Ethylbenzene to styrene in the presence of carbon dioxide over zirconia

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ZrO_2 itself was found be active for the dehydrogenation of ethylbenzene, especially in the presence of CO_2, which was aimed to be utilized as an oxidant. This positive effect of CO_2 was highly dependent on the crystalline phases of zirconia. The higher the tetragonal phase contained in ZrO_2, the higher the ethylbenzene conversion and styrene selectivity that were obtained. Highly tetragonal ZrO_2 was more active in oxidative dehydrogenation than monoclinic ZrO_2. The differences of catalytic activities could be ascribed to the differences of the surface area and CO_2 affinity related with surface basicity.

Keywords: ethylbenzene, oxidative dehydrogenation, styrene, carbon dioxide, ZrO_2, tetragonal, monoclinic

1. Introduction

Various reactions have been tried to transform carbon dioxide into valuable products by the help of catalytic methods. Most of them are concentrated on the utilization of carbon dioxide as a carbon source through catalytic reduction processes. However, carbon dioxide can play a role as an oxygen source or an oxidant in several oxidative conversions [1]. Commercially, styrene monomer (SM) is produced mainly by the dehydrogenation of ethylbenzene (EB) by using typical Fe–K–Cr oxide-based catalysts with superheated steam. Carbon dioxide formed as a by-product was known to deactivate the catalyst by the evaporation of potassium in this commercial process [2]. However, there have been some reports that carbon dioxide showed positive effects to promote catalytic activities of EB dehydrogenation over several catalysts [3–6].

Recently, zirconia is intensively studied in catalysis and material science. In catalysis, zirconia is important because it has moderate surface area, bifunctional properties of acid and base, reducing and oxidizing ability, and higher thermal stability. We had found that zirconia has good catalytic activity in the dehydrogenation of EB in the presence of carbon dioxide. Zirconia has also the advantage of high thermal stability, because the dehydrogenation of EB is performed at around 600 °C in the commercial process. Zirconia has three types of crystalline structures namely monoclinic, tetragonal, and cubic phase. The phase of zirconia is changed from monoclinic to tetragonal above 1170 °C and the cubic phase appears above 2370 °C. In 1965, Garvie explained the stability of metastable tetragonal zirconia below 1000 °C with the factor of particle size and surface free energy. Monoclinic zirconia has lower molar free energy than tetragonal zirconia, but tetragonal zirconia has lower surface free energy than monoclinic zirconia. As a result, metastable tetragonal zirconia can be stabilized if the particle size is smaller than the critical size of 300 Å. It is possible to make zirconia with a metastable tetragonal phase by changing the preparation methods, but it is not easy to sustain the tetragonality after high-temperature calcination [7]. There are many reports about the catalytic properties of zirconia, but studies on the effect of zirconia phase on catalytic activity are rare. In this study, we prepared zirconias with different tetragonal fractions and performed the catalytic activity test of the EB dehydrogenation into SM in the presence of CO_2 and characterized them by CO_2 TPD, BET analysis, XRD, and TG-DTA.

2. Experimental

Hydrous zirconia was obtained by the hydrolysis of zirconyl(IV) chloride with an aqueous ammonia solution (25 wt%). The preparation methods are described in figure 1. Filtered precipitates were washed with hot distilled water until they passed the $AgNO_3$ test. Dried hydrous zirconia was calcined at 625 °C for 4 h with 1 °C/min ramp rate.

The EB dehydrogenation to SM was carried out in a conventional fixed-bed reactor made of quartz tube at 600 °C under atmospheric pressure. The preheating zone was kept at 125 °C to prevent the condensation of EB. One gram of catalyst was placed on a fritted quartz disk in the reactor. Total reactant flow rate was 20 ml/min and CO_2/EB mole ratio was 5.4. The liquid products were collected every hour and analyzed by a FID gas chromatograph (Donam Corp., DS6200) equipped with a methyl silicon capillary column (J&W, DB-1).

