Catalyst synthesis and evaluation using an integrated atomic layer deposition synthesis–catalysis testing tool

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An integrated atomic layer deposition synthesis-catalysis (I-ALD-CAT) tool was developed. It combines an ALD manifold in-line with a plug-flow reactor system for the synthesis of supported catalytic materials by ALD and immediate evaluation of catalyst reactivity using gas-phase probe reactions. The I-ALD-CAT delivery system consists of 12 different metal ALD precursor channels, 4 oxidizing or reducing agents, and 4 catalytic reaction feeds to either of the two plug-flow reactors. The system can employ reactor pressures and temperatures in the range of 10^{-3} to 1 bar and 300–1000 K, respectively. The instrument is also equipped with a gas chromatograph and a mass spectrometer unit for the detection and quantification of volatile species from ALD and catalytic reactions. In this report, we demonstrate the use of the I-ALD-CAT tool for the synthesis of platinum active sites and Al_2O_3 overcoats, and evaluation of catalyst propylene hydrogenation activity. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4928614]

I. INTRODUCTION

Atomic layer deposition (ALD) has become a useful, high-precision tool for the synthesis of supported catalytic materials.[1] ALD is a thin film growth technique that makes use of a sequence of self-limiting surface reactions to deposit materials in a conformal, layer-by-layer fashion.[2] The technique is similar to chemical vapor deposition (CVD), but the self-limiting nature of the ALD reactions ensures that only single monolayers or sub-monolayers of materials are deposited in each cycle and that surfaces are coated uniformly. Catalyst synthesis by ALD has been used to prepare the majority of relevant catalyst compositions, affording a wide range of supported active sites with various metal nuclearities (isolated metal atoms,[3] metal clusters,[4] nanoparticles,[5–7] and films).[8–10]

Our group recently developed an integrated instrument capable of both ALD synthesis and catalyst performance evaluation in a single reactor (I-ALD-CAT). The I-ALD-CAT system is equipped with an ALD manifold for catalyst synthesis on a solid support loaded in a plug-flow reactor. Immediately after the catalyst synthesis by ALD, the instrument can be switched to "*catalysis mode*" for reactivity testing using gas-phase probe reactions. This instrument is capable of performing both catalyst synthesis and reactivity testing functions in an efficient, *in situ* procedure utilizing (1) a large number of ALD precursors (both support and catalyst), (2) an integrated ALD-Catalytic plug flow reactor with fast thermal cycling, and (3) on-line gas chromatograph (GC) and mass spectrometer (MS) for ALD byproducts and catalytic product analyses.

Current catalysis research approaches that utilize ALD as a synthesis tool involve the catalyst synthesis and reactivity evaluation as two separate processes. Typically the materials are (1) prepared by deposition of the catalytic components from solution or gas-phase onto a solid support, (2) removed from the synthesis vessel, (3) loaded into the catalytic reactor, (4) pretreated, and evaluated for catalytic activity.[1] The I-ALD-CAT instrument combines all of these steps into a single, streamlined, automated process. Various equipment for high-throughput experimentation has been commercially developed to automate and parallelize catalyst discovery.[11–14] However, the range of accessible material structures and compositions is expected to be much broader with the I-ALD-CAT tool. Furthermore, the integration of the ALD manifold to the plug-flow reactor unit allows for immediate *in situ* evaluation of reactive catalytic species without decomposition due to exposure to air or moisture. This feature makes the I-ALD-CAT instrument a highly suitable tool for the reactivity evaluation of air- and moisture-sensitive supported active sites and reactive surface intermediates, potentially harnessing mechanistic insights that are pertinent to the rational design of robust, high-activity catalytic systems.

