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Production of pure hydrogen and more valuable hydrocarbons from ethane on a novel highly active catalyst system with a Pd-based membrane reactor

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Abstract

Production of pure hydrogen and more valuable hydrocarbons from ethane on a novel highly active catalyst system with a Pd-based membrane reactor is studied at the mild reaction temperatures of 773–858 K and a wide SV range of ethane. Re/HZSM-5 is highly active for upgrading of ethane for production of hydrogen and more valuable hydrocarbons such as ethylene and aromatics (BTX) even at the relatively lower temperatures. Formation rates of the more valuable hydrocarbons and hydrogen are remarkably enhanced by selective permeation of hydrogen product in the membrane reactor. It is also found that formation rate of methane as a side product is effectively suppressed by selective permeation of hydrogen though the membrane tubes. Therefore, both ethane conversion and selectivity for production of hydrogen and more valuable hydrocarbons such as ethylene and BTX are greatly enhanced by application of the membrane reactor.

Keywords: Ethane dehydrogenation; Pd-based membrane reactor; Re/HZSM-5 catalyst; Production of pure hydrogen

1. Introduction

Hydrogen is an important clean energy source for use in fuel cell and also an important raw material for the chemical and petrochemical industries. Ethylene, propylene and aromatics such as BTX (benzene, toluene and xylenes) are the very important basic feedstocks for the production of wide variety of chemical products. Production of pure hydrogen and ethylene or BTX from ethane is highly desired in chemical industry. However, catalytic conversion of ethane into hydrogen and ethylene is one of the most challenging projects in catalytic science because of its high thermodynamic stability. High temperatures (about 923 K or higher) are necessary for ethane dehydrogenation into ethylene and hydrogen on the traditional mono-functional dehydrogenation catalyst such as Pt–Sn/Al_2O_3-based catalyst. The necessity to operate at such high temperatures introduces several potential problems. The thermal stability of the catalyst and the membrane tubes with the high temperatures tending to enhance catalyst and membrane materials sintering and coke deposition on the catalyst are certainly the major problems. Our previous works found that Re/HZSM-5 exhibits a unique high activity for activation of methane into hydrogen and higher hydrocarbons [1,2]. However, little attention has been paid to the catalytic performance of Re/HZSM-5 for activation of ethane. Recently, there has been an intense, worldwide effort on the integration of catalytic dehydrogenation reaction of hydrocarbons and separation process of H_2 product in palladium composite membrane reactors. The

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main motivation for applying membrane reactors for hydrocarbon dehydrogenation includes the direct production of pure hydrogen and the attainment of higher conversion and product yield. These efforts have been summarized in some recent review articles [3–5]. Production of pure hydrogen from ethane on the other type catalyst such as graphite-based catalyst by using membrane-type reactors at a relatively higher temperature has been reported [6]. The objective of the present study is to make the dehydrogenation of ethane feasible at relatively lower temperatures by using a novel highly active catalyst system and to produce pure hydrogen and other more valuable hydrocarbons such as ethylene, propylene and BTX (aromatics) by integration of the dehydrogenation of ethane and hydrogen separation with a Pd-based membrane.

2. Experimental

2.1. Membrane reactor

The Pd-based membrane reactor is commercially available one supplied by REB Research & Consulting Co. It is with 16 mm diameter and by 254 mm tall and contains four membrane tubes with 3 mm diameter and by 178 mm tall. The scheme for the membrane reactor is shown in Fig. 1. The REB Research membranes are made by palladium coating high permeability alloy tubes and are effectively 100% selective to hydrogen. The details about manufacture and performance of the REB membranes have been described in [7,8]. H_2 was permeated through the membrane into the tubes and removed by pump immediately after produced. Ultra highly pure H_2 was produced because the selectivity for hydrogen permeation through the membrane tubes is 100%.

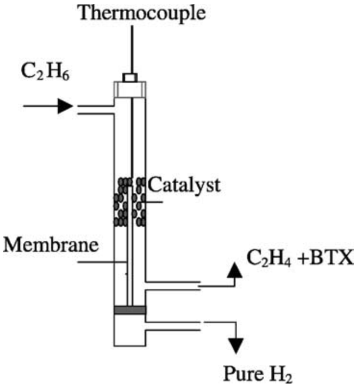

Fig. 1. Schematic illustration of the membrane reactor.

