# Oxidative Dehydrogenation of Propane over Nanostructured Membrane Catalyst

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## Introduction

Oxidative dehydrogenation (ODH) of propane is an attractive route to the production of propylene for petrochemical and energy industries and requires novel selective catalytic materials in order to avoid complete oxidation to CO and $CO_2$. The use of a nanostructured membrane based on anodic aluminum oxide (AAO) can provide a significant advantage to oxidation reactions by reducing the contact time of the desired product with catalysts, thereby minimizing over-oxidation. [1] Furthermore, recent works focused on the development of ODH vanadium based catalysts have shown the importance of the choice of the support metal oxides, such as MgO, $Al_2O_3$, $Nb_2O_5$ or $TiO_2$, on the dispersion and electronic properties of the dispersed vanadium species by influencing the rates and selectivity of the catalytic chemical reactions. [2]

In this paper we describe the characterization and catalytic performances in the reaction of ODH of propane over new nanostructured membrane catalysts composed of vanadium species supported on different metal oxides ($Al_2O_3$, $Nb_2O_5$, $TiO_2$), which have been fabricated using the combination of AAO and atomic layer deposition (ALD). [3] The aim of this study is to determine the role played by the nanostructured materials and the nature of the support oxide on the reactivity of these AAO membrane catalysts in terms of activity and selectivity to propylene**.**

## Materials and Methods

The fabrication of AAO membranes has been developed for growing the alumina nanopores in the center of an aluminum ring by two-step anodizing pure Al foil (0.5 mm, 99.999%, Sigma-Aldrich) in aqueous oxalic acid solution. The nanoporous AAO membranes were coated by ALD using alternating exposures to $Al(CH_3)_3$ (TMA, Aldrich) and $H_2O$. Next, the $TiO_2$ or $Nb_2O_5$ ALD coatings were carried out by using respectively $TiCl_4$/H2O and $Nb(OC_3H_7)_5/H_2O_2$ cycles. Then, one or two monolayers of the catalytic $V_2O_5$ were deposited by using respectively 1 or 2 cycles of $VO(OC_3H_7)_3$ in $H_2O_2$. The quality of the ALD coatings on the AAO membrane has been verified by SEM and the amount of vanadium deposited on the support has been determined by XRF spectroscopy. The characterization of the VOx species supported on various oxides has been investigated by using XRD, IR and UV Raman spectroscopy, XAFS analysis.

ODH of propane was performed at atmospheric pressure in a freestanding AAO (FAAO) quartz flow reactor from 500 to 580°C by employing 10 $mL.min^{-1}$ total flow of reactants in Ar carrier gas ($C_3H_8$: $O_2$ = 1) with gas analysis by on-line gas chromatography. For each experiment, membrane catalyst was deposited on a porous frit between two quartz rings in a quartz tube of 20 mm internal diameter and calcined under 20% $O_2$/Ar at 500°C during 4h.

## Results and Discussion

The resulting membranes obtained with these electrochemical conditions are typically about 70 µm thick with uniform, hexagonal and parallel pores of 40 nm. Layer-by-layer ALD coatings leads to the deposition of the various oxides uniformly along the strength of the nanopores of the membrane and to the control of the vanadium density in the catalytic materials as reported on the Table 1.

Regarding the catalytic properties of the nanostructured vanadium oxides membrane catalyst in the ODH of propane, the reactivity (TOF) is two times greater for $VO_x/TiO_2$/AAO than $VO_x/Al_2O_3$/AAO and $VO_x/Nb_2O_5$/AAO catalysts (Table 1). This trend is attributed to the higher dispersion of the VOx species on the $TiO_2$ from the UV Raman spectra. We also show that the nature of the oxide support has an important effect on the selectivity to propylene which reaches to 82% for $VO_x/Al_2O_3$/AAO catalyst and decreases in the following order: $Al_2O_3$ (82 %) > $Nb_2O_5$ (57 %) > $TiO_2$ (46 %) at 530°C and for a conversion of propane ~ 3%.

**Table 1. Physicochemical and catalytic properties of various nanostructured vanadium-oxides AAO membrane catalysts (reaction conditions: T = 530 °C, conversion of propane ~ 3 %)**

| Catalyst | $V.nm^{-2}$ | TOF $x10^{-3}$ ($molC_3H_6.mol^{-1}V.s^{-1}$) | $\%C_3H_6$ | %CO | $\%CO_2$ |
|---|---|---|---|---|---|
| $VO_x/Al_2O_3$/AAO | 8.5 | 5.5 | 82 | 13 | 5 |
| | 14.5 | 4.4 | 37 | 32 | 30 |
| $VO_x/TiO_2$/AAO | 7.5 | 8.2 | 46 | 30 | 24 |
| $VO_x/Nb_2O_5$/AAO | 10 | 3.9 | 57 | 23 | 20 |

## Significance

This work shows that the combination AAO and ALD is a flexible and efficient approach to the synthesis of ultra-uniform nanostructured catalytic membranes with precise control of pore wall composition and catalyst loading. These new nanocatalysts exhibit high selectivity to propylene. Then AAO platform coupled with ALD coating is ideal for studying the fundamentals of ODH catalysis and these materials may be promising candidates for future industrial applications.

## References

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