Dehydrogenation of ethylbenzene to styrene in the presence of CO_2 over calcined hydrotalcite-like compounds as catalysts

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Calcined hydrotalcite-like compounds were effective catalysts for the dehydrogenation of ethylbenzene in the presence of CO_2 as an oxidant. X-ray diffraction patterns suggested that the catalyst components are distributed uniformly. The activity (areal rate) of Fe(1)/Al(2)/Zn(6) oxide catalyst (molar ratios in parentheses) was the highest among the catalysts tested.

KEY WORDS: ethylbenzene; styrene; dehydrogenation; hydrotalcite; CO_2

1. Introduction

Styrene is an important starting compound for the synthesis of many polymers. About 3 million tons of styrene is produced annually in Japan. Styrene is commercially produced by the Fe–K-based catalytic dehydrogenation of ethylbenzene in the presence of a large quantity of steam at 873–973 K. In the present commercial process, a large amount of latent heat from the condensation of steam is dissipated at a liquid-gas separator. The steam plays three important roles in the dehydrogenation: (1) it reduces the partial pressure of ethylbenzene, increasing the equilibrium yield of styrene; (2) it prevents coke deposition; and (3) it ensures that the active species in the catalyst remains a weak oxidant. Recently, as a substitute for steam, CO_2 gas has received much attention as a co-feed gas for the dehydrogenation of ethylbenzene [1–3]. CO_2 is as effective as steam in reducing the partial pressure of ethylbenzene, preventing coke deposition, and ensuring that the catalyst remains a weak oxidant. We have estimated that the energies required for the steam and CO_2 processes are about 1.5×10^9 and 1.9×10^8 cal per ton of styrene, respectively [1,4]. Thus dehydrogenation using CO_2 could be an energy-saving process.

The Fe–K-based catalysts used for the present commercial dehydrogenation process are not effective for the dehydrogenation of ethylbenzene in the presence of CO_2. Thus a high-performance catalyst is required. Several research groups have reported high-performance catalysts for the dehydrogenation of ethylbenzene using CO_2 as a co-feed gas [2,3,5–9], and we have prepared Fe_2O_3/Al_2O_3-based catalysts by a coprecipitation method [1,4,10]. More work, however, is needed to develop new methods of preparation for control of active species and to develop catalysts with improved activity and long-term stability.

Recently, layered materials have been used as precursors of metal oxide catalysts for various reactions. Calcined layered materials give highly dispersed mixed metal oxides with large surface areas, uniform particle sizes, and pronounced basic properties [11,12]. Thus, calcined layered materials could be useful precursors of metal oxide catalysts for the catalytic dehydrogenation of ethylbenzene. However, so far there have been no reports describing the use of calcined layered materials as catalysts for the dehydrogenation of ethylbenzene in the presence of CO_2.

In this report, we describe the preparation of iron-based oxide catalysts from precursor hydrotalcite-like compounds. These compounds are layered materials with the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^+[A^{n-}]_{x/n}\cdot nH_2O$, where M is a metal, A is an anion, usually carbonate in natural minerals, and $0.25 \leqslant x \leqslant 0.33$. We report herein the catalytic performance of calcined hydrotalcite-like compounds for the dehydrogenation of ethylbenzene in the presence of CO_2 as oxidant, and the effect of adding a promoting element to the catalysts.

2. Experimental

2.1. Catalyst preparation

Hydrotalcite-like compounds were prepared by the precipitation method. Solution A was prepared by mixing solutions of metal nitrates (200 ml) in the desired molar ratios. Solution B (200 ml) was prepared by dissolving 24 g (0.6 mol) of sodium hydroxide and 20 g (0.19 mol) of sodium carbonate in 200 ml of deionized water. Under vigorous stirring, solution B was added slowly to solution A until the pH was 10–11. The precipitates were aged at 343 K for 18 h in a thermostatic bath. The resulting product was filtered, washed thoroughly with deionized water until the

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Table 1
Activities of various calcined hydrotalcite-like compounds as catalysts for dehydrogenation of ethylbenzene to styrene in the presence of CO_2[a]

