated ALD: (i) depositing a template (right) onto an existing catalyst

surface, (ii) using ALD to synthesize an inert oxide film, 2 nm thick around, but not over, the templates, and (iii) treating the materials in O₃ to remove the templates, revealing the underlying catalyst surface. (b) Selective photocatalytic oxidation and reduction of mixtures on CAL-templated nanocavities. Reprinted with permission from [389]. Copyright © 2012, Rights Managed by Nature Publishing Group.

6.4 Oxide ALD using single-molecule sacrificial templates: Atomically-precise “bottom-up” synthesis of selective catalysts.

Crystalline microporous oxides such as aluminosilicate zeolites are widely used as catalysts in fuels and commodities chemicals upgrading [390]. The materials typically have pore with diameters of 0.3–1.0 nm. This pore size range enables microporous oxides to catalyze chemical transformations with excellent selectivity via reactant or transition-state shape selectivity. Recently, Notestein and co-workers demonstrated a novel approach for “bottom-up” synthesis of a shape-selective catalyst using ALD [389]. Therein, an ultrathin and cavity-containing oxide sieving layer was constructed on the surfaces of larger non-porous oxide catalyst particles by the new technique of molecular-templated ALD. As shown in the schematic illustration in Fig. 72a, an appropriate template molecule was first grafted onto an existing TiO₂ photocatalyst surface. The template molecule is selected to be unreactive towards the ALD precursors so as to remain uncovered by the ALD film. Next, an ALD alumina film is selectively deposited on the TiO₂ surface surrounding the template molecule to a thickness less than the template height. Finally, the template molecule is removed using O₃ to reveal the underlying catalyst surface and activate the catalyst. The lateral dimension and depth of the nanocavity could be tuned by controlling the size the template molecule and the number of ALD alumina cycles, respectively. Using appropriate templates, the nanocavity dimensions were in the supermicroporous region (diameters of 1–2 nm), where shape-selectivity is expected to occur for many reactants (Fig. 72b). Indeed, the authors demonstrated that these nanocavities resulted in a high selectivity (up to 9:1) towards less sterically-hindered reactants in otherwise unselective, competitive photocatalytic oxidation and transfer hydrogenation.

6.5 Oxide ALD on carbon materials

Oxides supported on carbon-based materials including CNTs, graphene and activated carbon etc., are of great interest in both heterogeneous and electrocatalysis [391–394]. These oxide/carbon hybrid materials have strong chemical attachment and electrical coupling

between the electrocatalytic oxide nanoparticles and the carbon support, leading to nonprecious metal-based electrocatalysts with improved activity and durability for the oxygen reduction reaction for fuel cells and oxygen/hydrogen evolution reactions [394].

Fig. 73. (a) ALD of Al₂O₃ on pristine graphene, scale bar is 200 nm. (b) ALD of Al₂O₃ on PTCA-coated graphene, scale bar is 500 nm. (c) Schematics of Al₂O₃ deposition on various graphene substrates. Reproduced with permission from [150]. Copyright 2008 American Chemical Society. Copyright © 2008, American Chemical Society.

ALD provides an alternative way to directly deposit highly dispersed oxide species onto carbon-based materials with high homogeneity and precise control over coverage [126]. However, it turned out that the chemically inert nature of pristine graphitic carbon inhibits the nucleation of ALD materials, since the initiation of ALD growth requires functional surface groups or defects that act as nucleation sites for the ALD precursors. In these cases, the carbon surface must be functionalized prior to the ALD (also seen in the review paper elsewhere by Pinna et al. [126] and the references therein). For instance, George et al. found that Al₂O₃ ALD on untreated multiwall carbon nanotubes (MWCNTs) resulted in isolated Al₂O₃ nanospheres rather than a continuous film (Fig. 74a) [395], which was attributed to the low density of defects or active chemical species on the MWCNT surface. Once the MWCNTs were functionalized by a layer of adsorbed NO₂ and TMA, a smooth and conformal Al₂O₃ coating was achieved (Fig. 74b). Dai et al. also reported that Al₂O₃ ALD preferentially grew on the edges and defect sites of pristine graphene sheets (Fig. 73a), suggesting that the chemical groups on the edge and defect sites act as nucleation sites to

interact with the Al_2O_3 ALD precursors, whereas the basal plane of pristine graphene lacks such interactions [150]. When perylene tetracarboxylic acid (PTCA) was used to functionalize the graphene sheets, the perylene core could interact with the basal plane of graphene through π – π interaction, while the carboxylic acid groups could interact and react with the ALD precursors. The resulting PTCA functionalized graphene could be uniformly coated with ultrathin Al_2O_3 layer (Fig. 73b).

