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Application of membrane reactor for dehydrogenation of ethylbenzene

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Abstract

Two types of membrane reactors have been constructed in order to evaluate the influence of membrane reactor configuration on the performance of the dehydrogenation of ethylbenzene in a porous alumina membrane reactor. The type I construction combine reaction and separation in the same space. The type II configuration is comprised of three parts, i.e., reaction prior to separation, reaction and separation, and reaction after separation. The results showed that the overall yield of styrene in Type I is only 4% higher than that of the fixed bed reactor at 893 K, while 11% enhancement in yield to styrene was obtained with Type II through optimizing the reaction conditions.

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1. Introduction

Dehydrogenation of ethylbenzene is a thermodynamically limited reaction, it is usually operated in the reaction conditions of high temperature (893 K) and low pressure in order to obtain conversion of commercial significance. However, if one of the products can be simultaneously removed from the reaction system when reaction is proceeding, then the conversion can exceed thermodynamic limitation. Based on this idea, much attention has been paid to the application of membrane reactors which can combine the catalytic reaction with the separation process in a single unit in dehydrogenation reactions [1–11].

Membranes prepared with palladium and its alloys can selectively separate hydrogen (almost 100%) from other gases. Therefore, palladium membrane reactors have been used in almost all the reaction processes which involved hydrogen, such as, dehydrogenation of cyclohexane to cyclohexene [1] or benzene [2–5], dehydrogenation of C_2–C_5 to the corresponding olefins [5–7], and steam-reforming of methane [8]. All the above mentioned reactions can greatly exceed the thermodynamic limitation when the reactions are carried out in palladium membrane reactors. However, the application of palladium reactors in large scale industrial processes is limited by its high cost, difficulty in fabrication, and low permeability. In order to overcome these shortages, a porous ceramic membrane reactor with high permeability but relatively low separation factor has been studied recently for its application in catalytic dehydrogenation [9–12].

Porous ceramic membranes usually can enrich one component of a gas mixture through Knudsen diffusion. However, the separation factor of Knudsen diffusion is very low, which equals to the square root of the ratios of the molecular weights of the separated gas. Higher value can be achieved if hydrogen is separated from other

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gases, especially from gases with higher molecular weights [13]. Nevertheless, due to the low separation factor of the porous ceramic membranes, the reactant in a porous ceramic membrane reactor can permeate from the reaction zone to the permeation zone even for hydrogen separation. Since the permeated reactant is not completely converted to products, the conversion of a dehydrogenation reaction in the permeation zone will decreases. As a whole, it will diminish a part of the increment in conversion in the reaction zone. Therefore, it is necessary to improve the separation factor of the porous ceramic membrane in order to fully exploit the advantages of the membrane reactor. One of the methods is to carefully modify the microstructure of the membrane, and the other one was to mindfully choose a reactant which has a higher molecular weight, such as cyclohexane [9] and ethylbenzene [10,11] etc.

In this paper, the results on the application of a porous alumina membrane reactor for the dehydrogenation of ethylbenzene were presented. Our research object here is to get a better understanding of how to use the porous ceramic membrane reactors in the process of the catalytic dehydrogenation reaction.

2. Experimental

2.1. *Configuration of the membrane reactor*

Fig. 1 shows the configuration of a porous alumina membrane reactor. The membrane reactor is divided by the porous alumina membrane into two zones. The first zone is called the reaction zone, in which catalysts are loaded and the dehydrogenation reaction is carried out. The other zone is called the permeation zone in which the purge gas is fed. Hydrogen permeated from the reaction zone was simultaneously taken away from the reaction system by the purge gas. The differences of the two types of membrane reactors are: Type I combined reaction and separation in the same space, while Type II was consisted of three parts, i.e., reaction prior to separation, reaction and separation, and reaction after separation.

2.2. *Porous alumina membrane*

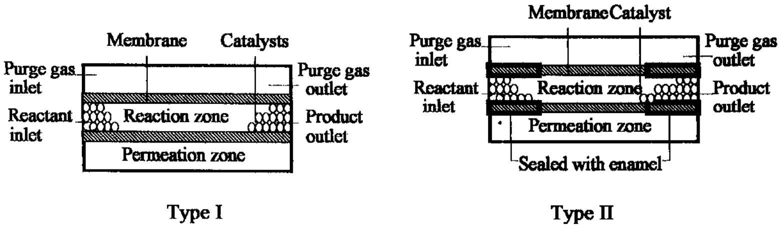
The membranes used here were tubular porous alumina membranes with permeation area between 0.8 and $2.7 \cdot 10^{-3}$ m^2. The permeation properties of the membrane were: H_2/N_2 separation factor 2.8–3.2; H_2 flux $7.0 \cdot 10^{-7}$ mol/ $m^{-2} \cdot s^{-1} \cdot Pa^{-1}$.

