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Dehydrogenation of ethylbenzene to styrene over Fe_2O_3/Al_2O_3 catalysts in the presence of carbon dioxide

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Abstract

Thermodynamic consideration of the dehydrogenation of ethylbenzene clearly indicates that the equilibrium yield of styrene for the dehydrogenation in the presence of CO_2 is much higher than that for the dehydrogenation in the presence of steam. A two-step pathway for the dehydrogenation in the presence of CO_2 appears to provide higher equilibrium yield of styrene at a given temperature. The amount of energy required for the new process using CO_2 is much lower than that for a typical present commercial process using steam. An Fe_2O_3(10 wt.%)/Al_2O_3(90 wt.%) catalyst prepared by a coprecipitation method was found to be effective for the dehydrogenation of ethylbenzene to produce styrene in the presence of CO_2. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Ethylbenzene; Styrene; Dehydrogenation; Carbon dioxide; Fe_2O_3/Al_2O_3 catalysts

1. Introduction

Styrene is one of the most important basic chemicals as a monomer of polymers. About 3 million tons of styrene is annually produced in Japan. It is commercially produced by the dehydrogenation of ethylbenzene in the presence of a large quantity of steam at high temperatures of 600–700°C. It has been pointed out that the present commercial processes waste a large amount of latent heat of steam condensation at a liquid–gas separator following a reactor. Recently, CO_2 has received much attention as a co-feed gas for the dehydrogenation, because it is always gaseous throughout the dehydrogenation process. The authors reported that the energies required for producing styrene by a present commercial process using steam and also by a new process using CO_2 were estimated to be 1.5×10^9 and 1.9×10^8 cal per *t*-styrene, respectively [1,2]. Therefore, the dehydrogenation process using CO_2 could be an energy-saving process. Since Fe–K based catalysts used for present commercial dehydrogenation processes do not work effectively in the presence of CO_2, a high performance catalyst has been required for the dehydrogenation of ethylbenzene in the presence of CO_2. Other groups presented several catalysts for the dehydrogenation using CO_2 [3–5], and the authors also reported that iron oxide based catalysts were effective for this dehydrogenation [1,2].

In the present work, first we revealed the advantages of usage of CO_2 instead of steam for the dehydrogenation of ethylbenzene to styrene on the basis of thermodynamic considerations. Then we investigated the effects of supports on the performance of iron oxide-based catalysts, the effectiveness of a coprecipitation method for preparing a iron–aluminum oxide catalysts.

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One-step pathway

$Ph\text{-}CH_2CH_3 + CO_2 \rightarrow Ph\text{-}CH{=}CH_2 + CO + H_2O$ [Eq. 1]

Two-step pathway

$Ph\text{-}CH_2CH_3 \rightarrow Ph\text{-}CH{=}CH_2 + H_2$ [Eq. 2]

$H_2 + CO_2 \rightarrow H_2O + CO$ [Eq. 3]

Scheme 1.

2. Thermodynamic considerations

2.1. Equilibrium yield of styrene in the dehydrogenation of ethylbenzene

The thermodynamic data of the substances were taken from 'MALT2', which is a software of thermodynamic database supplied by Kagaku-Gijutsu-sha, which is a Japanese software company. There are two possible reaction pathways for the dehydrogenation in the presence of CO_2 as shown in Scheme 1, one-step pathway shown in Eq. 1 and two-step pathway via Eq. 2 followed by Eq. 3 in Scheme 1. Simple dehydrogenation in commercial processes using steam proceeds via Eq. 2 only. If the reaction of Eq. 1 is followed by the water gas shift reaction (reverse reaction of Eq. 3), there will be no thermodynamical difference between the one-step pathway and the two-step pathway. In this study, we supposed that the water gas shift reaction would not take place in the one-step pathway. The equilibrium yields of styrene for the three reaction pathways including the simple dehydrogenation were calculated by using the equations shown in calculation 1. The equilibrium constants (K_1–K_4) were calculated by MALT2 for given temperatures.

