Development of Highly Selective Oxidation Catalysts by Atomic Layer Deposition

Energy Systems Division

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Project Objective:

The goal of the project is to develop new techniques for the manufacture of catalysts by atomic layer deposition (ALD) for the selective oxidative dehydrogenation of alkanes, for example, ethane to ethylene, propane to propylene, and butane to butadiene. The specific project objective is to demonstrate the catalyst manufacturing techniques by developing, characterizing, testing, and evaluating new catalysts for the selective oxidative dehydrogenation of alkanes on existing catalytic substrates in conventional reactors and in single-pass catalytic reactors utilizing AAO/ALD catalytic membranes.

Background:

The domestic chemical industry has identified improved separation and catalytic processes as a high priority research need for improving the energy efficiency of hydrocarbon processing. Recent advances at Argonne National Laboratory both in material synthesis techniques and in computational studies of these techniques on supported vanadate catalyst systems suggest that new efficient and more specific catalysts can be developed. The material synthesis techniques have been verified by the production of uniquely specific catalysts for the oxidative dehydrogenation reaction of cyclohexane to cyclohexene, resulting in increased product yield and improved product selectivity. In response to a solicitation from the Industrial Technology Program, Argonne National Laboratory and its partners, Northwestern University (Center for Catalysis and Surface Science, and Institute for Environmental Catalysis) and Ineos

Technologies (formerly BP Amoco Chemicals), propose to develop new catalytic synthesis techniques. Successful completion of this project will advance the state-of-the-art, increase the understanding, and accelerate the development of highly selective catalytic materials for the domestic chemical industry. Successful implementation of the anticipated results of this project will result in significant energy, environmental, and economic benefits.

1. ALD Process Development

Figure 1 illustrates the principle synthetic concept that motivated this project. By depositing a series of ALD coatings on a substrate, we can individually tune the physical and chemical properties of the substrate to generate a catalyst that is highly selective and active, and combines both catalytic and separations functions in a single unit. In this example, the anodic aluminum oxide (AAO) membrane with intrinsic 40 nm pores is first coated by ALD with Al_2O_3 to uniformly shrink the pore size to 10 nm to alter the transport/filtering properties. Next, ~ 0.5 nm ALD TiO_2 is deposited to act as the catalytic support layer. Finally, a single cycle of ALD V_2O_5 is performed to deposit isolated VO_x species on the surface to serve as the active catalyst.

Figure 1: ALD synthesis of nanostructured catalyst using AAO membrane as template for growth.

To synthesize and evaluate the selective oxidative dehydrogenation (ODH) catalysts in this project, we first had to develop new ALD processes for depositing the necessary catalytic materials: silica, vanadia, niobia, molybdenum oxide, and tungsten oxide. These processes had to be compatible with the high surface area substrates required for effective catalysts. Moreover, we had to develop methodologies for coating and characterizing these high surface area substrates including mesoporous granular materials such as silica gel, and the nanoporous AAO membranes. These development activities will be detailed in the following sub-sections. Our primary focus was on vanadia catalysts given their high activity for ODH. In addition, we pursued mixed-metal (V-Nb-Mo and V-Nb-W) catalysts based on the high selectivity demonstrated by these materials for ethane ODH.

1.1 Silica ALD

The ALD of silica (SiO_2) was needed in order to coat the convert the native alumina surface of the AAO membranes into SiO_2 to be used as the support layer for the subsequent deposition of the vanadia and mixed-metal catalysts. We performed experiments examining improved methods for preparing SiO_2 films by ALD. The existing method that uses alternating $\text{SiCl}_4/\text{H}_2\text{O}$ exposures suffers from several limitations including the need for high deposition temperatures of 400°C , very large reactant exposures as well as etching and corrosion problems from the SiCl_4 precursor and the HCl byproduct. The improved method utilized alternating exposures to tris-dimethylamino silane ($\text{SiH}(\text{N}(\text{CH}_3)_3)_3$) and ozone, O_3 . In situ measurements performed using a quartz crystal microbalance (QCM) demonstrated self-limiting growth at 200°C using reactant exposures $\sim 10^3$ times lower than with $\text{SiCl}_4/\text{H}_2\text{O}$. The growth

was self-limiting and showed a modest growth rate of $\sim 0.23 \text{ \AA/cycle}$ using exposure times $>6\text{s}$ for the $\text{SiH}(\text{N}(\text{CH}_3)_3$ and 5 s for the O_3 . Although we were successful in developing this SiO_2 ALD process, we elected later in the project to use Nb_2O_5 as the support layer for the vanadia catalyst and as a consequence we did not ultimately utilize the SiO_2 ALD for catalyst synthesis.