The ability to evaluate a broad range of structural motifs makes the I-ALD-CAT instrument a powerful synthesis tool for understanding and advancing catalysis science. For example, this instrument can be employed for (1) the synthesis of single oxide and mixed-oxide thin film supports on a variety of scaffolds, (2) the deposition of supported (sub)nanometer metal or alloy particles or clusters at high density, (3) the preparation of active single oxide and mixed-oxide monolayers, and (4) construction of oxide pores/cavities around
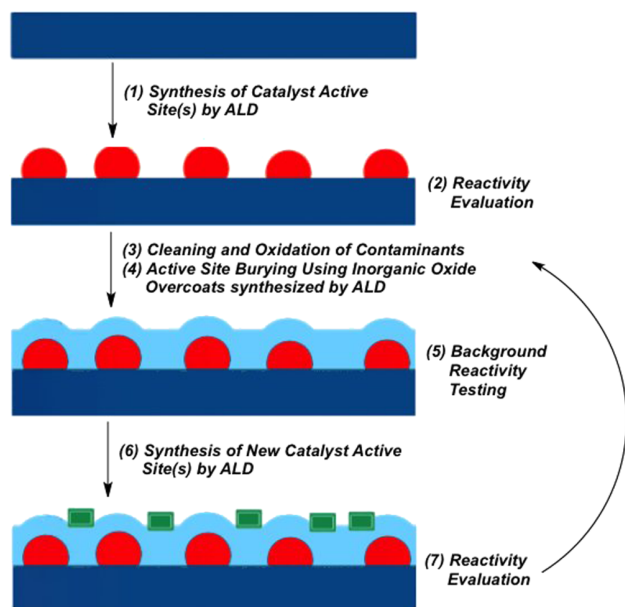
FIG. 1. High-throughput approach to catalyst synthesis by ALD and reactivity evaluation using the I-ALD-CAT tool.

particles or clusters with atomic precision to inhibit sintering, control accessibility to reagents and provide an enzyme-like environment for catalysis.

In addition to synthesizing and testing new materials, multiple catalyst compositions on a single scaffold can be prepared through reiterative (1) *catalyst deposition*, (2) *reactivity testing*, and (3) *overcoating* experiments. Each time a catalyst evaluation is completed, the surface can be buried using a multilayer inorganic oxide overcoat (Figure 1). Completely overcoating the catalytic sites or particles will eliminate the previous catalyst and at the same time create a fresh scaffold surface for constructing the next catalyst. Thus, many catalyst formulations can be rapidly evaluated.

In this paper, we report the development of the I-ALD-CAT tool and demonstrate its use in the processes identified above as key steps for *in situ* catalyst synthesis and reactivity evaluation. The I-ALD-CAT tool was successfully used in (1) the deposition of platinum active sites and Al_2O_3 overcoats by ALD and (2) platinum-catalyzed propylene hydrogenation experiments.

II. I-ALD-CAT DESIGN

The I-ALD-CAT tool combines an ALD manifold with a plug-flow reactor unit. This instrument has the capability of catalyst synthesis by ALD on an inorganic oxide support loaded in a plug-flow reactor, after which, the catalyst activity testing can be immediately carried out. The I-ALD-CAT system is equipped with an ALD manifold that delivers gaseous reagents which include 12 different ALD precursors, 4 oxidizing or reducing agents for ALD, and 4 catalytic reaction feeds to either of the two plug-flow reactors. The system can employ reactor pressures and temperatures in the range of 10^{-3} to 1 bar and 300–1000 K, respectively. The instrument is also equipped with a gas chromatograph (GC-flame ionization detector (FID)/thermal conductivity detector (TCD)) unit and a MS for the detection and quantification of volatile species generated during ALD and catalytic reactions. We will present each part of the system and how this is achieved in turn.

