# Dehydrogenation of ethane over gallium oxide in the presence of carbon dioxide

**Kiyoharu Nakagawa,[a,b] Masato Okamura,[a] Naoki Ikenaga,[a] Toshimitsu Suzuki*[a,b]† and Tetsuhiko Kobayashi[c]**

[a] *Department of Chemical Engineering, Faculty of Engineering, and*
[b] *High Technology Research Center, Kansai University, Suita, Osaka, 564-8680, Japan*
[c] *Osaka National Research Institute, AIST, MITI, Ikeda, Osaka 563-8577, Japan*

**Gallium oxide is found to be an effective catalyst for the dehydrogenation of ethane to ethene in the presence of carbon dioxide at 650 °C, giving 18.6% ethene yield with a selectivity of 94.5%.**

Ethene is predominantly produced by steam cracking of naphtha, ethane or liquid petroleum gas at high temperatures at short residence time.

In order to reduce energy consumption of ethene production, oxidative dehydrogenation of ethane is proposed [eqn. (1)].

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O \qquad (1)$$

The reaction becomes exothermic and thermodynamically could be possible at relatively low temperatures. However, it is necessary to remove heat from the reaction and to avoid over oxidation to $CO_2$ to give high selectivity towards ethene. Recently, a great variety of catalysts have been developed and tested for this reaction.[1–3] In the oxidative dehydrogenation of propane, Burch and Crabb[4] pointed out that thermal non-catalytic oxidative cracking of propane proceeded to give propene in the same yield as compared to catalyzed runs which were operated about 50 °C lower than that of non-catalyzed runs. This suggests that catalyzed oxidative dehydrogenation of lower alkanes is not highly superior to thermal oxidative pyrolysis.

Recently, several attempts have been made to use carbon dioxide as an oxidant for coupling of methane,[5] dehydrogenation of ethylbenzene[6] or propane.[7] However, the role of $CO_2$ in these reactions is still not clear. In addition, the effects of $CO_2$ on the conversion and yield of the product are not significant.

Here, we study the dehydrogenation of ethane to ethene over several metal oxide catalysts, and we have found that $CO_2$ markedly promoted dehydrogenation of ethane over $Ga_2O_3$ catalyst.

The catalysts used were commercially available MgO, $Al_2O_3$, $SiO_2$, CaO, $TiO_2$, $V_2O_5$, $Cr_2O_3$, $Mn_3O_4$, $Fe_3O_4$, ZnO, $Ga_2O_3$, $Y_2O_3$, $ZrO_2$, $Nb_2O_5$, $MoO_3$, $In_2O_3$, $SnO_2$, $La_2O_3$, $CeO_2$, $Ta_2O_5$ and $Tl_2O_3$. The reaction was carried out with a fixed-bed flow type quartz reactor (i.d. 10 × 350 mm) at atmospheric pressure. Using 200 mg of a catalyst, 5 ml $min^{-1}$ of $C_2H_6$ and 25 ml $min^{-1}$ of $CO_2$ were introduced. The runs were conducted for 30 min and products were analyzed by gas chromatography.

Fig. 1 shows ethene yields on the various metal oxide catalysts. Thermal dehydrogenation occurred to give only 2.3% of ethene yield. Equilibrium conversion of ethane to ethene is *ca.* 50% at 650 °C at a $C_2H_6$–Ar (or $CO_2$) ratio of 1 : 5. MgO, CaO, $SiO_2$, $Ta_2O_5$, $Al_2O_3$, $SnO_2$, $MoO_3$, and $Tl_2O_3$ did not show any catalytic activity while $CeO_2$, $Nb_2O_5$, $Fe_3O_4$, and $ZrO_2$ exhibited only slight catalytic activity. The order of the activity of oxides at the reaction temperature of 650 °C was as follows: $Ga_2O_3 > Cr_2O_3 > V_2O_5 > TiO_2 > Mn_3O_4 > In_2O_3 > ZnO > La_2O_3$. The $C_2H_4$ selectivities in all the metal oxide catalysts were $> 85\%$ in the dehydrogenation of ethane in the presence of $CO_2$. As expected, $Cr_2O_3$ and $V_2O_5$ exhibited high activities. These catalysts are known to be active catalysts for dehydrogenation of alkanes. $Ga_2O_3$ afforded the highest yield of ethene (18.6%) amongst the various metal oxide catalysts. However, little work has dealt with $Ga_2O_3$ catalyst in the dehydrogenation of propane.[8]