1.2 Vanadium Oxide ALD

Vanadium oxide (V_2O_5) ALD was accomplished using alternating exposures to vanadium (V) tris-isopropoxide (VOTP) and hydrogen peroxide (H_2O_2). QCM measurements showed self-limiting growth at $\sim 0.45 \text{ \AA/cycle}$ using a deposition temperature of 100°C and exposure times of $>0.25\text{s}$ for the H_2O_2 and $>0.25 \text{ s}$ for the VOTP (Figure 2). These studies utilized a vaporization temperature for the VOTP of 45°C . It was also possible to deposit the vanadia using H_2O in place of the H_2O_2 , but in this case the growth rate was only $\sim 0.32 \text{ \AA/cycle}$. These observations were confirmed by ex situ spectroscopic ellipsometry, scanning profilometry, and scanning electron microscopy measurements for films prepared using 50-2000 V_2O_5 ALD cycles which revealed a growth rate of $0.41 \text{ \AA/cycle}$ in good agreement with the QCM. We established that the growth was constant over the range of deposition temperatures of $70\text{-}150^\circ\text{C}$. At higher temperatures, the growth rate increased dramatically due to thermal decomposition of the VOTP precursor. The films were smooth and amorphous as deposited (0.33 nm RMS roughness for 800 nm film) but crystallized upon annealing above $\sim 200^\circ\text{C}$. Using in situ QCM we confirmed that the ALD V_2O_5 proceeded promptly and without any apparent nucleation delay on ALD TiO_2 surfaces prepared in situ using alternating exposures to TiCl_4 and H_2O_2 .

We also examined an alternative precursor for the V_2O_5 ALD, bis-pentamethyl cyclopentadienyl vanadium (II), or $\text{V}(\text{Me}_5\text{Cp})_2$ which had been custom-synthesized by the group of Tobin Marks at Northwestern University. We found the growth to be very similar to that of the VOTP, with a growth rate of $0.4 \text{ \AA/cycle}$ at a deposition temperature of 120°C . However, the $\text{V}(\text{Me}_5\text{Cp})_2$ required a higher vaporization temperature of 100°C and longer exposure times of $>2 \text{ s}$ due to the lower vapor pressure of this compound versus the VOTP. For these reasons, we elected to proceed with the VOTP for the remainder of the project.

1.3 Niobium Oxide ALD

An ALD process for Nb_2O_5 was developed using alternating exposures to niobium (V) ethoxide ($\text{Nb}(\text{OEt})_5$) and either H_2O_2 or H_2O . These studies utilized a vaporization temperature for the $\text{Nb}(\text{OEt})_5$ of 110°C and a growth temperature of 200°C . In this case, both the H_2O_2 or H_2O yielded a similar growth rate of $0.45 \text{ \AA/cycle}$ for the Nb_2O_5 . The optimal timing sequence was determined using in-situ quartz crystal microbalance (QCM) measurements. These measurements also verified the self-limiting surface reactions for this system. Next, Nb_2O_5 films were deposited on flat, $\text{Si}(100)$ surfaces and analyzed using ellipsometry, SEM and energy-dispersive x-ray analysis (EDAX) to determine the film thickness, surface morphology and chemical composition, respectively. In addition to the pure Nb_2O_5 films, we also studied the ALD of $\text{Nb}_2\text{O}_5/\text{V}_2\text{O}_5$ mixed oxide films using in-situ QCM, ellipsometry and EDAX measurements (Figure 3). These analyses confirmed that we can deposit these mixed-metal oxides with atomic-level control over both film thickness and stoichiometry. We deposited both Nb_2O_5 and V_2O_5 films by ALD onto nanoporous anodic aluminum oxide (AAO) membranes by extending the exposure times of the precursors relative to those used for the flat $\text{Si}(100)$ surfaces.

Figure 3: In situ QCM measurements performed during alternating growth of V_2O_5 and Nb_2O_5 ALD films. These data indicate that the V_2O_5 grows readily on the Nb_2O_5 and vice versa, as expected given that the ALD surface chemistries for these two materials are very similar.

