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Development of High Temperature Catalytic Membrane Reactors

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for

High Temperature Catalytic Membrane Reactors

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George Gallaher, Thomas Gerdes, Ruth Gregg, Diane Flowers,
Jeffrey C. S. Wu, Chi-li Lin, and Paul K.T. Liu

Aluminum Company of America
1135 William Pitt Way
Pittsburgh, PA 15238

MASTER

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Executive Summary

Early efforts in 1992 were focused on relocating the membrane reactor system from Alcoa Separation Technology, Inc.'s Warrendale, PA facility to laboratory space at the University of Pittsburgh Applied Research Center (UPARC) in Harmarville, PA following the divestiture of Alcoa Separations to US Filter, Inc. Reconstruction was completed in March, 1992, at which time the reactor was returned to ethylbenzene dehydrogenation service.

Efforts on ethylbenzene dehydrogenation to styrene focused on optimizing hybrid reactor performance relative to packed bed operation. A 5.5% styrene yield improvement was demonstrated for the hybrid (1st stage packed bed, 2nd stage 40Å membrane) reactor compared to a two stage packed bed reactor. Conditions for this study were 600°C, atmospheric feed pressure, a pressure ratio of 0.25, a liquid hourly space velocity of 0.5 hr⁻¹, and a diluent to ethylbenzene molar ratio of 10. These conditions approximate those encountered industrially.

Carbon deposition led to a decline in membrane permeability from approximately 110 m³/m²/hr/atm for the thermally treated membrane to a steady state value of approximately 5 m³/m²/hr/atm under reaction conditions. This permeability value allowed for sufficient H₂ transport across the separating layer without significant bypassing of the reactant ethylbenzene. In post operation characterization, the carbon layer was removed by oxidation. Pore enlargement was observed in the underlying γ -Al₂O₃ layer due to attack from alkali leaching from the commercial catalyst. The carbon deposition appeared to counteract this Al₂O₃ transformation and as a result, the membrane reactor was able to permselectively separate H₂ from the reaction zone resulting in the observed enhanced yield.

In midyear, the reactor system was converted to light alkane dehydrogenation and a study of isobutane dehydrogenation was undertaken. This reaction is of great industrial interest since isobutene is a key intermediate for the production of the octane enhancer methyl tert-butyl ether (MTBE). Demand for MTBE is quickly outstripping isobutene production capacity, providing a significant economic incentive for developing process improvements for this reaction. Additionally, isobutene production involves an energy intensive separation of the reactant alkane from the product olefin. Process improvements should lead to substantial energy savings for this increasingly important commercial reaction.

First efforts on this reaction revealed that stainless steel reactors, which were previously suitable for ethylbenzene dehydrogenation, produce severe coking as a side reaction. Selectivities to coke formation in excess of 60% were observed at reaction temperatures well below those employed commercially. Several inert quartz modules were tried, but proved too fragile and unsuitable due to membrane leakage. An aluminum alloy passivated stainless steel module has recently been obtained and tested. This module improvement has significantly reduced the coking in the reactor under commercial conditions and this problem is now considered resolved.

The kinetics and performance of three commercial catalysts have been evaluated in quartz packed bed reactors. With two Cr/Al₂O₃ catalysts, one from Engelhard and one from United, industrially observed yields and selectivities have been observed in the laboratory. The packed bed kinetic results have been incorporated into an existing membrane reactor model in order to predict attainable isobutene yield improvements in hybrid and single stage membrane reactors. In the hybrid configuration, where the existing packed bed would be followed by a second stage membrane reactor, an 8% isobutene yield improvement is theoretically possible with current 40Å Knudsen membrane technology. H₂ selective membranes have been developed in our laboratory which closely balance the membrane permeation performance to the reaction kinetics. The ultimate isobutene yield improvement for the hybrid concept using these H₂ selective membranes is 26%. However, attainment of this theoretical maximum would require significant enhancement in membrane module packing density. For second generation reactors where existing packed beds are replaced with H₂ membrane reactors, isobutene yield improvements above existing packed bed technology approach 15% for single stage reactors. Enhancements in H₂ permeability and membrane module packing density will be necessary to realize this second generation concept. Nevertheless, the required level of advancement appears possible at this juncture.

Outside interactions in 1992 included presentation of the current styrene reactor results at the 5th Annual North American Membrane Society Meeting in Lexington, KY, and publication of the results reported in 1991 in *Separation Science and Technology*. Discussions were held with two potential industrial endusers and information is currently being exchanged on a nonconfidential basis. Both endusers are interested in participating in the Phase II program. In Phase II, these endusers would perform economic analyses of the potential commercial processes, conduct parallel studies to verify our results, and perform pilot scale testing of the technology. Interaction with the University of Wisconsin primarily involved maintaining a supply of membranes for their work and receiving updates on their efforts to synthesize a permselective Fe₂O₃ membrane on an asymmetric tubular support. No successful membranes were received or tested.

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1.0 Introduction

In 1992, the catalytic membrane reactor system was relocated from Alcoa Separation Technology, Inc.'s Warrendale, PA facility to laboratory space at the University of Pittsburgh Applied Research Center (UPARC) in Harmarville, PA following the divestiture of Alcoa Separations to US Filter, Inc. The system was reconstructed and returned to ethylbenzene dehydrogenation operation in March, 1992.

Efforts on ethylbenzene dehydrogenation to styrene focused on optimizing hybrid reactor performance relative to packed bed operation. Following this, the reactor system was converted to isobutane dehydrogenation. Experimentation on isobutane dehydrogenation focused on design of an inert reactor, evaluation of commercial light alkane dehydrogenation catalysts, and modeling of membrane reactor performance relative to the performance of a packed bed reactor.