2.2. Catalyst preparation and reduction

Re/HZSM-5 catalyst was prepared by impregnating NH_4ZSM-5 ($SiO_2/Al_2O_3 = 30$) with NH_4ReO_4 aqueous solution, followed by drying at 383 K for 6 h and calcination at 773 K for 6 h. The samples were finally pressed, crushed and sorted into 20–40 meshes. The catalyst was reduced into metallic state by the mixture of hydrogen and nitrogen at 623–673 K for 2 h in the reactor before the reaction. The loadings of Re is about 5% in weight.

2.3. Catalytic tests and analysis of products

Catalytic tests were carried out with about 0.2–2 g catalyst placed in the fixed bed continuous-flow membrane reactor. After the catalyst was reduced into metallic state by H_2/N_2 at 623–673 K ethane feed was introduced into the reactor and passed through the catalyst bed. Flow rate of ethane feed was controlled by a mass flow rate-controller. The catalytic reaction was conducted in the membrane reactor at the pressure of 100 KPa and ethane SV of 340–4800 ml/h/g. The products were withdraw periodically from the outlet of reactor and analyzed by a two on-line gas chromatography of Shimadzu GC-14B and GC-8A equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD), respectively. The hydrocarbon products were separated on a 4 mm × 1 m Porapak P column and CH_4, CO, CO_2, H_2 and N_2 were separated on a 4 mm × 1 m active carbon column. Conversion, selectivity and formation rates of products were calculated by an internal standard analyzing method. About 2.41% N_2 is added into ethane feed as the internal standard. The method is presented briefly as follows. Even if the total flow rate changed at outlet from inlet of reactor ($F_{\mathrm{Total}}^{\mathrm{inlet}}$, $F_{\mathrm{Total}}^{\mathrm{outlet}}$). Flow rate of the non-reactive internal standard gas (F_{st}) doses not change.

$$F_{\mathrm{st}} = F_{\mathrm{Total}}^{\mathrm{outlet}} \times X_{\mathrm{st}}^{\mathrm{outlet}} = F_{\mathrm{Total}}^{\mathrm{inlet}} \times X_{\mathrm{st}}^{\mathrm{inlet}}$$

Here, X_{st} refer to concentration of the internal standard gas. Formation rate of i product (F_i) can be calculated as

$$F_i = F_{\text{Total}}^{\text{outlet}} \times X_i^{\text{outlet}} = F_{\text{st}} \times \frac{X_i^{\text{outlet}}}{X_{\text{st}}^{\text{outlet}}}$$

Ethane conversion (C_{ethane}) can be calculated as

$$C_{\text{ethane}} = \frac{F_{\text{ethane}}^{\text{inlet}} - F_{\text{ethane}}^{\text{outlet}}}{F_{\text{ethane}}^{\text{inlet}}} = 1 - \frac{F_{\text{ethane}}^{\text{outlet}}}{F_{\text{ethane}}^{\text{inlet}}} = 1 - \frac{F_{\text{st}} \times X_{\text{ethane}}^{\text{outlet}}}{X_{\text{st}}^{\text{outlet}} \times F_{\text{ethane}}^{\text{inlet}}}$$

Selectivity of hydrocarbon product is calculated as, S_{HC} is the formation rate of i product (F_i)/consumption rate of ethane.