Fig. 76. TEM (a, c, e) and HRTEM (b, d, f) images of ZrO_2 –GNS nanocomposite prepared at 150 °C (a, b), 200 °C (c, d) and 250 °C (e, f) with 10 cycles. Reproduced with permission from [396]. Copyright © 2012 Elsevier Ltd. All rights reserved.

A common method to generate oxygen-containing sites on carbon surfaces is to chemically treat the carbon using mineral acids such as HNO_3 , H_2SO_4 , or a strong oxidizing agent such as O_3 [127–129]. Sun et al. systematically investigated the ALD of ZrO_2 on graphene nanosheets (GNS) using alternating exposures to tetrakis(dimethylamido)zirconium(IV) (TDMAZ) and water at 150, 200 and 250 °C [396]. Therein, the GNS were prepared by

thermal reduction of graphite oxide. FTIR measurements showed a strong peak located at 3450 cm^{-1} , corresponding to the stretching vibration of hydroxyl groups ($-\text{OH}$). HRTEM showed that ZrO_2 nanoparticles were formed on GNS after 10 cycles of ZrO_2 ALD at all temperatures (Fig. 74). The reaction of TDMAZ with widely-separated surface $-\text{OH}$ groups during the first cycle was suggested to initiate the ZrO_2 nanoparticle growth. In addition, the crystallinity of the deposited ZrO_2 was found to depend highly on the deposition temperature. The ZrO_2 deposited at $150\text{ }^\circ\text{C}$ was amorphous (Fig. 74a,b), but at a deposition temperature of $250\text{ }^\circ\text{C}$ the ZrO_2 was crystalline (Fig. 74e,f). The interplanar spacing of the crystalline nanoparticles was measured to be 0.298 nm , agreeing well with the lattice distance between (101) planes of tetragonal ZrO_2 , as seen in Fig. 74d. With increasing ALD cycles, the ZrO_2 nanoparticles coalesced so that the growth mode transitioned from “island growth” to “layer-by-layer growth”.

6.6 Summary

As a consequence of the self-limiting, surface-controlled reactions that define ALD, it is possible to coat surfaces with metal oxide species for catalysis with precise control over the structure to create isolated monomers, two-dimensional polymers, or three-dimensional, thin-film crystals using ALD techniques [10, 368, 369]. Furthermore, the dispersion of the catalytic surface species synthesized by ALD is frequently higher than that of conventional techniques, and this in turn provides higher catalytic activity [10]. The ALD of metal oxides inside of mesoporous zeolites or on the surface of hierarchical structures provides a powerful means to tune the pore size and to enhance the acid catalytic activity [373, 374]. Recently, Kuech et al. demonstrated that Mg-Al oxide ALD on $\gamma\text{-Al}_2\text{O}_3$ particles with varied Mg/Al atomic ratios resulted in a systematic variation of the acid and base site areal densities [397].

The low deposition temperatures typical in metal oxide ALD often leads to amorphous films, and in some cases this produces unique and beneficial electronic properties [382]. In cases where crystalline metal oxides are desired, post-annealing in an oxygen environment can improve the crystallinity of the ALD oxide film and improve the quality of interface between the ALD layer and the substrate. The precise control over the film thickness and the capability to build complex structures comprised of multiple layers of different oxides or blends of oxide materials make ALD an extremely powerful method for constructing nanostructured architectures with optimized photocatalytic performance.

While the growth of oxides onto carbon-based materials using ALD has not been extensively explored, this strategy nevertheless holds great promise in catalysis, and

especially in electrocatalysis. The chemically inert nature of pristine graphitic carbon leads to inhibits the nucleation of ALD growth, and various methods have been demonstrated to impart functional groups prior to ALD that permit smooth, continuous films. Nonetheless, careful control over the density of functional groups might produce a high dispersion of catalytic species on carbon-based materials with extremely high homogeneity [59].

