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# $CO_2$ utilization for the formation of styrene from ethylbenzene over zirconia-supported iron oxide catalysts†

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**Dehydrogenation of ethylbenzene with carbon dioxide has been carried out over zirconia-based catalysts. Carbon dioxide in this reaction was found to play a beneficial role as an oxidant for promoting catalytic activity. The addition of a ceria promoter to zirconia improved the catalytic activity significantly, which was attributed to increasing basicity as well as oxygen vancancies. The loading of iron oxide onto only zirconia among zirconia-related materials is effective for improving the activity. Copyright © 2000 John Wiley & Sons, Ltd.**

**Keywords: $CO_2$; oxidant; ethylbenzene; styrene; ceria–zirconia; iron oxide**

## INTRODUCTION

The utilization of carbon dioxide, which is a main contributor to the greenhouse effect, has been of global interest from both fundamental and practical viewpoints.[1] Carbon dioxide might also be utilized as an oxygen source or oxidant because it can be considered a nontraditional or mild oxidant and oxygen transfer agent.[2,3] It has been recently reported that carbon dioxide can be utilized as an oxidant for the oxidative conversions of alkanes, alkenes, and alcohols[4] and that oxygen generated during $CO_2$ reduction can participate in both partial oxidation and dehydrogenation.[4,5]

Catalytic dehydrogenation of ethylbenzene (EB) is important in the manufacture of a styrene monomer (SM), which needs a large excess amount of superheated steam for preventing catalyst deactivation due to coke formation as well as enhancing catalytic activity. We have previously reported that $CO_2$ could also play a role in the EB dehydrogenation over supported iron oxide catalysts as an oxidant with improved coke stability.[6,7] The redox nature of the $Fe^{2+}/Fe^{3+}$ couple[8] and oxygen-deficient $Fe_3O_4$ as an active phase[6,9] in the EB dehydrogenation were expected to promote catalytic activities in the EB dehydrogenation with $CO_2$ through an oxidative pathway. Zirconia is useful for a catalyst support because it has moderate surface area, adjacent acid–base pair sites to show amphoteric properties, oxygen vacancy, and good thermal stability. We have also found that zirconia exhibits good catalytic activity in the EB dehydrogenation in the presence of $CO_2$.[10] Here we report that the modification of zirconia with ceria or loading of $Fe_3O_4$ improves the catalytic activity and stability under $CO_2$ atmosphere for EB dehydrogenation.

## EXPERIMENTAL

$ZrO_2$, Ce–$ZrO_2$ (20 wt% $CeO_2$), and Si–$ZrO_2$ (20 wt% $SiO_2$) supports were purchased from MEL Chemicals. Iron oxide catalysts supported on these supports were prepared by deposition of an aqueous iron(II) sulfate solution onto supports under $N_2$ at 60 °C followed by precipitation at $pH = 10–11$. Prior to the catalytic activity test, all the catalysts were pretreated under helium at 600 °C for 1 h. The catalytic activity test for EB dehydrogenation in the

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presence of $CO_2$ was tested in a fixed bed reactor at 600 °C, and is described elsewhere.[9] The molar ratio of $CO_2$ to EB was 5 and the LHSV of EB was 1 $h^{-1}$. The liquid products were collected every hour and analyzed by gas chromatography (Donam Corp., DS6200) equipped with a flame ionization detector. FT-IR spectroscopic studies were performed in a quartz vacuum cell using self-supported wafers. IR spectra were recorded on a Nicolet (Magna 560) FT-IR spectrophotometer at room temperature, of which the spectral resolution was 4 $cm^{-1}$. Temperature-programmed desorption (TPD) profiles of $CO_2$ on fresh catalysts after adsorption of $CO_2$ at 30 °C were obtained using a gravimetric analyzer (Hiden, IGA-002).

