Nanostructured Membrane Catalysis in ODH of Cyclohexane

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Introduction

The porous anodized aluminum oxide (AAO) membrane features a highly ordered array of nano-pores. The unique structure of the AAO membrane makes this material a strong candidate for a highly selective catalysis system.[1] When reactants flow through the nano-pores, the limited thickness of the membrane shortens the contact time between reactants and catalyst and reduces undesired over reactions.

The oxidative dehydration (ODH) of alkanes is a promising way to produce alkenes due to its thermodynamically favorable and environmentally friendly nature. However, the major challenge of ODH reactions is over-oxidation to products which are thermodynamically more stable.[2] The membrane system is ideal for studying these reactions because of its excellent selectivity to the initial products.

Materials and Methods

The AAO membranes were prepared by anodic oxidation of aluminum in a 0.3M oxalic acid solution at a potential of 40 V.[3] The anodization was carried out in a masking fixture in which the perimeter of an aluminum disc was effectively separated from the electrolyte so that the AAO membrane was seamlessly mounted on an aluminum ring support. The vanadium oxide catalysts were loaded onto the membranes either by incipient wetness impregnation (WI) or by atomic layer deposition (ALD). Catalytic experiments were carried out in a metal reactor constructed from a standard Swagelok VCR fitting in which the membrane was placed between the sealing glands, and the Al ring was used as the gasket. The ODH of cyclohexane was studied in the temperature range 400 to 500°C at atmospheric pressure. Pure oxygen was used as the oxidant, and the reactant gas has the composition 1% cyclohexane, 2% oxygen, and the balance helium. The reactants and products were analyzed by a GC equipped with a TCD and an FID detector.

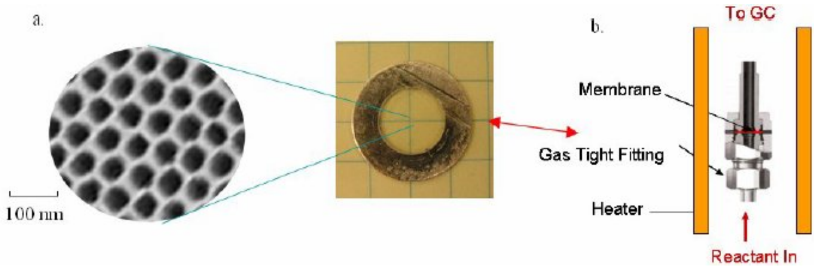


Figure 1. The AAO membrane mounted on the aluminum ring **(a)** and the metal reactor **(b)**

Results and Discussion

When the reactants flow through the nano-pores, the membrane can be regarded as an array of "nano-reactors". A plug flow with dispersion model is applied to analyze their performance. However, it is shown that Knudsen diffusion is the dominant factor influencing the performance of the nano reactor while the contribution from mass flow is limited. A large deviation from plug flow is expected in the nano pores.

As shown in Fig. 2, the vanadium oxides supported on membranes have much better selectivity to partial oxidation products than supported on a powder. Since the reaction of cyclohexene 5 to 10 times faster than for cyclohexane, the membrane system effectively reduces over-oxidation by decreasing the residence time of partial oxidation products in the catalytic layer.

Different forms of vanadium oxide show different activities in ODH of cyclohexane. The isolated form synthesized by ALD has a lower specific activity than the polymeric form. Wet impregnated samples fall between ALD samples, which implies that all forms of vanadium oxides (isolated, polymeric, and V_2O_5 crystal) are present on the surface. Both the conversion/selectivity patterns and the activation energies change remarkably on different metal oxide supports at the same loading of the vanadium demonstrating that the V-O-surface bond also plays an important role in the ODH reaction.

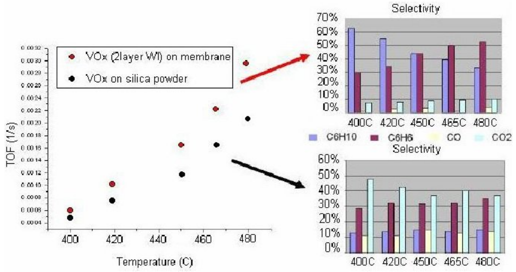
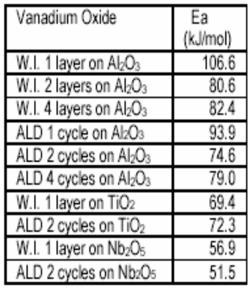


Figure 2. Catalysis of VOx supported on the silica powder V.S. on the membrane



Vanadium Oxide	Ea (kJ/mol)
W.I. 1 layer on Al_2O_3	106.6
W.I. 2 layers on Al_2O_3	80.6
W.I. 4 layers on Al_2O_3	82.4
ALD 1 cycle on Al_2O_3	93.9
ALD 2 cycles on Al_2O_3	74.6
ALD 4 cycles on Al_2O_3	79.0
W.I. 1 layer on TiO_2	69.4
ALD 2 cycles on TiO_2	72.3
W.I. 1 layer on Nb_2O_5	56.9
ALD 2 cycles on Nb_2O_5	51.5

Table 1. Activation Energies

Significance

The exploration of nanostructured membrane catalysts extends the application of nano technology in the traditional heterogeneous catalysis field. The catalytic performance for selective oxidation of cyclohexane contributes to the understanding of hydrocarbon ODH reactions with supported vanadium oxide catalysts.

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References

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