A. The ALD-CAT manifold

The I-ALD-CAT design was implemented by ARRADIANCE (ARR-100000 GEMSTAR-CAT Dual System, Figures 2 and 3). The upper manifold (UM) consists of three 200 °C standard manifolds (M_1–M_3) equipped with 12 ALD precursor material bottles (PR_1–PR_{12}), six of which allow for assisted precursor dosing (PR_7–PR_{12}). Nitrogen-assist during the ALD pulsing is carried out by an external ALD carrier gas (N_2) controlled by a mass-flow controller (MFC_1). The ALD manifold is also equipped with a 175 °C manifold (M_4) with four external ALD gas ports for reducing agents and oxidizing agents necessary for the ALD synthesis methods. ALD and catalysis experiments can be carried out in an automated fashion and the flow of gaseous reactants is controlled by 200 °C upper and lower process selection manifolds (UM and LM) equipped with heated lines. The ALD synthesis of catalysts and reactivity evaluation can both be conducted in the two, independent 700 °C tube reactors (R_1 and R_2). Reactor temperature monitoring is carried out through a thermocouple installed in each reactor chamber. (Note: The current reactor tube design does not allow insertion of a thermocouple directly into the ALD substrate bed.) 406 mm stainless steel tube reactors with internal diameters ranging from 3.18 mm
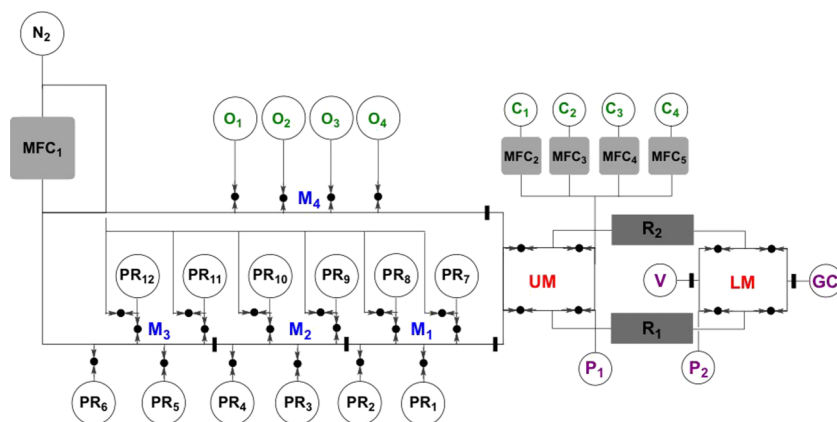

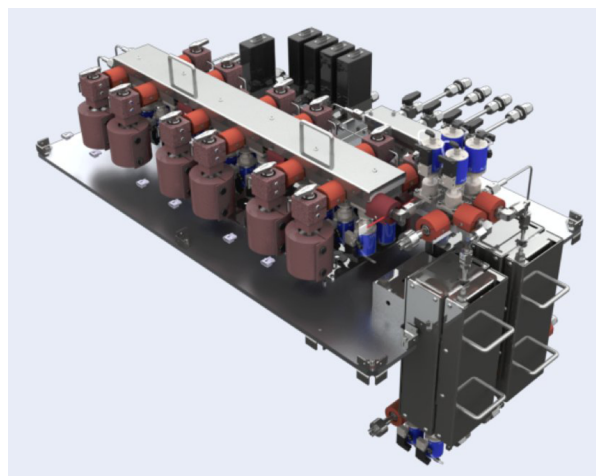FIG. 2. Schematic representation of the HT-ALD-Cat instrument.

FIG. 3. ALD and plug-flow reactor manifold of ARR-100000 GEMSTAR-CAT Dual System. The metalorganic manifold of the GEMSTAR-CAT Dual System consists of three (3) manifolds that connect through VCR-4 fittings. Each manifold is entirely made of welded 316L stainless steel and is approximately 26 cm long × 15 cm wide. Each manifold unit consists of (1) a Stewart Warner (SW) settable temperature control zone up to 200 °C, (2) four VCR-4 connected heated material bottle interfaces with four software settable control zones for the material bottles up to 200 °C and a manual isolation valve for each material bottle, and (3) six high speed ALD Diaphragm Valves (DV) with 1.5″ C-Seal interface. Four of the DV valves are dedicated for manifold injection of precursors and two are for separate bottle injection of inert gases (N_2 or Argon) on two of the material ports. The latter is a *vapor-push mechanism* that allows for material pressure to be raised and facilitate injection of precursors with low heated vapor pressures. The ALD manifold is also equipped with a 1/4″ central mass flow controlled VCR-4 connection for inert carrier gas connection. The entire unit is strategically insulated to ensure minimal cold spot locations.