7 Conclusions and outlook

Catalyst synthesis with precise control over the catalytic active site structure on the atomic level is essential for understanding catalyst behavior and ultimately for the rational design of advanced catalysts with high performance. The unique self-limiting feature of ALD allows conformal deposition of catalytic materials on catalyst supports with high surface area and porosity. These catalytic materials can be precisely constructed on the support surface in a digital, step-by-step fashion by controlling the ALD cycles. As a consequence, ALD provides a “bottom-up” approach for nanostructuring supported catalysts with near atomic precision.

ALD has demonstrated the capability to achieve precise control over the particle size, composition and structure of supported metal nanoparticles. The resulting metal catalysts typically have a high dispersion, and show higher activity compared to catalysts prepared by conventional methods. Although ALD processes are carried out at elevated temperatures, single-atom metal catalysts can be prepared by carefully controlling the nucleation sites and deposition temperature. In addition, selective metal ALD on metal surfaces but not on supports enables the atomically-precise synthesis of supported bimetallic nanoparticles, a long-standing goal in catalyst synthesis, by digitally tailoring the ALD pulse sequences: the size of the bimetallic particles is determined by the total number of ALD cycles performed, the composition is dictated by the relative number of ALD cycles used for each component, and the structure of the bimetallic nanoparticles is controlled by the order in which the individual cycles are executed. Such cycle-by-cycle “bottom up” bimetallic (or multiple components) nanoparticle growth on supports shows obvious advantages over conventional methods. However, it should be noted that surface segregation of metal atoms can occur in some cases, leading to different structures than intended.

ALD has proven effective for tailoring the catalytic performance and enhancing the stability of metal catalysts using ultrathin oxide overcoats. The conformality and thickness control afforded by ALD provide advantages over other alternative methods such as CVD and sol-gel chemistry. Besides improving the stability of metal catalysts against sintering and leaching, the activity and selectivity can be remarkably improved by ALD oxide overcoats.

Differences in the oxide overcoat thickness and composition can both affect the catalytic activity. While the porosity within the oxide overcoat might have a remarkable impact on the catalyst selectivity via the confinement effect. In particular, selectively blocking the low-coordination sites of metal nanoparticles with ALD oxide overcoats, while leaving the terrace site accessible, provides a new ideal model system for elucidating the individual roles of the low-coordinated and terrace sites of metal nanoparticles in structure-sensitive reactions. When undesired side reactions take place at the low-coordination metal sites, preferential blocking of these undesirable sites by oxide overcoats would produce a more selective catalytic material.

Cycle-by-cycle “bottom up” fabrication catalytic metal oxide species on a support by ALD also makes it advances in precise synthesis of supported metal oxide catalysts, where the structures of catalytic active sites is tuned from isolated metal oxide species, to two-dimensional aggregates, and to large islands. Meanwhile, the catalyst acidity can be precisely modified by depositing different oxide materials. The low deposition temperatures typical in metal oxide ALD often leads to amorphous films, and in some cases this produces unique and beneficial electronic properties. In cases where crystalline metal oxides are desired, post-annealing in an oxygen environment can improve the crystallinity of the ALD oxide film and improve the quality of interface between the ALD layer and the substrate. The precise control over the film thickness and the capability to deposit complex structures comprised of multiple layers of different oxides or blends of oxide materials make ALD an extremely powerful method for constructing nanostructured architectures with optimized photocatalytic performance.

ALD has commercialized in the microelectronics industry to manufacture a range of different devices, while synthesizing catalysts using ALD are oftentimes considered slow and expensive due to the limitations of current ALD strategies, equipment, and high cost of precursors. Moreover, ALD on powders at a commercial scale is still not realized, scaling up the process remains as the main technical challenge. Current work at the laboratory scale has demonstrated that ALD in a fluidized-bed reactor with a batch type process, or spatial ALD with continuous operation is potentially possible for scaling up. In addition, performing ALD at atmosphere pressure might be beneficial to decrease the cost, and simplify the requirements for the reactor design facilitating the development of scaling-up process.

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