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TECHNICAL NOTE

Dehydrogenation of Ethylbenzene to Styrene in an Inorganic Membrane Reactor

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ABSTRACT

A new kind of inorganic membrane featuring H_2 permeability of 10^{-6} mol/(m^2·s·Pa) magnitude and H_2/EB selectivity over 75 is applied in a membrane reactor for dehydrogenation of ethylbenzene (EB) to styrene. At a temperature range of 560–600°C, an EB liquid hour space velocity (LHSV) of 0.5–1.0/hour and a water/EB molar ratio of 9.86–16.42, the membrane reactor improves styrene yield to a maximum of 21.5% and a top per-pass stryrene yield of 75%, which is 10% above that obtained in a fixed bed.

Key Words. Inorganic membrane reactor; Dehydrogenation of ethylbenzene; Styrene

INTRODUCTION

The dehydrogenation of ethylbenzene (EB) to produce styrene is a commercial process of high importance, while its product yield is thermodynamically limited by the reverse reaction. To achieve conversions above the theoretical equilibrium, early work tested semipermeable membranes where only hydrogen diffused through a palladium alloy membrane (1). Problems of low permeability and hydrogen embrittlement of palladium restricted this approach. In

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recent years, permselective ceramic membranes, characterized by high permeability but relatively low selectivity, have been the focus of several studies to remove H_2 in situ with a certain separation factor (2). While using permselective membranes, all the species pass through the reactor walls by pore diffusion, thus causing the loss of feed. The experimental results suggested it was possible to raise EB conversion by 15% at most (3) or styrene yield by 4% (4) above the conventional fixed-bed processes, but that is only comparable to the improvement with a semiselective membrane reactor.

The membranes previously employed have been ceramic tubes with narrow pore diameters distributed around 3–4 nm, where the Knudsen diffusion mechanism is expected to prevail (3). Badra (5) concluded from simulation that under the Knudsen diffusion mechanism, the feed losses are too high to obtain a favorable result, so there is the need to modify the pore structure of the ceramic membranes that are normally designed for ultrafiltration purposes.

The focus here is to employ our newly modified ceramic membrane, with separation factors for H_2/EB that are over 10 times the values possible from Knudsen diffusion, to test its enhancement effect in the dehydrogenation of ethylbenzene.

EXPERIMENTAL

Figure 1 is a schematic flow diagram of the reactor system. EB and water are pumped through a coil pipe which is long enough to guarantee the vaporizing and heating of feed to the reaction temperature. A noncatalytic tubular membrane filled with crushed catalyst pellets of 20–40 mesh is sealed on the ends with graphite (Fig. 2), and settled in a constant temperature region of the furnace. Feed passes through the tube side while purge gas (N_2) blows shell-sided cocurrently. Tests were also made to simulate the fixed-bed reaction where a stainless steel tube of the membrane size is installed.

Gas outlets are condensed with cold traps, and the uncondensible vapor is vented after its flow rate is measured with bubble meters. To acquire the overall reaction results in the membrane reactor, the condensed hydrocarbons from either flowing side were mixed before sampling. The samples were composed of styrene, ethylbenzene, toluene, and benzene. They were analyzed with GC to obtain the molar compositions X_i, and

$$C_{EB} = (1 - X_{EB}) \times 100\%; \quad Y_{St} = X_{St} \times 100\%; \qquad (1)$$
$$S = (Y_{St}/C_{EB}) \times 100\%$$

where C_{EB} is the conversion of EB, Y_{St} is the yield of styrene, and S is its selectivity.

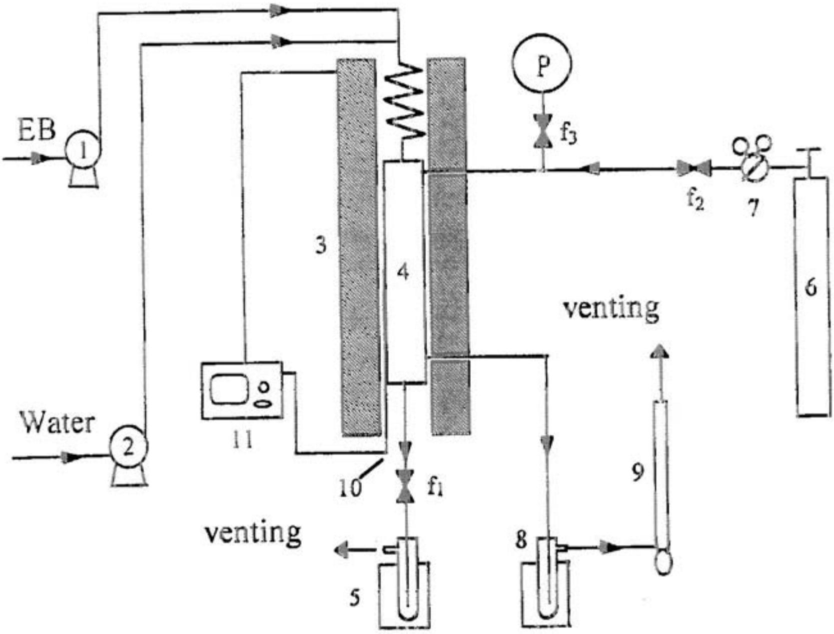

FIG. 1 Schematic flow diagram of the reactor system. (1, 2) Syringe pumps; (3) tubular furnace; (4) reactor; (5, 8) cold traps; (6) N_2 cylinder; (7) pressure controlling valve; (9) bubble meter; (10) thermocouple; (11) temperature controller; f_1–f_3, needle valves.