1.4 Molybdenum oxide ALD

We evaluated several precursors for the ALD of molybdenum oxide, MoO_3 . The first precursor that we tested was diethyl-benzyl Mo ($\text{Mo}(\text{EtBz})_2$), however we failed to observe self-limiting ALD using this compound. The second precursor was molybdenum(IV) oxide acetylacetonate ($\text{MoO}_2(\text{acac})_2$). At a deposition temperature of 200°C and a vaporization temperature of 150°C and using O_3 as the co-reactant, in situ QCM measurements showed a growth rate of $\sim 0.3\text{--}0.4 \text{ \AA/cycle}$. Spectroscopic ellipsometric measurements of the MoO_3 films deposited on silicon substrates using 10-300 ALD MoO_3 cycles yielded a somewhat higher growth rate of 0.47

Figure 4: EDAX cross-sectional maps showing distribution of elements within a single silica gel particle. Mo is localized only near the outer edge of the particle indicating incomplete infiltration.

Å/cycle. However, the MoO_3 growth was not found to be self-limiting, but rather the thickness increased steadily with increasing $\text{MoO}_2(\text{acac})_2$ exposure times. For this reason, we evaluated a third ALD MoO_3 precursor, molybdenum(IV) oxide tetramethyl-heptanedionate, $(\text{MoO}_2(\text{thd}))_2$. At a deposition temperature of 210°C and a vaporization temperature of 180°C , in situ QCM measurements showed mass uptake using either H_2O , H_2O_2 , or O_3 as the oxygen source but the largest growth rate was obtained using the O_3 . Next, MoO_3 coatings were prepared on high surface area silica gel substrates and self-limiting growth was observed at $0.7 \text{ Wt\%/cycle}$ using the $100 \text{ m}^2/\text{g}$ substrate material as determined using X-ray fluorescence measurements. However, subsequent cross-sectional scanning electron microscopy with energy-dispersive analysis of X-rays (SEM-EDAX) revealed that only the outer ~ 10 micron perimeter of the 100 micron sized silica gel particles was coated (Figure 4). We believe the incomplete infiltration of the MoO_3 into the mesoporous silica gel resulted from thermal decomposition of the O_3 on the MoO_3 surface. Due to these difficulties in achieving satisfactory conformal coatings of the MoO_3 , we elected to proceed with WO_3 instead.

1.5 Tungsten oxide ALD

We pursued tungsten oxide (WO_3) ALD using the approach of first depositing metallic W using alternating exposures to disilane (Si_2H_6) and tungsten hexafluoride (WF_6) followed by calcining to form the oxide. In situ QCM measurements revealed the W ALD to be self-limiting over a range of deposition temperatures between 125 – 300°C , and this finding was corroborated using ellipsometry, stylus profiling, and cross-sectional SEM measurements for ALD W films deposited on planar silicon substrates. The growth rate increased with increasing deposition temperature from $m=3.1 \text{ Å/cycle}$ at 125°C to $m=8.2 \text{ Å/cycle}$ at 300°C (Figure 5). We found the conformality of the ALD W films to be superb. We deposited uniform W films inside of AAO membranes, carbon aerogels, and mesoporous silica gel substrates, and in all cases cross sectional SEM-EDAX measurements verified complete and uniform infiltration of these substrates by the ALD W films. We discovered that the post-deposition calcining to form the oxide had to be performed slowly and with care to avoid a thermal runaway condition caused by the exothermic tungsten oxidation reaction. By limiting the oxygen partial pressure to be only a few Torr, and performing the oxidation at temperatures below 100°C , we found that the oxidation could be well-controlled.

Due to the inhibited growth of the W ALD on metal oxide surfaces, the W growth per cycle varied initially with the number of ALD W cycles performed, at least in the early stages of growth. For instance, using the same silica gel substrate with $100 \text{ m}^2/\text{g}$ specific surface area,

Figure 5: ALD tungsten thickness versus cycles as measured by ellipsometry for films prepared on silicon at different temperatures. ALD temperatures (in $^\circ\text{C}$) and growth rate (m) for each trace are indicated.

the W loading resulting from 1, 2, and 3 W ALD cycles was 12, 47, and 110 wt%, respectively, on an Al_2O_3 surface, versus 2, 11, and 25 wt%, respectively, on a Nb_2O_5 surface. This behavior was reproducible, and consequently it was possible to control precisely the W loading if the nucleation behavior was taken into account.