Fig. 1 shows the dependence of the equilibrium yield of styrene on the reaction temperature in the dehydrogenation of ethylbenzene in the presence of CO_2 or steam. The equilibrium yield of styrene in the presence of CO_2 either via one-step pathway or two-step pathway is higher than that in the presence of steam. Accordingly, the usage of CO_2 instead of steam could provide several advantages for the dehydrogenation process such as the reduction of the reaction temperature, energy saving in the distillation process of styrene, and so on.

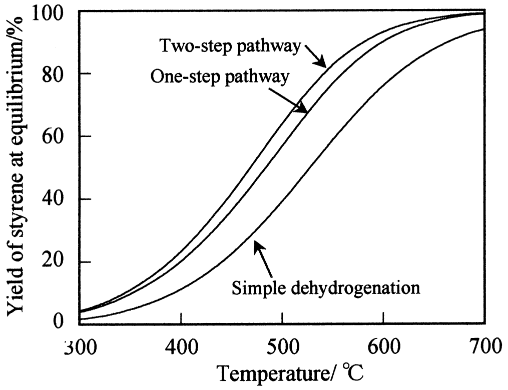


Fig. 1. Yield of styrene at equilibrium in the dehydrogenation of ethylbenzene in the presence of CO_2 or H_2O. Simple dehydrogenation: H_2O/ethylbenzene = 9; One step pathway, two step pathway: CO_2/ethylbenzene = 9.

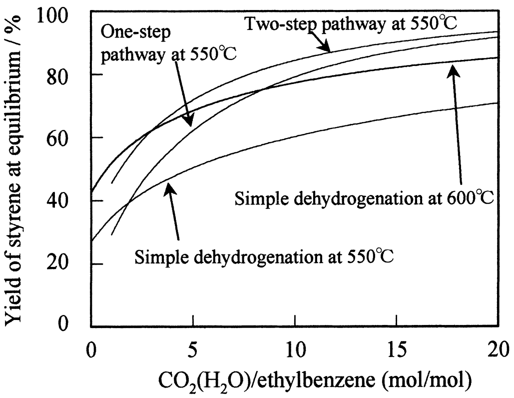


Fig. 2. Effects of the ratio of CO_2/ethylbenzene or H_2O/ ethylbenzene on the yield of styrene at equilibrium.

Since a large amount of energy is needed to produce a high purity CO_2 from exhaust gases by membrane separation or by absorption method, it might be necessary to use a smaller amount of CO_2 or a lower purity CO_2 as a co-feed gas. Fig. 2 shows effect of the ratio of CO_2 or H_2O to ethylbenzene on the equilibrium yield of styrene. In the case of the ratio of CO_2/ethylbenzene >8 for one-step pathway or in the case of the ratio of CO_2/ethylbenzene >3 for two-step pathway, the equilibrium yield of styrene in the dehydrogenation in the presence of CO_2 at 550°C is higher than that in the presence of steam at 600°C.

Fig. 3 shows the effect of CO_2 content of a co-feed gases on the yield of styrene at equilibrium, where

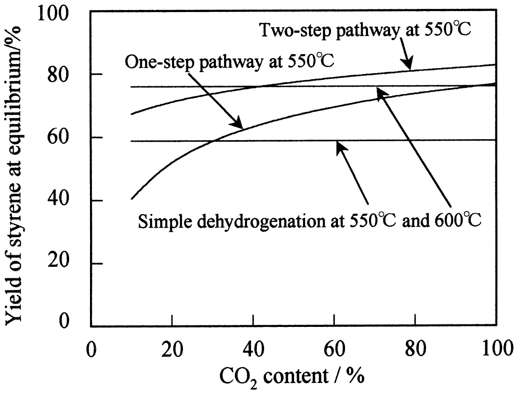
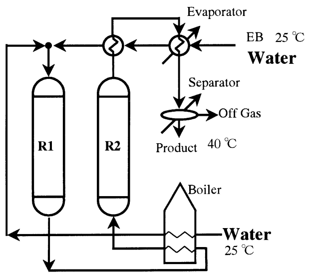


Fig. 3. Effect of CO_2 content of a co-feed gas on the yield of styrene at equilibrium. Simple dehydrogenation: H_2O/ethylbenzene = 9; One-step pathway, two-step pathway: (CO_2 + N_2)/ethylbenzene = 9.