CO_2 TPD experiments were carried out using a flow system equipped with TCD. Before experiment, the sample

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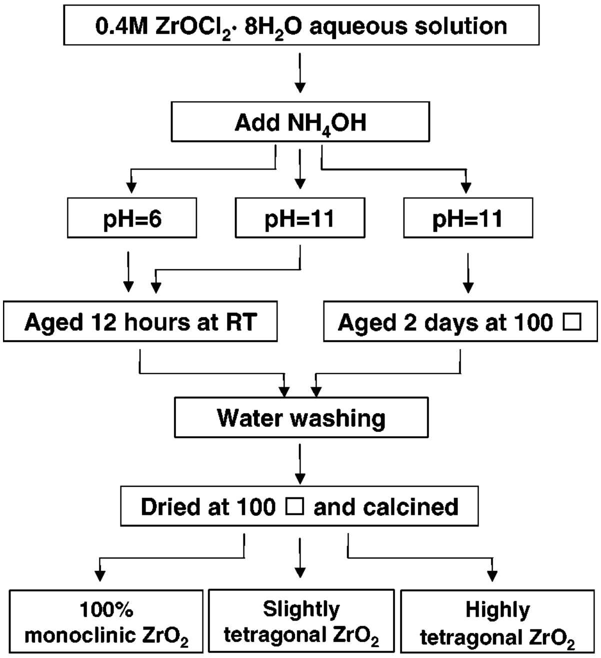

Figure 1. Preparation of zirconias with different tetragonal fraction.

was pretreated at 600 °C for 1 h in He. Then, it was cooled down and CO_2 was adsorbed at RT. The sample was heated again from RT to 600 °C with a heating rate of 5 °C/min under 30 ml/min of He flow.

The BET specific surface areas and pore volumes were measured by nitrogen adsorption at 77 K (Micromeritics, ASAP-2400). XRD patterns were recorded using a Rigaku 2155D6 diffractometer (Ni-filtered Cu Kα, 40 kV, 50 mA). TG-DTA analysis was carried out using a Setaram TGDTA 92-12. Temperature was raised from RT to 850 °C with a heating rate of 10 °C/min under 30 ml/min of air flow.

3. Results and discussion

Our group previously found that zirconia is a promising material for the EB dehydrogenation using carbon dioxide during the study of supported iron oxide catalysts [8]. Commercial zirconia (Strem Co.) showed very good catalytic activity (EB conversion >40%) compared with γ-alumina, silica, and zeolite materials under the same reaction conditions. Most of commercial zirconia has 100% monoclinic phase. Therefore, zirconias with different tetragonal fractions were prepared to study the effect of zirconia phase on EB dehydrogenation. Their structures were identified by XRD analysis. Monoclinic zirconia has a characteristic $(11\bar{1})$ peak at $2\theta = 28.1°$ and a (111) peak at $2\theta = 31.4°$ and tetragonal zirconia has a characteristic (111) peak at $2\theta = 30.1°$. The amount of tetragonal phase was calculated by the following equation (I means intensity of peaks):

$$\%\ \text{tetragonal} = I(111)_{\rm t}/\left[I(111)_{\rm t} + I(111)_{\rm m} + I(11\bar{1})_{\rm m}\right].$$

Table 1

BET specific surface area, pore volume, and average pore size of catalysts.

Property	m-z		21t-z		45t-z	
	Fresh	Used (6 h)	Fresh	Used (6 h)	Fresh	Used (10 h)
BET specific surface area (m^2/g)	23	16	45	28	119	85
Pore volume (cm^3/g)	0.087	0.063	0.110	0.063	0.343	0.164
Average pore diameter (Å)	154.9	157.2	96.8	88.7	114.6	76.9

