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

Naoki Mimura and Masahiro Saito

Global Warming Control Department, National Institute for Resources and Environment (NIRE), 16-3 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

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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 steam used in commercial processes. The dehydrogenation of ethylbenzene over the catalyst in the presence of CO_2 was considered to proceed both via a one-step pathway and via a two-step pathway. CO_2 was found to suppress the deactivation of the catalyst during the dehydrogenation of ethylbenzene.

Keywords: ethylbenzene, styrene, dehydrogenation, carbon dioxide, Fe_2O_3/Al_2O_3 catalyst

1. 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 873–973 K. It has been pointed out that the present commercial processes consume a large amount of energy because all the latent heat of condensation of steam is not recovered at a liquid–gas separator following a 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. The authors reported that the energies required for producing styrene by a present commercial process using steam and by a new process using CO_2 were estimated to be 1.5×10^9 and 1.9×10^8 cal/t-styrene, respectively [1]. 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 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 [2–4], and the authors also reported that iron-oxide-based catalysts were effective for the new dehydrogenation [1].

In the present paper, we report the effects of supports for iron-oxide-based catalysts on their performance, the effectiveness of a coprecipitation method for preparing iron–aluminum oxide catalysts, the pathway of the dehydrogenation of ethylbenzene over the catalyst and the suppression of the catalyst deactivation by the addition of CO_2.

2. Experimental

Iron-oxide-based catalysts were prepared by an impregnation method or a coprecipitation method. In the case of preparing the catalysts by an impregnation method, Al_2O_3 (JRC-ALO4, or prepared by 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 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 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 then dried at 393 K. The precursors prepared by both methods, except Fe/AC, were calcined in air at 1023 K for 5 h. Then, they were pelletized at 200 kg/m^2, and then 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 or 0.8 g) was treated with CO_2 or He as the 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 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 268 K and analyzed by a FID gas chromatograph. The gaseous products passing through the trap were analyzed by an on-line TCD gas chromatograph.

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

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3. Results and discussion

Table 1 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.

Columns 1–3 in table 1 clearly indicate that alumina is much better as a support than SiO_2 and AC. Columns 3–5 suggest that the coprecipitation method could provide a highly active Fe_2O_3/Al_2O_3 catalyst. Since Fe_2O_3 alone or Al_2O_3 alone was not highly active, as shown in table 1, some special interaction between iron oxide and alumina might be necessary for a highly active catalyst. Figure 1 shows XRD patterns of the Fe_2O_3/Al_2O_3 catalyst shown in column 5 before and after the dehydrogenation. The XRD pattern before the reaction gave no significant peaks corresponding to a composite oxide between iron and aluminum such as $FeAlO_3$ or $FeAl_2O_4$, but only broad peaks assigned to γ-Al_2O_3 as indicated by asterisks in figure 1. 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 the reaction for 6.5 h, the bulk structure of the catalyst might be unchanged during the reaction.

Figure 2 shows the effect of the ratio of Fe_2O_3 to Al_2O_3 on its activities at 0.42 and 6 h. Although the catalysts containing more than 15 wt% of Fe_2O_3 were more active at 0.42 h than the catalysts containing less than 15 wt% of Fe_2O_3, the catalysts with higher content of Fe_2O_3 were considerably deactivated after 6 h. On the other hand, the catalyst containing 10 wt% of Fe_2O_3 maintained its initial activity for 6 h and exhibited the highest activity among the

Table 1
The performances of various iron-oxide-based catalysts for the dehydrogenation of ethylbenzene in the presence of carbon dioxide.[a]

No.	Catalyst	Method of preparation	Yield (%) Styrene	Benzene	Toluene	Selectivity to styrene (%)
1	Fe_2O_3/SiO_2 (10/90 wt%)	Impregnation	6.9	0.6	0.2	89.7
2	Fe_2O_3/AC (10/90 wt%)	Impregnation	8.6	0.8	0.5	86.3
3	Fe_2O_3/Al_2O_3[b] (10/90 wt%)	Impregnation	20.3	0.6	0.3	95.7
4	Fe_2O_3/Al_2O_3[c] (10/90 wt%)	Impregnation	24.4	0.6	0.4	96.2
5	Fe_2O_3/Al_2O_3 (10/90 wt%)	Coprecipitation	33.2	0.9	0.6	95.7
6	α-Fe_2O_3	Reagent	3.1[d]	0.5[d]	0.1[d]	83.1[d]
7	Al_2O_3	JRC-ALO4	9.0	0.8	0.4	88.4
8	Al_2O_3	Precipitation	6.8	0.8	0.3	85.8
9	None	–	2.0	0.4	0.1	78.3

[a] The reaction conditions were as follows: temperature = 823 K, flow rate of ethylbenzene = 0.5 mmol/min, CO_2/ethylbenzene = 11, and the yield and selectivity was observed at 6 h.
[b] The Al_2O_3 is JRC-ALO4 (the reference catalyst provided by Catalysis Society of Japan).
[c] The Al_2O_3 is prepared from $Al(NO_3)_3$ and Na_2CO_3 by precipitation method.
[d] Observed at 2.17 h.