This report summarizes the effort in 1992 on the development of ceramic membranes as dehydrogenation reactors. In addition, outside interactions on behalf of this investigation are discussed.

2.0 Ethylbenzene Dehydrogenation

Efforts in 1992 on ethylbenzene dehydrogenation to styrene focused on optimizing the performance of the hybrid reactor (1st stage packed bed, 2nd stage membrane) vs. the two stage packed bed reactor. In addition, characterization of the membrane following ethylbenzene dehydrogenation was performed.

2.1 Reaction Studies

2.1.1 Methodology

The reactor system used in this study is shown schematically in Figure 1. Water and ethylbenzene liquids are fed to vaporizers via variable flow Harvard Apparatus syringe pumps. These pumps can deliver the liquid feed rates of approximately 20 $\mu\text{L}/\text{minute}$ necessary to achieve LHSV's of 0.4 hr^{-1} . The vaporizers are of thermosyphon design. In the lower section, large volumes of vapor are generated. Much of this flow condenses in a cold arm on the side. A large circulating flow of vapor is thus set up. A small portion of this recirculation is drawn through a needle valve on the top of the vaporizer and fed to the system. Ethylbenzene and water vapor are carried to the reactor by flowing N_2 .

The membrane reactor is housed in a seven zone furnace. Three zones heat the preheater section and four zones are localized around the membrane module. The four zones around the module can be independently adjusted to yield an isothermal temperature profile along the membrane reactor. Temperature profiles within $\pm 1^\circ\text{C}$ are routinely achieved. A N_2 purge is provided on the permeate side of the

Figure 1: Schematic of the Ethylbenzene Dehydrogenation Reaction System

membrane module. High temperature pressure transducers are located at the inlet and outlet of the reactor to monitor feed, reject, and permeate pressures.

A bypass is installed around the reactor. During startup, the feed flow is diverted around the reactor so that steam and ethylbenzene vapor flows can stabilize. The reactor is heated to temperature at approximately 10°C/minute in flowing N₂. Once the feed flow and reactor temperature stabilize, the feed is switched into the reactor. This procedure protects the catalyst and membrane from the flow fluctuations that can occur during this transient period.

A detailed schematic of the membrane module is shown in Figure 2. The ceramic membrane is sealed in the stainless steel module via packing glands and graphite ribbon packing. The membrane tube is packed with a commercial, potassium-promoted iron oxide styrene catalyst from United Catalysts. The commercial pellets are crushed and sieved through 14 mesh onto 28 mesh before packing to increase packing density in this benchscale configuration. A four point thermocouple is placed in the catalyst bed to monitor reaction temperatures at the inlet and outlet of the reactor as well as at points 1/3 and 2/3 of the way along the bed. In addition, three single point thermocouples are placed along the shell side of the module to monitor permeate temperatures.

Permeate and reject streams exit the furnace and flow to separate dual FID/TCD gas chromatographs for simultaneous online sampling. The analytical protocol uses a Hayesep D column on the TCD side and a Porapak Q column on the FID side. H₂, N₂, CO, CO₂, CH₄, and water are analyzed on the TCD side. The Hayesep D column gives a particularly nice peak for water with no detectable permanent holdup and little peak tailing. Methane, ethylene, ethane, benzene, toluene, ethylbenzene, and styrene are analyzed on the FID side. The sample is injected at 40°C. This temperature is held for 2 minutes before ramping at 25°C/min to 245°C followed by another hold period. All products elute within 20 minutes. Total turnaround for the analysis is 30 minutes.

The streams exit the GC's and pass through condensers. The condensable fractions are collected and the gas flow rates are measured with bubble meters before venting to a fume hood.

2.1.2 Results and Discussion

The primary reaction results are shown in Figures 3 and 4 and Table 1. Figure 3 compares the styrene yield from the hybrid reactor with that from the two stage packed bed as a function of temperature. Selectivities as a function of temperature are compared in Table 1. The effect of diluent ratio on the performance of the two reactors is

Figure 2 Schematic of the Ceramic Membrane Reactor

**Figure 3: Styrene Yield as a Function of Temperature
Hybrid vs. Packed Bed Reactor**

Table 1 Selectivities Under Ethylbenzene
Dehydrogenation Hydrid vs. Packed Bed Reactor

Temperature (°C)	Styrene		Benzene		Toluene	
	Membrane	Packed Bed	Membrane	Packed Bed	Membrane	Packed Bed
530	0.98	--	0.01	--	0.01	--
535	--	0.98	--	0.01	--	0.01
550	0.96	0.96	0.02	0.02	0.03	0.02
575	0.94	0.95	0.02	0.02	0.04	0.03
600	0.93	0.93	0.02	0.03	0.05	0.04

**Figure 4: Styrene Yield as a Function of Diluent/Ethylbenzene Ratio
Hybrid vs. Packed Bed Reactor**

shown in Figure 4.

The results shown in Figures 3 and 4 represent a condensation of all the data points taken for each reaction run. As noted previously (1), variations in ethylbenzene space velocity and water to ethylbenzene molar ratio occur during a typical run despite the best attempts to keep these parameters constant. In addition, the N_2 used to sweep the ethylbenzene and steam into the reactor provides an additional dilution effect. Styrene yield is expected to vary with both space velocity and total diluent to ethylbenzene ratio.

The results reported in 1991 Topical Report (Gallaher, et al., 1992; Gallaher, et al., 1993) were based on a linear regression of the yield data vs. water to ethylbenzene ratio only. For the results reported here, the raw data has been regressed against two independent variables, ethylbenzene space velocity and total diluent to ethylbenzene ratio. The regression equations were then used to determine values of styrene yield at fixed values of both ethylbenzene space velocity and total diluent to ethylbenzene ratio.