3. Results and discussion

3.1. Catalytic performance of Re/HZSM-5 for conversion of ethane

The traditional mono-functional catalyst of Pt/Al_2O_3 or $Pt\text{-}Sn/Al_2O_3$-based catalyst is only active for conversion of ethane into ethylene and hydrogen at the relatively higher reaction temperatures. In order to make the dehydrogenation of ethane feasible at relatively lower temperatures, the catalytic performance of Re/HZSM-5 as a novel catalyst system is studied for dehydrogenation of ethane because of the unique high activity of Re/HZSM-5 even for the dehydrogenation of methane. Formation rates of different products for catalytic conversion of ethane on Re/HZSM-5 at 818 K and different SV of ethane are shown in Fig. 2. It is clear in Fig. 2 that a large amount of hydrogen and ethylene, propylene, aromatics (BTX) are produced as the major products on Re/HZSM-5 catalysts. Both the olefin products (ethylene and propylene) and the aromatics product (BTX) are highly desired in chemical industry as the basic chemical feedstocks. A little amount of methane is also produced as a side product. It is indicated from Fig. 2 that Re/HZSM-5 exhibits a quite high activity for dehydrogenation of ethane even at a relatively lower reaction temperature of 818 K although the major product is the mixture of ethylene, propylene and aromatics (BTX). We can see in Fig. 2 that the formation rates of hydrogen, ethylene and propylene are increased sharply with increasing ethane SV. However, formation rates of BTX and methane have no increase with increasing ethane SV. This indicates that the selectivity to different product for dehydrogenation or dehydro-condensation of ethane on Re/HZSM-5 catalyst is well controlled by variation of ethane SV. Higher ethane SV is favorable for high selectivity to ethylene and propylene and lower ethane SV is favorable for high selectivity to BTX. A high selectivity to ethylene and propylene of about 70–80% at ethane conversion of 9–25% has been achieved at 818 K. The hydrogen is also produced in a large amount at the same time.

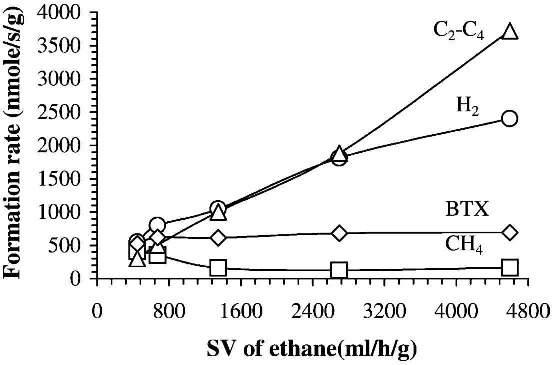

Fig. 2. Formation rates of the products for dehydrogenation of ethane on Re/HZSM-5 at 818 K and different SV of ethane.

3.2. Effect of hydrogen permeation on catalytic conversion of ethane in the membrane reactor

In order to enhance the dehydrogenation of ethane and to produce pure hydrogen directly, catalytic dehydrogenation of ethane and hydrogen separation are integrated with the Pd-based membrane reactor. The high activity of novel Re/HZSM-5 catalyst for dehydrogenation of ethane makes it possible that dehydrogenation reaction of ethane proceeds in the Pd-based membrane reactor at relatively more mild reaction temperatures of 773–858 K. The produced H_2 was selectively permeated through the membrane tubes and removed by pump immediately. The selectivity for hydrogen permeation through the membrane is 100% and ultra highly pure H_2 was produced as a result. The formation rates of the products for dehydrogenation

Table 1
Effect of H_2 separation on the dehydrogenation reaction of ethane at different temperatures[a]

Temperature (K)	H_2 removed (%)	Formation rate (nmol/s/g)				
		CH_4	C_2H_4	C_3	BTX	H_2
773	74	80	1308	212	652	–
	0	240	916	240	432	1904
793	81	124	1400	280	1016	–
	0	276	1000	300	672	2480
818	81	276	1776	388	1564	–
	0	788	1520	488	1268	3528
858	93	892	2152	452	4432	–
	0	3040	1736	716	3088	6892

[a] SV of ethane = 2700 ml/h/g.