2.3. *Catalyst*

A potassium promoted iron oxide type catalyst for the dehydrogenation of ethylbenzene was a commercially product of the Dalian Institute of Chemical Physics. The physical parameters were: specific area 3–4 m^2/g; packed density 1.2–$1.4 \cdot 10^3$ kg/m^3; and particle size 20–30 mesh. In order to obtain steady state reaction results, the catalyst had been tested in the dehydrogenation of ethylbenzene for two weeks in a fixed-bed reactor before it was used in membrane reactor. No deactivation of the catalyst was observed during a period of 1000 h.

2.4. *Reaction conditions*

Catalyst loading was 10 ml; bed height 37 mm; LHSV 1.0 h^{-1}; H_2/ethylbenzene (volume ratio)



Type I

Type II

Fig. 1. Configuration of membrane reactors.

1.3–1.6; the reaction was carried out isothermally at a temperature of 893 K.

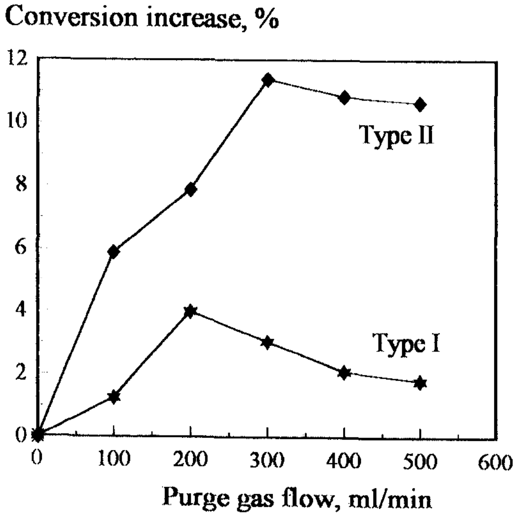
2.5. *Product analysis*

Products coming from the reaction zone and the permeation zone were collected separately every 0.5 h, then mixed and 0.2 μl of the product was taken, and analyzed by gas chromatography. In this way, the overall conversion and selectivity were obtained.

3. Results and discussion

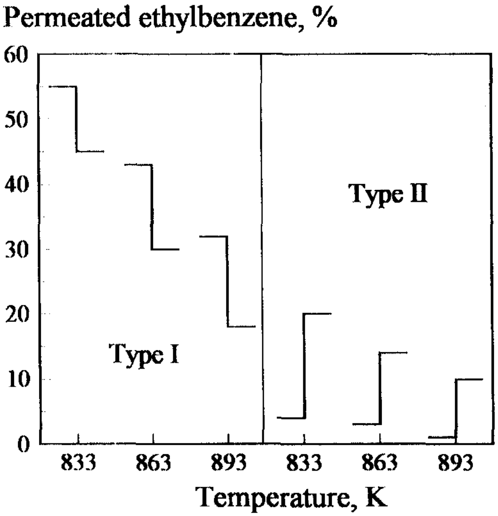
It has been demonstrated that the conversion of dehydrogenation of ethylbenzene can be increased with a membrane reactor. In this paper, the 'conversion increase' is used in order to evaluate the effectiveness of the membrane reactor. The 'conversion increase' is referred as:conversion increase = $\text{conversion}_{\text{membrane}} - \text{conversion}_{\text{fixed-bed}}$.

The purge gas fed in the permeation zone can make the mass transport easier, and it will accelerate the permeation of both the product (such as hydrogen) and the reactant (such as ethylbenzene), from the reaction zone to the permeation zone, due to the poor separation properties of the porous alumina membrane. Consequently, the conversion of dehydrogenation of ethylbenzene will be increased by hydrogen removal (positive effects), and decreased by reactant removal (negative effects). Therefore, it is very important to optimize the purge gas flow in order to achieve a higher conversion of dehydrogenation of ethylbenzene in a porous alumina membrane reactor.



Temperature:893K

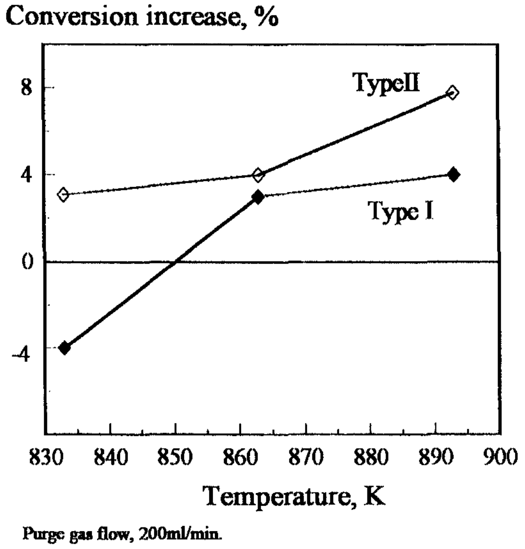
Fig. 2. Purge gas flow effects.



Purge gas flow:0-300ml/min.

Fig. 3. Permeation of ethylbenzene.