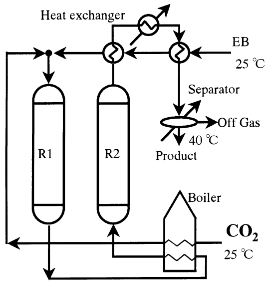
the ratio of a co-feed gas, which is CO_2 + N_2 or H_2O, to ethylbenzene is fixed to 9. The equilibrium yield of styrene in the two-step dehydrogenation at 550°C is higher than that in the simple dehydrogenation at 600°C when CO_2 content is higher than 40%. However, the equilibrium yield of styrene in the one-step dehydrogenation at 550°C is lower than that in the simple dehydrogenation at 600°C when CO_2 content is lower than 95%. Figs. 2 and 3 clearly suggest that the two-step pathway should be more effective than one-step pathway for obtaining higher equilibrium yield of styrene.

2.2. Estimation of energy required for producing styrene

Fig. 4 shows the model flow diagrams of a typical commercial process using steam and of a new process using CO_2. Table 1 gives basic parameters for the model processes. In our previous study [1], the reaction pathway of the new process using CO_2 was postulated to be one-step. In the present study, the reaction pathway has been postulated to be two-step, because the two-step pathway was found to be more effective than one-step pathway as described above. Table 2 summarizes the energy required for producing styrene by the dehydrogenation of ethylbenzene in the presence of CO_2 as well as in the presence of steam. The energy required for producing styrene in the presence of CO_2 is 1.5×10^8 cal per *t*-styrene, which is 20% lower than that via one-step pathway estimated in our previous study. On the other hand, the commercial process using steam requires 10 times the energy required for the two-step dehydrogenation in the presence of CO_2. Consequently, the dehydrogenation in the presence of CO_2 could be an energy saving process. However, the economic study was not performed on the new process in the present study because the authors have not investigated what kinds of facilities would be required for the new process.



A model of commercial process



A model of new process

Fig. 4. Model process of the commercial process using steam and new process using CO_2 for the production of styrene by the dehydrogenation of ethylbenzene.

3. Test of various iron oxide-based catalysts for the dehydrogenation of ethylbenzene in the presence of CO_2

3.1. Experimental

Iron oxide-based catalysts were prepared by an impregnation method or by a coprecipitation method. When the impregnation method was employed for catalyst preparation, Al_2O_3 (JRC–ALO4, which is

Table 1
Basic parameters for the model processes

	Commercial process		New process
Reaction temperature[a]	630°C		580°C
Pressure	Atmospheric pressure[b]		
Component of feed gas	H_2O/EB = 9		CO_2/EB = 9
Temperature of starting materials		25°C	
Temperature of products and off gases		40°C	
Reaction pathway	Simple dehydrogenation		Two-step pathway
Yield of styrene	R1: 35%	R2: 35%,	Total: 70%
Selectivity of styrene		100%	
Thermal efficiency of boiler		90%	
Thermal efficiency of heat exchanger and evaporator		100%	

[a] The temperature at the top of R1.
[b] The pressure in a typical present commercial plant is about 0.5–0.8 atm.

Table 2
Energy required for producing styrene

		Commercial process (10^8 cal per *t*-styrene)	New process (10^8 cal per *t*-styrene)
Input (1)	Boiler	17.8	11.7
	Evaporator	2.2	–
Output (2)	Combustion of off-gas	5.0	5.6
	Surplus energy	–	4.6
Energy required	(1)–(2)	15.0	1.5

one of the reference catalysts supplied by Catalysis Society of Japan, or prepared by a precipitation method from $Al(NO_3)_3 \cdot 6H_2O$ and sodium carbonate, <0.18 mm), SiO_2 (CARIACT Q-3, Fuji Silisia Chemical Ltd., 0.075–0.5 mm) or AC (activated carbon, Shirasagi, Takeda Chemical Industries Ltd., 0.18–0.30 mm) were used as supports. A slurry composed of an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ and the support was stirred for 2 h, before vacuum-drying at 100°C. The coprecipitation method was carried out as follows: Both an aqueous solution (300 ml) containing $Fe(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 6H_2O$ (Fe + Al = 0.30 mol) and an aqueous solution (300 ml) of Na_2CO_3 (0.495 mol) were simultaneously added to vigorously stirred distilled water. The precipitate was washed with distilled water, filtered, and dried at 120°C. The precursors prepared by both methods except Fe/AC were calcined at 750°C for 5 h in air, and pelletized to 0.18–0.3 mm. An Fe/AC catalyst was used without further treatment after vacuum-drying.