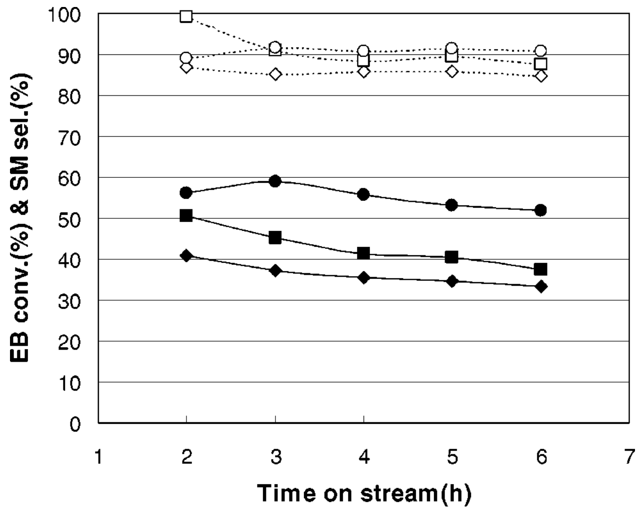

Figure 2. EB conversion and SM selectivity of catalysts on the dehydrogenation of EB. EB conversion: (◆) m-t, (■) 21t-z, and (●) 45t-z; SM selectivity: (◇) m-t, (□) 21t-z, and (○) 45t-z.

XRD result showed that the samples have 100% monoclinic, 21 and 45% of tetragonal structure and they were designated as m-z, 21t-z, and 45t-z, respectively. The more tetragonal the zirconia, the broader the XRD peak and this means the order of crystal size is m-z (480 Å) > 21t-z (220 Å) > 45t-z (170 Å). The crystal size is calculated by the Scherrer equation and an Al_2O_3 single crystal was used for the determination of instrumental line broadening. The small crystal size of 45t-z is the characteristic of hydrothermal synthesis. BET specific surface area, pore volume, and average pore size of fresh and used catalysts are summarized in table 1. The order of BET specific surface area is 45t-z > 21t-z > m-z and the order of pore volume is the same as that of BET specific surface area in the fresh catalyst. These physical properties are well correlated with the difference in particle size. Especially, the surface area of 45t-z is 119 m^2/g after calcination at 625 °C and this is a very high surface area compared with that of commercial zirconia (below 50 m^2/g).

Figure 2 shows EB conversion and SM selectivity for these catalysts in CO_2 atmosphere. The liquid product was

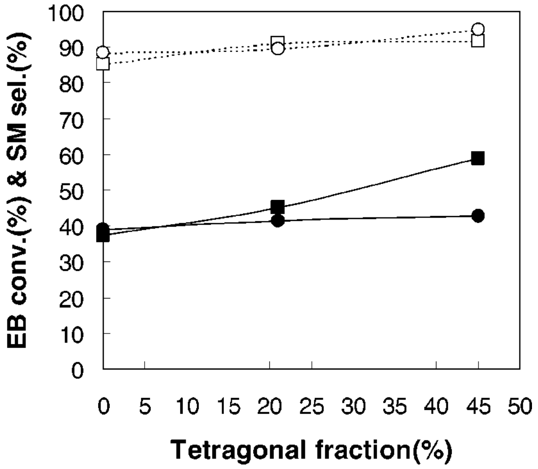

Figure 3. EB conversion and SM selectivity of catalysts with different tetragonal fractions under different carriers. EB conversion: (■) CO_2 and (●) N_2; SM selectivity: (□) CO_2 and (○) N_2.

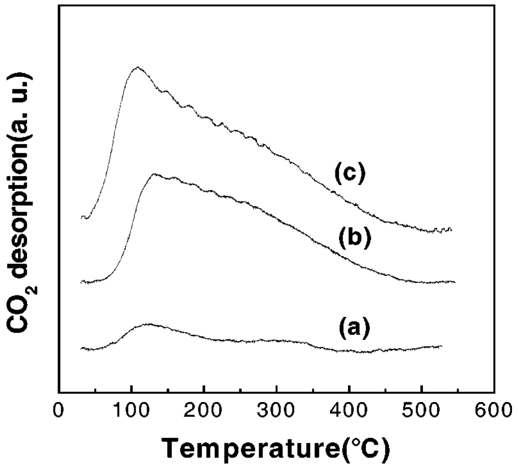

Figure 4. CO_2 TPD spectra of (a) m-z, (b) 21t-z, and (c) 45t-z.

collected after 2 h from the start of reaction to obtain steady-state result. The reaction equations of EB dehydrogenation are as follows:

$$\text{Ph–CH}_2\text{CH}_3 + CO_2 \rightleftharpoons \text{Ph–CH=CH}_2 + H_2O + CO$$

