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Dehydrogenation of ethylbenzene to styrene in the presence of CO_2†

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The relationship between the yield of styrene and the energy required for separation by the model distillation system clearly indicates that it is possible to save energy by a new process using CO_2.

An Fe_2O_3(10 wt%)–Al_2O_3(90 wt%) catalyst prepared by a coprecipitation method was found to be effective for dehydrogenation of ethylbenzene to produce styrene in the presence of CO_2, instead of the steam used in commercial processes. The dehydrogenation of ethylbenzene over the catalyst in the presence of CO_2 was considered to proceed both *via* 45% of a one-step pathway and *via* 55% of a two-step pathway. CO_2 was found to suppress the deactivation of the catalyst during the dehydrogenation of ethylbenzene. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: ethylbenzene; styrene; dehydrogenation; CO_2; Fe_2O_3/Al_2O_3 catalyst; energy-saving

INTRODUCTION

Styrene is one of the most important basic chemicals as a raw material of polymers. It is commercially produced by the dehydrogenation of ethylbenzene in the presence of a large quantity of steam at high temperatures of 873 to 973 K. It has been pointed out that the present commercial processes consume large amounts of energy because not all the latent heat of condensation of steam is recovered at the liquid–gas separator following the reactor. Recently, CO_2 has received much attention as a co-feed gas instead of steam, because it is always gaseous throughout the dehydrogenation process. We have already reported on the energies required for producing styrene by the present commercial process using steam and by the new process using CO_2 (shown in Table 1).[1] Therefore, the dehydrogenation process using CO_2 could be an energy-saving process. Since Fe–K-based catalysts used for the present commercial dehydrogenation processes do not work effectively in the presence of CO_2, a high-performance catalyst for the dehydrogenation of ethylbenzene in the presence of CO_2 has been required. Other groups presented several catalysts for the dehydrogenation using CO_2,[2–5] and the authors also reported that iron-oxide-based catalysts were effective for the new dehydrogenation.[1]

In the present paper, we report on the energy required for separation of the mixture of ethylbenzene and styrene, which presents one of the advantages of using CO_2 instead of steam, and several properties of iron-oxide-based catalysts for the dehydrogenation of ethylbenzene in the presence of CO_2.

DETERMINATION OF THE ENERGY REQUIRED FOR SEPARATION

The equilibrium yield of styrene is increased by using CO_2 instead of steam.[1] In the commercial processes, a large amount of energy is required for separation of the mixture of ethylbenzene and styrene, because boiling points are very near (ethylbenzene: 136 °C; styrene: 145 °C.) In this section, the relationship between the yield of styrene and the energy required for separation by distillation is investigated. The model distillation system for determining the energy required for separation is shown in Fig. 1. The flow rates, reflux ratio, reboiling ratio and temperature were calcu-

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Table 1 Energy required for producing styrene[a]

		Commercial process 10^8 cal/styrene-t	New process 10^8 cal/styrene-t
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

[a] This table is reproduced from Ref. 1(b).

lated using a personal computer using the software 'EQUATRAN'. The results are presented in Fig. 2, and they clearly indicate that it is possible to save energy for separation by the new process using CO_2.

EXPERIMENTAL

Iron-oxide-based catalysts were prepared by an impregnation method or a coprecipitation method. In the case of catalysts prepared by an impregnation method, Al_2O_3 (JRC-ALO4, 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 activated carbon (AC; Shirasagi, Takeda Ltd, 0.18–0.30 mm) were used as supports. After a slurry composed of an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ and the support was stirred for 2 h, the slurry was vacuum dried at 373 K. The coprecipitation method was carried out as follows: both the 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 then dried at 393 K. The precursors prepared by both methods, except for Fe–AC, were calcined in air at 1023 K for 5 h. Then they were pelletized at 200 kg

