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Palladium membrane reactor for the dehydrogenation of ethylbenzene to styrene

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Abstract

The Pd membrane was made by the electroless plating of Pd on the oxidized porous stainless steel (PSS) support with a 0.5 μm grade. The dehydrogenation of ethylbenzene to styrene was carried out in both the Pd membrane reactor and fixed-bed reactor at temperatures from 450 to 625°C and 1.2 atm pressure with a steam/ethylbenzene ratio of 6.8. As the result of the removal of hydrogen, the ethylbenzene conversion in the Pd membrane reactor was about 10% higher than that in the fixed-bed reactor for temperatures above 600°C. More importantly, the styrene selectivity in the Pd membrane reactor was ∼15% higher than that in the fixed-bed reactor. © 2001 Published by Elsevier Science B.V.

Keywords: Dehydrogenation; Fixed-bed reactor; Pd membrane reactor; Ethylbenzene

1. Introduction

In a membrane reactor, the chemical conversion and product purification by separation take place in the same device. For reactions limited by thermodynamic equilibrium (e.g., most dehydrogenation reactions), the removal of products by a membrane reactor can improve the conversion beyond the static equilibrium and the reaction may become limited by the kinetics associated with the reaction system and the catalyst.

Palladium membranes have drawn increasing attention in recent years due to their unique property of being only permeable to hydrogen. Palladium and its alloy membranes were prepared on stainless steel supports by the electroless plating technique by Mardilovich et al. [1] and Li et al. [2] and on porous alumina supports by Paglieri et al. [3], on alumina supports by sputtering by McCool et al. [4] and by the metal-organic chemical vapor deposition (MOCVD) by Morooka et al. [5]. The electroless plating technique has the advantages of easy operation and simple equipment.

A number of reactions have been investigated using inorganic membrane reactors [6–8]. A widely studied class of reactions in membrane reactors is the dehydrogenation of hydrocarbons. The instantaneous removal of hydrogen in the reaction zone by permeation through a membrane can, in principle, increase the conversion.

Itoh et al. [9] studied the dehydrogenation of cyclohexane to benzene in a Vycor glass membrane reactor with a mean pore size of 40 Å. The conversion at 200°C and 1 atm pressure was 45% versus the 19% equilibrium value. Champagnie et al. [10] investigated the ethane dehydrogenation in an alumina membrane reactor. The pore size of the top layer of the membrane was 50 Å. The ethane conversion was appreciably higher than the corresponding equilibrium value. For instance, at 640°C, the measured conversion was 25% versus the 15% equilibrium conversion.

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Compared to porous membrane reactors, palladium membrane reactors give considerably higher hydrogen selectivity. The hydrogen produced in the reaction can be more selectively removed from a palladium membrane reactor. Therefore, the increase in conversion in the Pd membrane reactor should, in general, be higher than those in a porous membrane reactor. For example, the conversion in the reaction of cyclohexane to benzene was 99.7% in a Pd–Ag membrane reactor [11]. On the other hand, the conversion of the same reaction in a porous membrane reactor was only 45% [9].

Styrene is one of the most important monomers and extensively used for the manufacturing of plastics and synthetic rubbers. Ninety percent of the world styrene capacity is produced via the catalytic dehydrogenation of ethylbenzene. Wu et al. [12] studied the dehydrogenation of ethylbenzene in an alumina membrane reactor with 40 Å pore size. Their experimental results showed that the conversion of ethylbenzene increased ~15% compared to the conversion in a packed-bed reactor. Becker et al. [13] also investigated the dehydrogenation of ethylbenzene in an alumina membrane reactor. Ten to fifteen percent higher ethylbenzene conversion than the fixed-bed reactor was obtained in the membrane reactor. It should be pointed out, however, porous membrane reactors allow the purge gas to diffuse to the permeate side. The increase in conversion in the porous membrane reactor can, at least, in part be attributed to the dilution effect.

The objective of this study was to investigate the dehydrogenation of ethylbenzene to styrene experimentally in the palladium membrane reactor. The advantages of the palladium membrane reactor over the fixed-bed reactor for the dehydrogenation was explored by performing the reaction in both types of reactors under identical reaction conditions.