1.6 Conformal ALD Coating of AAO Membranes

The AAO membranes were prepared using a two-step anodization process with high purity aluminum disks carried out in 0.3 M oxalic acid at a constant potential of 40 volts, resulting in 40 nm pores with an average pore to pore separation of 110 nm. The thickness (pore length) of the AAO membranes, $\sim 70\ \mu\text{m}$ in this case, was controlled by the duration of the second-step anodization and was verified using cross-sectional SEM measurements. The aluminum disk were masked during fabrication to preserve an aluminum border around the perimeter of the AAO discs. This enabled the membrane to be sealed in the catalyst testing reactor using commercial compression fittings (VCR glands). Before any catalyst was loaded, the AAO pores were coated with at least 1 nm of Al_2O_3 to completely cover electrolyte impurities incorporated into the oxide material during anodization. The layer-by-layer growth of alumina was achieved by alternatively exposing the AAO substrates to trimethyl aluminum and water for 8 cycles using a quasi-static reactor operation mode in which the reactor is pumped down to 0.1 Torr after each dose and purge. The ALD precursor partial pressures and exposures times were increased when coating the AAO membranes as compared to coating planar substrates in order to facilitate the gaseous diffusion into the very high aspect ratio AAO pores. Figure 6 shows cross-sectional EDAX measurements for the V, O, and Al following ALD V_2O_5 in the AAO membrane. The relatively constant V EDAX signal across the ~ 70 micron thickness of the AAO indicates uniform infiltration of the AAO.

In the course of preparing the ALD/AAO catalysts, we discovered a novel technique for depositing materials at controlled depths within porous substrates based upon the passivating effect produced by one precursor to prevent the adsorption of a second precursor. For example, a surface exposed to trimethyl aluminum is not reactive towards diethyl zinc. This effect, combined with Knudsen diffusion in which the precursor exposure times dictate the depth of penetration of the deposited layer, enables spatially controlled “stripe coating” within porous supports. We used this method to deposit stripes of ZnO , TiO_2 , V_2O_5 , and Nb_2O_5 at specified depths within AAO membranes. The stripes were visualized by cross-sectional elemental mapping of the coated AAO membranes. The factors controlling the stripe locations and widths

Figure 6: Cross sectional EDAX measurements showing uniform infiltration of the high aspect ratio (L/D~1500) AAO membrane by the V_2O_5 ALD coating.

were identified by comparing the experimental results with the results of Monte Carlo simulations. This new technique opens up potential applications in sensors, separation devices, and multi-step catalysts. For example, Figure 7 shows a stripe of TiO_2 prepared at a depth of ~20 microns within a 70 micron thick AAO membrane. One potential application for this method to catalysis is that a series of stripes of different catalytic material could be prepared so as to effect an $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ sequential catalytic conversion within a single membrane.

We used ~1cm AAO membranes for the development work in this project. However, we identified a commercial partner (Synkera, Inc.) capable of fabricating large area AAO membranes for scale-up. Figure 8 shows a photograph of an AxA inch AAO membrane fabricated by our partner.

1.7 Conformal ALD Coating of Porous Powders

Prior to the ALD coating in powders, fixtures were designed and fabricated to allow small quantities (~1 g) of porous powders to be coated with catalytic layers inside of the existing ALD viscous flow reactors at Argonne. In addition, characterization facilities were commissioned. An Oxford instruments ED2000 X-ray fluorescence (XRF) spectrometer was acquired and installed in our ALD laboratory. This instrument was used to determine the composition of the ALD layers deposited on both flat test substrates as well as on the high surface area catalytic support powders and membranes. We used the XRF to verify the self-limiting growth of ALD ZnO monolayers on gram-quantities of high surface area silica powder. In addition, we used cross-sectional SEM and EDAX measurements of individual silica particles to prove that the ZnO completely and uniformly infiltrates these silica supports. We have also used XRF to quantify the V_2O_5 coverages on AAO membranes. X-ray photoelectron spectroscopy (XPS) and

inductively coupled plasma atomic absorption spectroscopy (ICP-AES) measurements were performed at Ineos on the silica powder coated materials. These measurements confirmed the anticipated loadings, and also identified possible contamination that may arise from the commercially obtained ALD precursors.

Our initial studies of ALD in the high surface area porous powders revealed that the optimized ALD process conditions developed for ALD growth on wafers and during QCM studies are not directly applicable. In order to better understand the interplay between process and reactor conditions on the ALD coating of high-surface area and high-aspect ratio substrates, a benchmarking study was performed on the silica gel catalyst support powders using the very well understood zinc oxide ALD process comprising the precursors diethyl zinc (DEZ) and H_2O .