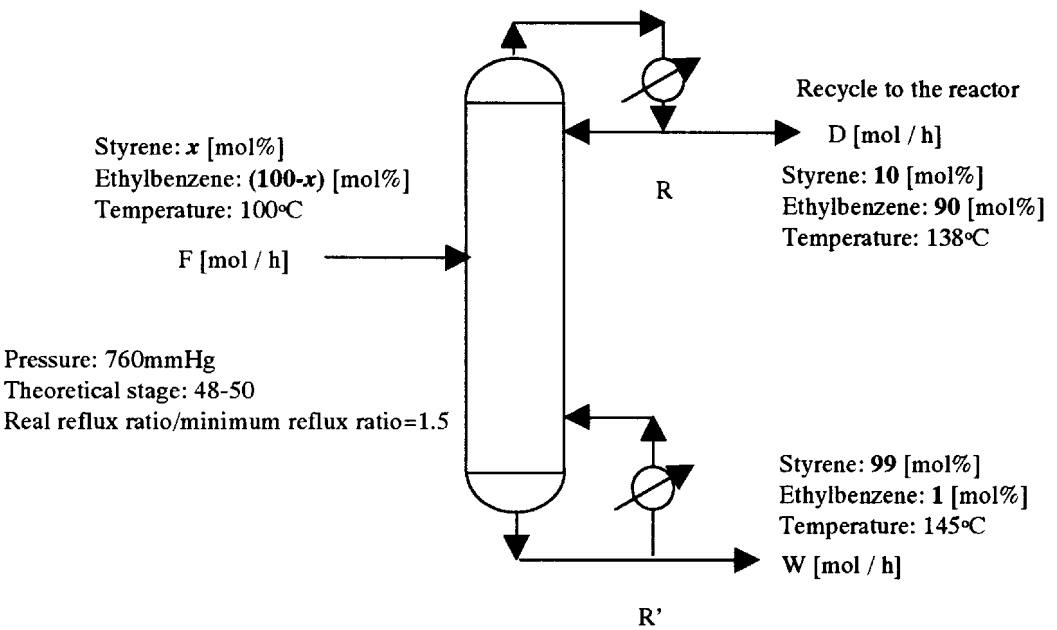

Figure 1 The model distillation system to determine the energy required for separation.

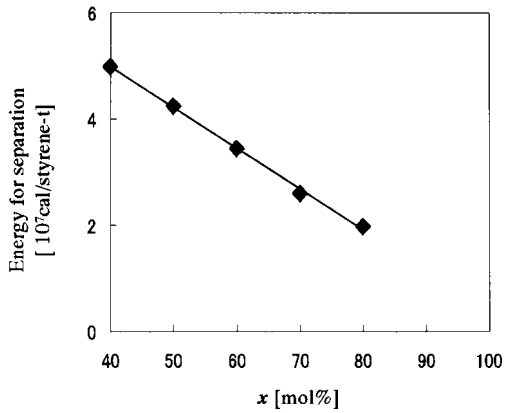

Figure 2 Energy required for separation.

m^{-2}, and crushed and sieved to 0.18–0.3 mm. The Fe–AC catalyst was used without further treatment after vacuum drying.

The dehydrogenation of ethylbenzene was carried out using a quartz tube reactor. Before the reaction, the catalyst (1.4 g or 0.8 g) was treated with CO_2 or He as a co-feed gas for 15 min at 823 K. Then, the dehydrogenation was performed at 823 K under atmospheric pressure. The molar ratio of the co-feed gas to ethylbenzene was selected to be 11, because to typical ratio of steam to ethylbenzene in a commercial process is 7 to 12. The flow rate of ethylbenzene was fixed at 0.50 mmol min^{-1}. The products were liquified by a cold trap at 268 K and analyzed using flame ionization detector gas chromatograph. The gaseous products passing through the trap were analyzed using an on-line thermal conductivity detector gas chromatograph.

Catalysts were analyzed with power X-ray diffraction (XRD) using a Rigaku RAD-3A X-ray diffractometer with Cu Kα radiation.

RESULTS AND DISCUSSION

Table 2 shows the catalytic performances of various iron-oxide-based catalysts for the dehydrogenation of ethylbenzene in the presence of CO_2 at a time on stream of 6 h. Toluene and benzene were detected as by-products in liquid products, whereas only CH_4 was detected as a by-product in gaseous products.