2. Experimental

2.1. Palladium membrane preparation

A porous 3161 stainless steel (PSS) tube with an OD of 12.7 mm and a wall thickness of 1.6 mm, purchased from Mott Metallurgical, was used as supports for the preparation of Pd membranes. The grade of these PSS supports was 0.5 μm (95% rejection) with the largest pore diameter of 5 μm and an average pore diameter of 3 μm. The porosity of the PSS support was about 17%. The non-porous stainless steel tubes were welded to both ends of the PSS tube for ease of Pd deposition, gas permeation measurements and reaction studies.

The PSS support was cleaned in an ultrasonic bath with alkaline solution, followed by sequentially rinsing in tap water, deionized water and isopropanol. After drying at 120°C for about 2 h with a heating and cooling rate of about 2°C/min, a metal oxide surface layer was created by oxidizing the cleaned PSS support at 800°C under air atmosphere for 4 h in a furnace with a heating and cooling rate of 3°C/min [14].

The electroless plating was used to deposit the Pd layer on the oxidized PSS support. The electroless plating included primarily the surface activation and plating steps. The surface activation consisted of successive immersions of the PSS support in the acidic $SnCl_2$ (sensitizing) and acidic $PdCl_2$ baths followed by the electroless plating in the plating bath. The detailed procedure for the electroless plating can be found in our previous work [1].

Before carrying out reaction experiments, the palladium membrane was characterized by conducting H_2 and Ar permeation tests. Scanning electron microscopy (SEM, JEOL JSM-840 and AMR 1610) with energy disperse spectrometer (EDS) was used to examine the PSS support and the membrane.

2.2. Experimental setup

Fig. 1 is the schematics of the setup for the dehydrogenation study. A cylindrical ceramic heater was used to provide the heat required for the reaction. The temperature of the heater was controlled by an Omega temperature controller and measured by a thermocouple placed in the middle of the catalyst bed. The pressure was maintained at about 1.2 atm.

Ethylbenzene (Alrdich, 99.8%) and water were fed simultaneously by a syringe pump (equipped with two syringes of different sizes) to the evaporator (~200°C), where ethylbenzene and water were vaporized. The mixture of steam and ethylbenzene was then passed through the preheating and mixing zone

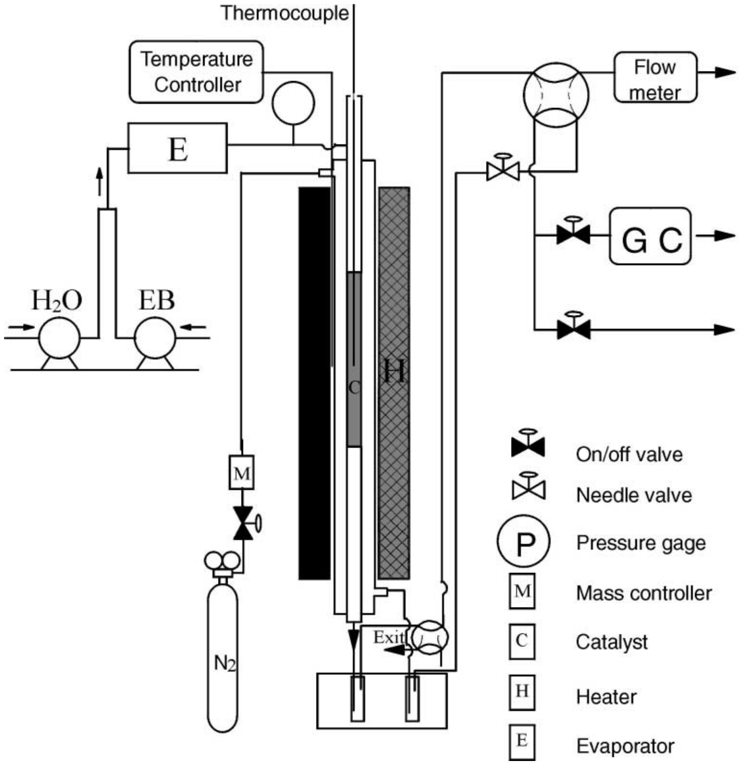

Fig. 1. Schematic diagram of the Pd membrane reactor set-up.

and was heated further to the reaction temperature when the mixture entered the catalyst bed.

The reaction was carried out at temperatures ranging from 450 to 625°C and 1.2 atm pressure with a steam/ethylbenzene ratio of 6.8. The catalyst used in the reaction was iron oxide promoted by potassium oxide supplied by United Catalysts [13]. The size of catalyst particles was 40–60 meshes. 12.1 g catalyst was packed in the tube side while argon was used as the purge gas in the shell side.