The ZnO study provides a benchmark for evaluating other ALD coatings onto the same powders. In particular a 3-cycle application of DEZ/ H_2O onto a $100\text{ m}^2/\text{g}$ silica gel yielded an 8.0% weight gain of ZnO. Next, we coated commercial silica gel (Silicycle S10040M, $100\text{ m}^2/\text{g}$, 100 micron particle size) using ALD Al_2O_3 to characterize how ALD performs on these high aspect ratio, high surface area materials. Figure 9a shows EDAX elemental maps of the Al concentration taken from individual grains coated using TMA exposure times of 5, 15, 30, and 90 s. It is clear that the coating occurs from the outside of the particles first and progresses inward as the exposures approach saturation. Figure 9b shows that the weight gain and the EDAX intensity both saturate at ~70s exposure time, and this corresponds well to the predicted value based on the surface area of the silica gel and the TMA partial pressure. Figure 9c shows that the weight gain of the silica gel increases linearly with increasing Al_2O_3 ALD cycles as predicted for layer-by-layer coating in the limit where the silica gel pore size does not change significantly.

Using lessons learned from the benchmarking studies, a successful process for ALD vanadium oxide was developed where a 5.4% weight gain for a 3-cycle exposure was observed on powders. Both of these values are consistent with growth rates observed for the same ALD reactants on flat substrates. For the V_2O_5 ALD using alternating exposures to VOTP and H_2O_2 , we also observed saturating in the weight gain versus

Figure 9: (a) Cross-sectional EDAX maps of Al in silica gel after ALD Al_2O_3 coating illustrating that this porous material coats from the outside progressively inward with increasing exposure times; (b) Uptake measurements versus TMA exposure during Al_2O_3 ALD in silica gel showing saturation behavior; (c) weight gain versus number of ALD Al_2O_3 cycles demonstrating linear growth.

Figure 10: Uptake measurements versus VOTP and H_2O_2 exposure during V_2O_5 ALD in silica gel showing saturation behavior. Photo shows uniform coloration of the V_2O_5 -coated silica gel at saturation.

exposure times as illustrated in Figure 10. In this case, saturation required 250s, and this is a consequence of the lower vapor pressure for VOTP compared to TMA. The initially white silica gel powder became a uniform yellow color when saturation of the V_2O_5 ALD was achieved. For sub-saturating exposures, the color was still uniform across the powder bed, but the shade was lighter. This behavior is consistent with the ALD coating occurring essentially uniformly on the entire powder bed, but with the infiltration occurring progressively into the individual particles with longer exposure times, analogous to the behavior shown in Fig. 9 for the ALD Al_2O_3 in the silica gel. Similarly, we achieved good saturation and uniform infiltration of the S10040M silica gel powder using the alternating $Nb(OEt)_5/H_2O$ exposures for Nb_2O_5 ALD as shown in Figure 11. Using 3 ALD Nb_2O_5 cycles, we found saturating loadings of ~ 1 wt% Nb_2O_5 using $Nb(OEt)_5$ exposure times of 300s (Fig. 11a). Moreover, cross sectional EDAX elemental mapping of the Nb revealed uniform infiltration of the high aspect ratio and high surface area silica gel substrate (Fig. 11b).

Finally, we synthesize ALD coatings of the mixed-metal catalyst materials inside of the silica gel nanoporous powder substrates. Using the processes for the ALD Nb_2O_5 , V_2O_5 , and W described above, we prepared a sample using all three processes in succession and subsequently analyzed the material using XRF measurements (Fig. 12). We found that the loadings of the Nb, W, and V were consistent with our expectations, thereby confirming our ability to synthesize complex, mixed-metal catalysts on high surface area powders using ALD.

Figure 11: (a) Uptake measurements versus $Nb(OEt)_5$ exposure during Nb_2O_5 ALD in silica gel showing saturation behavior. (b) EDAX cross sectional elemental maps showing uniform infiltration of the ALD Nb_2O_5 .

Figure 12: XRF measurement of Nb-W-V mixed-metal catalyst showing the presence of all three metals at the expected loading.

2. Facilities and Equipment Development

In addition to the ALD process development described in Section 1, there was significant facilities and equipment development required for this project in order to develop the necessary custom infrastructure to manufacture and test the catalysts.

2.1 AAO Fabrication Facility

Anodic aluminum oxide (AAO) membranes consist of a uniform array of hexagonal cells, extending from the surface through the width of the membrane. Generation of AAO membranes requires a series of electrochemical anodizations (30 volts max) to form the pores and chemical

etchings to remove unwanted material. To facilitate catalyst testing in the AAO membranes, a facility was installed for producing batches of 8 membranes with an integral aluminum border to permit sealing of the catalyst membrane using VCR face-seal glands. In this way, the catalyst testing gas mixture can be forced to flow through the AAO pores without bypass. Fabrication of AAO membranes is an electrochemical process consisting of the following steps:

- Annealing of sample – e.g., at 500°C in a tube furnace in an argon atmosphere
- Electropolishing of sample – e.g., at 0°C in a perchloric acid / ethanol solution
- First anodization – e.g., at 3°C in an oxalic acid solution
- Removal of preliminary AAO – e.g., at 60°C in a chromic acid / phosphoric acid solution
- Second anodization (if necessary) – e.g., at 3°C in an oxalic acid solution
- First Etching – at room temp in a copper chloride / hydrochloric acid solution
- Second Etching (If necessary) – at 30°C in a phosphoric acid solution
- Chemical and/or microstructural Analysis

Figure 13 describes the AAO fabrication facility. The top right image shows the anodization bath and current source. The top left image shows the AAO fixture which is designed to accommodate 8 polished Al discs in separate anodization volumes. The bottom left image shows a photograph of the resulting AAO membrane retained in the integral aluminum sealing ring, and the bottom right image is an SEM micrograph of the AAO showing the 40 nm diameter pores in an hexagonal arrangement.

Figure 13: AAO fabrication facility.

2.2 Catalyst Testing System

A Catalyst Test Station (CTS) was custom designed and built for the evaluation of powder and membrane catalysts in flowing gaseous reactions at atmospheric pressure and up to 650°C temperature (Figure 14). Catalyst Test System flows metered amounts of a mixture of hydrocarbon gases (methane, methanol, propane or ethane) and oxidizers (water or oxygen) using an Ar carrier gas through a heated (100-650°C) reactor fixture containing up to 1.0 gram of a catalyst

Figure 14: Catalyst testing system.

powder or an AAO membrane. The gases are supplied from high pressure gas cylinders using two-stage regulators set to 30 psig. The working pressure in the catalyst reaction zone will be maintained at or below 10 psig depending on the flow rate, amount of catalyst, and temperature. In this dual testing system, one system is optimized for testing the catalysts prepared on powder supports, and the other system is optimized for testing the catalysts prepared on AAO supports.

An AAO membrane testing fixture was designed and constructed allowing propane and oxygen to be delivered on opposite sides of the catalytic membrane to evaluate the effect of this asymmetric reactant distribution on the membrane performance (Figure 15). A series of AAO catalytic membranes was prepared by ALD using V-based catalysts for use in the new testing fixture. These membranes had 20-40 nm pores and the V catalyst was applied uniformly throughout the pores. These tests

did not indicate any advantage in terms of propylene yield for the asymmetric flow configuration. This is believed to result from rapid diffusion of the reactants through the 20-40 nm pores. Under the conditions used for these tests, the rapid reactant diffusion apparently negates the effect of delivering the reactants on opposite sides. Smaller membrane pores or higher pressures which reduce this diffusion might enhance the propylene yield. Alternatively, the propylene yield might be enhanced by applying the catalyst at discrete depth locations within the pores using stripe coating.

Figure 15: Schematic diagram of AAO membrane testing fixture for catalyst testing system.

2.3 Large Substrate Reactor

A new deposition chamber for our viscous flow ALD coating system was designed and constructed to allow coating of large format, up to 12"x18" AAO membranes similar to that shown in Figure 8. This is a scale-up of over 1000x compared to the 0.5" diameter AAO we have used previously. This was a cross flow system with a Kalrez O-ring seal capable of heating to 300°C (Figure 16).

Figure 16: Photograph of large substrate reactor for ALD coating AAO membranes of up to 12x18".

2.4 Powder Coating Reactor

To perform the scale up of ALD coating on porous powders such as the silica gel substrate from 1g to 1 kg, a powder coating reactor was designed and constructed. The powder coating reactor uses a rotating drum to agitate the powder during coating, and utilizes static dosing of metered quantities of the ALD precursors to maximize precursor utilization (Figure 17). An internal ducted fan circulates the precursor during the doses for more effective coating. The system is integrated with a residual gas analyzer for endpoint detection of the ALD cycles. The system is designed for the batch coating of 10^4 m^2 of high surface area substrates.

Figure 17: Powder coating reactor, shown partially constructed

2.5 Beneq TFS500

To complete the scale-up of the AAO membrane coating, a commercial ALD coating system (Beneq TFS500) for coating multiple, large-format AAO membranes with catalyst layers was installed and commissioned (Figure 18). Large-format membranes have been coated successfully. We completed the demonstration of coating a large format (8"x8") porous membrane with an ALD layer (bottom right photo in Figure 18). This represents a scale up of 400x in surface area compared to the prototype membranes used for the development work in this project.

Figure 18: Beneq TFS500 ALD coating system. Right hand side shows several views of inner chamber batch reactor capable of coating multiple, large area porous membrane substrates. Bottom most image shows porous membrane following ALD coating with Al_2O_3 performed in the Beneq.