## RESULTS AND DISCUSSION

We have previously shown that for EB dehydrogenation with $CO_2$ an active phase of iron oxide would be a rather reduced iron oxide like $Fe_3O_4$.[6] In this work, the main iron oxide over supported iron oxide catalysts is also considered to be $Fe_3O_4$. Figure 1 presents the catalytic activities of the supported iron oxide catalysts for the EB dehydrogenation with $CO_2$ according to iron oxide loading based on $Fe_3O_4$. These data were collected after 2 h of reaction. For $ZrO_2$- and Ce–$ZrO_2$-supported catalysts, the optimal loadings of $Fe_3O_4$ are 2 wt% and 5 wt%, respectively. It is evident that at more than 2% $Fe_3O_4$, Ce–$ZrO_2$-supported catalysts are more active than $ZrO_2$-supported ones. Table 1 compares the catalytic activities of various catalysts in terms of EB conversion and selectivity to SM. A commercial catalyst ($K_2O$–$Fe_2O_3$), which has high and stable activity under steam flow, exhibits much lower activity in the presence of $CO_2$ compared with other $ZrO_2$-based or supported iron oxide catalysts. Zirconia itself seems to be a good catalytic material for the EB dehydrogenation. Its catalytic activities are much improved by the modification of zirconia with cerium or silicon. The effect of iron oxide loading onto zirconia materials is different according to the promoter added to zirconia. Zirconia with 2 wt% $Fe_3O_4$ shows a little higher activity than zirconia itself, whereas the loading of iron oxide on Ce–$ZrO_2$ gives a negative effect on the activity. On the other hand, the loading of iron oxide on Si–$ZrO_2$ has no effect on the catalytic activity. All the catalysts except the commercial one are deactivated as the reaction proceeds, though the degree of deactivation is much different according to the type of catalyst, suggesting that the deactivation is still proceeding even in the presence of $CO_2$. Among zirconia materials, the deactivation of Si–$ZrO_2$ is much faster than the others. $Fe_3O_4$-loaded catalysts exhibit a more stable activity in terms of EB conversion than their supports except Si–$ZrO_2$ system.

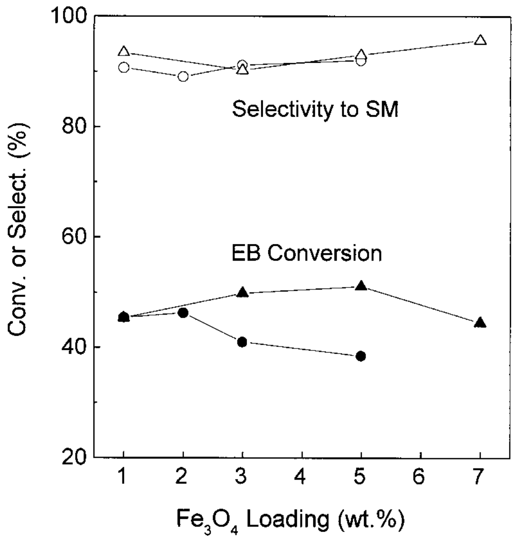

**Figure 1** Effect of iron oxide loading over zirconia (square symbol) and ceria-modified zirconia (triangle symbol) in the dehydrogenation of EB into styrene with $CO_2$. Reaction conditions: *see* Table 1.

Contrary to the activity trend in the presence of

**Table 1** Comparison of catalytic activity in the EB dehydrogenation with $CO_2$ over various catalysts[a]

| | After 2 h | | After 6 h | |
|---|---|---|---|---|
| Catalyst | *X*(EB) (%) | *S*(SM) (%) | *X*(EB) (%) | *S*(SM) (%) |
| $K_2O$–$Fe_2O_3$[b] | 23.5 | 88.0 | 22.2 | 87.1 |
| $ZrO_2$ | 43.7 | 91.7 | 36.0 | 90.6 |
| Ce–$ZrO_2$ | 57.0 | 90.0 | 46.8 | 87.8 |
| Si–$ZrO_2$ | 59.7 | 89.4 | 36.6 | 84.7 |
| $Fe_3O_4$–$ZrO_2$[c] | 46.2 | 89.1 | 40.4 | 87.5 |
| $Fe_3O_4$/Ce–$ZrO_2$[d] | 51.0 | 93.0 | 45.4 | 90.5 |
| $Fe_3O_4$/Si–$ZrO_2$[e] | 58.2 | 93.3 | 37.1 | 91.9 |

[a] Reaction conditions: temp., 600 °C; LHSV, 1 $h^{-1}$, $CO_2$/EB = 5 (molar ratio); designation: EB conversion for *X*(EB) and selectivity to SM for *S*(SM).

[b] Commercial catalyst (Nissan Girdler, G-64 JX).

[c] 2 wt% $Fe_3O_4$.

[d] 5 wt%.