The reaction products exited from the tube side at the bottom of the reactor. The liquid products were collected in a tube immersed in an ice bath. The liquid samples were injected by a syringe to the HP 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID) for the composition analysis. Gas-phase products samples were analyzed by a second on-line HP 5890 GC equipped with a thermal conductivity detector (TCD). The major components of the gas-phase products were H_2 with less than about 5% of CO_2, CO, CH_4, and C_2H_4.

3. Results and discussion

The effect of using the Pd membrane reactor on the reaction conversion was studied by carrying out the dehydrogenation of ethylbenzene to styrene in both the Pd membrane and conventional fixed-bed reactors under identical reaction conditions. The parameters used in the study are defined as follows:

$$\text{contact time (h)} = \frac{\text{weight of catalyst in packed bed}}{\text{weight of reactant per hour}} \tag{1}$$

The weight hourly space velocity (WHSV), the reciprocal of contact time, was also used. The ethylbenzene conversion (X), styrene selectivity (S) and yield (Y) are defined as

$$X = \frac{\text{ethylbenzene consumed}}{\text{ethylbenzene}|_{\text{IN}}},$$

$$S = \frac{\text{styrene produced}}{\text{ethylbenzene consumed}}, \qquad Y = X \times S$$

3.1. H_2 and N_2 permeation

A Pd membrane reactor was prepared by the electroless plating of Pd on an oxidized PSS support. The Pd membrane was characterized by the H_2 and N_2 gas permeation prior to loading the catalyst into the reactor for the reaction study. Fig. 2 presents the H_2 permeation flux and the H_2/N_2 selectivity as a function of the difference of the square root of pressure at 600°C. The H_2/N_2 selectivity decreased with the increase of the pressure difference due to the difference in the pressure dependence of the hydrogen and nitrogen fluxes as discussed in detail by Mardilovich et al. [1]. Furthermore, since the hydrogen permeation flux through the palladium bulk was considerably higher than its flux through the grain boundary and possibly some small defects, the Sievert's law was still valid as demonstrated by the excellent fit of the data by the straight line shown in Fig. 2. It is believed that the selectivity of about 350 was sufficiently high for the membrane reactor study. Although no long term stability study was available at the reaction temperature of 600°C, the Pd/oxidized PSS membrane has been shown to be stable for over 6000 h in the temperature range 350–450°C in our recently issued patent [14].

3.2. Effect of the ratio of purge gas to reactant feed

The benefit of the Pd membrane reactor for the dehydrogenation of ethylbenzene was mainly derived from the removal of the H_2 produced during the reaction. At any given temperature, the flow rate of the purge gas in the shell side affected the removal rate of the H_2 from the Pd membrane surface. In order to examine the effect of the ratio of the purge gas to the reactant feed on the conversion, the ratio was changed by varying the purge gas flow rate while keeping the reactant feed constant. The dehydrogenation of ethylbenzene was carried out in the Pd membrane reactor at 600°C with different purge gas flow rates at a constant contact time of 8.3 h. Fig. 3 shows the conversion as a function of the ratio of the purge gas flow rate to the reactant feed at 600°C. The degree of the removal of hydrogen directly reflected the advantages of the Pd membrane reactor. Since the higher the ratio was, the lower the H_2 concentration in the shell side. This not only gave a larger driving force for the H_2 permeation across the Pd membrane but also reduced the mass transfer resistance between the membrane surface and the bulk of the purge gas. Therefore, as observed in Fig. 3, the conversion increased as the ratio was increased. However, for the ratio greater than about 15,

