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DEHYDROGENATION OF ETHYLBENZENE TO STYRENE USING COMMERCIAL CERAMIC MEMBRANES AS REACTORS

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ABSTRACT

The catalytic dehydrogenation of ethylbenzene to styrene in a membrane reactor was studied at 600° to 640°C. The reactor selected in this study is a commercial alumina membrane tube with 40Å pore diameter packed with granular catalysts. One of the reaction products, hydrogen, was separated through the membrane. Therefore, the catalytic dehydrogenation was enhanced by reducing the hydrogen partial pressure in the reactor. The conversion of ethylbenzene increased ~15% compared to the conversion in the packed-bed reactor. The hydrothermal stability of membrane reactor after reactions was examined by nitrogen permeation test and SEM. It indicated that the pore diameter increased to 60 ~ 90Å and the microstructure of membrane remained intact.

INTRODUCTION

There are numerous (predominantly gas phase) reactions in the chemical and petroleum processes which are thermodynamically limited. Production of styrene from ethylbenzene falls in this category. To overcome the thermodynamic constraint, it is commercially operated at high- temperature and low-pressure conditions. This results in sacrificing the selectivity for styrene with a concommitant increase in reactor size and higher recycle ratios. It has been known in the reaction engineering world that there exists a need for a reactor capable of

in-situ separations. Such reactors can help the thermodynamic equilibrium to shift favorably and a higher conversion ratio can be realized. Catalytic membrane reactors offer a promising solution to overcome the thermodynamic limitation.

The concept of catalytic membrane reactors has been reported in the literature. The enhanced conversion for the dehydrogenation of ethylbenzene to styrene has been demonstrated in a recent study [1] using laboratory developed membranes packed with formed catalysts. This study suggests ~15% improvement in the conversion yield is possible, which could lead to significant energy savings in the catalytic conversion and the product separation. Our focus here is to employ the commercially available ceramic membranes to develop a state-of-the-art reactor containing existing catalysts for the production of styrene from ethylbenzene. By combining the advantages of using the existing ceramic membrane/support with commercial catalysts may play a significant role towards accelerating the commercialization of the catalytic membrane reactor technology.

LITERATURE REVIEW

Styrene Production

Styrene production by dehydrogenation of ethylbenzene is described in the literature [2-6]. The reaction is carried out adiabatically or isothermally at 550° to 650°C, and 1.1 to 2.0 atm. The equilibrium favors styrene production at these conditions. Temperatures above 650°C are avoided because the undesirable by-products (coke, methane, ethylene, benzene, and toluene) are formed in excessive amounts. Large amounts of superheated steam (i.e., ethylbenzene/water = 1/6~1/15) are fed with the ethylbenzene to the reactor. The steam supplies some of the heat for the dehydrogenation reaction, favors the products by diluting the reaction mixture, and oxidizes the coke formed on the catalyst surface. The catalysts in commercial use are all iron oxide, doped with potassium carbonate and several other metals at lower levels.

Catalytic Membrane Reactors

The use of catalytic ceramic membranes has been reviewed in a recent publication [7]. Most of them deal with theoretical calculation or laboratory study with experimental membranes. None of them have employed commercially available membranes to study catalytic reactions with commercial interests. Alumina membranes have been used for dehydrogenation of methanol [8], but the membrane composition showed very little selectivity for desirable products (e.g., formaldehyde). Supplying oxygen from the "back" side of the membrane, however, reduced the extent of coke buildup on the membrane.

Anodic oxide alumina membranes combined with platinum have been used for hydrogenation and dehydrogenation reactions [9], but the anodic oxide membranes have relatively large pores (800 to 2500Å) and are not easy to apply to a support

which is stable at temperatures above 200°C. Alumina-palladium membranes have been used for hydrogen separation [10] in the catalytic membrane reactors, as have porous glass-palladium membranes [11].

A system combining an alumina membrane with regular pelletized dehydrogenation catalysts has recently been described [1, 12-14]. The examples in this patent application were dehydrogenation of propane to propene, dehydrogenation of methylbutenes to isoprene, and dehydrogenation of ethylbenzene to styrene. In each case a pelletized catalyst of the type used for the respective reactions was placed in the membrane system, which was downstream of an ordinary bench-scale dehydrogenation reactor. The membrane reactor is specified as having 0.01 μm average pore size. The total yield of the dehydrogenated organic compound was higher in the system with the catalyst + membrane reactor than it was with an ordinary reactor alone. For the styrene case [1], the yield was 65.2% (94% selectivity for styrene) compared to 50.7% yield with the conventional packed bed catalytic reactor. The feed gas to the membrane reactor was 75 mol% H_2O - 25 mol% styrene and the reaction was carried out at 4 bar and 625°C.

Gas Permeation Mechanisms in Microporous Inorganic Membranes

Gas permeation through microporous inorganic membranes, in general, can be described by one or more of the following four mechanisms: Knudsen diffusion, Poiseuille flow, surface diffusion, and molecular sieving [15]. Molecular sieving requires very small pore size, i.e., <10Å, to achieve gas separations. Although this mechanism is very selective and desirable, the pore size of the existing ceramic membrane is much larger than this range. Molecular sieving, therefore, cannot be achieved with the existing membranes.