Entries 1 to 3 in Table 2 clearly indicate that alumina is much better as a support than SiO_2 and AC. Entries 3 to 5 suggest that the coprecipitation method could provide a highly active Fe_2O_3–Al_2O_3 catalyst. Since neither Fe_2O_3 alone nor Al_2O_3 alone were highly active, as shown in Table 2, and some special interaction between iron oxide and alumina might be necessary for a highly active catalyst. The XRD pattern before the reaction gave no significant peaks corresponding to a composite oxide between iron and aluminum, such as $FeAlO_3$ or $FeAl_2O_4$; only broad peaks assigned to γ-Al_2O_3 were present These findings suggest that the active sites composed of iron and aluminum might be amorphous and/or highly dispersed. Since the XRD pattern of the catalyst was hardly changed during

Table 2 Yields and selectivities of styrene by the dehydrogenation of ethylbenzene over iron-oxide-based catalyst in the presence of CO_2

No.	Catalyst	Yield (%)	Selectivity (%)	Method of preparation
1	Fe_2O_3–SiO_2 (10 wt%–90 wt%)	6.9	89.7	Impregnation
2	Fe_2O_3–AC[d] (10 wt%–90 wt%)	8.6	86.3	Impregnation
3	Fe_2O_3–Al_2O_3[a] (10 wt%–90 wt%)	20.3	95.7	Impregnation
4	Fe_2O_3–Al_2O_3[b] (10 wt%–90 wt%)	24.4	96.2	Impregnation
5	Fe_2O_3–Al_2O_3 (10 wt%–90 wt%)	33.2	95.7	Coprecipitation
6	α-Fe_2O_3	3.2[c]	83.1[c]	Reagent
7	Al_2O_3	9.0	88.4	JRC-ALO4
8	Al_2O_3	6.8	85.8	Precipitation
9	None	2.0	78.3	—

The yield and selectivity were observed at 6 h.
[a] The Al_2O_3 is JRC-ALO4 (the reference catalyst provided by the Catalysis Society of Japan).
[b] The Al_2O_3 is prepared from $Al(NO_3)_3$ and Na_2CO_3 by the precipitation method.
[c] 2.17 h.
[d] AC: activated carbon.

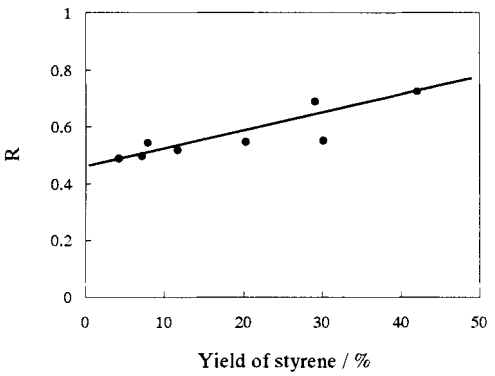

Figure 3 Relationship between R and the yield of styrene. R = CODH/(yield of styrene); reaction temperature: 823 K; pressure: 1 atm; CO_2/ethylbenzene: 11.

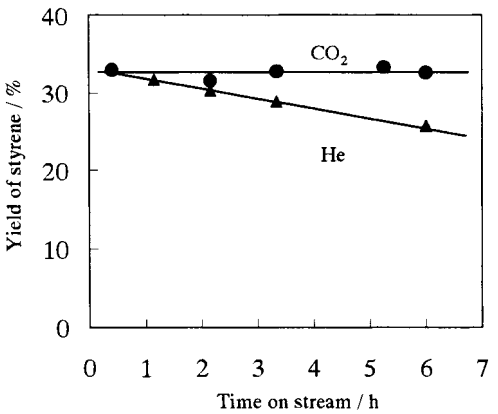

Figure 4 Effect of co-feed gases on the deactivation of an Fe_2O_3–Al_2O_3 catalyst Catalyst weight: 1.4 g (CO_2), 0.8 g (He); reaction temperature: 823 K.

the reaction for 6.5 h, the bulk structure of the catalyst might be unchanged during the reaction.

There are two possible reaction pathways for the dehydrogenation in the presence of CO_2, as shown in Scheme 1: a one-step pathway, shown in Eqn [1], and a two-step pathway *via* Eqn [2] followed by Eqn [3]:

$$\mathrm{Ph{-}CH_2CH_3 + CO_2 \rightarrow Ph{-}CH{=}CH_2 + CO + H_2O} \quad [1]$$

$$\mathrm{Ph{-}CH_2CH_3 \rightarrow Ph{-}CH{=}CH_2 + H_2} \quad [2]$$

$$\mathrm{H_2 + CO_2 \rightarrow CO + H_2O} \quad [3]$$

Scheme 1.

