ELSEVIER

Catalysis Today 45 (1998) 61–64

CATALYSIS TODAY

Dehydrogenation of ethylbenzene over iron oxide-based catalyst in the presence of carbon dioxide

N. Mimura[a,*], I. Takahara[a], M. Saito[a], T. Hattori[b], K. Ohkuma[c], M. Ando[d]

[a] *National Institute for Resources and Environment (NIRE), 16-3 Onogawa, Tsukuba-shi, Ibaraki 305, Japan*
[b] *Department of Applied Chemistry, Nagoya University, Furocho, Chikusa-ku, Nagoya 464-01, Japan*
[c] *Systems Research and Development Institute of Japan, 16-5 Tomihisacho, Shinjuku-ku, Tokyo 162, Japan*
[d] *Japan Fine Ceramics Association, Halifax Onarimon Bldg. 6F, 3-24-10, Nishi-shinbashi, Minato-ku, Tokyo 105, Japan*

Abstract

The energy required for a new process using CO_2 for the dehydrogenation of ethylbenzene to produce styrene was estimated to be much lower than that of the present commercial process using steam. A Fe/Ca/Al oxides catalyst was found to exhibit high performance in the dehydrogenation of ethylbenzene in the presence of CO_2. And the deactivation of the Fe/Ca/Al oxides catalyst was restrained by the action of CO_2.

Keywords: CO_2; Ethylbenzene; Styrene; Iron oxide-based catalyst

1. Introduction

Styrene is one of the most important substances as a raw material of polymers. In Japan, 1.5 million tons of styrene is produced every year. It is commercially produced by the dehydrogenation of ethylbenzene (reaction (2)), which is made from benzene and ethylene (reaction (1)).

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5–C_2H_5 \qquad (1)$$

$$C_6H_5–C_2H_5 \rightarrow C_6H_5–C_2H_3 + H_2 \qquad (2)$$

A large quantity of high temperature steam (steam/ethylbenzene=7–12 mol mol^{-1}) is used in the commercial plant. The important roles of the steam in the dehydrogenation of ethylbenzene are considered as follows:

1. The medium for supplying heat to the endothermic dehydrogenation.
2. Dilution of ethylbenzene to increase equilibrium conversion.
3. Avoiding coke deposition on the catalyst.

It has been pointed out that latent heat of condensation of steam is lost at a separator in a commercial process. Recently, dehydrogenation of ethylbenzene in the presence of carbon dioxide instead of steam has been studied [1,2]. It is considered that carbon dioxide can play above-mentioned three roles.

In this paper, we will also report a result of calculation of energy required to produce styrene in comparison between a present commercial process using excess steam and a new process using carbon dioxide, and some experimental results of the dehydrogenation of ethylbenzene in the presence of CO_2.

---

[*] Corresponding author. Tel.: +81-298-58-8176; fax: +81-298-58-8176; e-mail: mimura@nire.go.jp

0920-5861/98/$ – see front matter
PII: S0920-5861(98)00246-6

2. Experimental

The iron oxide-based catalysts were prepared by a coprecipitation method. In a typical experiment, 1.4 g of catalyst (0.18–0.30 mm) was set in a quartz tube reactor. Ethylbenzene was fed through a vaporizer, and was mixed with CO_2. The dehydrogenation was conducted at 550°C under atmospheric pressure. The product which was cooled to liquid by a trap was analyzed by GC.

3. Results and discussion

3.1. *Thermodynamic consideration of the dehydrogenation of ethylbenzene*

There might be two possible pathways for the dehydrogenation in the presence of CO_2, as shown in Fig. 1. Fig. 2, which shows the effect of temperature on the equilibrium yield of styrene, clearly indicates that the yield of styrene in the presence of CO_2 is much higher than that of the process using steam. On the other hand, at given temperature, the two step pathway appears to be more favorable for the yield of styrene.