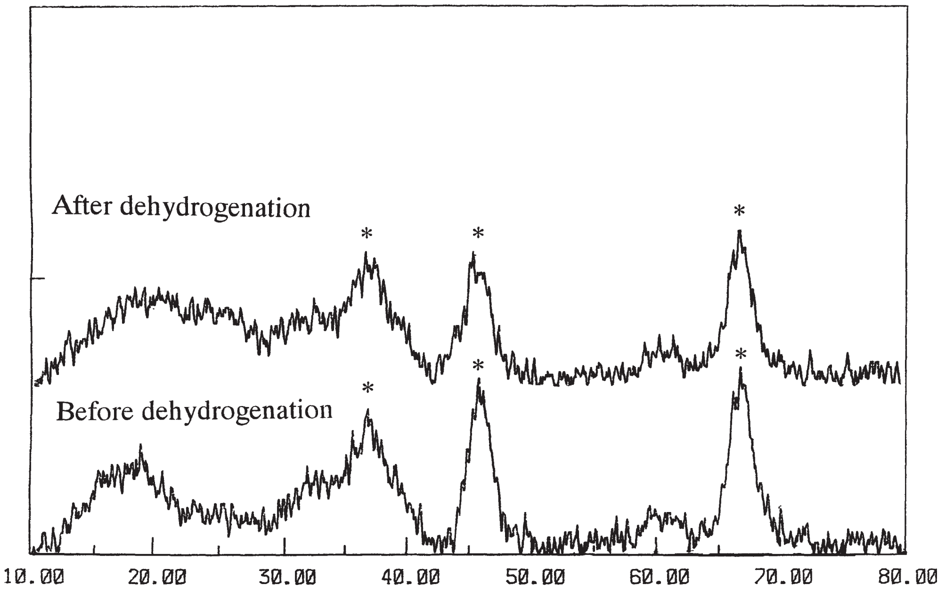


Figure 1. XRD patterns of Fe_2O_3/Al_2O_3 catalyst before and after dehydrogenation. (∗) γ-alumina.

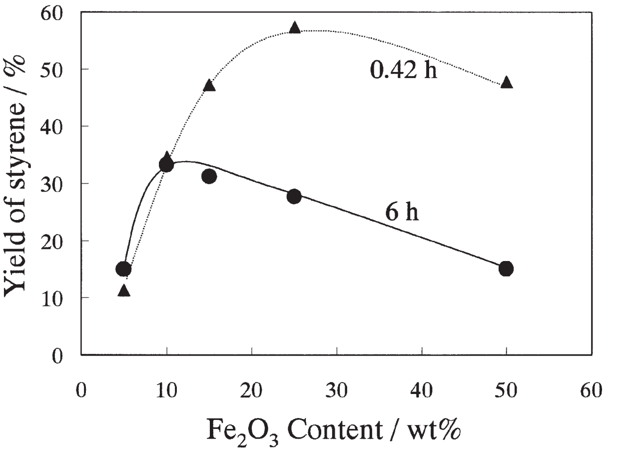


Figure 2. Effect of the weight ratio of Fe_2O_3 to Al_2O_3 in the catalyst on its activity. The yields of styrene were measured at 0.42 h (▲) and 6 h (●).

catalysts tested. This catalyst might be suitable for long-term operation.

There are two possible reaction pathways for the dehydrogenation in the presence of CO_2, as shown in equations (1)–(3), where the one-step pathway is shown in equation (1) and the two-step pathway is via equation (2) followed by equation (3):

$$\text{Ph–CH}_2\text{CH}_3 + CO_2 \rightarrow \text{Ph–CH=CH}_2 + CO + H_2O \quad (1)$$

$$\text{Ph–CH}_2\text{CH}_3 \rightarrow \text{Ph–CH=CH}_2 + H_2 \quad (2)$$

$$H_2 + CO_2 \rightarrow CO + H_2O \quad (3)$$

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, which hereinafter is represented by 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 equations (4) and (5):

$$\text{Ph–CH}_2\text{CH}_3 + CO_2 \rightarrow \text{Ph–CH}_3 + 2CO + H_2 \quad (4)$$

$$\text{Ph–CH}_2\text{CH}_3 + 2CO_2 \rightarrow \text{Ph–H} + 4CO + 2H_2 \quad (5)$$

Methane was detected as a by-product, which was produced by hydrocracking, as shown in equations (6) and (7):

$$\text{Ph–CH}_2\text{CH}_3 + H_2 \rightarrow \text{Ph–CH}_3 + CH_4 \quad (6)$$

$$\text{Ph–CH}_2\text{CH}_3 + 2H_2 \rightarrow \text{Ph–H} + 2CH_4 \quad (7)$$

The yield of CO produced only by the CO_2 decomposition, which is hereinafter represented by CODC, was calculated by the following equation:

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

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

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

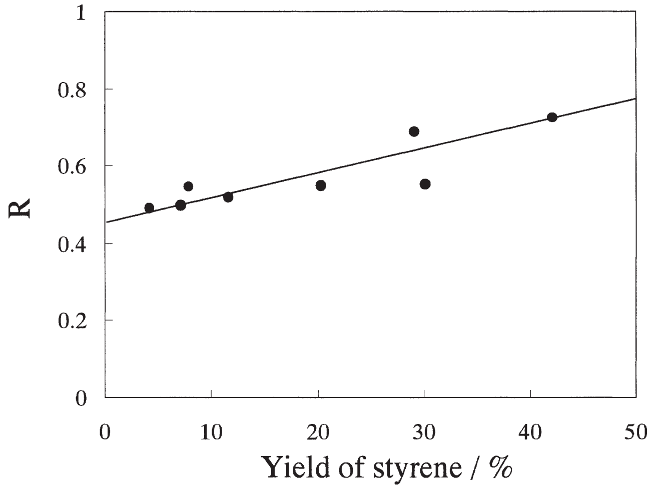
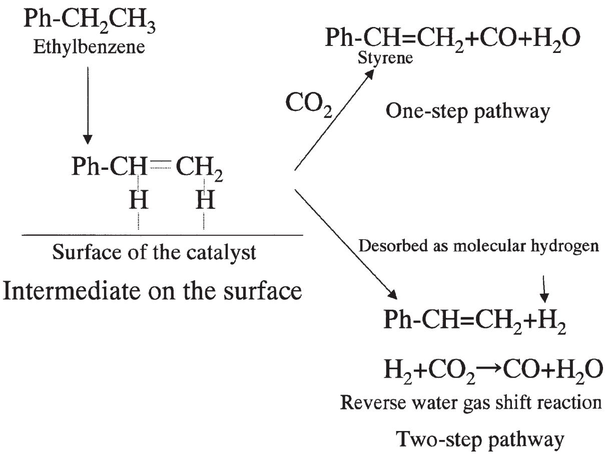


Figure 3. Relationship between R and the yield of styrene. R = CODH/(yield of styrene), reaction temperature = 823 K, pressure = 1 atm, CO_2/ethylbenzene = 11.



Scheme 1.

When the dehydrogenation proceeds only via the one-step pathway, R should be 1 at any yield of styrene. On the other hand, R should increase from zero with increasing yield of styrene for two-step dehydrogenation. Figure 3 shows the relationship between R and the yield of styrene. R was found to increase almost linearly from 0.45 at the styrene yield of zero with increasing the yield of styrene. This finding suggests that the dehydrogenation of ethylbenzene over the Fe_2O_3/Al_2O_3 catalyst in the presence of CO_2 should simultaneously take place both via one-step and two-step pathways, as shown in scheme 1. 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 H_2 molecule, and then the H_2 produced react with CO_2 to produce CO and H_2O by the reverse water gas shift reaction. 45% of styrene might be produced by the one-step pathway and 55% of styrene by the two-step pathway under the reaction conditions shown in figure 3.

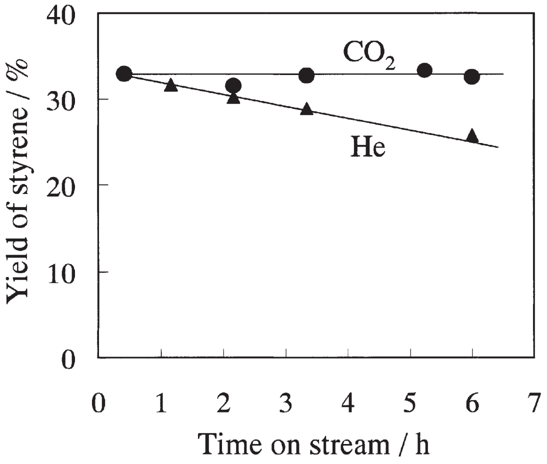


Figure 4. Effect of co-feed gases on the deactivation of a Fe_2O_3/Al_2O_3 catalyst. Catalyst weight = 1.4 g (CO_2), 0.8 g (He); reaction temperature = 823 K.

Figure 4 shows the activity of the Fe_2O_3/Al_2O_3 (10/90 wt%) catalyst in the presence of CO_2 or of He as a function of time on stream. Since the initial yield of styrene in the presence of He (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 He 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 He, 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 H_2 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.

4. Conclusions

1. A Fe_2O_3/Al_2O_3 (10/90 wt%) catalyst prepared by a co-precipitation method was effective for the dehydrogenation in the presence of CO_2.
2. The dehydrogenation of ethylbenzene over an Fe_2O_3/Al_2O_3 catalyst in the presence of CO_2 was considered to proceed both via a one-step pathway and via a two-step pathway.
3. CO_2 suppressed the deactivation of the catalyst during the dehydrogenation.

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