As a rule of thumb, Knudsen diffusion dominates when the mean free path is greater than ten times the pore diameter [16]. The mean free path can be estimated according to the equation in literature [17]. Table 1 gives the estimated mean free path values at atmospheric pressure for several gaseous species encountered in the catalytic dehydrogenation of ethylbenzene to styrene. It is evident from Table 1 that the values of mean free path for all species at temperatures in the range of 400° to 650°C are 15-100 times larger compared to the pore diameter of the membrane. Thus, Knudsen diffusion mechanism is expected to prevail under the operating conditions.

TABLE 1. Estimated Mean Free Path Values at Atmospheric Pressure

	Mean Free Path, Å, 1 atm		
	Temperature		
Component	25°C	400°C	650°C
H_2	1018	2595	3727
Ethylbenzene	126	429	666
Styrene	126	430	670
Benzene	170	570	878
N_2	639	1733	2467
He	1442	3695	5305

In this study on styrene production, the reaction is likely to be operated at a low pressure (0-2 atm) and 300 to 600°C. Surface diffusion by hydrogen, styrene, ethylbenzene and other products is believed to be insignificant. Poiseuille flow will be minimal unless membranes with a large pore diameter are employed. Accordingly the separation efficiency could be estimated based on the square root of molecular weight ratio as described in Eq. 1. Since the inverse square root of the hydrogen and ethylbenzene molecular weight ratio is about 7, the existing membranes are anticipated to provide a separation factor of ~7 for the proposed dehydrogenation process.

$$D_k = \frac{2}{3} r \sqrt{\frac{8000\,RT}{\pi M}} \qquad \text{Eq. 1}$$

where
- r: pore radius, m
- R: gas constant, 8.313, Pa-m^3/mole-K
- M: molecular weight, g/mole
- D_k: Knudsen effective diffusivity, m^2/sec

EXPERIMENTAL

Membrane Material

In this study, a transitional alumina membrane tube (frequently referred as γ-alumina) with 40Å pore size, 1/4" ID (Membralox®, Alcoa) was chosen as the primary candidate. To improve hydrothermal stability, the membrane was modified chemically for use in the selected conditions containing concentrated steam at 600°C. Figure 1 shows the schematic of a four-layered membrane/support structure. It consists of three thin membrane layers on a microporous support. The top layer has a pore size of about 40Å, the next adjacent layer has a 0.2μm pore size

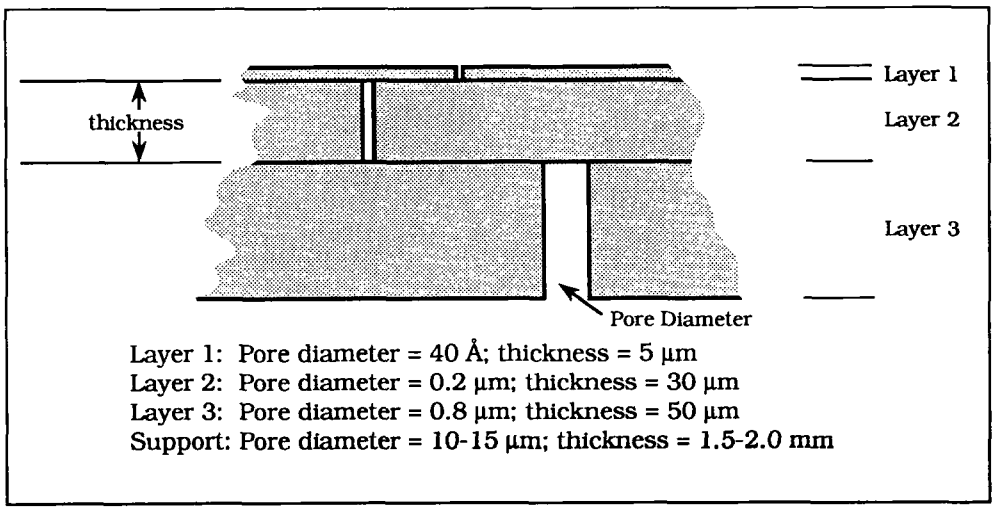

FIGURE 1. Schematic of Multilayer Alumina Membrane Structure

which is supported on approximately 0.8μm pore size layer. This sandwiched structure is supported on a very open porous support with openings of approximately 10-15μm. This asymmetric configuration with an extremely thin top layer and a very porous support provides a superior permeability, which is uniquely suitable for gas separations. The pore volume versus pore diameter distribution data for each layer obtained from mercury porosimetry analysis is shown in Figure 2.

Catalysts Preparation

Instead of using commercial catalysts, granular oxide catalysts were synthesized in the laboratory according to the recipe listed in the literature [18-19]. Alumina-supported iron oxides were prepared by ion-exchanging with an iron precursor solution. Granular activated alumina was placed in a glass column with a porous distributor in the bottom. The ion exchange solution was circulated through the alumina particulate bed with a peristaltic pump. The pH of solution was adjusted in a large beaker which also served as the ion exchange solution reservoir. The pH was controlled at 3.5 by a Cole-Parmer digital Chemcadet® model 5652-00 pH controller which fed acid (HNO_3) and basic (NH_4OH) solutions by actuating metering pumps. The ion exchange solution was iron (III) oxalate. The ion exchange experiment was carried out for 120 minutes. The iron (III) deposition is accompanied by a progressive darkening of the solids color (from white to yellow to red-brown). The ion-exchanged catalysts were calcined at 700° or 800°C. Potassium doped catalyst was prepared by incipient wetness method. 0.646 ml of K_2CO_3 (1.0 M) was used per gram of catalyst. After K_2CO_3 treatment, the catalyst was dried at 250°C. The composition of the developed catalyst is listed in Table 2. The surface area of the ion-exchanged catalysts was found to be only slightly lower than that of alumina calcined under similar conditions.