3.2. *Estimation of energy required for dehydrogenation processes*

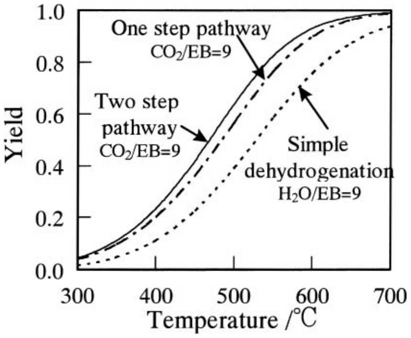
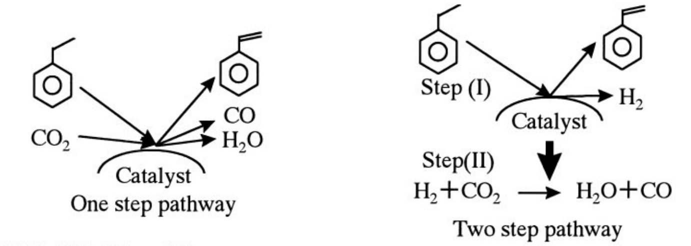


Fig. 2. Equilibrium yield of styrene in the dehydrogenation of ethylbenzene.

Fig. 3 shows model flow sheets for a typical present commercial process and new process using CO_2. Table 1 gives some basic parameters corresponding to the production of styrene via steam process and CO_2 process. In the presence of CO_2 the temperature of the dehydrogenation was assumed to be 50 K lower than that for commercial process on the basis of equilibrium styrene yield shown in Fig. 2. Table 2 summarizes the estimated energies required to produce styrene by dehydrogenation of ethylbenzene in the presence of CO_2 as well as in the presence of steam. The quantity of energy required for the new process using CO_2 is much lower than that for the present process. Energy consumption at the reactor and the separator is represented in Table 3. A large quantity of energy as latent heat of steam condensation is lost at the separator in the present process. Consequently the dehydrogenation in the presence of CO_2 should be an energy-saving process.

3.3. *Development of catalysts*

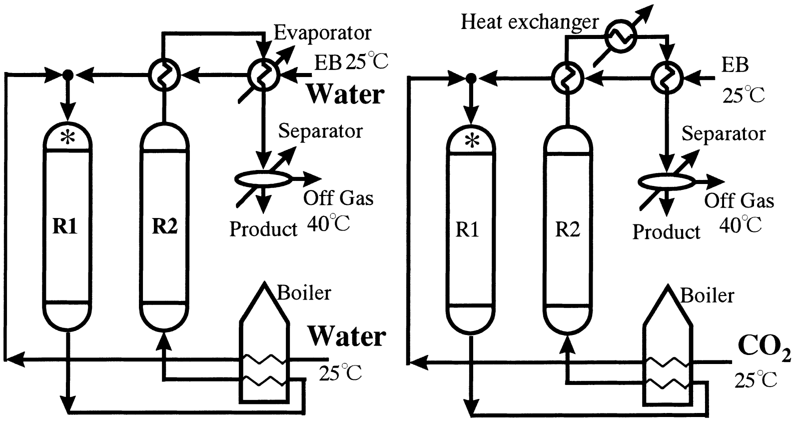
Fig. 4 shows the activities of several kinds of iron oxide-based catalysts. A Fe/Ca/Al oxides catalyst



$$C_6H_5\text{-}CH_2CH_3 + CO_2 \longrightarrow C_6H_5\text{-}CH{=}CH_2 + CO + H_2O$$

$$C_6H_5\text{-}CH_2CH_3 \rightarrow C_6H_5\text{-}CH{=}CH_2 + H_2$$
$$CO_2 + H_2 \rightarrow CO + H_2O$$

Fig. 1. Pathways for the dehydrogenation of ethylbenzene in the presence of CO_2.



Commercial process

New process

Fig. 3. Flow sheets of a present commercial process and a new process.

exhibited the best performance among the catalysts tested. Fe/Ca/Al and Fe/Al oxide catalysts were highly active, whereas Fe/Ca and Ca/Al oxide catalysts were extremely low in activity. The selectivities of Fe/Al oxides and Fe/Ca/Al oxide catalysts were almost the same (97% at 5.25 h), and the main byproducts were benzene and toluene. Therefore the addition of an optimum amount of CaO to Fe/Al based catalyst could suppress the deactivation of the catalyst during long term reaction. Further experiments are under achievement to elucidate precisely the role of CaO.