of ethane under the conditions of hydrogen permeation and without hydrogen permeation are listed in Table 1. We can see from Table 1 that 74–93% of produced hydrogen can removed from the product by selective permeation of hydrogen product through the membrane tubes at the temperature range 773–858 K. It is indicated in Table 1 that the formation rates of ethylene and BTX products are remarkably enhanced by removal of the hydrogen through selective permeation at 773–858 K. It is also of significance that the formation rate of methane as a side product is effectively suppressed by selective hydrogen permeation through the membrane tubes in the membrane reactor at a temperature range 773–858 K. The side product of methane is considered to be produced by the hydro-cracking of ethane on the catalyst. The hydro-cracking of ethane is suppressed by the removal of hydrogen through selective permeation. Therefore, the hydrogen separation from the product not only enhances the dehydrogenation reaction of ethane but also suppress the side reaction of ethane hydro-cracking. As a result, high selectivity of ethylene or BTX is attained and production of hydrogen is maximized by integration of dehydrogenation and hydrogen separation with the membrane reactor. Since the selectivity to ethylene or to BTX is well controlled by SV of ethane, effect of selective permeation of hydrogen product through the membrane tubes on the formation rates of ethylene and BTX have been studied at a wide range SV of ethane. The formation rates of the products for dehydrogenation of ethane under the conditions of hydrogen permeation and without hydrogen permeation at 793 K and ethane SV of 340–2700 ml/h/g are listed in Table 2. It is indicated in Table 2 that the formation

Table 2
Effect of H_2 separation on catalytic conversion of ethane at different SV[a]

SV of C_2H_6 (ml/h/g)	H_2 removed (%)	Formation rates of products (nmol/s/g)				
		CH_4	C_2H_4	C_3	BTX	H_2
340	89	180	180	108	700	–
	0	296	85	97	355	504
670	91	144	358	138	796	–
	0	300	256	176	550	878
1350	91	220	952	260	1242	–
	0	604	536	368	732	1886
2700	81	124	1400	280	1016	–
	0	276	1000	300	502	2480

[a] Reaction temperature: 793 K.

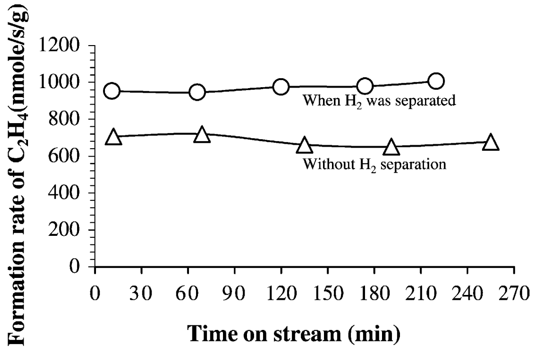

Fig. 3. Formation rate of C_2H_4 with time on stream on Re/HZSM-5 at 793 K and SV of 1350 ml/h/g.

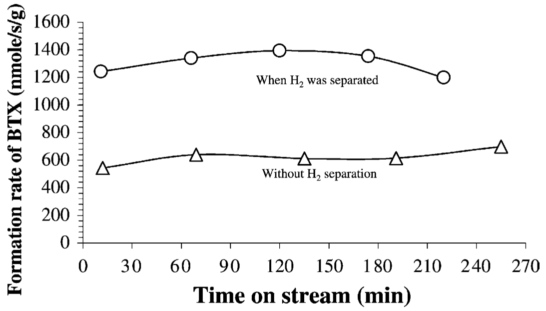

Fig. 4. Formation rate of BTX with time on stream on Re/HZSM-5 at 793 K and SV of 1350 ml/h/g.

rates of ethylene and BTX are remarkably enhanced and formation rate of methane is effectively suppressed by removal of hydrogen at the wide ethane SV range 340–2700 ml/h/g. We also can see from Table 2 that formation rate of the BTX (benzene, toluene and xylene) are difficult to be increased by increasing SV of ethane if without removal of hydrogen. However, the situation changes and the formation rate of BTX is greatly increased by increasing SV of ethane if hydrogen is removed by selective permeation as shown in Table 2. Therefore, the dehydro-condensation of ethane into BTX is effectively promoted by the hydrogen separation even at the high SV of ethane. The activity maintenance of the catalyst for production of ethylene and BTX with time on stream in the membrane reactor is shown in Figs. 3 and 4.