TABLE 2. Characteristics of Iron Oxide/Alumina Catalyst Particles

Sample	Temperature (°C)	K_2O (wt%)	Fe_2O_3 [(a)] (wt%)	N_2 BET S.A. (m^2/g)	Phase[(b)]
I-1	520	0	0	228.0	γ-alumina
I-Fe_2O_3-1	800	0	2.10	163.7	γ-alumina
I-Fe_2O_3-2	800	4.25	2.03	143.1	γ-alumina
I-Fe_2O_3-3	800	0	3.55	167.7	γ-alumina
I-Fe_2O_3-4	800	5.74	2.87	132.5	γ-alumina

(a) Determined from X-ray fluorescence.
(b) Determined from X-ray diffraction.
I-1: Alumina before ion exchange.
I-Fe_2O_3-1 and I-Fe_2O_3-2: Ion exchanged.
I-Fe_2O_3-3 and I-Fe_2O_3-4: First ion exchanged, calcined at 570°C, then second ion exchanged.

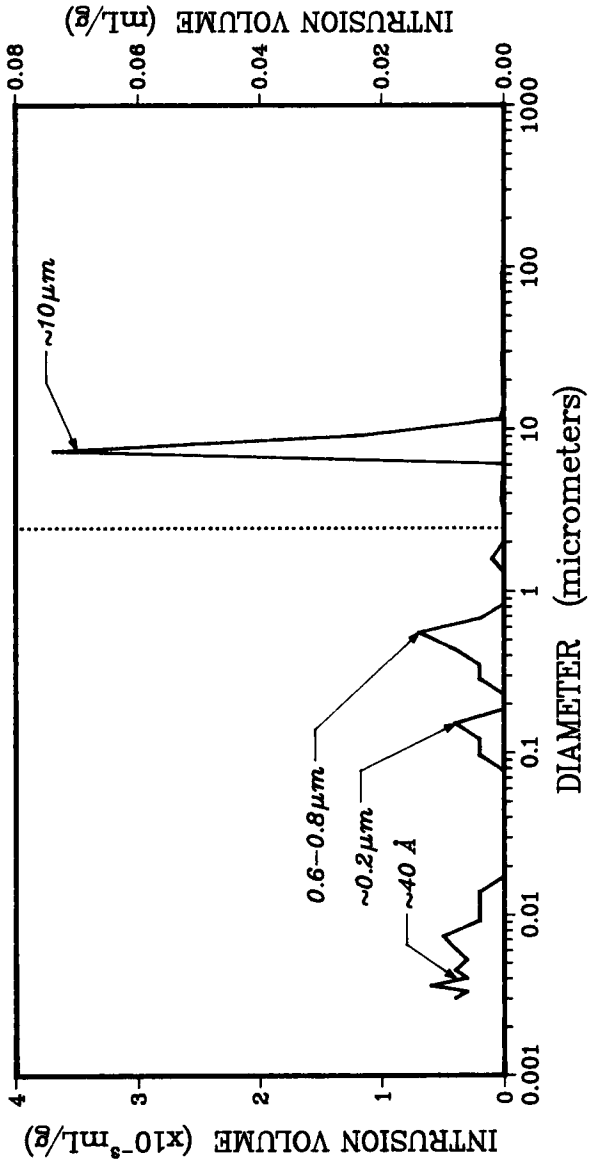

FIGURE 2 Pore Diameter versus Mercury Intrusion Volume

Apparatus

Figure 3 is the schematic of the bench-top catalytic membrane reactor for conversion of ethylbenzene to styrene. Ethylbenzene was generated through a saturator with nitrogen as carrier gas, whose flowrate was regulated by a mass flow controller. The concentration of ethylbenzene was controlled by the saturator temperature. The feed rate of ethylbenzene was measured by a bypass condenser line. An HPLC pump was used to supply water. The N_2, ethylbenzene and water mixture was preheated to the reaction temperature in the first section of an oven before entering the reactor. Feed, reject, and permeate stream pressures were measured by pressure transducers. The reactor pressure can be adjusted by the back pressure regulator. The permeate and reject pressures can be controlled independently by a separate back pressure regulator.