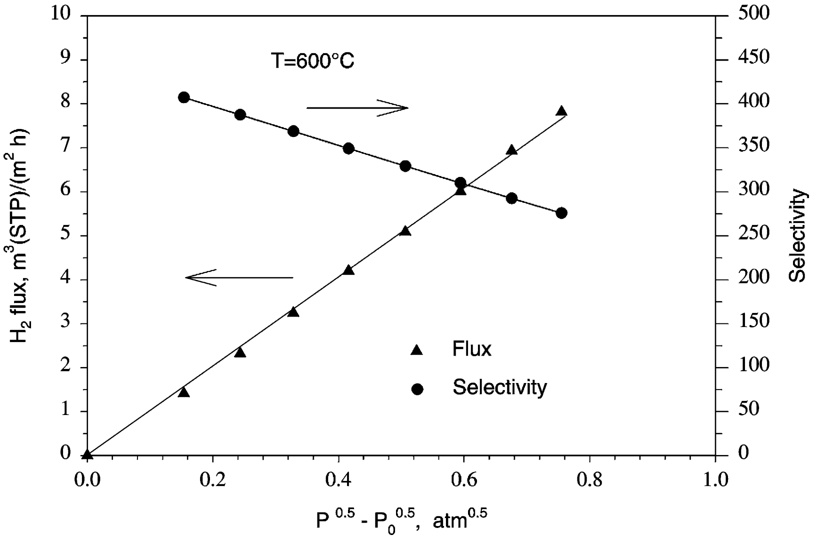

Fig. 2. The H_2 flux and selectivity of H_2/N_2 through the Pd membrane reactor at 600°C.

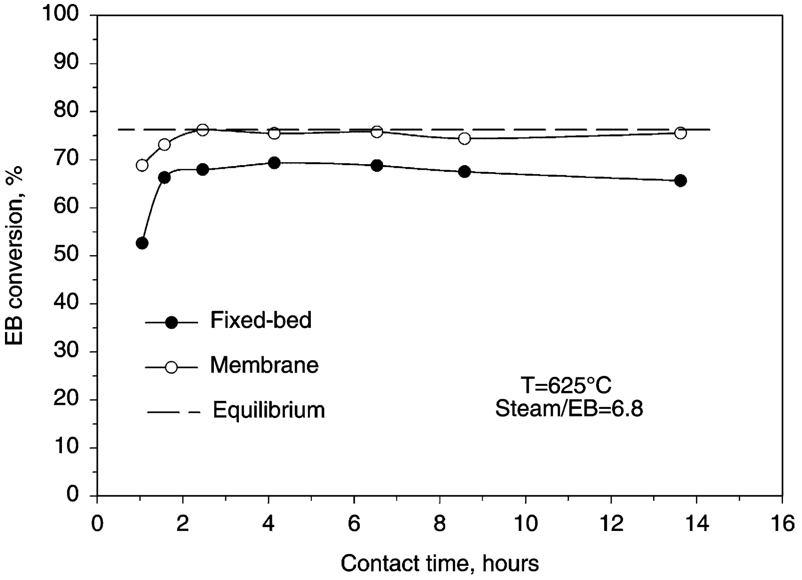

Fig. 3. Ethylbenzene conversion as a function of the ratio of purge gas to reactant feed.

the conversion was almost constant, indicating that the purge flow rate was sufficiently high for the removal of the produced hydrogen from the membrane reactor. Therefore, for all experiments, the ratio of the purge gas to the reactant feed was kept greater than 15.

3.3. Effect of contact time

Prior to the investigation of the effects of the contact time on the conversion, both the external and internal mass transfer resistance effects on the reaction rate were investigated by varying the reactant flow rate and the catalyst particle size, respectively. The conditions for the reaction study reported in this paper were outside both mass transfer controlled regions [15].

The effects of the contact time on the conversion were investigated by performing the dehydrogenation of ethylbenzene (EB) in both the Pd membrane and fixed-bed reactors. Fig. 4 presents the steady-state EB conversion as a function of the contact time at 600°C. For contact times greater than about 3 h, the conversions were essentially constant for both the Pd membrane and fixed-bed reactors.

The rate of the dehydrogenation reaction was described by the following equation [16]:

$$r = k\left(P_{\mathrm{EB}} - \frac{P_{\mathrm{ST}}P_{\mathrm{H_2}}}{K_{\mathrm{p}}}\right)$$

where r and k are the reaction rate and reaction rate constant, respectively, P_{EB}, P_{ST} and $P_{\mathrm{H_2}}$ are the partial pressures of ethylbenzene, styrene and hydrogen, respectively, and K_{p} is the equilibrium constant. The removal of the reaction product hydrogen from the reaction zone in the Pd membrane reactor lowered the hydrogen partial pressure i.e., the value of the second term in the rate expression. The reaction rate was, therefore, increased, resulting in the steady state conversion in the membrane reactor being about 10% higher than the fixed-bed reactor. This shows clearly the advantage of using a membrane reactor to remove the product from the reaction zone. The conversion in the membrane reactor did not, however, exceed the thermodynamic equilibrium. This is due, in part, to the fact that the activity of the catalyst used in the study was not high enough to allow the dehydrogenation reaction to achieve the thermodynamic equilibrium. Furthermore, the thermodynamic equilibrium calculation was based on the single main reaction of the styrene production. The comparison between the calculated ideal equilibrium conversion and the conversion in an actual reactor may not be appropriate due to the possibility of the existence of side reactions. One way to increase the conversion is to utilize a more active catalyst as also suggested by Raich and Foley [17] in their