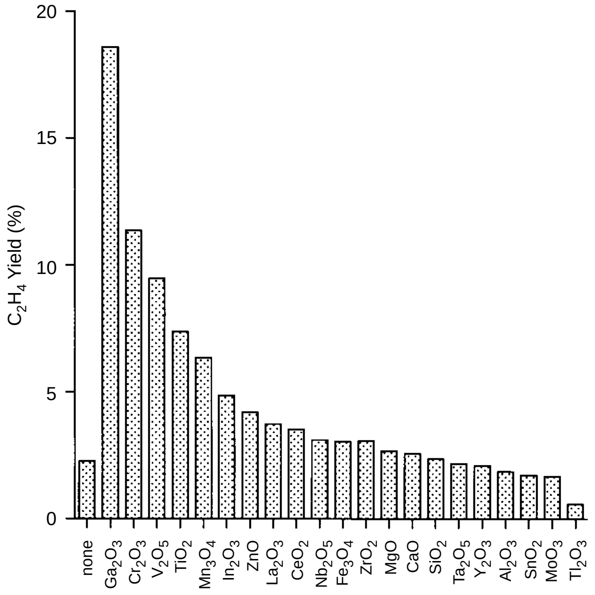

**Fig. 1** Dehydrogenation of $C_2H_6$ in the presence of $CO_2$. Catalyst 200 mg; temperature: 650 °C; $C_2H_6 : CO_2$ = 5 : 25 ml $min^{-1}$; SV = 9000 $h^{-1}$ ml (g cat)$^{-1}$.

Table 1 lists ethene yields on $Ga_2O_3$, $Cr_2O_3$, and $V_2O_5$ catalysts in the presence and absence of $CO_2$. The activity of the $Ga_2O_3$ catalyst in the presence of $CO_2$ was twice that in the absence of $CO_2$. Dehydrogenation of $C_2H_6$ in the presence of $CO_2$ over $Ga_2O_3$ catalyst produced mainly $C_2H_4$, CO, $H_2$ and $H_2O$. The yield of ethene with the $Cr_2O_3$ catalyst in the presence of $CO_2$ was slightly higher as compared to the run in Ar. The promoting effect of $CO_2$ in the dehydrogenation of $C_3H_8$ on $Cr_2O_3/SiO_2$ has been reported,[5] but the increase in the propene yield was only 2.6% at 550 °C. On the other hand, the effect of

**Table 1** Dehydrogenation of ethane in the presence of carbon dioxide[a]

| Catalyst | Surface area/ $m^2\ g^{-1}$ | Conv. (%) $C_2H_6$ | Yield (%) $C_2H_4$ | Selectivity (%) $C_2H_4$ | $CH_4$ | $C_3H_8$ |
|---|---|---|---|---|---|---|
| $Ga_2O_3(CO_2)$ | 9.8 | 19.6 | 18.6 | 95.0 | 3.8 | 1.0 |
| $Ga_2O_3$(Ar) | 9.8 | 9.6 | 9.0 | 94.0 | 5.0 | 0.7 |
| $Cr_2O_3(CO_2)$ | 2.8 | 12.1 | 11.4 | 93.8 | 5.8 | 0.4 |
| $Cr_2O_3$(Ar) | 2.8 | 10.4 | 10.2 | 97.6 | 1.8 | 0.6 |
| $V_2O_5(CO_2)$ | 3.5 | 9.8 | 9.5 | 97.1 | 2.9 | — |
| $V_2O_5$(Ar) | 3.5 | 12.5 | 11.5 | 91.7 | 7.4 | 0.9 |

[a] Reaction conditions: 650 °C, SV = 9000 $h^{-1}$ ml (g cat)$^{-1}$. Composition of the feed gas; $C_2H_6 : CO_2$(Ar) = 5 : 25 ml $min^{-1}$.

$CO_2$ on the yield of ethane with $V_2O_5$ in the presence of $CO_2$ was slightly detrimental. $CO_2$ promoted dehydrogenation of ethane exclusively over $Ga_2O_3$ catalyst. To our knowledge, such a marked promotion effect of $CO_2$ in a hydrocarbon conversion process has never been previously observed. The role of $CO_2$ in dehydrogenation of $C_2H_6$ over $Ga_2O_3$ catalyst is, as yet, unclear. With $CO_2$ considerable amounts of CO and $H_2O$ were formed during the reaction, indicating reaction of $CO_2$ with $H_2$. The amount of $H_2O$ was 1.09 mmol and that of CO was 1.07 mmol at 650 °C after 0.5 h. Dehydrogenation of $C_2H_6$ was strongly inhibited when $Ga_2O_3$ was impregnated onto a basic oxide such as MgO or $La_2O_3$. Another characteristic feature in the reaction in $CO_2$ is the increase in the yield of $CH_4$. From these findings the role of $CO_2$ may be as follows: slightly acidic $CO_2$ may strongly adsorb onto basic sites of gallium oxide, and as a result, the acidity of $Ga_2O_3$ would be enhanced. This possibility is reinforced by the fact that after dehydrogenation a certain amount of carbon was formed on the catalyst ($Ga_2O_3$, $Cr_2O_3$, and $V_2O_5$). Dehydrogenation of ethane would be catalyzed by acid sites on $Ga_2O_3$.

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## Notes and References

† E-mail: tsuzuki@ipcku.kansai-u.ac.jp

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