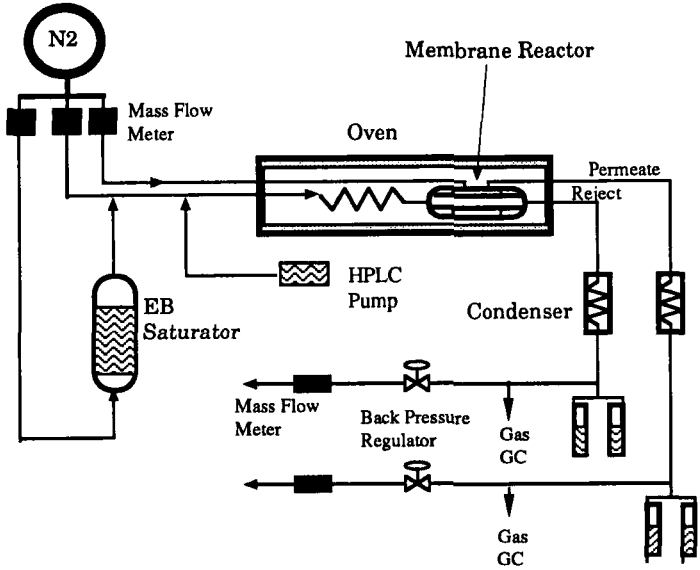

FIGURE 3: Membrane Reactor System

The membrane module assembly is shown in Figure 4. The condensable liquid products from permeate and reject streams were separated from the gaseous products by condensers at 15°C. Liquid-phase product was collected and injected to GC for analysis. Gas-phase product samples were analyzed by an on-line GC, and gas flow rates were measured by a mass flow meter in each stream. Parallel to the membrane module, a stainless tube of equivalent dimensions packed with similar catalysts was used as a control for evaluating the catalyst activity.

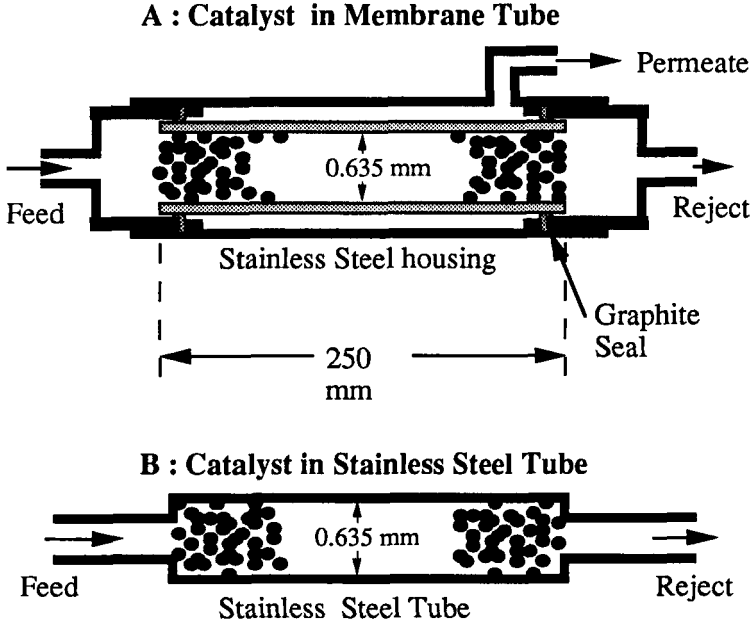

FIGURE 4 : Dehydrogenation Reactor Configurations

Reaction Procedure

Ethylbenzene was vaporized and carried by nitrogen (50 ml/min) in a saturator at 134°C at a rate of ~2.5 ml/min. Water (0.25 to 1.4 ml/min) was added to minimize coking. The water/ethylbenzene molar ratio was lower than the ratio normally used in industrial practice. The reasons were (1) the heat needed for the endothermic reaction was supplied by the oven, not by steam, which is normally used as the heating source in the industrial operation; thus, no excess water was necessary, and (2) this amount of added water was found sufficient to keep coking insignificant after the reaction reached the steady state.

The reaction was studied in the temperature range of 600°-660°C. Approximately 8 grams of catalyst was loaded in a 250 mm long membrane tube or a stainless steel tube of equivalent size. The pressure of the reject stream was kept higher than that of the permeate to minimize back diffusion. The reject pressures were varied from 1.0 to 3.0 psig. The permeate pressures were 0.0 to 1.0 psig. Depending on the experimental conditions (temperature, reject and permeate pressures), the pressure at the inlet of the reactor was varied from 2 to 9 psig. The permeate gas flow rate was adjusted to about 10%-15% of the total gas product. More than 98% of the liquid product was recovered from the reject stream.

Product Analysis

Liquid product was analyzed by Hewlett-Packard chemstation model 5890 Gas Chromatograph equipped with a 6'×1/8" stainless steel column from Supelco (5% SP 1200, 1.75% Bentone 34 on 100/120 supelcoport). 0.2μl of the sample was injected with a syringe. Gas samples were drawn from both reject and permeate side streams. These were injected on-line by a pneumatic valve to Hewlett-Packard 5880 gas chromatograph equipped with twin 10'×1/8" stainless steel columns (100/120, Carbosieve S-II).

RESULTS AND DISCUSSION

The conversion and selectivity referred to in this study are defined as follows:

$$\text{Conversion (\%)} = \frac{\text{moles of total liq. prod. - moles of ethylbenzene in liq. prod.}}{\text{moles of total liq. product}} \qquad \text{Eq. 2}$$

$$\text{Selectivity (\%)} = \frac{\text{moles of styrene in liq. prod.}}{\text{moles of total liq. prod. - moles of ethylbenzene in liq. prod.}} \qquad \text{Eq. 3}$$

Activity of Granular Catalysts

In order to determine the activity of the catalyst, the dehydrogenation reaction was performed by packing catalysts in a non-porous stainless tube. After several reaction runs, coke was found on the surface of the catalyst. Visual observation showed that coking was more serious for the catalyst without potassium than with potassium. Thereafter, potassium doped ion-exchanged catalysts were selected for further study evaluating membrane reactors.