It is clear in Fig. 3 that the enhanced formation rate of ethylene is quite stable with time on stream even if the hydrogen is continuously removed from the product by selective permeation into the membrane tubes in the reactor. Fig. 4 indicates that formation rate of BTX is about doubled by removal of hydrogen and the enhanced formation rate of BTX is maintained well with time on stream in about 4 h of time on stream. Figs. 3 and 4 indicate that the durability of both the membrane for hydrogen permeation and the catalyst activity for ethane conversion are quite well in several hours of time on stream under the reaction conditions of selective permeation of hydrogen product. Table 3 gives the results about the effect of hydrogen permeation on the conversion of ethane and the distribution of products at 793 K and ethane SV of 340–2700 ml/h/g. We can see from Table 3 that the conversion of ethane is evidently enhanced by selective permeation of hydrogen from the product at the lower SV of ethane. However, the selectivity of ethylene and BTX is enhanced and selectivity to methane is suppressed

Table 3
Effect of SV on conversion of ethane and distribution of products[a]

SV of C_2H_6 (ml/h/g)	H_2 removed (%)	Conversion (%)	Distribution of products (%)			
			CH_4	C_2H_4	C_3	BTX
340	89	35.9	16.1	14.8	8.8	54.5
	0	32.5	35.9	9.7	11.3	40.9
670	91	25.7	10.3	21.6	10.8	54.6
	0	21.8	23.2	17.0	11.5	46.7
1350	91	22.4	7.8	31.8	9.8	45.0
	0	22.3	26.9	22.8	15.8	30.7
2700	81	18.3	4.6	47.7	9.6	34.4
	0	18.3	12.6	42.9	13.1	28.8

[a] Reaction temperature: 793 K.

Table 4
Comparison of catalytic performance of Re/HZSM-5 with Mo/HZSM-5 for dehydrogenation of ethane[a]

Catalyst	H_2 removed (%)	Formation rates of products (nmol/s/g)				
		CH_4	C_2H_4	C_3	BTX	H_2
Re/HZSM-5	89	180	180	108	700	–
	0	296	85	97	355	504
Mo/HZSM-5	93	326	85	84	919	
	0	605	45	70	513	637

[a] Temperature = 793 K and SV = 340 ml/h/g.

by the selective permeation of hydrogen even more effectively at the higher SV of ethane as shown in Table 3.

3.3. Comparative study of Re/HZSM-5 and Mo/HZSM-5 catalysts for conversion of ethane

It is well known that Mo/HZSM-5 is also a highly active catalyst for dehydrogenation of methane into hydrogen and hydrocarbons [9]. Therefore, the catalytic performance of Mo/HZSM-5 is compared with Re/HZSM-5 for dehydrogenation of ethane. Table 4 lists the formation rates of product for dehydrogenation of ethane on Re/HZSM-5 and on Mo/HZSM-5 in the membrane reactor at a mild reaction temperature of 793 K and ethane SV of 340 ml/min/g. Re/HZSM-5 and Mo/HZSM-5 shows evidently different catalytic performance for ethane conversion. Mo/HZSM-5 exhibits higher selectivity to BTX and Re/HZSM-5 exhibits higher selectivity to ethylene. In addition, Re/HZSM-5 shows lower activity for formation of methane than Mo/HZSM-5. In addition, formation rates of ethylene and BTX are greatly enhanced and formation rate of methane is suppressed effectively by the selective permeation of hydrogen on both the catalysts. Therefore, Re/HZSM-5 is the more promising catalyst for dehydrogenation of ethane for production of ethylene and pure hydrogen than Mo/HZSM-5 catalyst. Mo/HZSM-5 is relatively more suitable for use to catalyze the dehydro-condensation of ethane to produce BTX and hydrogen.

4. Conclusion

Re/HZSM-5 is highly active novel catalyst for upgrading of ethane to produce hydrogen and more valuable hydrocarbons of ethylene and aromatics (BTX) even at the relatively lower temperatures. The high catalytic activity of Re/HZSM-5 makes it feasible for integration of ethane conversion and hydrogen separation with a Pd-based membrane reactor for production of pure hydrogen and ethylene or BTX at the relatively mild temperatures. Selectivity to ethylene or BTX is well controlled by variation of ethane SV. High SV of ethane is favorable for production of ethylene and low SV of ethane is more favorable for production of BTX. The selective permeation of hydrogen product not only remarkable enhances the production of ethylene and BTX but also effectively suppresses the formation of the side product of methane.

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