

# Mesoporous catalytic membranes: Synthetic control of pore size and wall composition

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Atomic layer deposition (ALD) on anodic aluminium oxide (AAO) is shown to be a facile, flexible route to the synthesis of catalytic membranes with precise control of pore wall composition and diameters. The oxidative dehydrogenation of cyclohexane was shown to depend strongly on pore diameter and to be more specific than similarly active alumina powder catalysts.

**KEY WORDS:** AAO; ALD; alumina; anodic aluminium oxide; atomic layer deposition; cyclohexane; membranes; oxidative dehydrogenation.

Micro and mesoporous catalytic materials, predominantly in the form of zeolites, have gained wide acceptance as industrial catalysts for oil refining, petrochemistry, and organic synthesis, particularly for molecules with kinetic diameters below 1 nm. Here we report the first demonstration that ultra-uniform inorganic catalytic membranes, synthesized using a combination of anodic aluminum oxidation (AAO) [1–4] and atomic layer deposition (ALD) (a facile, flexible functionalization route) [5–7], have novel catalytic properties. Atomic level control of both the pore diameter and the pore wall composition along the *entire* pore length offers catalyst environments that include larger pores than conventional mesoporous materials (for efficient in-diffusion of large/elaborate molecular precursors or feedstock molecules, and for out-diffusion of large/elaborate product molecules), tailored channel sizes and wall compositions (including tailored channel surfaces ranging from hydrophobic to hydrophilic in nature), catalyst mobility constraints to hinder agglomeration, and flow control of reagents in and out of the catalyst.

Mesoporous and microporous catalytic material syntheses are often approached in a “one step” process (e.g., Zeolites [8–11]). In this paper, we present an approach based on two steps: production of a stable mesoporous scaffold and then carefully controlled modification of the scaffold, where each step can be optimized independently. A related two step synthesis

method utilizing a wet chemical modification method has been reported [12]. The modification method described here is based on gas phase deposition allowing directed control of the pore wall composition and diameter.

AAO membranes are an appealing scaffold with highly-aligned, parallel pores and narrow pore diameter distributions. Electrochemical conditions can be arranged to produce most probable pore diameters in the range 20–400 nm [1–4, 13, 14] and membrane thicknesses in the range 0.5 to >250  $\mu\text{m}$ . Prior catalytic studies using AAO showed interesting yield enhancements, but were limited to unreleased (pore blocked) films [15–18]. Moreover, as-grown AAO membranes suffer from poorly defined pore wall morphology and composition with significant (5%) amounts of incorporated electrolyte anions [19, 20].

For this work, highly-ordered, 70  $\mu\text{m}$  thick AAO scaffolds produced in oxalic acid [13, 14] are used. A typical plan view Secondary Electron Micrograph (SEM) of a scaffold is displayed in figure 1a. The hexagonal arrangement of pores (dark features) is clearly evident on this length scale; over longer distances the registry is less well defined. ALD was used to precisely control the chemical composition and diameter of the AAO scaffold pores. ALD is a growth technique that uses alternating, saturating reactions between gaseous precursor molecules and a substrate to deposit films in a layer-by-layer fashion [21]. By repeating the binary reaction sequence in an ABAB... fashion, films of micrometer thickness can be deposited with atomic layer

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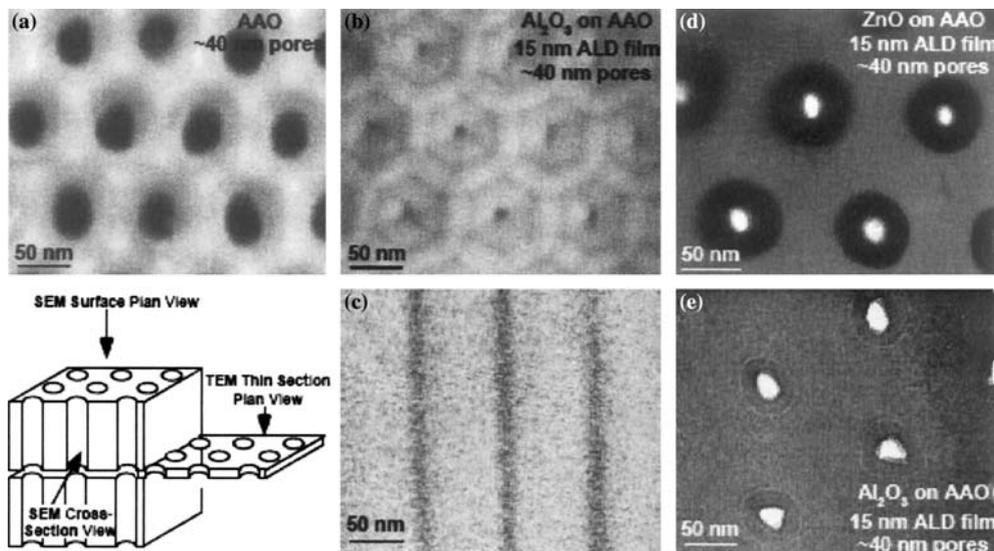