The conversion on the selected granular catalysts ranged from 15% to 18% at 600°C (Figures 5 and 6), which is lower than the literature reported value for the commercial catalyst [22]. At 640°C, the conversion increased to 38%~48%, approaching the equilibrium limit [22]. It is believed that the retention time selected in this study is not sufficient for reaching the equilibrium at a lower temperature, i.e., 600°C. At an elevated temperature, i.e., 640°C, the increase in reaction rate allows the reaction to approach equilibrium with the selected retention time. The selectivity, 85% to 94%, falls in the range reported in the literature [6]. In summary, the activity of the ion-exchanged catalyst doped with potassium appears sufficient for evaluating the membrane reactor conducted in this study.

Activity of Membranes Packed with Granular Catalysts

Alcoa's 40Å membranes were selected for the evaluation of ceramic membrane reactors. Activities of the membranes packed with granular catalysts were compared with those of the stainless steel reactor used as control. Figures 7 and 8 show the conversion of ethylbenzene dehydrogenation at different reaction temperatures. These data indicate that the conversion is enhanced in the membrane reactor. For I-Fe_2O_3-2 catalyst (Figure 7), the conversion increased from 18% to 22% at 600°C and from 38% to 53% at 640°C. For I-Fe_2O_3-4 catalyst with a higher iron-loading (Figure 8), the conversion increased from 15% to 42% at 600°C, and 48% to 65% at 640°C.

The selectivity for styrene is shown in Figures 9 and 10. The catalyst packed in the membrane tube gave a higher selectivity (2%-5% higher) than that observed in the stainless steel tube at 640°C. The use of the membrane-reactor configuration not only enhances the catalytic conversion but also improves the styrene selectivity. This phenomenon is in contrast to the observation with the traditional reactor: selectivity is inversely proportional to conversion. Since hydrogen is selectively removed from styrene through the permselective membrane, the selectivity reduction as a result of approaching equilibrium conversion no longer exists [23]. No selectivity improvement was observed for I-Fe_2O_3-4 at 600°C, which was probably masked by the nearly three-fold increase in conversion (15% to 42%).