(oxidative dehydrogenation)

$$\text{Ph–CH}_2\text{CH}_3 \rightleftharpoons \text{Ph–CH=CH}_2 + H_2$$

(simple dehydrogenation)

Tetragonal rich zirconia had higher conversion and selectivity than monoclinic zirconia in CO_2 flow. In the case of 45t-z, EB conversion was above 50% and SM selectivity was above 90% after 6 h reaction. This catalytic activity was maintained after 10 h reaction in 45t-z. All zirconias showed a decrease in EB conversion of about 10% and the same SM selectivity from 2 to 6 h. The color of used catalysts was black and this means the formation of coke. Therefore, we can suggest that the deposited coke inhibits EB dehydrogenation but does not affect SM selectivity over zirconia. The catalytic activity is not enhanced by the increment of tetragonal fraction when N_2 is used as a carrier gas (figure 3). Figure 3 shows that more oxidative dehydrogenation occurs over tetragonal rich zirconia. In the case of 45% tetragonal zirconia, the conversion difference is over 10% between CO_2 and N_2 atmosphere. Therefore, we thought the difference in conversion can be attributed to the oxidative dehydrogenation of ethylbenzene by help of oxygen originated from CO_2. We suggest that the activity difference between N_2 and CO_2 carrier can be correlated with the amount of the oxidative EB dehydrogenation.

CO_2 adsorption capacity may influence the EB dehydrogenation activity of catalysts because CO_2 is used as an oxidant. To study the CO_2 adsorption capacity of catalysts, CO_2 TPD was performed and the result was shown in figure 4. Tetragonal rich zirconia adsorbs more CO_2 than monoclinic zirconia. There are two CO_2 desorption peaks in m-z at about 125 and 330 °C. 21t-z and 45t-z show a broad desorption peak between 100 and 400 °C, which means there are more than three desorption peaks. It can be inferred that the lower temperature peak is related with monodentate carbonate species and the higher temperature peaks are related with bidentate and polydentate carbonate formed by the adsorption of CO_2. Rodriguez-Ramos et al. also reported similar CO_2 adsorption behavior over monoclinic and tetragonal zirconia by FT-IR, adsorption microcalorimetry, and CO_2 mass TPD experiment. They concluded that the crystallographic structure is the main factor determining the nature and density of the surface sites involved in the adsorption of CO_2 [9]. Considering the high surface area of tetragonal zirconia, 21t-z and 45t-z have still higher carbon dioxide adsorption capacity than m-z. 45t-z does not show a big difference in CO_2 adsorption capacity than 21t-z but the peak position is shifted to lower temperature, which means there are more easily accessible CO_2 adsorption sites in 45t-z. This CO_2 adsorption behavior is well matched with oxidative EB dehydrogenation activity. The better EB conversion and SM selectivity of tetragonal zirconia can be understood by the difference of CO_2 adsorption capacity and this can be explained by different basicity.

Figure 5 shows XRD patterns of fresh and used catalysts; m-z sustains the same structure, 21t-z shows a decrement of tetragonal fraction from 21 to 15%, and 45t-z sustains the same tetragonal fraction. The behavior of 21t-z is a general tendency because the oxidative dehydrogenation of EB produces water. Hydrothermal treatment at 600 °C would cause the growth of particle size which leads to the phase transition from metastable tetragonal to monoclinic. The crystal size of 45t-z did not change because the peak width is almost the same. It was a surprising and promising result that 45t-z sustains the same tetragonal fraction even after 10 h reaction. This can be explained by athermal kinetics postulated by Garvie [7]. During the heating cycle, domains of the tetragonal structure grow in a matrix of the monoclinic form. Strain at the domain boundaries brings the reaction to a halt after a short time, and a constant ratio of phase is observed at some temperature, T, in the transition