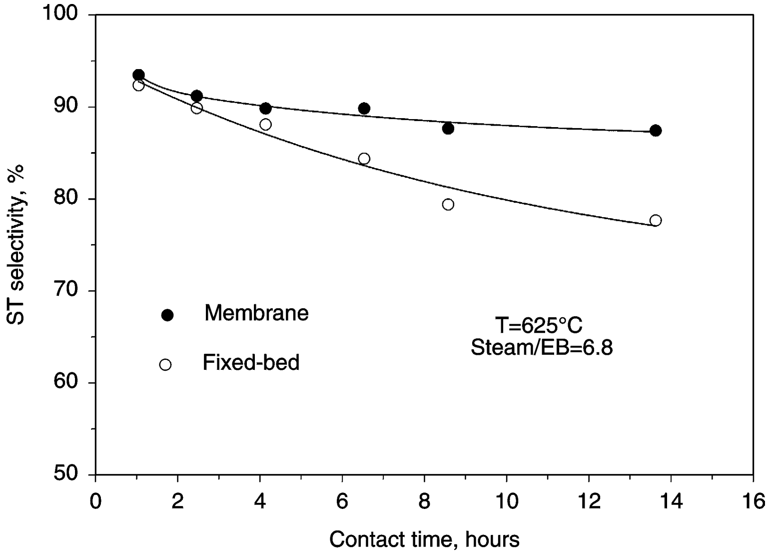

Fig. 4. Ethylbenzene conversion as a function of the contact time at 600°C.

investigation of the dehydrogenation of alkanes in membrane reactors.

A second way to increase the conversion is to use a long contact time to allow the reaction to proceed until the equilibrium was established. In the present study, the contact time was varied by changing the reactant flow rate while keeping the amount of the catalyst constant. Since the amount of the catalyst was kept constant, the superficial velocity of the reactant decreased as the contact time was increased. Therefore, a longer contact time resulted in a lower superficial velocity. For low superficial velocities, the mass transfer resistance between the catalyst surface and the bulk fluid might become a significant portion of the overall rate process. Therefore, further increase of the contact time would not lead to an increase of the conversion in both Pd membrane and fixed-bed reactors due to the possible existence of the external mass transfer resistance. Although the contact time could also be increased by increasing the amount of the packed catalyst while keeping the reactant flow rate constant, the maximum amount of the packed catalyst in the Pd membrane reactor was limited by the reactor volume. Since the reactor volume was already packed with the maximum amount of the catalyst, the contact time could only be increased by decreasing the reactant flow rate. As a result, the external mass transfer resistance between the bulk and the catalyst surface would increase when the reactant flow rate was decreased.

In addition to higher conversion, one of the most important advantages for a membrane reactor is its enhanced selectivity. Fig. 5 gives the selectivity in both Pd membrane and fixed-bed reactors as a function of the contact time at 600°C. Since the removal of the produced H_2 enhanced the desired reaction of styrene production and suppressed the side reaction in which H_2 was the reactant, the selectivity was higher for the membrane reactor than that for the fixed-bed reactor. The difference in the styrene selectivity ranges from a few percent to as high as about 15% in the range of the contact time investigated. The side reactions, which consumed ethylbenzene and was believed to be irreversible, continued to proceed as the contact time was increased. Therefore, the longer the contact time was, the more ethylbenzene was consumed in the side reactions, lowering the styrene selectivity for both Pd membrane and fixed-bed reactors. However, an additional benefit of the hydrogen removal in the Pd membrane reactor was that the styrene selectivity decreased more slowly due to the suppression of the side reaction in which hydrogen was a reactant as discussed above.