In Figure 3, the results from the regression analysis are reported at an ethylbenzene liquid hourly space velocity (LHSV) of 0.4 hr^{-1} and a total diluent to ethylbenzene ratio of 15. This LHSV is the designed target for the catalyst employed. The designed water to ethylbenzene ratio for this catalyst is approximately 10. The total diluent to ethylbenzene ratio of 15 represents a water to ethylbenzene ratio of 10 plus an addition 5 to 1 dilution of the ethylbenzene by the N_2 sweep gas. For the membrane, a pressure ratio (ie., permeate side pressure divided by tube side pressure) of 0.3 was maintained. As can be seen, styrene yield from the hybrid reactor was 9% greater than that from the packed bed reactor under these conditions.

In Table 1, the selectivity to the primary product styrene and the two major byproducts benzene and toluene are compared as a function of temperature for both reactors. As expected, selectivity to styrene declines as reaction temperature (and therefore total styrene yield) increases. However, the additional 9% styrene yield in the hybrid reactor comes at no loss in styrene selectivity compared to the packed bed reactor.

The effect of total diluent to ethylbenzene ratio is assessed in Figure 4. This was accomplished by varying the N_2 sweep gas flowrate at a constant water to ethylbenzene ratio. For these runs, the reaction temperature was 600°C , the targeted LHSV was 0.5 hr^{-1} , and the pressure ratio employed in the membrane reactor was 0.25. Extrapolation of the results to the target diluent to ethylbenzene molar ratio of the catalyst of 10, shows that the hybrid reactor outperforms the packed bed reactor by 5.5% in styrene yield.

2.2 Membrane Characterization

The critical characteristics that determine the performance of a microporous gas separation membrane are gas permeability through the membrane and the pore size through which the gas permeates. Permeability directly determines the flux through the membrane while pore size determines the transport mechanism. During reaction, only permeability can be monitored on line. The membrane employed in this study was subjected to an extensive post mortem characterization, including permeability, pore size distribution, SEM, and chemical analysis, following reaction.

2.2.1 Methodology

Gas Permeation

In gas permeation, the flux of gas through the membrane layer is measured as a function of total pressure, transmembrane pressure, and stage cut (ie., the fraction of gas fed to the membrane that permeates through it). Permeability results are reported as gas flow per unit transmembrane pressure per unit membrane surface area (ie., $\text{m}^3/\text{hr}/\text{atm}/\text{m}^2$).

To determine permeability, gas feed rates into the membrane are controlled by mass flow controllers. Total pressure, transmembrane pressure and stage cut are controlled by backpressure regulators on the exit permeate and reject lines. Feed, reject and permeate pressures are read by precision pressure transducers, and permeate and reject flowrates are measured by calibrated mass flowmeters.

Pore Size Distribution Analysis

For microporous membranes, pore diameter is one of the most critical factors in determining membrane performance. For the commercially available, asymmetric $40\text{\AA}$ $\gamma\text{-Al}_2\text{O}_3$ membrane however, the separating layer constitutes less than 0.2% by weight of the total sample. As a result, traditional techniques such as nitrogen adsorption or mercury intrusion do not have sufficient resolution to determine the pore size in this small layer.

A flow weighted pore size distribution analyzer has been developed which is capable of characterizing this thin layer. The details of the technique were originally developed from work performed at the Oak Ridge Gaseous Diffusion Plant and described by Fain (Fain, 1989).

The technique is based on the principle of condensation of a vapor in a capillary as described by the Kelvin Equation:

$$\ln(P_0/P) = 2\gamma V / (rRT) \quad (1)$$

where:

- P_0 = vapor pressure of condensable vapor
- P = partial pressure of condensable vapor
- γ = liquid surface tension of condensed vapor
- V = molar volume of condensed vapor
- r = pore radius where vapor is condensed
- R = gas constant
- T = temperature in the pore

A gas mixture which contains a condensable as well as a noncondensable gas is fed into the membrane tube and permeates through the membrane layer. When the partial pressure of the condensable gas is raised so as to satisfy Eqn. (1), vapor will condense in pores of radius r , thereby blocking them and resulting in a dropoff in flow. At a pressure approaching the saturated vapor pressure of the vapor, all pores in the membrane can be blocked and no permeate flow is observed. As the system pressure is stepwise lowered, pores are evacuated starting from the largest radius to the smallest. This change in flow can be monitored relative to partial pressure to give a flow weighted pore size distribution.

A schematic of the pore size distribution analyzer used in this study is shown in Figure 5. A stream of nitrogen or helium is saturated with cyclohexane by sparging through the temperature controlled saturator which is maintained so as to generate a 5% cyclohexane mixture. The membrane housing is immersed in a constant temperature bath and fed with a side stream from this flow. Total membrane pressure is varied by varying the reject flow while transmembrane pressure is maintained at a constant 15 Torr by controlling the permeate flow. Permeate and reject flows are monitored with mass flowmeters. Vacuum is drawn on the system with a vacuum pump. This system is interfaced with a Macintosh II computer for process control, data logging, and real time data analysis. Labview software from National Instruments is used for these purposes.