The dehydrogenation of ethylbenzene was carried out using a quartz tube reactor (d = 11 mm). Before the reaction, the catalyst (1.4 g) was treated with CO_2 or He as a co-feed gas for 15 min at 550°C. Then, the dehydrogenation was performed at 550°C under atmospheric pressure. The molar ratio of a co-feed gas to ethylbenzene was selected to be 11, because a typical ratio of steam to ethylbenzene in a commercial process is 7–12. The flow rate of ethylbenzene was fixed at 0.50 mmol/min. The products were liquefied by a cold trap at −5°C and analyzed by gas chromatography equipped with FID detector. The gaseous products after the trap were analyzed by an on-line TCD detector.

3.2. *Performances of the catalysts for the dehydrogenation*

Table 3 shows the properties of various iron oxide-based catalysts for the dehydrogenation of ethylbenzene in the presence of CO_2. Fig. 5 presents the yields of liquid products using the catalysts shown in Table 3 at 0.42 and at 6 h. The left bars and the right bars indicate the yields at 0.42 and at 6 h, respectively.

Table 3
Properties of various iron oxide-based catalysts

Catalyst number	Catalyst	Method of preparation	Surface area (m^2)	Density (g/ml)
1	Fe_2O_3/SiO_2 (10 wt.%/90 wt.%)	impregnation	381	0.93
2	Fe_2O_3/AC (10 wt.%/90 wt.%)	impregnation	611	0.37
3	Fe_2O_3/Al_2O_3[a] (10 wt.%/90 wt.%)	impregnation	138	0.70
4	Fe_2O_3/Al_2O_3[b] (10 wt.%/90 wt.%)	impregnation	142	0.64
5	Fe_2O_3/Al_2O_3 (10 wt.%/90 wt.%)	coprecipitation	160	0.64
6	α-Fe_2O_3	reagent	4.2	0.56
7	γ-Al_2O_3[a]	JRC–ALO4	177	0.67
8	None	–	–	–

[a] The Al_2O_3 is JRC-ALO4 (The reference catalyst supplied by Catalysis Society of Japan).
[b] The Al_2O_3 is prepared from $Al(NO_3)_3$ and Na_2CO_3 by precipitation method.

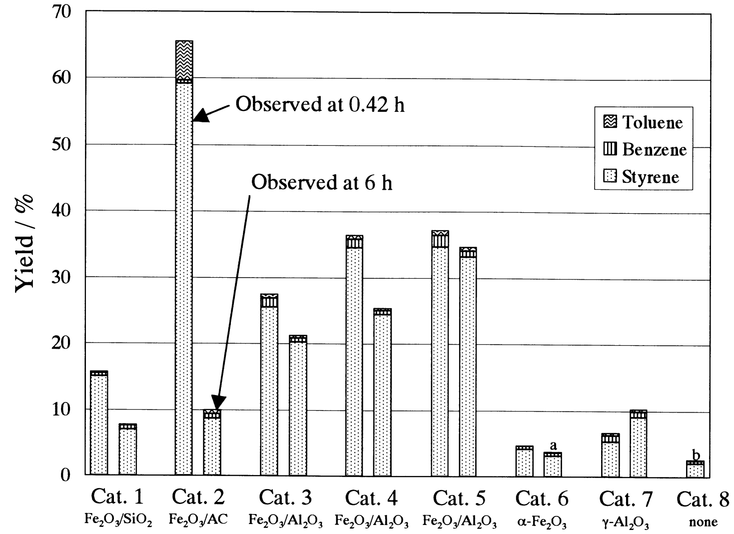


Fig. 5. The performances of various iron oxide-based catalysts for the dehydrogenation of ethylbenzene in the presence of carbon dioxide of the catalysts. Catalyst weight = 1.4 g; Temperature = 823 K; Ethylbenzene = 0.5 mmol/min, CO_2/ethylbenzene = 11; W/F = 47 g·h/mol; [a]Observed at 2.17 h; [b]Observed at 0.42 h.