Although it is difficult to compare the results obtained here with other studies in the literature due to the different operating conditions and catalysts used,

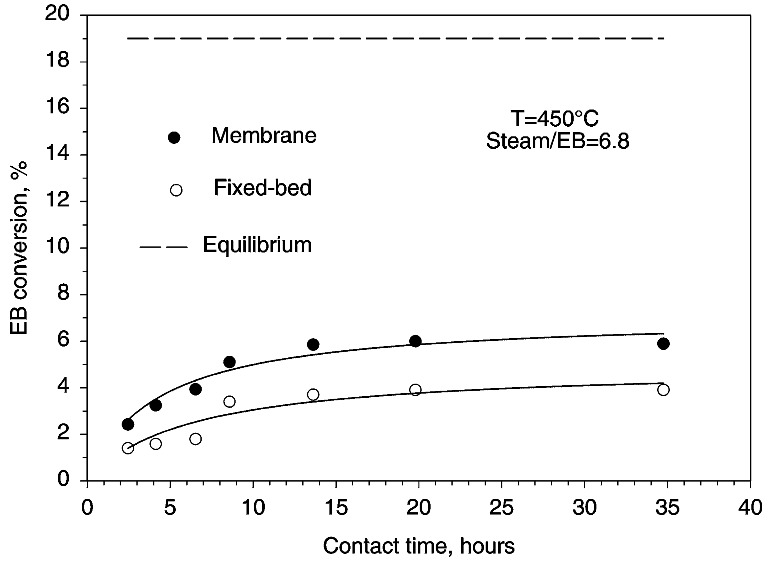

Fig. 5. Styrene selectivity as a function of the contact time at 600°C.

our results are comparable to those reported in the literature. For example, Becker et al. [13] reported an ethylbenzene conversion increase of approximately 15% at ~618°C, while Wu et al. [12] also reported an approximately 15% increase at 600–640°C. Both studies used porous alumina membrane reactor with a 40 Å pore diameter. Our results show a conversion increase of approximately 10% at 600°C. The difference between our results and the two previous studies is likely due to the different membrane reactors and operating conditions used. Furthermore, a porous membrane reactor generally gives a high permeation flux but low selectivity. As a result, the purge gas can easily permeate into the reaction side and the reactants can permeate to the purge gas side. This can cause the dilution in the reactant stream, thereby thermodynamically favoring a volume-increasing reaction.

The benefit of the Pd membrane reactor over a fixed-bed reactor for the dehydrogenation was less pronounced when the reaction rate was low. For instance, since the reaction rate at low temperatures was low, the use of the membrane reactor became less advantageous. Fig. 6 gives the ethylbenzene conversion as a function of the contact time at 450°C in both Pd membrane and fixed-bed reactors. At 450°C, the reaction rate was so low that the conversion was quite small and much less than the equilibrium conversion. Although the conversion for the membrane reactor was still higher than the fixed-bed reactor, the difference between the Pd membrane and fixed-bed reactors was relatively small.

3.4. *Effect of temperature*

The temperature has a strong effect on the reaction rate and the H_2 permeation flux through the Pd membrane. The dehydrogenation was carried out in both Pd membrane and fixed-bed reactors at temperatures ranging from 450 to 625°C with a steam/EB ratio of 6.8. Fig. 7 shows the conversion as a function of temperature with a contact time of 2.4 h. As expected, the conversion increased with increasing temperatures due to the high reaction rate at high temperatures. At the high temperature region (greater than about 550°C), more hydrogen was produced in the reaction and removed from the Pd membrane reactor. Consequently, as the temperature was increased, the conversion difference between Pd membrane and fixed-bed reactors was widened, exhibiting the increased benefits of the Pd membrane reactor. For instance, at 600 and 625°C, the conversions in the Pd membrane reactor were about 10% higher than those in the fixed-bed reactor. Furthermore, the conversions at 600 and 625°C in

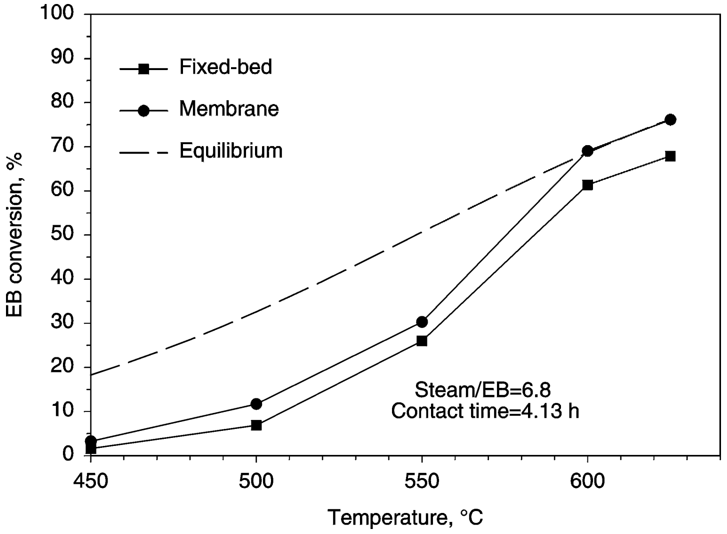

Fig. 6. Ethylbenzene conversion as a function of the contact time at 450°C.