Catalyst	Components (molar ratio or weight ratio)	Surface area ($m^2\ g^{-1}$)	Conversion of ethylbenzene[b] (%)	Areal rate ($\mu mol\ min^{-1}\ m^{-2}$)	Selectivity[b] (%)		
					Styrene	Benzene	Toluene
1	Fe/Mg (1/2)	24.5	16.4	2.39	97.0	1.2	1.8
2	Fe/Al/Mg (1/2/6)	60.8	27.0	1.59	95.9	2.2	1.9
3	Fe/Al/Mg (2/1/6)	75.9	28.0	1.32	95.4	2.5	2.1
4	Al/Mg (1/2)	116.1	0.81	0.02	71.6	12.3	12.3
5	Fe/Al/Zn/Mg (1/2/1.2/4.8)	91.7	40.8	1.59	94.4	4.4	1.2
6	Fe/Al/Zn/Mg (1/2/2.4/3.6)	80.9	40.0	1.77	94.5	4.2	1.5
7	Fe/Al/Zn (1/2/6)	22.1	25.7	4.15	91.4	6.2	2.3
8	Fe/Zn (1/2)	4.03	4.3	3.81	90.2	7.4	2.4
9[c]	Fe_2O_3/Al_2O_3 (10 wt%/90 wt%)	159.6	34.7	0.78	95.7	2.6	1.7

[a] Reaction conditions: temperature 823 K; flow rate of ethylbenzene 0.5 mmol min^{-1}; CO_2/ethylbenzene = 11/1 (mol/mol); catalyst weight 1.4 g.
[b] Observed at 25 min.
[c] Experimental data (except surface area) are from the literature [10].

filtrate showed no presence of NaOH, which was detected by using a pH meter, and subsequently dried at 373 K for 24 h. After X-ray diffraction measurement of the precursor, the hydrotalcite-like compound was calcined in air at 1023 K for 5 h.

2.2. Reaction

The dehydrogenation of ethylbenzene was carried out in a quartz tube down-flow reactor ($d = 11$ mm). Before the reaction, the catalyst (1.4 g, particle size 180–300 μm) was treated with CO_2 gas for 15 min at 823 K. Dehydrogenation was then performed at 823 K under atmospheric pressure. The molar ratio of CO_2 co-feed gas to ethylbenzene was set at 11, since the ratio of steam to ethylbenzene in the commercial process is typically 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 with a Shimadzu (Kyoto, Japan) GC-14A gas chromatograph equipped with a FID and TCD.

2.3. Analysis

The crystal structures of the catalysts were determined with a Rigaku (Tokyo, Japan) RINT-2000 X-ray powder diffractometer using Cu Kα radiation. The X-ray diffraction patterns were checked against a database (JADE version 5.0). The weight of carbon deposited on the catalyst during the dehydrogenation was measured with a TA Instruments (Delaware, USA) TGA 2950 thermogravimetric analyzer. Before analysis, samples were heated at 473 K for 10 min under a helium flow. The temperature was programmed to increase at a rate of 10 K min^{-1} from room temperature to 1073 K under circulation of dried air.

3. Results and discussion

Table 1 summarizes the results of this study. The data for catalysts 1–4 show that both Fe(III) and Al(III) must be present for high absolute activity per unit weight by increasing surface area; however, the areal rates were decreased by the addition of Al(III). These results are consistent with a previous report on Fe_2O_3/Al_2O_3 catalysts prepared by the coprecipitation method, shown on catalyst 9 in table 1 [10]. The conversion of catalysts 2 and 7 is almost the same, even though the surface area of catalyst 2 is larger than that of catalyst 7. This may reflect that the roles of zinc, which has an intrinsic activity for dehydrogenation, are decreasing surface area and increasing areal rate. The effect of adding Zn(II) to the catalyst may be seen by comparing the performances of catalysts 5–7. Significant synergistic effects (increased surface area) were observed when both Mg(II) and Zn(II) were components of the catalysts. Oxide catalysts containing three elements (Fe, Al and Zn) such as Fe(1)/Al(2)/Zn(6) (molar ratios in parentheses) were found to be highest areal rate for the dehydrogenation of ethylbenzene in the presence of CO_2. Table 2 presents components and contents of the gaseous phase using catalyst 7. It is considered that CO was produced by reverse water–gas shift reaction from formed H_2 and CO_2 as co-feed gas and a product of re-oxygenation of reduced surface species by CO_2, and that methane was produced hydrocracking of ethylbenzene. Ethylene might be formed by decomposition of ethylbenzene. Figure 1 presents the time course of areal rates and selectivities in the dehydrogenation of ethylbenzene in the presence of CO_2 using catalyst 7, which was the most active catalyst tested. The dehydrogenation activity decreased rapidly and the selectivity increased as the reaction proceeded. There are several possible causes for deactivation of the catalyst: (1) by-products of the dehydrogenation (hydrogen, carbon monoxide and so on) re-