In order to elucidate the pathway of the dehydrogenation over Fe_2O_3–Al_2O_3 catalysts, the yield of CO based on ethylbenzene supplied only by the dehydrogenation, (hereinafter termed CODH) as a function of styrene yield was examined by changing W/F at a CO_2/ethylbenzene ratio of 11. CO was also produced by the CO_2 decomposition of ethylbenzene, as shown in Scheme 2:

$$\mathrm{Ph{-}CH_2CH_3 + CO_2 \rightarrow Ph{-}CH_3 + 2CO + H_2} \quad [4]$$

$$\mathrm{Ph{-}CH_2CH_3 + 2CO_2 \rightarrow Ph{-}H + 4CO + 2H_2} \quad [5]$$

Scheme 2.

Methane was detected as a by-product, which was produced by hydrocracking as shown in Scheme 3:

$$\mathrm{Ph{-}CH_2CH_3 + H_2 \rightarrow Ph{-}CH_3 + CH_4} \quad [6]$$

$$\mathrm{Ph{-}CH_2CH_3 + 2H_2 \rightarrow Ph{-}H + 2CH_4} \quad [7]$$

Scheme 3.

The yield of CO produced only by the CO_2 decomposition, (hereinafter termed CODC) was calculated by the following equation:

$$\mathrm{CODC} = [4 \times (\text{yield of benzene}) + 2 \times (\text{yield of toluene}) - 2 \times (\text{yield of methane})]$$

Accordingly, CODH was determined by subtracting CODC from the total yield of CO. Then, R was defined as follows:

$$R = \mathrm{CODH}/(\text{yield of styrene})$$

When the dehydrogenation proceeds only *via* the one-step pathway, R should be unity at any yield of styrene. On the other hand, R should increase from zero with increasing yield of styrene for a two-step dehydrogenation. Figure 3 shows the relationship between R and the yield of styrene. R was found to increase almost linearly with increasing yield of styrene from 0.4 at a styrene yield of zero. This finding suggests that the dehydrogenation of ethylbenzene over the Fe_2O_3–Al_2O_3 catalyst in the presence of CO_2 should take place simultaneously *via* both one-step and two-step pathways. In the case of the one-step pathway, the intermediate absorbed on the catalyst would directly react with CO_2 to produce styrene, CO and H_2O. On the other hand, in the case of the two-step pathway, the intermediate would be dehydrogenated into styrene and molecular hydrogen, and then the hydrogen produced reacts with CO_2 to produce CO and H_2O by a reverse water-gas shift reaction. A total of 45% styrene might be produced by the one-step pathway and 55% styrene by the two-step

pathway under the reaction conditions shown in Fig. 3.

Figure 4 shows the activity of the Fe_2O_3–Al_2O_3 (10 wt%–90 wt%) catalyst in the presence of CO_2 or of helium as a function of time on stream. Since the initial yield of styrene in the presence of helium (48%) was about 45% higher than that in the presence of CO_2, the weight of the catalyst used for the dehydrogenation in the presence of helium was reduced in order to obtain the same initial yield of styrene as that for the dehydrogenation in the presence of CO_2. The catalyst was rapidly deactivated during the dehydrogenation in the presence of helium, whereas the deactivation of the catalyst was hardly observed during the dehydrogenation in the presence of CO_2. There might be two possible causes for the deactivation of the catalyst during the dehydrogenation. One is the reduction of active sites in the catalyst with hydrogen or CO produced during the dehydrogenation. The other one is the deposition of coke on the catalyst. The role of CO_2 in suppressing the catalyst deactivation is now under investigation.

CONCLUSIONS

The conclusions are as follows.

(1) It is possible to save energy in the separation of ethylbenzene and styrene by a new process using CO_2.
(2) The Fe_2O_3–Al_2O_3 catalyst prepared by a coprecipitation method was effective for the dehydrogenation in the presence of CO_2.
(3) The dehydrogenation of ethylbenzene over an Fe_2O_3–Al_2O_3 catalyst in the presence of CO_2 was considered to proceed *via* both one-step and two-step pathways.
(4) CO_2 suppressed the deactivation of the catalyst during the dehydrogenation.

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