In a typical experiment, full vacuum is drawn on the membrane to evacuate any condensed impurities while gas flow (either N_2 or He) is initiated to the saturator and allowed to equilibrate. The N_2 /cyclohexane mixture is then introduced into the membrane. The total pressure is raised to a sufficient level to fully condense the cyclohexane in the pores completely blocking permeate flow. The system pressure is then stepwise lowered. When a pressure equivalent to a pore radius as determined by Eqn. 1 is reached, those pores are evacuated and flow is initiated. Permeate flow is monitored for each increment and a distribution of incremental permeate flow versus system pressure results. This data is then analyzed via Eqn. 1

Figure 5: Schematic of the Pore Size Distribution Analyzer

taking into account the thickness of the adsorbed monolayer of cyclohexane on the pore wall. The result is a distribution of permeate flow versus pore radius and a flow weighted average pore radius can be calculated.

The primary advantage of this system is that it allows accurate pore size distribution measurement of the thin separating toplayer of the assymetric membranes. In addition, the distribution is based on incremental flow through the membrane rather than incremental volume desorbed (as in N_2 porosimetry) or incremental volume intruded (as in Hg porosimetry). This incremental flow relates directly to membrane performance in gas separation applications. Also, no assumptions are required regarding porosity or tortuosity. The technique is limited by the constraints of the Kelvin equation. As a result, the lower limit of pore diameter accessible with this technique is approximately 15Å. Below this diameter, surface interactions with the adsorbate become significant, and the assumptions under which the Kelvin equation is derived breakdown. Theoretically, there is no upper limit to the application of the Kelvin equation. However, as noted by Gregg and Sing (Gregg, et al., 1982), the relative pressures for given pore sizes at the upper end of the mesoporous regime are grouped so closely together that experimental error renders the results highly questionable. Therefore, this technique is only used for pore sizes up to approximately 500Å or less.

2.2.2 Results and Discussion

The permeability of the membrane used in this study as a function of time on stream under reaction conditions is shown in Figure 6. Volumetric flowrate is determined in this case from the observed molar permeation rate via the ideal gas law. This simplified estimate does not account for gas separation effects due to the multicomponent nature of the permeate, but is adequate to indicate general membrane performance.

As can be seen in Figure 6, permeation drops dramatically as soon as the membrane is exposed to the reaction mixture. This is due to carbon built up from catalytic coking at the high reaction. This build up also occurs on the catalyst. The catalyst is formulated with K^+ which catalyzes the reaction of coke with the steam added in the reaction feed to prevent catalyst deactivation. From Figure 6, the permeability through the reactor stabilizes at a value of approximately $5 \text{ m}^3/\text{hr}/\text{atm}/\text{m}^2$ throughout the reaction run. This nearly constant permeability represents a dynamic equilibrium between carbon deposition from coking and carbon removal from reaction with steam in the reaction feed. The observed permeability of $5 \text{ m}^3/\text{hr}/\text{atm}/\text{m}^2$ allows for sufficient H_2 transport without large-scale bypassing of ethylbenzene from the reaction zone. The observed yield improvement results from shifting the equilibrium by H_2 removal

Figure 6: Permeability of the Ceramic Membrane under Reaction Conditions

while maintaining the ethylbenzene reactant in the presence of the catalyst. The constant low permeability also suggests that for the conditions and reaction times employed here, the graphite seal used to mount the membrane in the reactor module is stable.

Following reaction, the membrane was removed from the reactor module and remounted in a test module for permeation and pore size distribution analysis. The N₂ and He permeabilities through the spent membrane are given in Table 2. Values of 2.2 m³/hr/atm/m² and 4.7 m³/hr/atm/m² are observed for N₂ and He respectively. The ratio of these permeabilities is an estimation of the separation factor for the this membrane. The observed ratio of 2.14 compares favorably with the ideal ratio of 2.65. For gas transport via Knudsen diffusion, this ideal ratio is equal to the square root of the ratio of molecular weights (ie., $(28/4)^{1/2} = 2.65$). Pore size distribution analysis was attempted but unsuccessful on this membrane due to the low permeability.

The membrane was then treated for 16 hours at 500°C in flowing air to burn off the coke deposited during reaction. After this treatment the membrane was remounted in the test module and its permeability rechecked. N₂ and He permeabilities increased to 21.3 m³/hr/atm/m² and 47.2 m³/hr/atm/m² respectively. Again the ratio of permeabilities of 2.22 compared favorably with the ideal ratio of 2.65. Pore size distribution analysis was successful on the membrane after burnout. The distribution results are shown in Figure 7. A flow weighted average pore radius of 55 Å (pore diameter = 110Å) was observed. This compares to a radius of 20Å (pore diameter = 40Å) for the fresh membrane before exposure to reaction. Additionally, 58% of the flow observed through this membrane during pore size analysis was attributable to pore diameters in excess of 500Å. Obviously significant changes are occurring in the γ -Al₂O₃ during reaction. These changes can be seen in the SEM micrographs in Figure 8.

From the wide view of the membrane surface in Figure 8a, defects in the membrane surface can be seen. From the magnified view of one of these defects in Figure 8b, the underlying 0.2 μ m α -Al₂O₃ structure can be seen. A large portion of this structure is thinly coated but some larger defects are observed. An EDAX pattern of this surface is shown in Figure 9. Peaks attributable to Al and O are expected and observed. However, a peak attributable to K is also observed. The obvious source of this K is leaching from the K⁺-promoted catalyst. Fresh and spent catalyst along with a sample of a fresh membrane and a sample of the membrane from the reactor were analyzed for K content. The results are summarized in Table 3. The fresh catalyst has a K content of 6.0%. This content falls to 4.9% in the spent catalyst. An unexposed membrane contains essentially no K, while the spent membrane has a K content of 0.24%.