to 6.35 mm with Variable Compression Ratio (VCR) -type connections can be installed in the reactor ovens. Each plug-flow reactor is connected to two lower manifold (LM) valves, one opens to the vacuum system (V) and the other to an on-line GC for quantitative analysis of gaseous products. Vacuum is achieved in the system using an Edwards vacuum pump model EIM-18. (Safety note: In order to ensure that no toxic gaseous byproducts are released during the ALD process, the low-pressure gas stream emerging from the ALD manifold is thermally degraded in a Mini-Mite™ tube furnace TF55030A set at 550 °C and then filtered through a Balston® compressed air and gas in-line filter regulator model AFR-940 before reaching the vacuum pump.) Real-time manifold pressure monitoring is made possible by the two vacuum gauges (P_1 and P_2) installed upstream and downstream of the plug-flow reactor chambers. When the instrument operates in catalysis mode, catalysis feed gases (C_1–C_4) are injected to the reactor through four MFC-controlled external carrier gas manifolds (MFC_2–MFC_5). The I-ALD-CAT tool can be operated for ALD synthesis or catalysis experiments in a fully automated mode using a GEMSTAR-CAT system control program.

B. The analytical tools

Monitoring of volatile organic species generated during the ALD process (e.g., protonated organic ligands) is performed using a residual gas analyzer (Stanford Research Systems RGA 200). The gas-phase sampling is carried out

through a leak valve connected to the lower manifold vacuum valve of each reactor. The RGA head vacuum is separately pumped with a built-in turbomolecular pump. When the I-ALD-CAT is in catalysis mode, gas chromatography (GC) analyses of the gaseous product stream is performed using an online Agilent 7890 unit equipped with a 6-port injection valve, a split/splitless injector, a flame ionization detector (FID), and a Thermal Conductivity Detector.

III. IMPLEMENTATION OF THE I-ALD-CAT TOOL

The atomic layer deposition of Al_2O_3 overcoats on supported platinum nanoparticles (~2.8 nm Pt/Al_2O_3 (NanoDur™)) was chosen to demonstrate the utility of the I-ALD-CAT tool for inorganic oxide synthesis, while gas-phase propylene hydrogenation was used as the catalyst activity probe reaction.

A. ALD method development

The online mass spectrometer plays a central role in the development of ALD methods using the I-ALD-CAT instrument. The ALD parameters (e.g., dose and evacuation times) for the Al_2O_3 deposition method presented in this paper were identified through real-time mass spectroscopic monitoring of the deposition reaction of trimethylaluminum (TMA) and water under various ALD conditions. For example, the manifold evacuation period required between each TMA and H_2O pulse was determined as the minimum time required (30 s) to detect baseline methane signal in the mass spectrometer.