Fig. 5 shows effects of feed gas on activities and selectivities of the Fe/Ca/Al oxides catalyst. The highest initial activity was exhibited in the presence of helium. However, the activity decreased rapidly. Although the initial yield in the presence of CO_2 was lower than the yield in the presence of helium, the deactivation rate of the catalyst was slower than that under helium. On the other hand, the activity under water and helium was very low. The selectivities of the catalyst in the presence of He or CO_2 were almost the same, however the selectivity in the presence of He and H_2O was much lower than under He or CO_2. In the light of this result, CO_2 prevents deactivation of the catalyst. In addition, compared with steam, CO_2 led to higher activity and selectivity.

Table 1
Basic parameters for the model processes

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

[a] Temperature at the top of R1, which is indicated by * in Fig. 3.

[b] The pressure in commercial plants are about 0.5–0.8 atm.

Table 2
Energy required for producing styrene

		Commercial process (10^8 cal/*t*-styrene)	New process (10^8 cal/*t*-styrene)
Input	Boiler	17.8	12.2
(1)	Evaporator	2.2	–
Output	Combustion of off gas	5.0	5.9
(2)	Surplus energy	–	4.4
Energy required	(1)−(2)	15.0	1.9 (6.3[a])

[a] Without the surplus energy recovered by heat exchanger (cf. Fig. 3).

Table 3
Energy consumption at the reactor and the separator

	Commercial process (10^8 cal/*t*-styrene)	New process (10^8 cal/*t*-styrene)
Consumption at the reactor	2.9	3.7
Energy lost at the separator	15	3.4

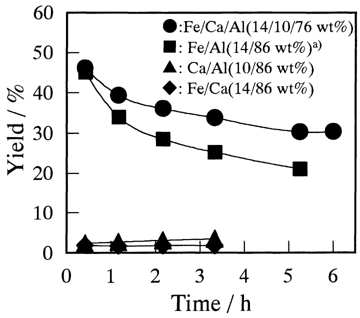


Fig. 4. Activities of Fe oxide-based catalyst. Feed gas: CO_2/EB=11, (a) catalyst weight=1.0 g.

4. Conclusion

The energies required for the present commercial process using steam and for the new process using CO_2 were estimated to be 1.5×10^9 cal/*t*-styrene and 6.3×10^8 cal/*t*-styrene, respectively. Therefore, the new process using CO_2 should be a "energy-saving process".

A Fe/Ca/Al oxides catalyst was found highly active and promising catalyst for the dehydrogenation of ethylbenzene in the presence of CO_2. And the deactivation of the Fe/Ca/Al oxides catalyst was restrained by the action of CO_2.

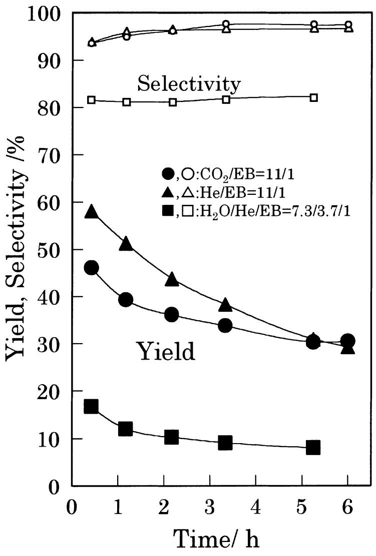


Fig. 5. Effects of feed gas on activities of the Fe/Ca/Al oxides catalyst.

References

[1] M. Sugino, H. Shimada, T. Turuda, H. Miura, N. Ikenaga, T. Suzuki, Appl. Catal. A 121 (1995) 125.
[2] S. Sato, M. Ohhara, T. Sodesawa, F. Nozaki, Appl. Catal. 37 (1988) 207.