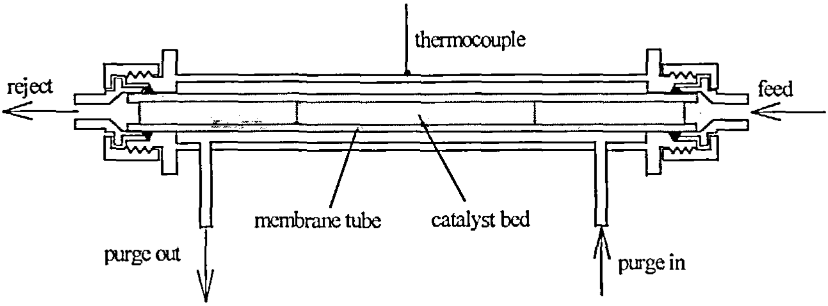

FIG. 2 Schematic diagram of membrane reactor.

RESULTS AND DISCUSSION

The membranes to be used were characterized by gas permeate experiments, where the H_2 permeability (F_H) and the separation factor of H_2/N_2 ($\alpha_{H/N}$) were measured at room temperature. Tubes with an H_2 permeability of 4–8 × 10^{-6} mol/(m^2·s·Pa) and $\alpha_{H/N}$ 2.8–3.5 were chosen.

Preparative tests were conducted at 580°C to determine the flow rate of purge gas, above which the EB conversion approaches a maximum. This value was found to be 2.0 mm/s (ambient conditions) and was therefore adopted for the remaining tests.

The factors considered below are the reaction temperature (*T*), the H_2O/EB molar ratio (*W*), the liquid hour space velocity of EB (*SV*), and the stability of the membrane.

Temperature (*T*)

Experiments carried out at $W = 13.14$ (or volumetric ratio = 2) and $SV = 1.0\ h^{-1}$ are illustrated in Fig. 3. They show the benefit of a membrane reactor (MR) as reflected by the increase of Y_{St} over a fixed bed (FB), reaching a maximum value of 21.5% at 560°C, but the improvement decreases as the

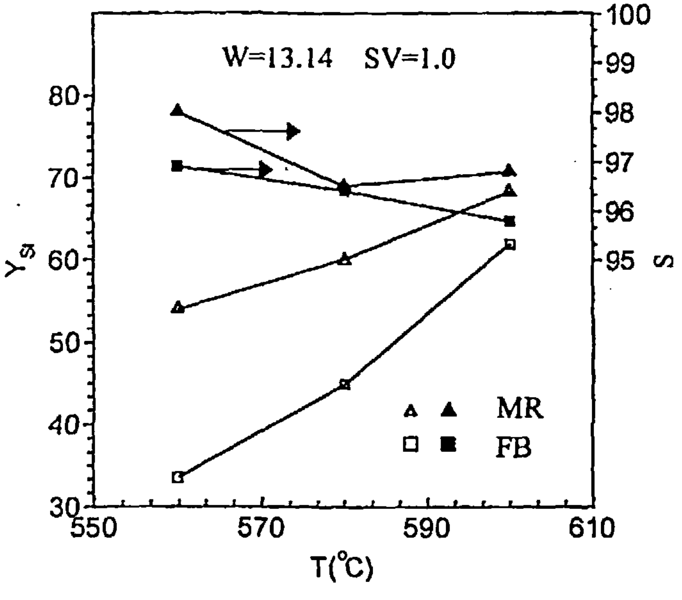

FIG. 3 Reaction results at different temperatures.

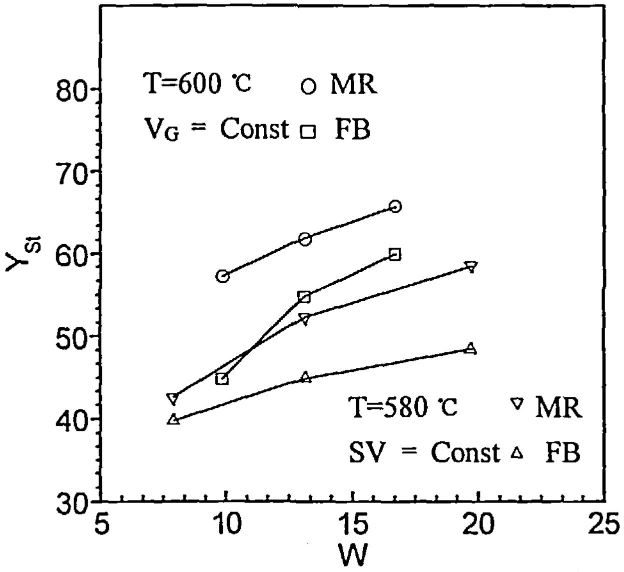

FIG. 4 The effects of *W*.

temperature rises. Also, the selectivities of products are little improved over the fixed bed. Subsequent computer simulation showed that a decrease in the permeability of the membrane, due to enhancement of coking with a rise of temperature, is probably responsible for this trend. Lower temperatures result in low conversion, so they were not tested.