Confirmation of the self-limiting nature of ALD half reactions is a critical element in ALD method development. This feature is usually determined through mass gain measurements per ALD cycle using a quartz crystal microbalance (QCM) installed in viscous flow ALD reactor units.[15] The current design of the I-ALD-CAT instrument does not include a QCM accessory in the reactor; hence, a mass gain-based approach in determining self-limiting surface reactions is not possible. However, the online mass spectrometer unit provides the advantage of real-time monitoring of the formation of precursor breakdown products (e.g., CH_4 from TMA and H_2O dosing) under ALD conditions. TMA and H_2O dosing experiments were conducted to determine if the TMA and H_2O half-reactions proceed in a self-limiting fashion. Figure 4(a) shows the methane generation plot for a one-cycle Al_2O_3 deposition experiment. The first TMA pulse resulted in the most intense methane signal while pulses 2–4 resulted in decreasing methane signal intensities. No further decrease in the methane signal was observed between pulses 4 and 5, potentially indicating complete surface coverage with aluminum alkyl species. Pulses 6–25 resulted in increased methane signal intensity. The observed methane generation pattern for pulses 6–25 was also observed in control experiments where TMA was pulsed into an empty reactor tube (Figure 4(b)). This mode of methane generation is an indication that during pulses 6–25 (Figure 4(a)), no further TMA surface deposition occurs, and the concentration of TMA that decomposes in the mass spectrometer approaches the levels detected for pulsing into an empty reactor.
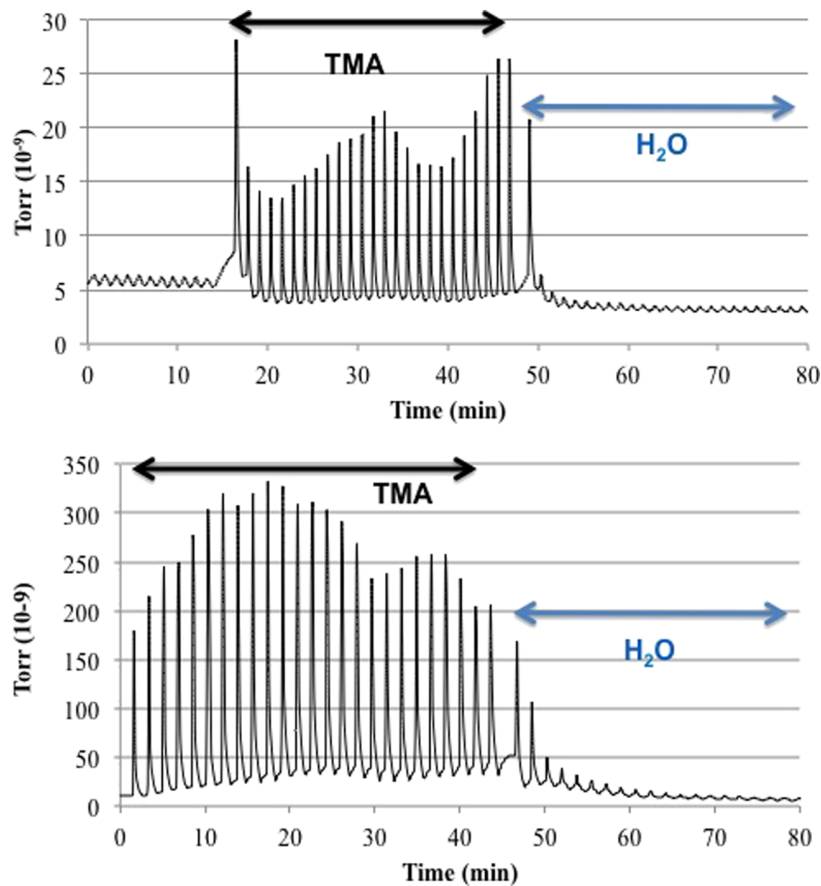
FIG. 4. Mass spectrometric monitoring of methane generated during one-cycle Al_2O_3 deposition at 175 °C. TMA pulse: 50 ms (1 Torr); H_2O pulse: 50 ms (1 Torr).

H_2O pulsing experiments (Figure 4(a)) shows that complete hydrolysis of grafted alkyl aluminum sites is achieved within the first four pulses, as indicated by the baseline methane signal. Multiple TMA-H_2O pulsing experiments were then conducted to determine the reproducibility of the ALD deposition cycles. Figure 5 shows a repeatable methane generation pattern from a 10-cycle Al_2O_3 deposition experiment.