Figure 1. (a) Plan view SEM image of surface of the original 40 nm AAO material. (b) Plan view SEM image of the surface of the 40 nm AAO material coated with 15 nm of alumina. (c) Cross sectional view of 40 nm AAO material coated with 15 nm of alumina taken from the center of the AAO membrane (note that the coating is uniform despite the high aspect ratio). (d) Plan view TEM thin section image taken from the center of a 40 nm AAO membrane coated with 15 nm of ZnO. (e) Plan view TEM thin section image taken from the center of a 40 nm AAO membrane coated with 15 nm of  $\text{Al}_2\text{O}_3$  (note that the ALD coating conformally coats pores with eccentric pore shapes).

precision. Current viscous flow reactor designs, allow this monolayer by monolayer growth to proceed very rapidly, resulting in growth rates as high as  $0.1 \mu\text{m/h}$  [6]. Binary reaction sequences have been developed to deposit a wide variety of materials including oxides, nitrides, sulfides and metals [22]. ALD composite oxides can also be formed by depositing alternating layers (“nanolaminates”) [6] or partial layers of the component oxides at a specific ratio that controls the composition of the composite layer. Because gas transport into mesoporous and microporous materials is diffusion-limited, surfaces at the entrance to the AAO membrane will receive reactant exposures that are  $\sim 10^3$  larger than interior surfaces. Despite this, ALD has a demonstrated ability to coat mesoporous materials [5, 23] including AAO [7]. The key to fabricating uniform nanoporous membranes from AAO templates is the “self-limiting” nature of the ALD binary reaction scheme.

Previously, ALD has been used to coat alumina powder catalysts with vanadate [24–29]. When compared with conventionally impregnated catalysts, the ALD catalysts were more highly dispersed and more easily reduced. Moreover, for propane dehydrogenation reactions, the rate of propene formation by the ALD catalysts was higher than that achieved by conventionally impregnated catalysts [27].

We have synthesized extremely uniform AAO membranes and subsequently applied highly conformal ALD coatings with atomic layer precision using a wide variety of materials ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{V}_2\text{O}_5$ , and Pd) to narrow the pore diameters from 38 to 5 nm. Figure 1b and c demonstrate a membrane with 10 nm pores produced by depositing 15 nm ALD  $\text{Al}_2\text{O}_3$  on an

AAO scaffold with an initial pore diameter of 40 nm. Figure 1c is a cross sectional SEM demonstrating that the pores have been narrowed uniformly throughout their entire pore length. Figure 1d demonstrates that the ALD coating technology can be extended to ZnO. The darkened circles in this Transmission Electron Micrograph (TEM) are the ZnO coating while the AAO pores are the bright central regions. Note that the highly conformal ALD coating exaggerates the ellipticity of pores that are initially non-circular. EDAX images (not shown) reveal that the Zn is uniform throughout the membrane. The TEM in figure 1e shows a region of an ALD  $\text{Al}_2\text{O}_3$  coated AAO membrane having many irregular pores and again illustrates the superb conformality of ALD.

To test the catalytic behavior of these membranes, two ALD coated membranes, with 1 and 15 nm  $\text{Al}_2\text{O}_3$  ALD coating and thus 38 and 10 nm pore diameters, respectively, were tested and compared to both an uncoated AAO membrane and a conventional high surface area  $\gamma$ -alumina powder catalyst ( $180 \text{ m}^2/\text{g}$ ). The membranes had approximately one monolayer of vanadium oxide added as the active species by standard impregnation to a loading of  $12 \mu\text{mol V}^{5+}/\text{m}^2$  of ammonia metavanadate followed by drying at  $150 \text{ }^\circ\text{C}$  for 3 h and calcination at  $500 \text{ }^\circ\text{C}$  for 5 h. The alumina powder was impregnated at 20 wt.%  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  to obtain a comparable conversion efficiency to the membrane catalyst. It should be noted that both the ALD and incipient wetness coatings cover the pore walls and the AAO membrane front and back surfaces. The pore wall to surface area ratio is 111 and 874 for the 10 and 38 nm membranes, respectively.