3. ALD Catalyst Testing

3.1 Catalyst Testing at Ineos

A set of ALD catalysts was prepared at Argonne in which the number of ALD cycles for niobia was varied while keeping constant the loading of vanadia. The goal of this catalyst set was to investigate the necessary thickness of the niobia layer. In addition, a set of ALD catalysts was prepared in which the niobia, vanadia, and tungsten catalysts were blended in a cycle-by-cycle basis. The goal of this set of catalysts was to optimize on the formulation of the niobia/vanadia/tungsten catalysts. These two sets of ALD catalysts were shipped to Ineos for testing. Ineos tested these materials and identified an optimal ordering of the Nb and V layers to achieve maximal propylene yield in the oxydative dehydrogenation of propane. These tests also revealed that the effect of the tungsten was minimal. A brief description of these catalysts is given in Table 1, and the test results are summarized in Figure 19. The highest propylene yields were obtained for the 1 cycle V on 12 cycle Nb samples prepared on the CP8020 substrate. The CP8020 is a proprietary silica gel produced by Ineos having a bimodal pore size distribution.

<u>Argonne Sample ID</u>	<u>INEOS Calcined Sample ID</u>	<u>Description</u>	<u>Support</u>
JL_ALD_006	22129-72-A	3 cycles V (3% V)	CP8020
JL_284	22129-72-B	12 cycles Nb, 1 cycle V (1% V)	CP8020
JL_285	22129-72-C	12 cycles Nb, 1 cycle V, 1 cycle W	CP8020
JL_296	22129-108-A	12 cycles Nb	CP8020
JE_1260	22129-108-B	12 cycles Nb, 1% V (wet impregnation)	CP8020
JE_1261	22129-108-C	12 cycles Nb, 3% V (wet impregnation)	CP8020
JL_314	22195-123-A	12 cycles Nb	Silacyle
JL_315	22195-123-B	12 cycles Nb, 1 cycle V	Silacyle
JL_316	22195-123-C	12 cycles Nb, 2 cycles V	Silacyle
JL_317	22195-123-D	12 cycles Nb, 4 cycles V	Silacyle
JL_320	22195-123-E	12 cycles Nb, 2 cycle V, "1 ML" Mo (wet impregnation)	Silacyle

Table 1: Description of ALD catalysts prepared on silica gel substrates and tested for propane ODH at Ineos

3.1 Catalyst Testing at Argonne

An additional set of catalysts was prepared at Argonne to evaluate the effects of the Nb_2O_5 support layer thickness, the structure of the silica gel support, the ALD pulse sequence for the Nb and V components, as well as the inclusion of ALD Mo to make a three-metal catalyst. These catalysts were tested at Argonne in propane ODH using the catalyst testing system shown in Figure 14, and the results are summarized in Figure 20. One important and surprising finding was that the pore structure of the support has a profound influence on the catalytic behavior. This can be seen in Fig. 20 which shows much higher yields for the catalysts prepared on the Ineos-proprietary CP8020 silica gel which has a bimodal pore size distribution (1.5 and 20 nm pores), as compared to the commercial Silicycle S10040M which has a nearly identical specific surface area, but a mono-modal pore size distribution (30 nm pores).

Finally, a pair of identical vanadia catalysts was prepared, with the only difference being that in one case the vanadia was deposited by ALD, and in the second case the vanadia was deposited using conventional incipient wetness impregnation (IWI). These catalysts were tested at Argonne for ethane ODH and the results are shown in Fig. 21. Figure 21 shows that the ethylene yield from the ALD vanadia catalyst is up to 3x higher compared to the IWI catalyst. The much higher yield for the ALD catalyst results from the higher dispersion afforded by ALD. As deposited by ALD, the vanadia species are isolated, thus avoiding the formation of polymers which tend to form the combustion products (CO and CO_2) rather than the desired ethylene.

4. Accomplishments

4.1 Patents

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4.2 Publications

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4.3 Presentations

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Chicago Catalysis Club 2007 Spring Meeting, Chicago, IL, "Development of Highly Selective Oxidation Catalysts by Atomic Layer Deposition", J. W. Elam, Contributed Talk (May, 2007).