Table 2 Permeability of the Spent Ethylbenzene Membrane

Membrane	Permeability (m ³ /m ² /hr/atm)	
	N ₂	He
E 13009 Before Burn Out	2.2	4.7
E 13009 After Burn Out	21.3	47.2

**Figure 7: Pore Size Distribution Analysis
E13009-Spent Styrene Membrane after Burnout**

Figure 8: SEM Micrographs of Spent Styrene Membrane Surface

8b): Magnified View of Membrane Surface

8a): Wide View of Membrane Surface

Figure 9 EDAX Analysis of Spent Styrene Membrane Surface

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Table 3 Alkali Analysis of Catalysts and Membranes

Sample	wt % K
Fresh Catalyst	6.0
Spent Catalyst	4.9
Fresh Membrane	0.00051
E 13009 - Spent Membrane	0.24

Transitional aluminas are known to be readily mineralized by alkali compounds, especially in the presence of water (Wefers, et al., 1987) to form alkali aluminates. This is likely to be the case here with the underlying γ - Al_2O_3 layer where pore enlargement was observed after removal of the dynamic carbon toplayer. Under reaction conditions, this carbon layer appears to be the functional separating membrane. Any defects in the underlying γ - Al_2O_3 are effectively filled with carbon deposits. This hypothesis is supported by the low permeability observed before burnout. After burnout, the permeability increases as these carbon deposits are removed. From pore size distribution analysis of the burnt out membrane, 58% of the flow is through the enlarged pores of the γ - Al_2O_3 layer. The conclusion is that for run times up to several hundred hours as employed here, the membrane reactor is capable of Knudsen separation, and enhanced yields are possible as long as the carbon deposits are maintained. The impact of exposure times up to one year, which will be encountered in industrial operation, remain to be determined in pilot scale operation.

3.0 Isobutane Dehydrogenation

The dehydrogenation of isobutane to isobutene suffers from similar thermodynamic equilibrium constraints as ethylbenzene dehydrogenation to styrene. Hydrogen produced in the main reaction inhibits complete conversion of reactant isobutane to product isobutene. Isobutene is an increasingly important industrial commodity as an intermediate for the production of the octane enhancer methyl tert-butyl ether (MTBE). Demand for MTBE currently outstrips capacity for isobutene production. Dehydrogenation capacity dedicated to isobutene production is currently in the design and construction phase. The demand for MTBE provides a strong economic incentive to pursue enhanced isobutene yields via a ceramic membrane reactor.

The most popular method for the dehydrogenation of light alkanes such as isobutane is the Houdry process (Kearby, 1955; Kearby, 1955; Hornaday, et al., 1961; Craig, et al., 1990). In the Houdry process, multiple packed beds of $\text{Cr}/\text{Al}_2\text{O}_3$ catalyst diluted with inert Al_2O_3 are operated in a cyclical semi-continuous mode. The feed flowrate is fixed at approximately 2 hr^{-1} LHSV. An individual reactor is operated adiabatically in the dehydrogenation mode for 5 to 20 minutes at temperatures from 500°C to 650°C depending on the light alkane being fed. Sub-atmospheric reactor pressures (typically 6 psia) are utilized to enhance olefin yield. During dehydrogenation, coke builds up on and deactivates the catalyst. After the 5 minute to 20 minute run, the reactor is evacuated then the catalyst is regenerated in flowing air. The heat from this exothermic regeneration is stored in the diluent Al_2O_3 providing the endothermic heat of reaction during dehydrogenation. Several packed beds are typically operated in parallel, with one under dehydrogenation while others are being purged and regenerated. In this manner, a continuous product stream is sent for downstream processing.

Industrially, isobutene yield is approximately 50% and selectivity of isobutane to isobutene is approximately 80%. Approximately 2 weight% coke is produced before regeneration. This amount of coke produces sufficient heat during regeneration to operate the next dehydrogenation cycle.

The downstream processing involves separating the product olefin from the unreacted alkane, which is then recycled back to the reactor train feed. The separation of close boiling alkanes and olefins is carried out in large distillation columns and consumes significant amounts of energy. Increased per pass yields would reduce the energy duty for these separations.

3.1 Methodology

The reactor system used for ethylbenzene dehydrogenation was modified in 1992 to accommodate gas phase feeds such as isobutane. A schematic of the modified system is shown in Figure 10. Isobutane, He, H₂, and air flows are controlled by mass flow controllers. As with ethylbenzene dehydrogenation, the reactor is housed in a 7-zone furnace capable of controlling the reactor temperature profile to within $\pm 2^\circ\text{C}$. Feed, reject, and permeate streams are analyzed by on-line gas chromatographs (gc's) equipped with dual thermal conductivity/flame ionization detectors. Hydrocarbons are separated on the FID side with a 14 ft. 0.19% pycric acid column using He as the carrier. He, H₂, CO, CO₂, and air are analyzed on the TCD side using a 10 ft. Haysep D® column with Ar as the carrier. The gc is operated isothermally at 35°C for the total analysis turnaround time of 20 minutes. Feed, reject, and permeate flows are monitored with bubble meters. A vacuum pump is installed on the permeate line. When operated, the vacuum pump allows attainment of membrane pressure ratios down to approximately 0.05.

In a typical run for isobutane dehydrogenation, the catalyst is exposed to pure alkane feed for run times up to 60 minutes at atmospheric pressure and temperatures up to 600°C. The reactor is evacuated with the vacuum pump then purge with He. When no hydrocarbons or H₂ are observed chromatographically, the catalyst is regenerated in flowing air. Regeneration continues until no CO₂ is observed by gc in the reactor effluent. The reactor is again evacuated with the vacuum pump then purged with He. When no air is observed by gc, the catalyst bed is mildly reduced for 15 minutes in flowing H₂. The reduction is followed by another evacuation, then purged with He. When no H₂ is observed, another dehydrogenation can begin. Total cycle time with 60 minutes reaction time on stream is approximately 3 hours.