Table 2
Components and contents of gaseous phase using catalyst 7[a]

Component	Content (%)
CO_2	97.1
CO	2.3
H_2	0.3
CH_4	0.2
C_2H_4	0.1
C_2H_6	Trace (<0.01)

[a] Reaction conditions are the same as in table 1.

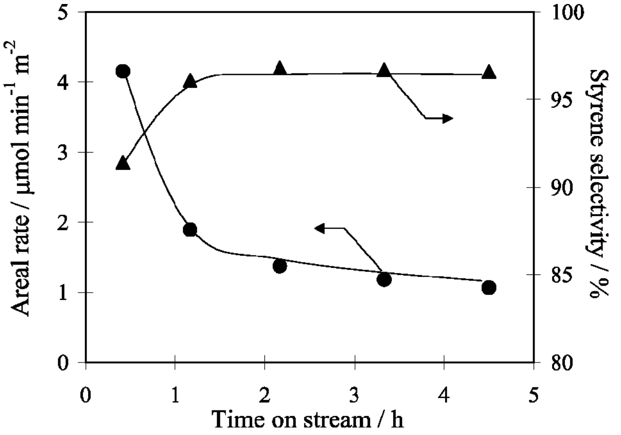

Figure 1. Time course of areal rate and styrene selectivity using catalyst 7.

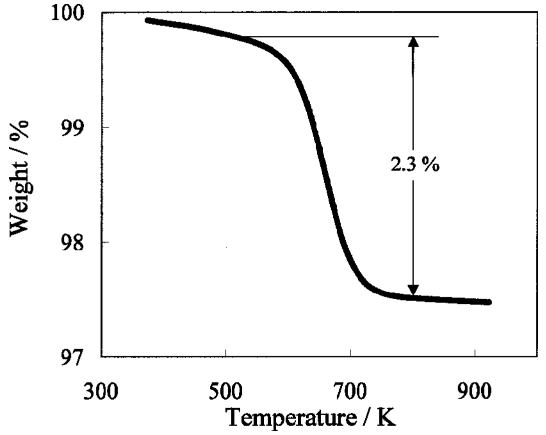

Figure 2. TGA profile of catalyst 7 after dehydrogenation for 5 h. Programmed rate 10 K min^{-1}; feed gas dried air.

duce active species to inactive species that adhere to the catalyst; (2) active species are covered by deposited coke; and (3) active species are gradually poisoned with water generated by the reverse water–gas shift reaction ($H_2 + CO_2 \rightleftharpoons H_2O + CO$). Figure 2 presents the TGA profile of catalyst 7 after dehydrogenation for 5 h. We assumed the weight loss in the TGA profile corresponded to the weight of coke deposited on the catalyst during the dehydrogenation. The weight of deposited coke was 2.3% of the catalyst weight. We consider this result to be evidence of (2). Mimura *et al.* [1] reported that the activity of Fe_2O_3/Al_2O_3-based catalysts for dehydrogenation of ethylbenzene is lower in steam, which may be regarded as evidence of (3). In the present study, we found no clear evidence of (1). We are currently investigating the deactivation of catalysts in an attempt to find evidence of (1).