B. Al_2O_3 ALD conditions

Al_2O_3 ALD was conducted using trimethylaluminum (TMA, 98%, Sigma-Aldrich) and deionized water as precursors.[16–18] 140 mg of the Pt/Al_2O_3(NanoDur) substrate was loaded into a 406 mm × 6.35 mm (i.d.) stainless steel tube reactor. The substrate was purged with N_2 (10 SCCM) for 30 minutes after reactor tube installation, and subsequently heated to 200 °C for 1 h under vacuum. The TMA–H_2O deposition experiments were carried out at 175 °C substrate temperature (Table I). During the course of ALD synthesis, the manifold upstream of the reactor (M_1–M_3, UM) was maintained at 135 °C, the reductant/oxidizer manifold (M_4) at 115 °C, and the LM at 175 °C. Both the TMA and H_2O bottles were kept at ambient temperature during the synthesis. In this report, one Al_2O_3 deposition cycle is comprised of five consecutive 50 ms (1 Torr) TMA pulses followed by five consecutive 50 ms H_2O (1 Torr) pulses. Each precursor pulse was carried out in a three-step sequence: (1) manifold evacuation to 1 Torr base pressure (30 s), (2) precursor pulse (50 ms) at 1 Torr pressure, and (3) 50 SCCM N_2 purge (30 s).
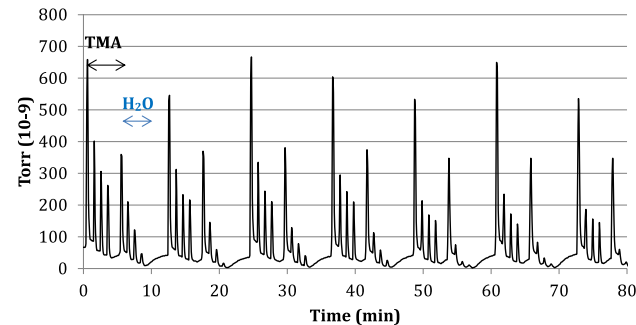

FIG. 5. Mass spectrometric monitoring of methane generated during a 10-cycle Al_2O_3 deposition experiment at 175 °C. Each cycle is comprised of four 50 ms (1 Torr) TMA and four 50 ms (1 Torr) H_2O pulses.

TABLE I. HT-ALD-CAT conditions for Al_2O_3 deposition.

HT-ALD-CAT section	Temperature (°C)
ALD manifold (M_1–M_3)	135
Red/ox manifold (M_4)	115
Upper manifold (UM) valves	135
Lower manifold (LM) valves	175
Reactor (R_1)	175

TABLE II. HT-ALD-CAT conditions for Al_2O_3 deposition.

HT-ALD-CAT section	Temperature (°C)
ALD manifold (M_1–M_3)	135
Platinum precursor (PR_2)	55
Red/ox manifold (M_4)	115
Upper manifold (UM) valves	135
Lower manifold (LM) valves	175
Reactor (R_1)	200

The success of each Al_2O_3 overcoating experiment was confirmed by the decrease in propylene hydrogenation activity of the resulting material measured at 30 °C. Complete overcoating of the Pt material was confirmed by the total suppression of propylene hydrogenation activity.

C. Thermal annealing of Al_2O_3 overcoat

When complete Pt overcoating was achieved, thermal annealing of the ALD-prepared Al_2O_3 overcoat was conducted to identify conditions under which pore formation and Pt exposure occur. The completely overcoated Pt catalysts were annealed at three different temperatures: 300 °C, 450 °C, and 600 °C. For each annealing experiment, the reactor was heated at the desired temperature for 1.5 h while maintaining a 20 SCCM N_2 flow (LM open to vacuum). The annealed catalyst was then cooled to 30 °C for propylene hydrogenation activity measurements.