3.2 Stainless Steel Packed Bed Results

The first study undertaken investigated isobutane dehydrogenation over an industrial 19% Cr/Al₂O₃ catalyst from Engelhard in a stainless steel packed bed. Results are summarized in Figure 11 and Table 4. From Figure 11, isobutane conversion increased steadily as reaction temperature was

Figure 10: Isobutane Dehydrogenation System Schematic

**Figure 11: Isobutane Dehydrogenation over Cr/Al₂O₃
in Stainless Steel Packed Bed**

⊖ Isobutane Conversion

⊞ Isobutene Yield

▲ Coke Yield

Table 4 Selectivities for Isobutane Dehydrogenation
over Cr/Al₂O₃ in a Stainless Steel Packed Bed

Temperature (°C)	Selectivities					
	Isobutene	C ₄	C ₃	C ₂	C ₁	Coke
450	77.5	0	2.5	0	0	19.5
500	77.0	0	4.3	1.0	0	17.3
525	33.0	0	5.3	1.3	0	60.7

increased from 450°C to 525°C. Isobutane yield increased from approximately 12% at 450°C to about 27% at 500°C. However, isobutene yield declined to approximately 16% at 525°C. This decline in isobutane yield was accompanied by an increase coke yield from about 6% at 500°C to nearly 30% at 525°C. Similarly, selectivity to isobutene fell from 77% at 500°C to 33% at 525°C while selectivity to coke increased from 17.3% to 60.7% over the same temperature range. After runs at 525°C, extremely long regeneration times (in excess of 4 hours) were required to eliminate CO₂ from the reactor regeneration effluent. When the module was disassembled, large amounts of rust were observed in the catalyst bed.

The large amount of coke production appeared to be due to catalytic decomposition of product isobutene on the stainless steel walls of the reactor (Satterfield, 1980). The observed rust was due to carburization of the stainless steel from the catalytic coking which was subsequently oxidized during regeneration. Industrial dehydrogenation reactors are lined with refractory brick insulation which circumvents this problem. These results pointed to the need for an inert reactor for further studies.

For packed bed studies, a quartz tube was found to be inert to the coking observed in the stainless steel packed bed. All experimental results reported below were obtained in such a packed bed. Three separate designs were attempted for quartz modules capable of sealing membrane tubes under reaction conditions. Besides the inherent fragility of a quartz module, in each case significant leakage resulting in feed bypassing the membrane element was observed. A passivated stainless steel module has been tested. The stainless steel surface was passivated by high temperature treatment with aluminum powders in a process known as alonizing available from Alon, Inc. in Tarentum, PA. As a result of this treatment, a durable aluminum alloy is formed on the stainless steel surface which is inert to catalytic coking and most corrosion. Alonized tubes are used in many petrochemical catalytic processes as well as in high temperature boilers and in Claus reactors where severe corrosion of ordinary surfaces would be expected. This alonized module permits effective sealing of the membrane elements in a passive yet durable module.

3.3 Packed Bed Catalyst Evaluations

The isobutane dehydrogenation activity of three commercial catalysts was evaluated in a quartz packed bed at 575°C and atmospheric pressure. Isobutane LHSV's were fixed at 2 hr⁻¹. Two commercial Cr/Al₂O₃ formulations, one from United and one from Engelhard, were tested along with a commercial 0.5% Pt/Al₂O₃ catalyst from Engelhard. The Cr/Al₂O₃ catalysts represent typical light alkane dehydrogenation catalysts. The Pt/Al₂O₃ formulation was a first attempt at a noble metal based system. Two new light alkane dehydrogenation processes, the Phillips Star® and the UOP Oleflex® processes, utilize proprietary Pt-based catalysts. High olefin yields along with longer cycle times before regeneration are reported (Meyers, 1986).

Total isobutane conversions at 575°C as a function of time on stream are shown in Figure 12. Isobutene yields are shown in Figure 13 while Figure 14 gives yields of the most significant side reaction, hydrogenolysis to C₃'s (propane + propylene). Observed selectivities to all gas phase products are summarized in Table 5. Total isobutane conversion rose slightly with time on stream for the United Cr/Al₂O₃ from 64.0% after 10 minutes to 65.5% after 30 minutes. For the Engelhard Cr/Al₂O₃, total isobutane conversion fell slightly from 55.0% after 10 minutes to 53.0% after 30 minutes. The total conversion over the Pt/Al₂O₃ was significantly lower than the conversions observed over both Cr/Al₂O₃ catalysts. Isobutene yield over the United Cr/Al₂O₃ fell from 55.0% after 10 minutes to 53.5% after 30 minutes. Isobutene yield was 48.5% over the Engelhard Cr/Al₂O₃ after 10 minutes declining to 46.5% after 30 minutes. Over the Pt/Al₂O₃ isobutene yield was approximately constant at 10% with increasing time on stream. The increased total conversion of isobutane over the United Cr/Al₂O₃ is attributable to an increase in C₃ yield as shown in Figure 14. For the Engelhard Cr/Al₂O₃, C₃ yield was lower than on the United Cr/Al₂O₃, and fell slightly with time on stream. C₃ yield over the Pt/Al₂O₃ fell from 2.6% after 10 minutes to 2.2% after 30 minutes. Isobutene selectivities were highest over the Engelhard Cr/Al₂O₃ at 87.4% and 87.7% after 10 minutes and 30 minutes respectively. Isobutene selectivity over the United Cr/Al₂O₃ was slightly lower at 86.6 % after 10 minutes and 81.7% after 30 minutes. Selectivities to C₃'s were comparable over both Cr/Al₂O₃ catalysts. The United formulation had slightly higher selectivities to the other byproducts (C₄'s, C₂'s, and excess methane) than the Engelhard version. Isobutene selectivities over the Pt/Al₂O₃ catalyst were dramatically lower while byproduct selectivities were all significantly higher than the Cr/Al₂O₃ catalysts. For each catalyst, the material balances were closed to within ±4% (typically ±2%) by the observed gas phase products, suggesting that catalyst coking was well within industrially observed limits.