Toluene and benzene were detected as by-products in the liquid products. The gaseous products were H_2, CO, CH_4 and C_2 compounds. Their yields in the dehydrogenation over catalyst 5 are shown in Table 4. Catalysts 1–3 in Table 3 clearly indicate that alumina is much better as a support than SiO_2 and activated carbon. Catalysts 3–5 suggest that high performance Fe_2O_3/Al_2O_3 catalysts could be prepared by the co-precipitation method. Since Fe_2O_3 alone or Al_2O_3 itself was not highly active as shown in Table 3, some special interaction between iron oxide and alumina might be necessary high activity.

Table 4
Gaseous products using catalyst 5 at 0.63 and 6 h[a]

Gaseous products	Yield (%)	
	0.63 h[b]	6 h[b]
CO	28.6[c](2.6)[d]	21.5[c](2.0)[d]
CH_4	1.2[c]	0.6[c]
C_2	trace[c]	trace[c]

[a] H2 was not quantitatively determined.
[b] Time on stream during the reaction.
[c] The yield was based on ethylbenzene supplied to the reactor.
[d] The yield was based on CO_2 supplied to the reactor.

XRD analysis of catalyst 5 before and after reaction, effects of the ratio of Fe_2O_3–Al_2O_3 in the catalyst on the catalytic activity, the role of CO_2 in the dehydrogenation, and the reaction pathway over the Fe_2O_3/Al_2O_3 catalyst is reported elsewhere [6].

4. Conclusions

1. The yield of styrene at equilibrium in the dehydrogenation of ethylbenzene in the presence of CO_2 is much higher than that in the presence of steam.
2. The amount of energy required for the new process using CO_2 is about one tenth of that for the present commercial process using steam.
3. An Fe_2O_3/Al_2O_3(10 wt.%/90 wt.%) catalyst prepared by a coprecipitation method was effective for the dehydrogenation in the presence of CO_2.

5. Calculation

Equations used for calculating the equilibrium yield of styrene shown in Figs. 1–3.

One-step pathway

$$\frac{(x_1 P/a+b+d+x_1)^3}{\{(a-x_1)P/(a+b+d+x_1)\} \times \{(b-x_1)P/(a+b+d+x_1)\}} = K_1 \qquad \text{[Eq.4]}$$

Two-step pathway

$$\frac{(x_2 P/a+b+d+x_2) \times \{(x_2-y)P/(a+b+d+x_2)\}}{(a-x_2)P/(a+b+d+x_2)} = K_2 \qquad \text{[Eq.5]}$$

$$\frac{(x_2 P/a+b+d+x_2)^2}{\{(x_2-y)P/(a+b+d+x_2)\} \times \{(b-y)P/(a+b+d+x_2)\}} = K_3 \qquad \text{[Eq.6]}$$

Simple dehydrogenation

$$\frac{(x_3 P/a+c+x_3)^2}{(a-x_3)P/(a+c+x_3)} = K_4 \qquad \text{[Eq.7]}$$

a	Ethylbenzene supplied (suppose the ethylbenzene supplied to be 1 mol)
b	CO_2 (mol) supplied
c	Steam (mol) supplied
d	Nitrogen(mol) supplied
x_1	Yield of styrene, CO, or water via one-step pathway (mol)
x_2	Yield of styrene via two-step pathway (mol)
x_3	Yield of styrene or hydrogen via simple dehydrogenation (mol)
y	Yield of CO or water (mol)
P	Reaction pressure (suppose the pressure to be 1)
K_1–K_4	Equilibrium constants determined by MALT2
K_1	$K_2 \times K_3$
K_2	K_4
Content of CO_2 (%)	$b/(b+d) \times 100$

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