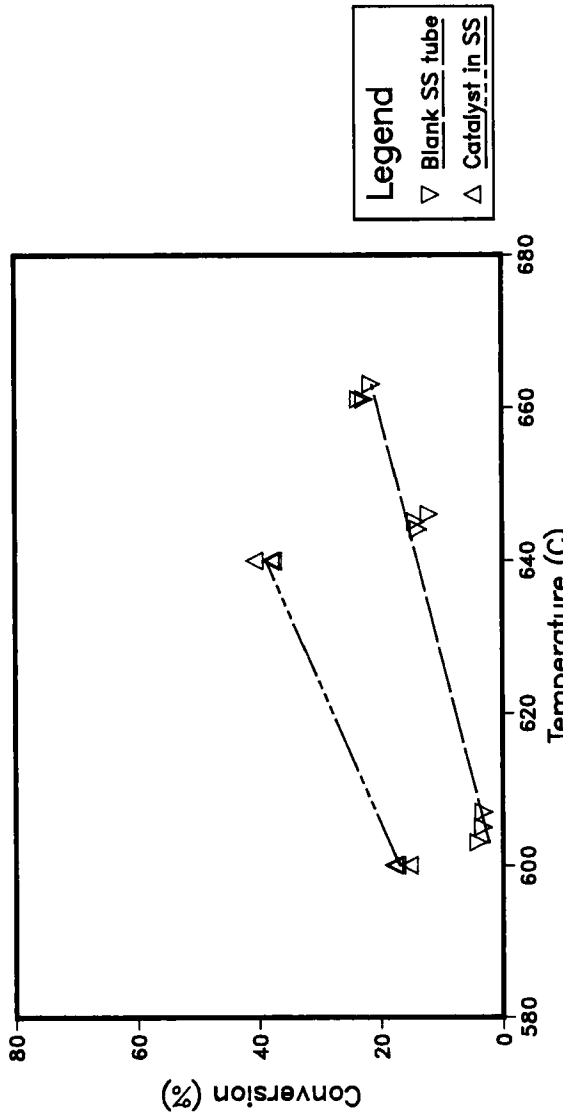

FIGURE 5. Ethylbenzene Dehydrogenation on I-Fe_2O_3-2 Catalysts

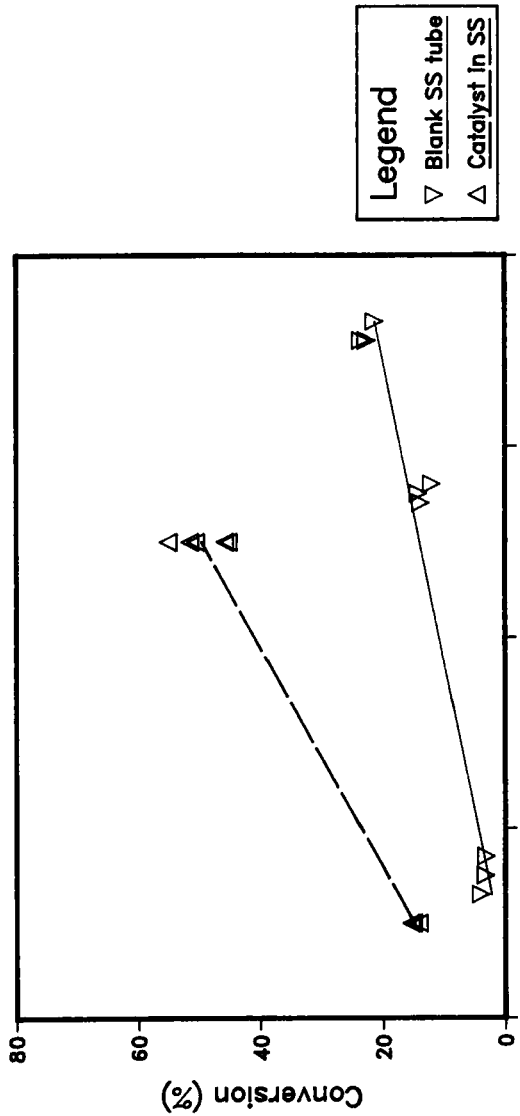

FIGURE 6. Ethylbenzene Dehydrogenation on I-Fe_2O_3-4 Catalysts

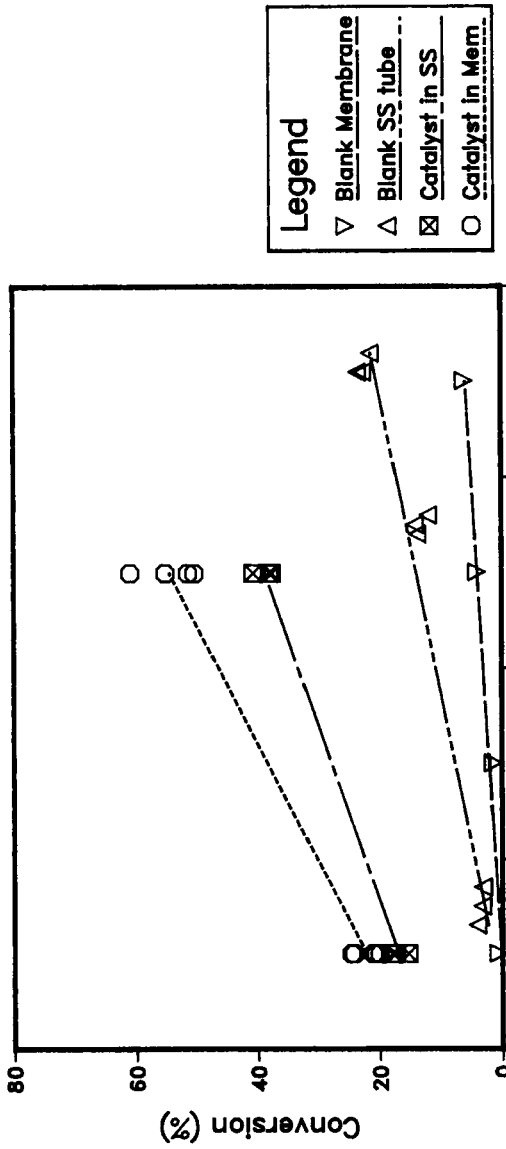

FIGURE 7. Ethylbenzene Dehydrogenation on I-Fe_2O_3-2 Catalysts

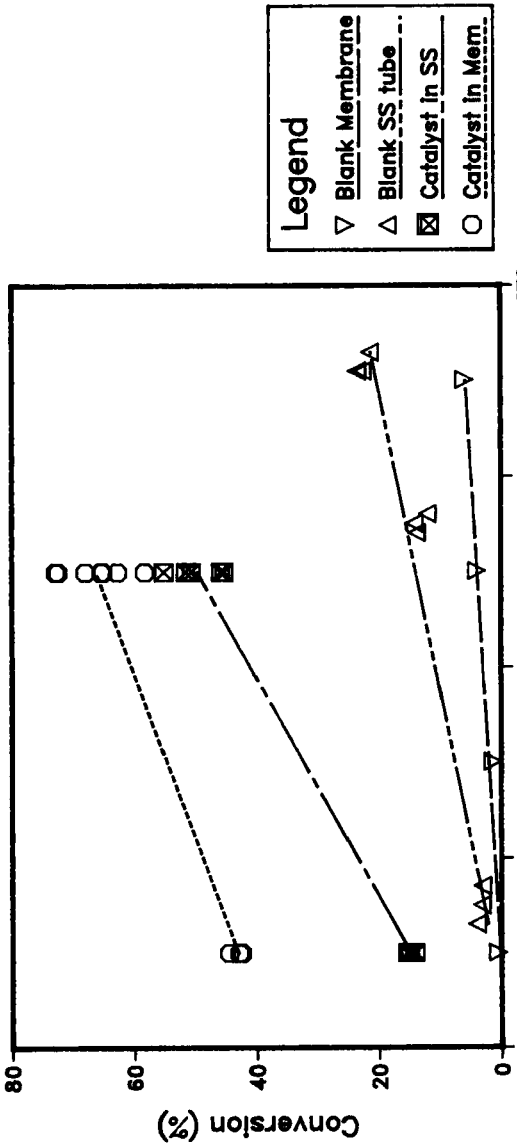

FIGURE 8. Ethylbenzene Dehydrogenation on I-Fe_2O_3-4 Catalysts

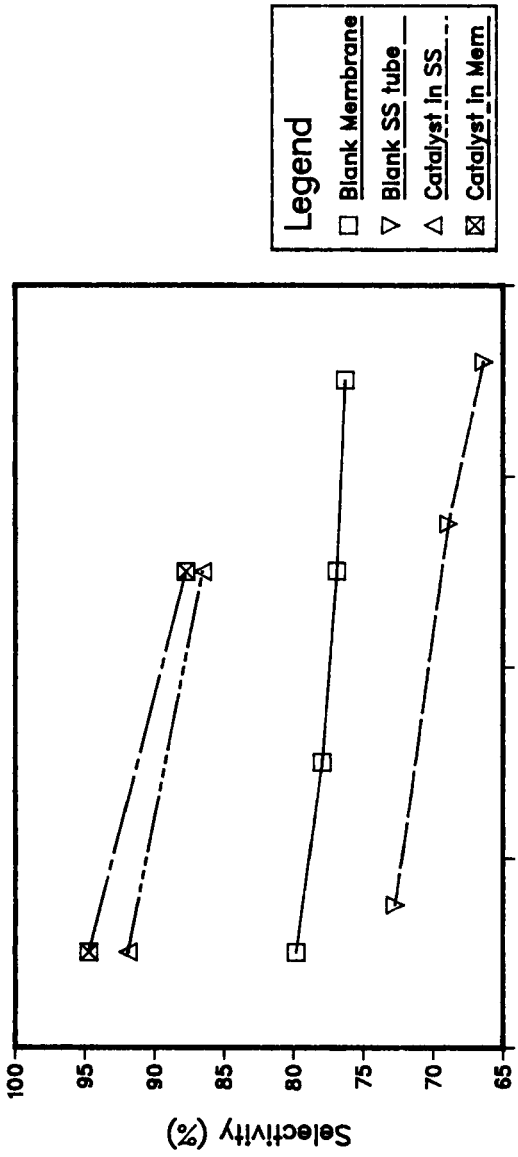

FIGURE 9. Styrene Selectivity of Ethylbenzene Dehydrogenation I-Fe_2O_3-2

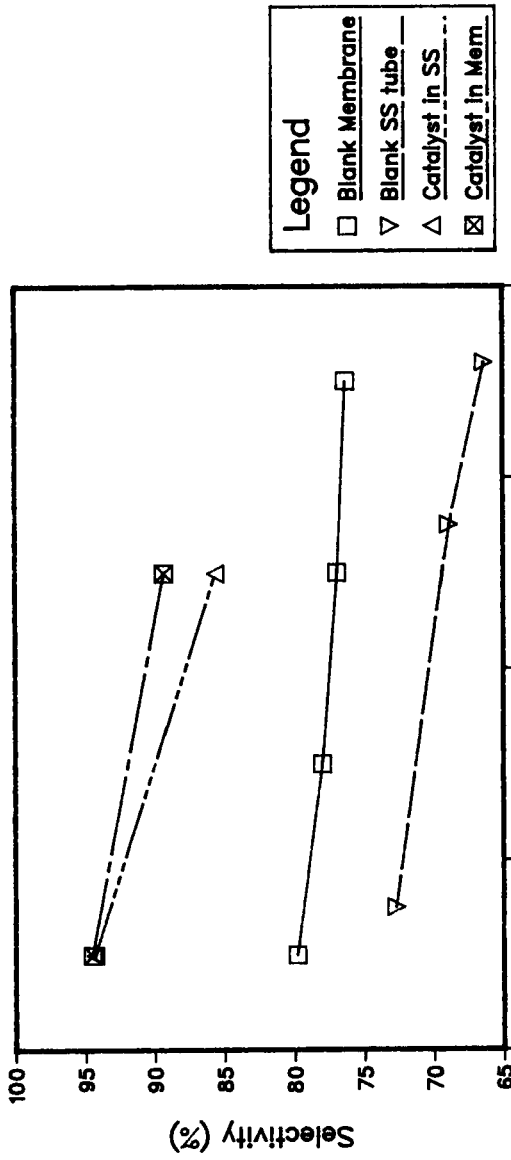

FIGURE 10. Styrene Selectivity of Ethylbenzene Dehydrogenation I-Fe_2O_3-4

The primary liquid by-products were benzene and toluene. The compositions of reject and permeate streams are listed in Table 3. Excluding nitrogen as the inert carrier gas, the major product was hydrogen. It primarily came from ethylbenzene dehydrogenation, and secondarily from water in the de-coking reaction. De-coking reaction also generates CO, CO_2 and methane. Methane may also come from the scission of the ethyl group in ethylbenzene since toluene and benzene were found in the liquid products. Trace amount of C_2 products (ethane, ethylene, and acetylene) was also detected in the gas phase, but not quantitatively measured.