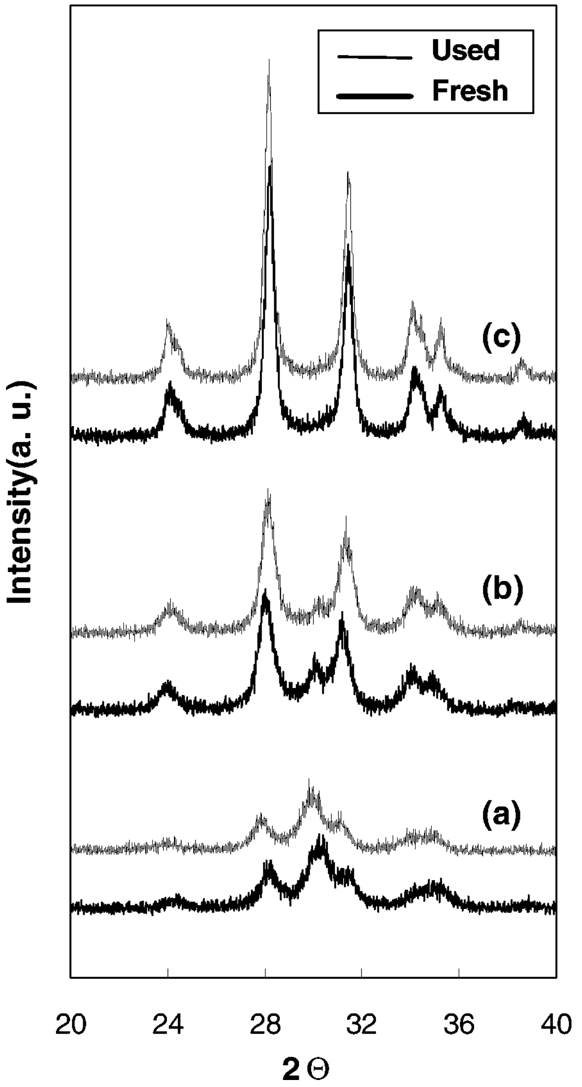

Figure 5. XRD patterns of fresh and used catalysts: (a) m-z, (b) 21t-z, and (c) 45t-z.

Table 2
Deposited coke amount, BET specific surface area, and pore volume of used catalysts corrected with the amount of coke.

Catalyst	Deposited coke (%)	BET specific surface area[a] (m^2/g)	Pore volume[a] (cm^2/g)
Used m-z (6 h)	4.8	17 ($\Delta = 26\%$)	0.066 ($\Delta = 24\%$)
Used 21t-z (6 h)	7.0	30 ($\Delta = 33\%$)	0.068 ($\Delta = 39\%$)
Used 45t-z (10 h)	20.5	107 ($\Delta = 10\%$)	0.206 ($\Delta = 40\%$)

[a] Δ: the difference between fresh and used catalysts.

region. This suggests that 45t-z calcined at 625 °C could form a stable phase at the reaction temperature 600 °C.

The amount of deposited coke calculated from TG-DTA analysis and BET specific surface area and pore volume corrected with the amount of coke are summarized in table 2. Used m-z and 21t-z show a similar decrease of BET specific surface area and pore volume which means m-z has no specific sites for coke formation. Used 45t-z, however, shows different coking behavior. The decrement of pore volume is four-fold as compared with the decrement of BET specific surface area. Table 1 shows a big decrement of average pore diameter for 45t-z. This means that 45t-z has specific sites for coke formation such as large pore and formed coke is more reactive in coke formation than fresh catalyst surface.

Tetragonal zirconia prepared by high-temperature aging showed high structure stability and small decrement of BET specific surface area after reaction at 600 °C. Our group will perform further study to elucidate the reaction mechanism of the oxidative EB dehydrogenation over pure zirconia and modified zirconia system.

4. Conclusion

Zirconias with different tetragonal fractions could be obtained by changing the preparation method. Highly tetragonal zirconia showed better EB conversion and SM selectivity than monoclinic zirconia in dehydrogenation of EB using carbon dioxide as an oxidant. The difference of catalytic activity can be ascribed to the difference of the surface area and CO_2 adsorption capacity related with surface basicity. Highly tetragonal zirconia showed better oxidative dehydrogenation ability, structural stability, and slightly decreased BET specific surface area after reaction at 600 °C for 10 h. Tetragonal zirconia prepared by high-temperature aging showed selective coking behavior compared with RT-aged zirconia. Therefore, highly tetragonal zirconia is more efficient in EB dehydrogenation and there is more possibility of improvement in the modification of tetragonal zirconia.

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