Fig. 2 shows the relationship between the 'conversion increase' and the purge gas flow. It can be seen that the 'conversion increase', at the beginning, increased greatly with the increasing of the purge gas flow, and reached a maximum value, then decreased slightly for both types of the membrane reactor. As mentioned above, the membrane permeation properties strongly influenced the effectiveness of the membrane reactor. Hydrogen permeation from reaction zone to permeation zone increased with the increase of the purge gas flow. This forced the reaction equilibrium to shift towards the hydrogen production side, and caused the conversion of dehydrogenation of ethylbenzene to increase, as shown in Fig. 2 (left hand). On the other hand, because of the limitation of membrane separation properties, the reactant (such as ethylbenzene) can also permeate through the membrane to the permeation zone in the case of hydrogen permeation, and the percentage of the permeated reactant also



Purge gas flow, 200ml/min.

Fig. 4. Temperature effects.

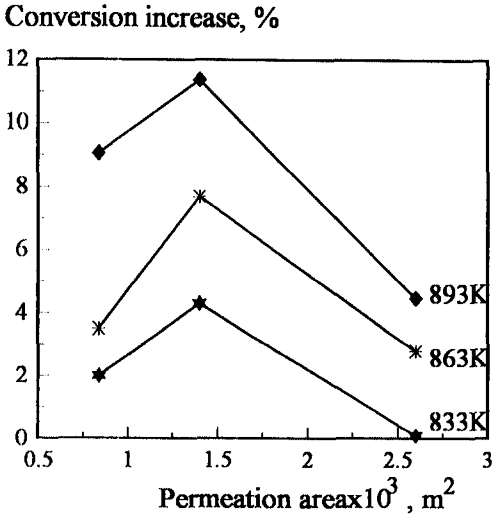
increased with the increase of the purge gas flow, as shown in Fig. 3. As the permeation of ethylbenzene increased, the negative effects become more and more important, and the conversion of dehydrogenation of ethylbenzene decreased slightly as the purge gas flow exceeded 200 ml/min for Type I and 300 ml/min for Type II (right hand in Fig. 2).

For Type I, the overall conversion is only 4% higher than that of fixed-bed reactor at 893 K, because much more ethylbenzene in the Type I membrane reactor permeated from the reaction zone to the permeation zone, as shown in Fig. 3. It can be seen that the percentage of permeated ethylbenzene reached nearly 30% at 893 K when the purge gas rate was 300 ml/min.

In Type II membrane reactor, a certain amount of ethylbenzene has been converted to styrene and hydrogen in the reaction prior to separation part, then the reaction mixtures with low concentration of ethylbenzene and high concentration of hydrogen and styrene passed through the reaction and the separation part, in which the permeation of ethylbenzene from the reaction zone to the permeation zone was much lower, as compared to the Type I membrane reactor, as shown in Fig. 3. However, the permeation of hydrogen and styrene will be greatly higher even for the membrane with a low separation factor. For further ethylbenzene conversion, the reaction after separation was carried out, and a 11% 'conversion increase' was obtained with Type II membrane reactor compared to a fixed bed reactor, as shown in Fig. 2.

Fig. 4 shows the temperature effects on the 'conversion increase' of membrane reactors. It can be seen that the 'conversion increase' increased with increasing temperatures for both types of membrane reactors. The reasons are: (1) with the increasing of temperatures, more hydrogen was produced and removed from the reaction system, i.e. positive effects increased with the increasing of temperatures; (2) the permeation of ethylbenzene decreased as the temperature was increased, as shown in Fig. 3, i.e. negative effects decreased with increasing temperatures. For Type I, the percentage of permeated ethylbenzene was more than 50% at a lower temperature (833 K). In this case, the negative effects predominated, and the 'conversion increase' decreased to some extent, as compared with a fixed-bed reactor, as shown in Fig. 4.

According to the above discussion, we can understand that the higher the permeation of hydrogen (positive effects), the lower the permeation of ethylbenzene (negative effects), and the more effective the membrane reactor. So the effectiveness of a membrane reactor greatly depends on the relative permeation of hydrogen



Purge gas flow, 300ml/min.

Fig. 5. Permeation area effects.

and ethylbenzene. Because the permeation of hydrogen and ethylbenzene has reverse effects, there will exist an optimal permeation area, as shown in Fig. 5. It can be seen that the 'conversion increase' is slightly increased when the permeation area of the membrane is small ($0.8 \cdot 10^{-3}$ m^2), which limited hydrogen permeation, but the 'conversion increase' is also slightly increased when the permeation area of the membrane becomes too large ($2.7 \cdot 10^{-3}$ m^2), which caused serious ethylbenzene permeation. Therefore, the optimal permeation area of the membrane used in this study was about $1.4 \cdot 10^{-3}$ m^2. It means the length of the membrane used here was about half the length of the catalyst bed.

4. Conclusions

The effectiveness of a membrane reactor is closely related to the membrane reactor configuration, the reaction temperature, the purge gas flow rates, and the membrane permeation area.

Acknowledgements

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