TABLE 3. Product Composition From Ethylbenzene Dehydrogenation in a Membrane Reactor Containing I-Fe_2O_3-2

	@ 600°C		@ 640°C	
	Reject* (mole%)	Permeate* (mole%)	Reject* (mole%)	Permeate* (mole%)
Ethylbenzene	51.0	64.8	28.0	33.5
Styrene	16.7	11.7	21.8	23.2
Toluene	0.7	1.0	1.4	3.2
Benzene	0.7	1.4	0.9	4.8
H_2	23.9	13.7	36.0	24.2
CH_4	1.3	0.9	2.8	3.2
CO	0.3	0.6	0.9	1.3
CO_2	4.6	5.9	8.1	6.5
C_2+	trace	trace	trace	trace
Reject/Permeate molar flow ratio	21.2		9.6	

* composition excluded water and nitrogen.

Material balance was performed for the run with I-Fe_2O_3-2 as catalysts. The result shows that the carbon and hydrogen balances are within ±5% error.

Activity of Ceramic Membranes and Stainless Steel Tubes

The activity of ceramic membrane and stainless steel tubes was examined. The alumina membrane showed a very low activity for ethylbenzene dehydrogenation, (e.g. <5% conversion, Figures 7 and 8). Its contribution to the catalytic activity is negligible. The stainless steel tube, on the other hand, showed some dehydrogenation activity, which increased along with the elevation of temperature. The tube used in this study was made up of 316 stainless steel which contains iron and chromium. The inner surface of the tube was probably coated with a layer of iron and chromium oxides under the reaction conditions which include a high

temperature and a high humidity. Therefore, this oxide layer might contribute to the significant catalytic activity observed in this study. In addition, residue of the catalyst adhered on the tube surface may contribute to the conversion. The styrene selectivity of the empty membrane and stainless steel tube was much lower than that obtained with catalysts (Figures 9 and 10). Since the ceramic membrane contributed insignificant activity, the enhanced conversion observed in our study was in all likelihood attributed to the removal of the reaction product, hydrogen.

Stability of Membrane

To evaluate the stability of the modified membranes at the proposed operating condition for dehydrogenation, fresh and used membranes were examined with Scanning Electron Microscopy (SEM) and gas permeation. Figure 11 shows the nitrogen permeation data of a fresh 40Å membrane and the modified membranes after exposure at the reaction condition. Since the use of steam is essential for the dehydrogenation, the hydrothermal stability was investigated first. After a fresh membrane was exposed to steam, the nitrogen permeation rate increased significantly, i.e., ~42%. The nitrogen permeation rate then increased very little in the next two reaction cycles. The observed permeability increase may be attributed to the pore growth in the presence of steam at the high temperature. The average pore sizes were determined from nitrogen permeability. The estimated pore size of the used membrane is 60Å to 90Å as compared to 40 Å of the fresh one. The pore diameter of 60~90Å is expected to perform gas separations within the Knudsen diffusion regime. SEM micrography of the used and fresh membranes showed no visual change in the layer thickness and the overall structure of the membrane.

CONCLUSION

Enhanced catalytic conversion using commercial ceramic membranes as a reactor has been demonstrated for an industrially important reaction. About 15% conversion increase was achieved over the control (i.e., a fixed-bed reactor) at conditions simulating the existing commercial operation. Significant increase in selectivity has been demonstrated with the catalytic membrane reactor. The commercial ceramic membrane after modification showed good hydrothermal stability under the reaction conditions. More study on the long-term stability of the membrane is underway.

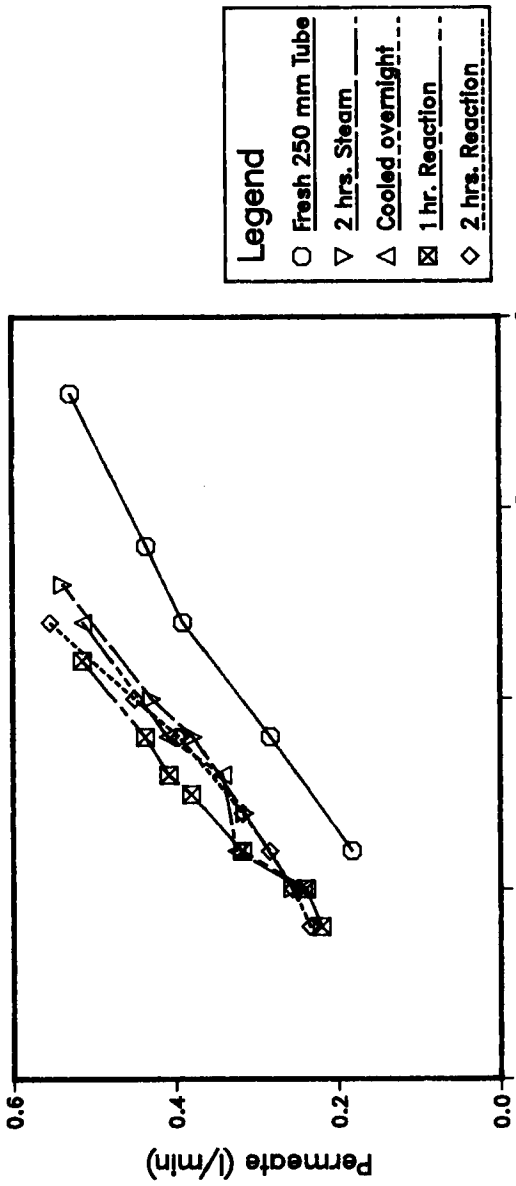

FIGURE 11. N_2 Permeation Through 40Å Membrane at 660°C

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