$CO_2$, the catalytic activity was hardly changed by the addition of a ceria promoter to $ZrO_2$ when nitrogen is used as a carrier gas.[11] The $CO_2$ conversion to CO during the EB dehydrogenation increased with the addition of the ceria. Moreover, the addition of a ceria promoter to $ZrO_2$ results in an increase of surface oxygen vacant sites together with basicity. These results indicate that an increase of conversion towards Ce–$ZrO_2$ is attributed to the oxidative dehydrogenation of EB by the help of oxygen originating from $CO_2$. A slight increment of conversion for 2 wt% $Fe_3O_4$–$ZrO_2$ over $ZrO_2$ may be due to the oxygen-deficient $Fe_3O_4$. However, it seems that the formation of $Fe_3O_4$ on Ce–$ZrO_2$ contributes to the decrease of the activity because $Fe_3O_4$ formed on the surface of Ce–$ZrO_2$ masks its active sites such as oxygen vacant sites.

Figure 2 shows the FT-IR spectra of zirconia, ceria–zirconia, and supported $Fe_3O_4$ catalysts according to desorption temperature after $CO_2$ adsorption. Hydroxyl groups on zirconia and ceria–zirconia are divided into a higher frequency part of

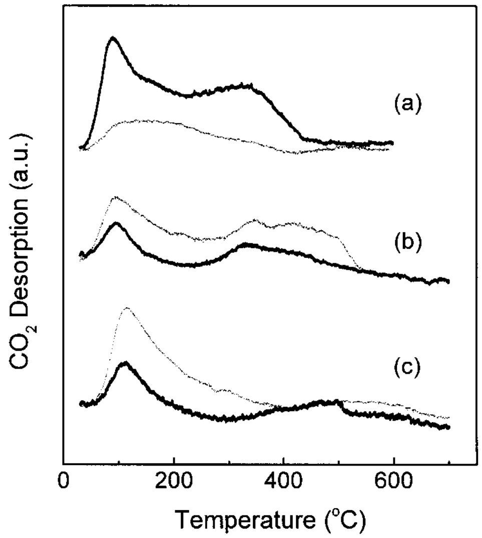

**Figure 2** $CO_2$ TPD profiles over (a) $ZrO_2$, (b) Ce–$ZrO_2$, and (c) Si–$ZrO_2$-supported $Fe_3O_4$ catalysts (thick line: supported $Fe_3O_4$ catalyst; thin line: support). Ramping rate: 10 °C $min^{-1}$.