Table 1  
Conversion and selectivity of  $\gamma$ -alumina and AAO supported  $V_2O_5$  catalysts for the oxidative dehydrogenation of cyclohexane

		$V_2O_5/Al_2O_3/AAO$ (10 nm)	$V_2O_5/Al_2O_3/AAO$ (38 nm)	$V_2O_5/AAO$ (40 nm)	$V_2O_5/\gamma-Al_2O_3$
Conversion (%)	$O_2$	5.1	9.9	3.7	6.6
	$C_6H_{12}$	3.0	4.2	4.0	4.4
Selectivity (%)	$C_6H_{10}$	29.8	8.5	6.9	3.1
	$C_6H_6$	14.5	28.9	19.0	33.3
	CO	13.7	19.1	23.5	20.1
	$CO_2$	41.9	43.5	50.5	43.5

The reaction was carried out in a conventional flow system using a quartz reactor with a feed mixture of He,  $O_2$  and cyclohexane at a ratio of 94.6:3.5:1. Reaction temperatures for these measurements were 450 °C. The carbon balance is within 2%. All AAO membranes have an AAO framework with 40 nm pores through a 70  $\mu$  membrane.  $V_2O_5/Al_2O_3/AAO$  membranes have been coated with 15 and 1 nm thickness of ALD  $Al_2O_3$ . The  $V_2O_5/AAO$  membrane had no ALD coat. All catalysts have  $\sim$ 1 monolayer of vanadium oxide produced using incipient wetness.

The well-studied reaction oxidative dehydrogenation (ODH) of cyclohexane was chosen to test catalytic behavior of our membranes because it can illustrate selectivity. ODH is an important class of catalytic reactions for conversion of short chain alkanes to alkenes exothermically [30]. ODH of cyclohexane can, for instance, produce both cyclohexene and cyclohexadiene (generally produced at low yield) – both useful intermediates for polyadditions. Further oxidation leads to the undesirable products benzene (because cyclohexane is mostly produced by hydrogenation of benzene [31]) and carbon oxides (CO and  $CO_2$ ).

Table 1 compares the selectivity to individual products (molar fraction of converted cyclohexane to that product) for vanadia-coated AAO membranes (with two pore diameters) to more conventional alumina catalysts at similar conversion efficiencies. The vanadia-coated AAO membranes exhibited higher selectivity for the partial oxidation product, cyclohexene, than vanadia supported on  $\gamma$ - $Al_2O_3$  catalysts. The lower selectivity for the conventional catalyst is not a consequence of different conversions since its cyclohexane conversion was lower, and conversion efficiency and selectivity are often inversely correlated. Instead, this may reflect a limiting of secondary oxidation reactions by a contact time of the reagents which is  $10^3$ – $10^4$  times shorter in the membrane channels than in the conventional catalyst bed. Among the membranes, the vanadia-coated AAO supported ALD membranes showed higher selectivity, especially the one with 10 nm channels. This may result from the uniformity of the  $Al_2O_3$  ALD coating. While the conversion percentages for  $O_2$  and  $C_6H_{12}$  are lower for the 10 nm membrane than its larger pore cousins, the conversion per mole vanadate is significantly higher. Since the mean free paths of molecules are 10–40 nm at these conditions, the molecular flux in the larger channels will be a combination of convective and diffusive (Knudsen) flow. The velocity profile of convective flow would be laminar in which the flow in the center is proportionately over-collected when sampling at the exit. Essentially, this portion of the sample bypasses the reactor without contact with the catalyst on the wall.

There is also a significant and repeatable difference in selectivity between 10 nm ALD pores and 38 nm pores. We are currently investigating the cause of this difference, which may result from changes in pore wall electronic structure or from flow dynamics. As one might expect, as the temperature is raised to increase conversion rates the specificity of the membranes decreases. In all cases the membranes outperform conventional supported alumina catalysts.

In summary, ultra-uniform inorganic catalytic membranes have been synthesized using a combination of AAO and gas phase ALD that exhibit a surprising specificity and conversion for ODH of cyclohexane to cyclohexene. These results demonstrate a new approach for tuning the catalytic properties of membranes that allows atomic level control of both pore wall diameter and composition.

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