D. Platinum ALD conditions

Platinum ALD was conducted using trimethyl(methyl-cyclopentadienyl)platinum(IV) (98%, Sigma-Aldrich) as precursor.[10] A three-cycle platinum ALD experiment was conducted on the overcoated (55 cycles Al_2O_3) Pt/Al_2O_3(NanoDur) substrate. Platinum deposition was carried out at 200 °C substrate temperature (Table II). During the course of Pt ALD, the manifold upstream of the reactor (M_1–M_3, UM) was maintained at 135 °C, the reductant/oxidizer manifold (M_4) at 115 °C, and the LM at 175 °C. The platinum precursor bottle was heated at 55 °C during the synthesis. In this synthesis, one platinum deposition cycle is comprised of five consecutive 50 ms (1 Torr) trimethyl(methylcyclopentadienyl)platinum(IV) pulses followed by five consecutive 0.1 s air (1 Torr) pulses. Each precursor pulse was carried out in a three-step sequence: (1) manifold evacuation to 1 Torr base pressure (30 s),
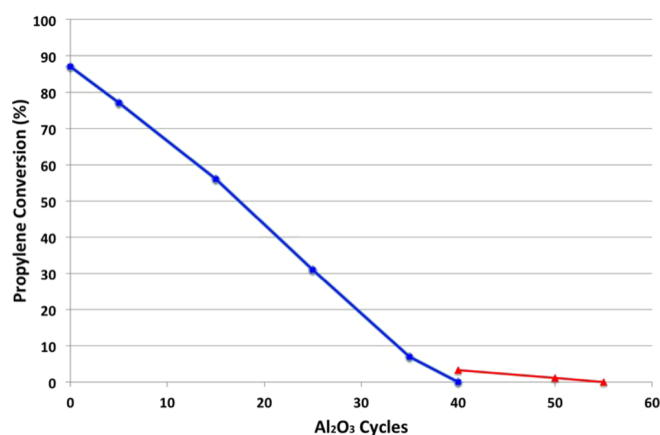

FIG. 6. Catalytic propylene hydrogenation activity as a function of Al_2O_3 deposition cycles; 1st Al_2O_3 overcoat (blue); 2nd Al_2O_3 overcoat (red). Note: The overcoated Pt/Al_2O_3 catalyst was annealed at 300 °C, 450 °C, and 600 °C prior to the application of the second overcoat.

(2) precursor pulse (50 ms to 0.1 s) at 1 Torr pressure, and (3) 50 SCCM N_2 purge (30 s).

E. HT-ALD *in situ* catalysis studies

In this study, catalyst reactivity evaluation was carried out using propylene hydrogenation at 30 °C as the probe reaction. After each ALD or annealing experiment, the upper and lower process selection manifolds (UM and LM) and the reactor (R_1) were cooled to 30 °C with 10 SCCM N_2 purge. Once the reactor temperature stabilizes at 30 °C, 10 ml/min 2.5 mol. % propylene in He (MFC_5) and 10 ml/min 2.5 mol. % hydrogen (MFC_3) in He were fed into the system. GC analysis of the product stream was performed using an online Agilent 7890 GC unit. The GC method employed a 60 m × 0.32 mm GS GasPro capillary column for the separation with cycle times in the order of 8 min.

F. Results and discussion

The utility of the HT-ALD-Cat tool for the application of inorganic oxide films/overcoats was successfully demonstrated through the application of multilayer Al_2O_3 overcoat on Pt nanoparticles (2.8 nm) on Al_2O_3 NanoDur. The propylene hydrogenation activity of Pt/Al_2O_3(NanoDur) at 30 °C decreases linearly with increasing number of Al_2O_3 deposition cycles (Figure 6). The first complete overcoating of the Pt sites was achieved after 40 Al_2O_3 cycles
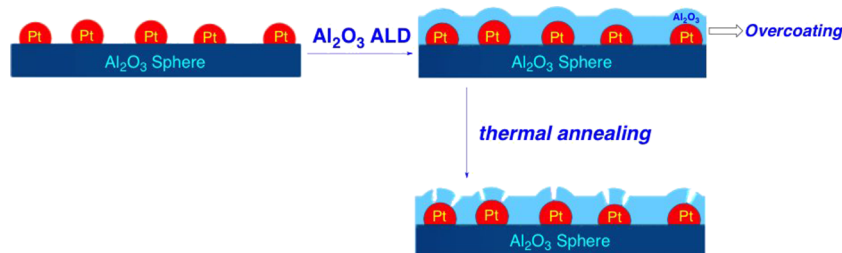