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4.3 Awards

R&D100 Award in 2012, “Large-Area Microchannel Plate (MCP)”

During our DOE ITP-funded project CPS 17784, we developed technology to apply thin film coatings by atomic layer deposition (ALD) inside of nanoporous membranes. The purpose of these coatings was to convert the chemically inert surface of the membrane into a catalytically active surface. For instance, beginning with an anodic aluminum oxide (AAO) membrane with 50 nm pores, 100 micron thickness, and 1cm² surface area, we first deposited 1-10 nm of TiO₂ by ALD to serve as a catalyst support layer, followed by a sub-monolayer of ALD V₂O₅. The resulting titania-supported vanadia surface is a highly active catalyst for oxidative dehydrogenation (e.g. propane to propylene). The benefit of the AAO membrane is that the highly uniform pore structure can serve to control precisely the catalyst contact time and consequently tune the selectivity of the catalyst. Moreover, we can precisely control the AAO pore size in the nm-regime by adjusting the thickness of the TiO₂ layer, and thereby combine gaseous separations with catalysis in the same porous structure. The initial development work in this catalysis project was performed using our existing bench-scale coating equipment and cm-sized AAO membranes to establish proof-of-concept. At the end of the project, we commissioned a commercial ALD coating system (Beneq TFS500) to fabricate large area (20x20cm) catalytic membranes as a demonstration of scale-up feasibility.

Recently we utilized the technology and equipment developed in our ITP-funded catalysis project for a different application: the fabrication of large area microchannel plate (MCPs). MCPs are solid state electron amplifiers used in image intensifiers (e.g. night vision), mass spectrometry, and particle detection. MCPs are comprised of thin glass plates of micron-scale capillaries, each of which acts independently to amplify weak electron signals by ~10,000x. Conventional MCP manufacturing is very expensive, and this has limited both the physical size of MCPs (typically ~1” diameter) as well as the range of potential applications for these devices. Using our ALD technology, we have developed a new method for manufacturing MCPs. We begin with porous capillary glass arrays fabricated by our industrial partner, Incom, Inc. The capillary glass has a porous structure nearly identical to that of the AAO we used to

Figure 22: We received an R&D100 Award in 2012 for our invention, “Large-Area Microchannel Plate (MCP)” based upon the technology and equipment developed in this program.

make catalytic membranes, with the exception of larger, micron-scale pores versus the nm-scale pores in AAO. Next, we deposit ALD coatings inside of the capillaries to impart the necessary electrical conductivity and electron-multiplying characteristics to the glass surface. Although the composition of the MCP coatings is different compared to the catalytic membranes, the ALD coating process and equipment are the same for both devices. We have successfully scaled-up our ALD manufacturing process to produce 8x8" MCPs which are the largest in the world, and our MCPs have been incorporated into functioning photodetectors. In addition to being up to 5x less expensive compared to conventional MCP manufacturing, the availability of very large MCPs (8x8") opens the door to new applications including: medical imaging, such as positron emission tomography (PET) scanners with 100x faster scanning; national security, including flat-panel neutron detectors that could be used to screen shipping containers or trucks for nuclear materials; large-area particle detectors essential to advancing large-scale, high energy physics experiments. We received an R&D100 Award in 2012 for our invention, "Large-Area Microchannel Plate (MCP)". This technology has been licensed by Incom, and we are currently engaged in transferring the Argonne MCP technology to Incom.

R&D100 Award in 2013, "Tunable Resistance Coatings"

A severe problem hampering the development of novel ion- and electro-optical devices as well as micro-electromechanical systems (MEMS) for use in science and industry is electrostatic charging. For instance, the digital pattern generator (DPG) is a 3D, multilayered microelectronic device capable of independently controlling one million electron beams. But the DPG suffers severe performance degradation when its insulating surfaces become electrostatically charged under operation. To solve this problem, Argonne developed Nanocomposite Charge Drain Coatings that can be deposited over complex 3D surfaces, such as the DPG chip, to eliminate electrostatic charging. The Argonne coating has a unique composition and nanostructure that provide unrivaled stability over a wide range of operating conditions and under very high electric fields. These coatings are fabricated using atomic layer deposition (ALD), an economical and production-worthy technology, and have enabled the DPG to achieve excellent performance and a long lifespan. This award is based on ALD technology developed under our DOE-ITP project, CPS 17784. In particular, the techniques for tungsten ALD, for blending ALD materials, and for coating complex, non-

Figure 23: We received an R&D100 Award in 2013 for our invention, "Charge Drain Coatings" based upon the technology and equipment developed in this program.

planar substrates such as the high aspect ratio AAO membranes and the porous silica gel powders were instrumental in the success of the charge drain coating invention. Furthermore, we utilized the equipment and facilities established under our DOE-ITP project to develop and produce the nanocomposite charge drain coatings and to perform the scale-up to larger substrate sizes.

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