The packed bed isobutene yields and selectivities over both Cr/Al₂O₃ catalysts compare quite well with the values reported in the literature (Kearby, 1955; Kearby, 1955; Hornaday, et al., 1961; Craig, et al., 1990). Both are good candidates for evaluation in the membrane reactor, especially since both have significant industrial marketshare. The Pt/Al₂O₃ catalyst studied here is a poor candidate for further study. The noble metal catalysts used industrially in the Phillips and UOP processes are probably variations of the platinum-rhenium reforming catalysts used in motor fuel production. The possibility of longer dehydrogenation run times makes noble metal based catalysts worth continued effort. Attempts will be made to secure commercial samples of such catalysts. Failing that, in house preparations will be pursued.

**Figure 12: Isobutane Conversion of Industrial Catalysts
as a Function of Time on Stream**

○ 19% Cr/Alumina-United

□ 19% Cr/Alumina-Engelhard

△ 0.5% Pt/Alumina-Engelhard

**Figure 13: Isobutene Yield of Industrial Catalysts
as a Function of Time on Stream**

○ 19% Cr/Alumina-United

□ 19% Cr/Alumina-Engelhard

▲ 0.5% Pt/Alumina-Engelhard

**Figure 14: C3 Yield of Industrial Catalysts
as a Function of Time on Stream**

○ 19% Cr/Alumina-United

□ 19% Cr/Alumina-Engelhard

△ 0.5% Pt/Alumina-Engelhard

Table 5 Selectivities of Industrial Catalysts for Isobutane
Dehydrogenation as a Function of Time on Stream

Catalyst	Selectivities					
	Time on Stream (min)	Isobutene	C ₄	C ₃	C ₂	C ₁
19% Cr/Al ₂ O ₃ - United	10	86.6	0.8	9.6	1.4	1.5
	30	81.7	1.1	13.0	2.4	1.8
19% Cr/Al ₂ O ₃ - Engelhard	10	87.4	0.7	10.2	0.8	0.8
	30	87.7	0.7	9.9	0.8	0.9
0.5% Pt/Al ₂ O ₃ - Englehard	10	58.7	15.4	15.4	1.7	2.5
	30	65.2	14.3	14.3	1.1	1.3

3.4 Modeling Results

The packed bed kinetic data obtained over the Engelhard Cr/Al₂O₃ were used in a mathematical model (Wu, et al., 1991) to estimate the performance of various membrane reactor configurations. These modeling results are summarized in Tables 6, 7, and 8.

Table 6 compares single stage membrane reactors to a single stage packed bed. The 40Å membrane with a H₂/N₂ separation factor represents a Knudsen separating membrane. The He permeability of 1 m³/m²/hr/atm for this membrane represents a membrane in which permeability has been reduced due to coking or due to perhaps intentional modification to reduce permeability. The H₂ selective membrane with a H₂/N₂ separation factor of 100 and a He permeability of 0.1 m³/m²/hr/atm is typical of the hydrogen selective membranes routinely produced in this laboratory. The hydrogen selective membranes with He permeabilities of 1.0 m³/m²/hr/atm and 5.0 m³/m²/hr/atm are representative of developmental membranes currently being synthesized in this laboratory. For all membranes, the pressure (P_r) was fixed at 0.05 and the stage cut (ie., the molar permeate flow divided by the total molar effluent flow) was allowed to vary.

As seen in Table 6, the single stage, 40Å membrane outperforms the single stage packed bed by 3.4% in isobutene yield. This is due to removal of H₂ from the catalyst reaction zone. Higher yield improvements have been reported in the literature utilizing 40Å Knudsen membranes. However, in those studies, the permeate side of the membrane was purged with an inert stream to enhance the partial pressure driving force for H₂ permeation. This inert also tends to permeate into the reaction zone, and much of the reported yield improvement results from a dilution effect within the catalyst bed rather than from selective H₂ removal. While yield improvement can be attained by dilution of the reacting mixture, downstream processing costs to separate, recover, and recycle this inert stream result in unfavorable economics for this approach. In this study, a true membrane reactor which relies on H₂ removal for yield enhancement is being pursued. For the H₂ selective membrane with a permeability of 0.1 m³/m²/hr/atm, the isobutene yield falls to 51.8% (an improvement of 1.6% vs. the packed bed). Isobutene yield improves to 54.9% for the H₂ selective membrane with a He permeability of 1.0 m³/m²/hr/atm. As the He permeability is increased to 5.0 m³/m²/hr/atm, single stage membrane reactor isobutane yield performance improves by 11.5% compared to the single stage packed bed. For each of the membranes in this modeling study except the H₂ selective membrane with the highest permeability, the increase in isobutene yield is only modest and probably within the experimental error of the existing reaction system. For the 40Å membrane this is due to permeation of the feed isobutane thereby bypassing the catalyst bed. For the two lower permeability H₂ selective membranes, the only modest increase in performance relative to the packed bed is due to insufficient H₂ being permeated from the reaction zone (ie., low stage cut).