FIG. 7. Al_2O_3 overcoating application by ALD, followed by thermal annealing of the Al_2O_3 overcoating.
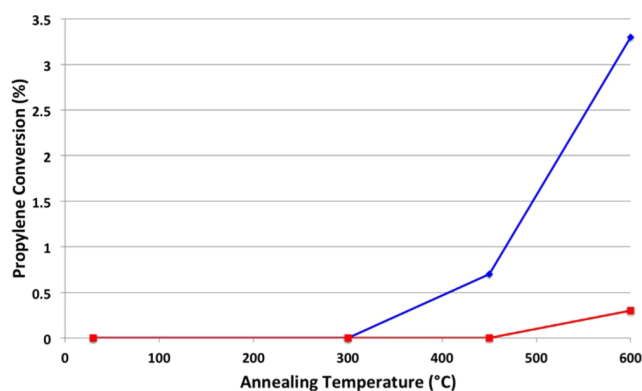
FIG. 8. Catalytic propylene hydrogenation activity after thermal annealing of Al_2O_3 overcoating. (a) Annealing of Al_2O_3 layer after the first 40 ALD cycles (blue); (b) annealing of Al_2O_3 layer after the additional 15 ALD cycles (red).

based on the complete loss of propylene hydrogenation activity.

Thermal annealing of the first complete overcoat (40-cycle Al_2O_3) at 300 °C, 450 °C, and 600 °C revealed that overcoat densification at 450 °C and 600 °C is sufficient to induce pore formation (Figure 7), as indicated by the resurrection of propylene hydrogenation activity at 30 °C (Figure 8). Application of 15 additional Al_2O_3 cycles (second overcoat) on the annealed catalyst afforded a material that is resistant to pore formation upon thermal treatment. Only background hydrogenation activity (0.5% propylene conversion at 30 °C) was observed after annealing at 600 °C. 90%–95% of the material can be recovered after each ALD synthesis and/or catalysis experiment. (Note: Some materials get trapped in the glass wool layers used to pack the substrate bed.) TEM imaging of

FIG. 9. TEM images of (a) Pt/Al_2O_3(NanoDur) substrate, (b) Pt/Al_2O_3(NanoDur) overcoated with 55 Al_2O_3 cycles, (c) and (d) showing Al_2O_3 layers/overcoating.

the Pt/Al_2O_3(NanoDur) overcoated with a total of 55 Al_2O_3 ALD cycles revealed platinum sintering, forming bigger Pt particles (~3.5 nm, Figure 9(b)). TEM characterization of the overcoated catalyst also showed regions where Al_2O_3 layers are visible (Figures 9(c) and 9(d)).

The three-cycle Pt ALD experiment on the fully overcoated material afforded a catalyst that hydrogenates 77% of the propylene at 200 °C (10 SCCM 2.5 mol. % propylene in He; 10 SCCM 2.5 mol. % H_2 in He). This result demonstrates the utility of the HT-ALD-CAT instrument for *in situ* active site synthesis. Our group has successfully extended this application to the deposition of single-atom active sites using organometallic manganese, zinc, and aluminum precursors. These findings will be reported separately.

IV. SUMMARY AND CONCLUSION

An I-ALD-CAT tool was developed by combining an ALD manifold with a plug-flow reactor system. The I-ALD-CAT is capable of *in situ* catalyst synthesis by ALD and reactivity evaluation through plug-flow reactor experimentation. This instrument is equipped with an ALD manifold that delivers gaseous reagents comprised of 12 different metal precursors, 4 oxidizing or reducing agents, and 4 catalytic reaction feeds to either of the two plug flow reactors. The system can employ reactor pressures and temperatures in the range of 10^{-3} to 1 bar and 300–1000 K, respectively. The instrument is also equipped with a GC unit and a MS for the detection and/or quantification of volatile species from ALD and catalytic reactions. The I-ALD-CAT was successfully employed in the application of platinum active sites and Al_2O_3 overcoating, and propylene hydrogenation activity testing under plug-flow conditions. The simplicity of the instrument design provides a model system that will enable the assembly of such ALD manifold–plug flow reactor hybrid instrument for lab-scale catalyst synthesis and reactivity studies.

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