the membrane reactor were close to the calculated equilibrium values. Temperatures greater than 625°C were not attempted since cracking of styrene tended to occur at temperatures above 630°C, leading to sever carbon deposition on the surface of the catalyst.

For the purpose of comparison, the Pd membrane reactor was characterized by the SEM analysis both before and after it was used for the membrane reactor study. Fig. 8 shows the micrograph of the unused Pd membrane, which exhibited the smooth surface of the Pd film. The microstructures of the Pd membrane after being exposed to temperatures from 450 to 625°C for

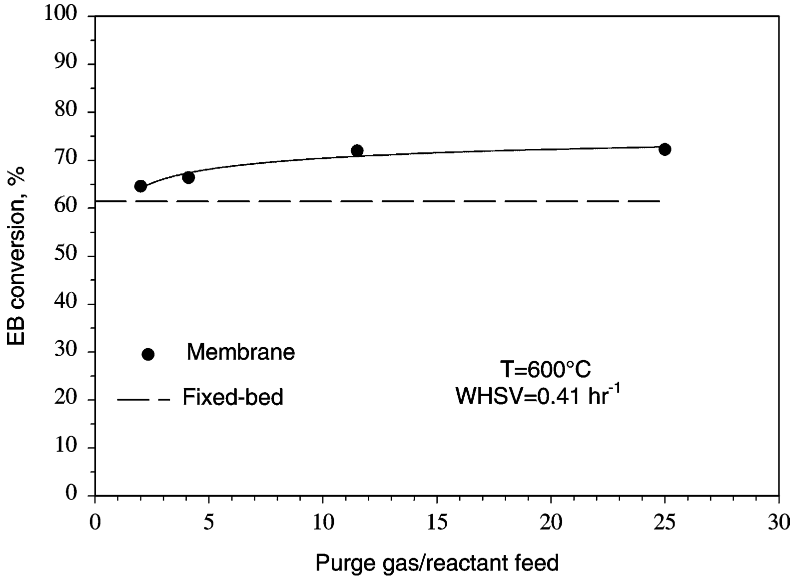

Fig. 7. Ethylbenzene conversion as a function of temperature.

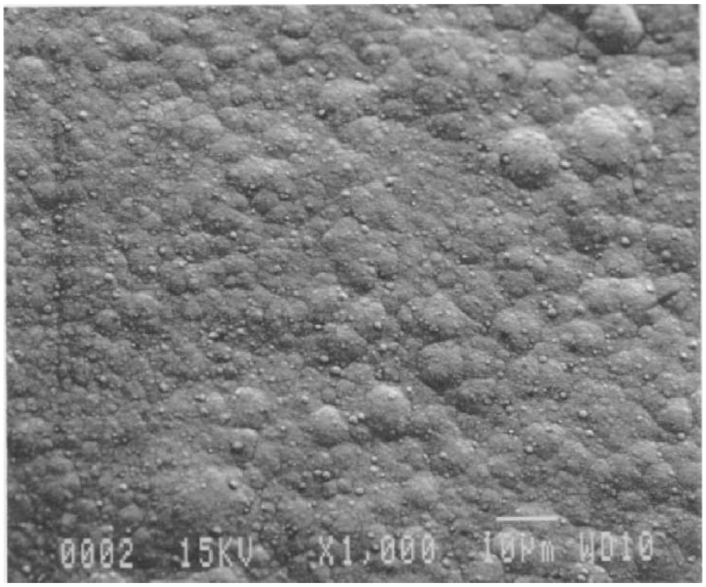

Fig. 8. Surface morphology of the Pd membrane before exposing to the dehydrogenation reaction.