Table 6 Modeling Comparison of Single Stage Packed Bed
and Membrane Reactors for Isobutane Yield

Reactor	Ideal H_2/N_2 Separation Factor	He Permeability ($m^3/m^2/hr/atm$)	Pr	Stage Cut	Isobutene Yield (%)
Packed Bed	--	--	--	--	50.2
40Å Membrane	3.74	1.0	0.05	0.518	53.8
H_2 Selective Membrane	100	0.1	0.05	0.024	51.8
		1.0	0.05	0.158	54.9
		5.0	0.05	0.343	61.69

Table 7 Modeling Comparison of Two Stage Packed Bed
and Membrane Reactors for Isobutane Yield

2nd Stage Reactor	Ideal H_2/N_2 Separation Factor	He Permeability ($m^3/m^2/hr/atm$)	Pr	Surface Area Increase Factor	Stage Cut	Isobutene Yield (%)
Packed Bed	--	--	--	--	--	60.4
40Å Membrane	3.74	1.0	0.01	1	0.5	68.4
H ₂ Selective Membrane	100	0.1	0.01	200	0.5	86.0

Table 8 Effect of Increasing Module Surface Area on Isobutane Yield from H₂ Selective Ceramic Membrane Reactors

Reactor	Ideal H ₂ /N ₂ Separation Factor	He Permeability (m ³ /M ² /hr/atm)	Pr	Surface Area Increase Factor	Stage Cut	Isobutene Yield (%)
Packed Bed	--	--	--	1	--	50.2
40Å Membrane	3.74	1.0	0.05	1	0.518	53.8
H ₂ Selective Membrane	100	0.1	0.05	200	0.506	65.9
		1.0	0.05	20	0.496	64.7
		5.0	0.05	4	0.494	64.5

The first generation concept for implementing ceramic membrane reactors industrially is as an add on stage to an existing reactor train. This configuration is attractive for several reasons. First the risk to the end user is minimized since the existing reactor train remains in place. Secondly, utilizing the first stage packed bed to the fullest minimizes reactant bypassing in the commercially available 40Å membrane. Modeling results for this scheme are given in Table 7 where a two stage packed bed is compared to two hybrid reactors. For the first hybrid reactor, the second stage is a 40Å Knudsen membrane reactor. The second hybrid reactor utilizes the currently available H₂ selective membrane. To attain sufficient stage cut in order to optimize isobutane yield, the available membrane surface area must be increased by a factor of 200 for the H₂ selective membrane (see discussion below for variable surface area reactor modules). The single stage packed bed from Table 6 is not fully equilibrated so the addition of a second packed bed increases the isobutene yield from 50.2% to 60.4%. Adding a 40Å Knudsen membrane reactor results in a further 8.0% increase in isobutane yield compared to the two stage packed bed. If the performance of the H₂ selective module could be increased so that a stage cut of 50% is attained (in the case shown by increasing surface area by a factor of 200), an isobutane yield of 86.0% is theoretically possible.

The only way to increase H₂ permeation rate from the reaction zone with membranes of fixed permeability operating at already low pressure ratios is to increase the membrane surface area. The results in Table 8 are for single stage packed bed and membrane reactors. In this study, the available surface area for the H₂ selective membranes is increased until a stage cut which optimizes isobutene yield is obtained. For each H₂ selective membrane, the optimum isobutane yield for a single stage with increased surface area is about 65%. This represents an isobutene yield improvement of approximately 15% over the single stage packed bed. For the membrane with a He permeability of 0.1 m³/m²/hr/atm, a 200 fold increase in surface area is required to attain this optimum yield. As the He permeability increases by an order of magnitude to 1.0 m³/m²/hr/atm, the increased surface area drops by an order of magnitude to a factor of 20 increase. A further increase in He permeability to 5.0 m³/m²/hr/atm results in 4 fold increase in surface area required to attain the optimum isobutene yield.

In Table 9, the sensitivity of this maximum isobutene yield to variable surface area is tested for the H₂ selective membrane with a He permeability of 1.0 m³/m²/hr/atm. From there it can be seen that nearly the same isobutene yield is obtained as surface area is increased from a factor of 12 to a factor of 40. For the single stage membrane reactor concept, these results suggest that both improved membrane permeability and increased membrane surface area (ie., packing density) will be important.

Table 9 Sensitivity of Isobutene Yield to Module Surface Area
for a H₂ Selective Ceramic Membrane Reactor

Surface Area Increase Factor	Stage Cut	Isobutane Yield (%)
12	0.428	64.219
16	0.463	64.559
20	0.496	64.661
24	0.525	64.501
40	0.640	63.429

4.0 Outside Interactions

In 1992, the ethylbenzene dehydrogenation results outline above were presented at the 5th Annual Meeting of the North American Membrane Society in Lexington, KY. In addition, the results outlined in the 1991 Topical Report were published in *Separation Science and Technology* (Gallaher, et al., 1993).

Potential joint development of ceramic membrane reactor technology for several dehydrogenation reactions were discussed with potential endusers including a publicly held chemical producer which is a major polypropylene supplier and a privately held firm with a variety of petrochemical interests including MTBE production. Discussions were held with the Sandia National Laboratory concerning a potentially useful styrene catalyst under development there. This catalyst is of interest to this program since it does not contain alkali promoters in its current formulation. Packed bed styrene performance data was forwarded to the Sandia group along with a sample of the commercial styrene catalyst used in this study.

Interaction with the University of Wisconsin was limited to maintaining their inventory of membrane tubes and discussing some limited results of their attempts to synthesize a 40Å Fe_2O_3 membrane. As of August, 1992, no defect free Fe_2O_3 membranes of any pore size had been synthesized. As a result none were available for testing in our reaction system.

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