Water Ratio (*W*)

From Fig. 4 we can see that though the value of Y_{St} in both reactors increases with *W*, the slopes of the curves are different. When the velocity of the feed gas mixture (V_G) is constant, the yield of the MR changes slower than that of the FB. When *SV* is constant, the trend is the opposite. By correlation of the experimental results with the model, it is concluded that these trends are due to changes in the permeation of water with *SV* and *W*.

Liquid Hour Space Velocity of EB (*SV*)

Table 1 gives the results at two *SV* values of Catalyst No. 1 and No. 2, purchased from different catalyst manufacturers. The rules are similar: as *SV* decreases, *S* decreases while Y_{St} and ΔY_{St} increase. The per-pass value of Y_{St}

TABLE 1
The Effect of SV for Two Catalysts, No. 1 and No. 2 (T = 600°C, W = 13.14)

Catalyst	No. 1				No. 2			
SV	1.0		0.5		1.0		0.75	
Reactor	MR	FB	MR	FB	MR	FB	MR	FB
C_{EB}	70.5	65.1	83.7	72.6	63.4	56.4	76.9	65.2
S	96.8	95.2	91.2	91.5	97.6	96.9	95.0	95.5
Y_{St}	68.3	62.0	76.4	66.4	61.9	54.6	73.1	62.3
ΔY_{St}	6.3	0	10.0	0	7.3	0	10.8	0

for No. 1 at SV = 0.5 is 76.4%, 10% higher than that in a fixed bed. Tests at lower SV are not listed because they were less profitable.

By comparison, Catalyst No. 1 is more active but has a lower selectivity than Catalyst No. 2. Because the selectivity of No. 2 is higher and hence it cokes less, we used it in tests of membrane stability.

Stability of Membrane

Repetitive reaction tests were performed with the same membrane, so the times the membranes were used before the test differ (Table 2), but the catalyst was renewed before each test. The sampling began when the stable state was attained in each test, normally about 2 hours after the temperature reached 600°C.

TABLE 2
The Stability Test of a Membrane (Catalyst No. 2 at T = 600°C)

SV (h^{-1}):	1.0				0.79		0.82	
W:	13.14				16.5		16.5	
Membrane used time before the test (h):	~20		~35		~25		~40	
Sample at (h)	C_{EB}	Y_{St}	C_{EB}	Y_{St}	C_{EB}	Y_{St}	C_{EB}	Y_{St}
0	62.95	61.0	63.4	61.9	69.3	66.6	69.1	65.2
0.5	64.5	62.0	63.9	59.2	70.8	69.1	70.4	64.3
1.0	62.4	60.8	65.2	62.5	70.7	67.9	69.1	65.8
1.5	62.9	61.2	63.2	60.3	70.2	68.5	69.7	64.8
2.0	66.3	63.8	67.5	63.45	74.35	73.3	70.0	65.45
2.5	63.4	59.9	62.75	60.0	77.0	73.7	72.5	70.1

By comparing the results listed in Table 2, we can see that the repetitiveness of the reaction is good for two different series of conditions ($SV = 1$, $W = 13.14$; $SV = {\sim}0.8$, $W = 16.5$), and the reaction results have little connection with the time the membrane has been used up to 40 hours. It is concluded that the membrane performs with satisfactory stability at 600°C and in a steam atmosphere.

CONCLUSION

The modification of the membrane applied to dehydrogenation of ethylbenzene seems successful. Further work is needed to optimize the value of the two contradictory factors of permeability and permselectivity in preparation of the membrane.

NOTATION

C_{EB}	conversion of EB
F_H	permeability of H_2 [mol/(m^2·s·Pa)]
S	reaction selectivity
SV	liquid hour space velocity of EB (h^{-1})
T	reaction temperature (°C)
V_G	gas velocity of the feed mixture (m/s)
W	molar ratio of H_2O/EB in feed
X_i	molar composition of component i, i = H, EB, St, W, N
Y_{St}	yield of styrene
ΔY_{St}	enhancement of Y_{St} in membrane reactor over that in fixed bed
$\alpha_{H/N}$	membrane permselective factor of nitrogen over hydrogen

Subscripts

H	hydrogen
EB	ethylbenzene
St	styrene
N	nitrogen

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