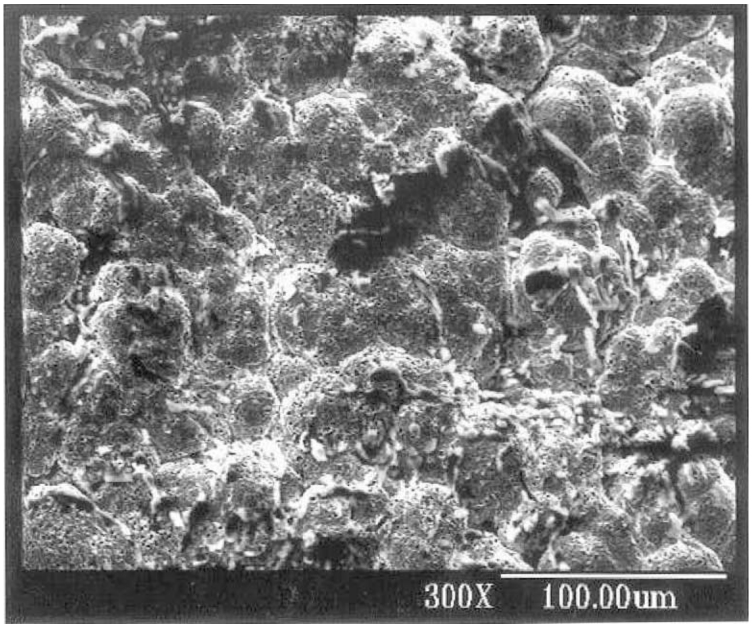

Fig. 9. Surface morphology of the Pd membrane after being exposed to the dyhydrogenation reaction at temperatures up to 625°C.

about 500 h are given in Fig. 9. The carbon deposition and intermetallic diffusion of components in the PSS support to the Pd layer might have contributed to the observed microholes and membrane swelling shown in Fig. 9. After the reaction study was completed, the Ar gas permeation test at 600°C showed an increase in Ar permeance from 0.0067 m^3 (STP)/(m^2 h atm) to 0.21, reducing the H_2/Ar selectivity to about 20. Since the membrane reactor was operated outside the thermal stability region of the present membrane, it was not surprising that the membrane deterioration took place. Since the molecular weights of both ethylbenzene and styrene are much higher than that of argon, the separation factors for H_2/ethylbezene and H_2/styrene would probably still be much higher than that of H_2/Ar, which was sufficiently high enough not to affect the ethylbenzene dehydrogenation reaction. The formation of the microholes in the Pd membranes that were exposed to high temperatures particularly above 550°C was also observed previously [18,19]. Galuszka et al. [18] found filamentous carbon formation on the Pd membrane and membrane swelling leading to its destruction for the methane conversion to syngas between 550 and 600°C. Collins et al. [19] observed the defect formation of the Pd membrane supported on porous α-alumina during the propane dehydrogenation at 525°C. They suggested that the deposited carbon diffused into the Pd films, causing stress and forming holes. Obviously, the degradation of the Pd membranes at high temperatures is a critical issue in its reaction and separation applications and further investigation is needed.

4. Conclusions

The Pd membranes were successfully prepared by the electroless plating of Pd on the oxidized PSS supports with a 0.5 μm grade. The dehydrogenation of ethylbenzene performed in the Pd/oxidized PSS membrane reactor showed that the ethylbenzene conversion was significantly enhanced as a result of the H_2 permeation through the Pd membrane reactor. The benefits of the Pd membrane reactor depended greatly on the degree of the hydrogen removal. The high ratio of purge gas to the reactant feed could increase the removal of hydrogen due to the large driving force for the hydrogen permeation and the reduction of the external mass transfer resistance between the membrane surface and the bulk of the purge gas. However, the ethylbenzene conversion was essentially constant for ratios greater than 15, indicating the ratio was large enough for the removal the produced hydrogen.

At high temperatures, more hydrogen was produced in the reaction and removed from the Pd membrane reactor. As a result, the advantage of the Pd membrane reactor over the fixed-bed reactor became more pronounced at high temperatures. The membrane reactor gave about 10% higher conversion than the fixed-bed reactor at 600°C with a steam/EB ratio of 6.8. More importantly, the membrane reactor gave higher styrene selectivity due to the increased rate of the main styrene production reaction coupled with the suppression of the side reaction.

The development of microholes and membrane swelling were observed by SEM after the membrane was used for the reaction study between 450 and 625°C for about 500 h. The deterioration of the membrane might be caused by the carbon deposition and intermetallic diffusion.

Acknowledgements

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