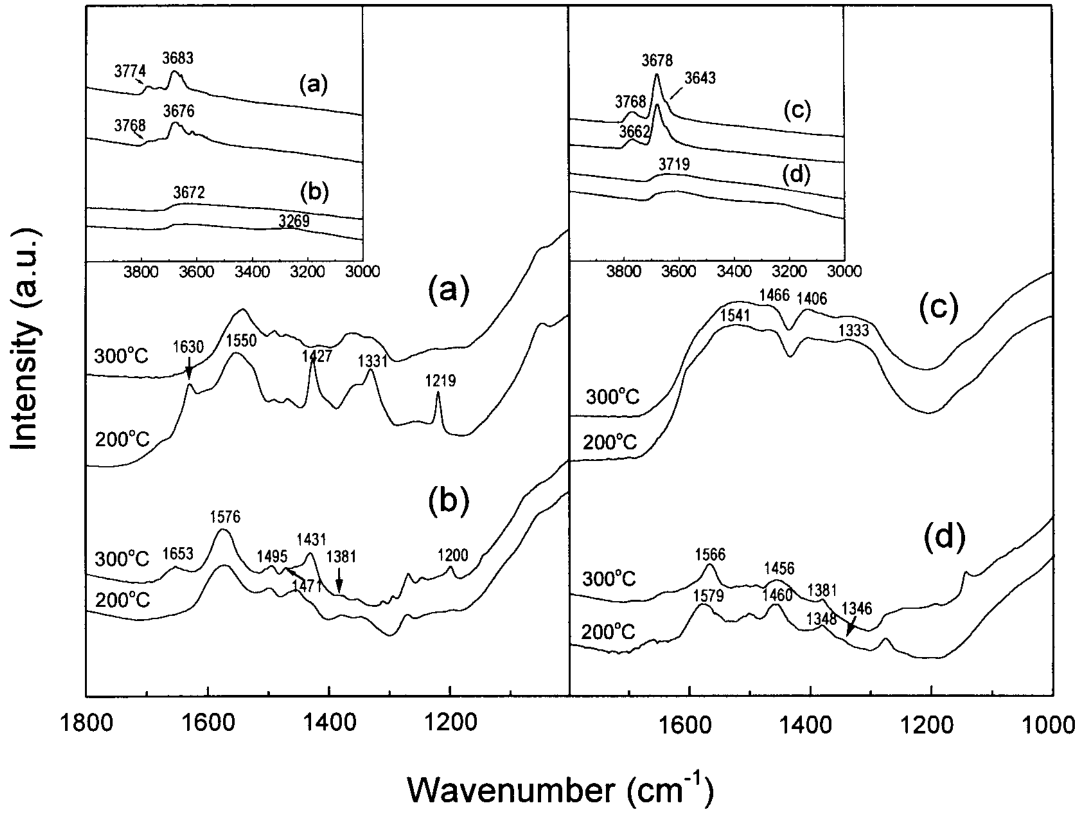

**Figure 3** FT-IR spectra of zirconia-based catalysts according to desorption temperature after adsorption of 10 Torr $CO_2$ at 30 °C for 30 min on each sample: (a) $ZrO_2$, (b) $Fe_3O_4$–$ZrO_2$, (c) Ce–$ZrO_2$, and (d) $Fe_3O_4$/Ce–$ZrO_2$.

3800–3720 cm$^{-1}$ and a lower frequency part of 3700–3620 cm$^{-1}$. The preceding bands in each part are assigned to low-coordinated $Zr^{4+}$ (or $Ce^{4+}$)—OH, whereas the subsequent bands are assigned to low-coordinated O—H derived from $H_2O$.[12] Low-coordinated $Zr^{4+}$ (or $Ce^{4+}$)—OH on Ce–$ZrO_2$ is dominant even after desorption of $CO_2$ at 300 °C. It has been reported that the formation of the stronger Lewis acid ($Zr^{4+}$ or $Ce^{4+}$) and base (surface $O^{2-}$) sites is favorable for $CO_2$ activation.[12,13] The more pronounced intensity attributed to the formation of planar polydentate carbonates (1466 and 1406 cm$^{-1}$) on Ce–$ZrO_2$ indicates the closeness of cations, which is characteristic of the tetragonal structure of $ZrO_2$.[14] For zirconia the bands assigned to bidentate carbonates (1550 and 1331 cm$^{-1}$) and hydrogen carbonates (1630, 1427, and 1219 cm$^{-1}$) disappear after evacuation at 300 °C, whereas the bands due to hydrogen carbonates (1653, 1431, and 1200 cm$^{-1}$) appear on supported $Fe_3O_4$ catalyst after evacuation at 300 °C. On the other hand, the loading of $Fe_3O_4$ on Ce–$ZrO_2$ has retained the same $CO_2$ adsorption sites as on $Fe_3O_4$–$ZrO_2$. Hence, ceria has a distinct contribution to the adsorption of $CO_2$ on zirconia and the loading of iron oxide on zirconia promotes the formation of more stable sites for $CO_2$ adsorption.

$CO_2$ TPD profiles of the catalysts to probe their surface basicities are illustrated in Fig. 3. The $CO_2$ adsorption sites are classified into three groups, i.e. weak sites (*ca* 100 °C) attributed to physisorption, moderate sites (*ca* 350 °C), and strong sites (above 400 °C). The loading of $Fe_3O_4$ on zirconia provides new $CO_2$ adsorption sites having moderate and strong adsorption strength. However, the loading of iron oxide on Ce–$ZrO_2$ causes a decrease of its surface basicity, which implies that the lesser activity of $Fe_3O_4$/Ce–$ZrO_2$ than Ce–$ZrO_2$ is ascribed to the loss of rather stable $CO_2$ adsorption sites, such as moderate and strong sites. In the case of Si–$ZrO_2$, its surface basicity upon loading $Fe_3O_4$ is not changed so much, except by decreasing the population of weak base sites. These TPD results lead to the suggestion that surface basicity of the $ZrO_2$-based catalysts in EB dehydrogenation with $CO_2$, of course, affects their activities, but these are not a decisive factor in deciding their activities. Instead, the weak surface basicity appears to cause fast deactivation of the catalyst, so rapid deactivation of the Si–$ZrO_2$ system is due to the lack of highly basic sites. In addition to the surface basicity, oxygen vacancies in the catalyst are considered to be an important factor for the catalytic activity in EB dehydrogenation with $CO_2$.[11]

## CONCLUSION

$CO_2$ was utilized as an oxidant in the EB dehydrogenation over zirconia-based catalysts to improve their activities. The modification of zirconia with ceria and the optimal loading of iron oxide made a pivotal contribution to the formation of strong $CO_2$ adsorption sites. Oxygen vacancy sites, as well as surface base sites over zirconia-based catalysts, were considered as active sites for the reaction.

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