Figure 3 shows the X-ray diffraction (XRD) patterns of catalyst 7 before calcination, after calcination, and after dehydrogenation. Figure 3(a) is the pattern of the hydrotalcite-like compound before calcination. Figure 3(b) is the pattern after calcination at 1023 K for 5 h. The pattern is broad, indicating that catalyst components are distributed uniformly. The XRD pattern reveals that three phases exist in the oxide: zinc oxide (ZnO) (○), franklinite ($ZnFe_2O_4$) (△), and gahnite ($ZnAl_2O_4$) (□). The XRD pattern in figure 3(c) is similar to that of figure 3(b); thus the bulk crystal structure of the catalyst was not changed in the reaction. We did not find any new phases such as metallic iron, which is a reduced Fe species. We believe that the three phases shown in the XRD patterns (figure 3 (b) and (c)) do not reveal the structure of the active species directly. The active species might be uni-

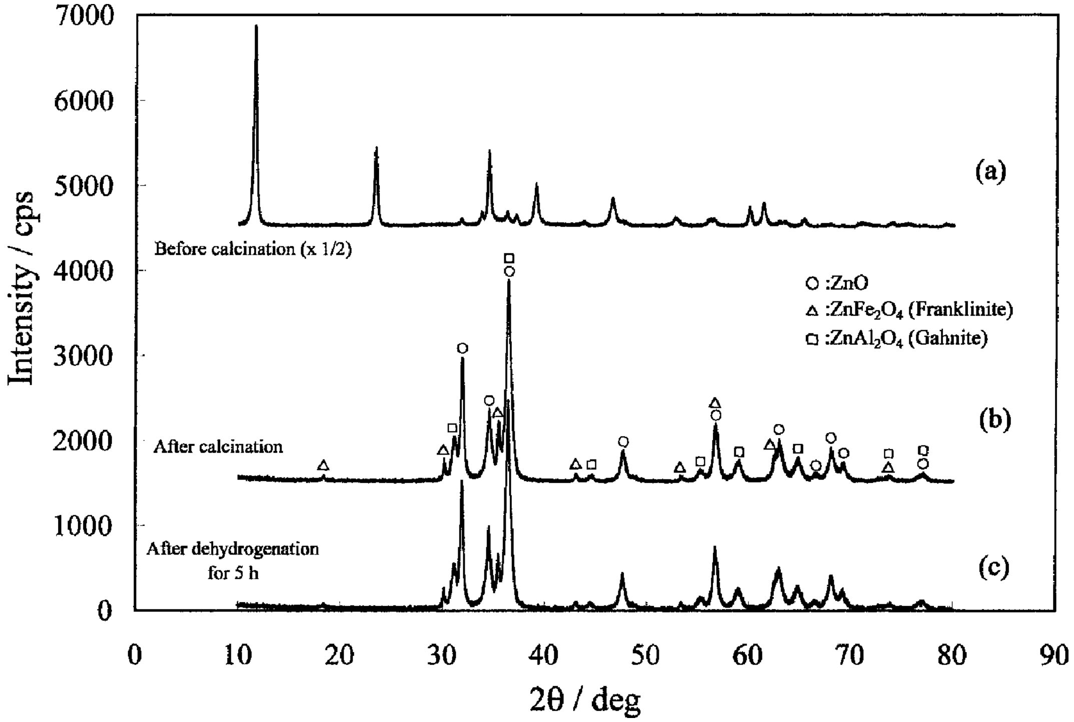

Figure 3. XRD patterns of catalyst 7. (a) Before calcination (hydrotalcite-like compounds), (b) after calcination at 1023 K for 5 h, before dehydrogenation, (c) after dehydrogenation for 5 h.

formly and widely dispersed on the amorphous-like catalyst. We are currently carrying out a detailed investigation of the active species.

4. Conclusions

Calcined hydrotalcite-like compounds were effective catalysts for the dehydrogenation of ethylbenzene in the presence of CO_2 as oxidant. XRD patterns suggested that the catalyst components are distributed uniformly. Oxide catalysts containing three elements (Fe, Al and Zn) were effective catalysts; an areal rate of 4.15 μmol min^{-1} m^{-2} was achieved with Fe(1)/Al(2)/Zn(6) (molar ratios in parentheses). Including both Mg(II) and Zn(II) in the catalysts produced a synergistic effect for increasing surface area and improving absolute activity per unit weight.

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