Promoting effect of carbon dioxide on the dehydrogenation and aromatization of ethane over gallium-loaded catalysts

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Ga_2O_3 and Ga_2O_3/TiO_2 catalysts were found to be effective agents for the dehydrogenation of ethane to ethene in the presence of carbon dioxide at 650 °C. The activity of the Ga_2O_3 and Ga_2O_3/TiO_2 catalysts in the presence of CO_2 was 2–4 times higher than that without CO_2. Ethene yields reached ca. 20–25% and selectivity was ca. 70–90% at 650 °C in the 17% ethane and 83% CO_2 feed at an SV of 9,000 ml/(g-cat h). The presence of CO_2 markedly promoted dehydrogenation of ethane over Ga_2O_3 and Ga_2O_3/TiO_2 catalysts. Furthermore, the promoting effect of CO_2 on the aromatization of ethane and ethene over a Ga_2O_3 + H/ZSM-5 catalyst was also observed above 650 °C. Aromatics yields were higher than those without CO_2.

Keywords: gallium oxide, titanium oxide, carbon dioxide, oxidative dehydrogenation

1. Introduction

The industrial demand for alkenes is increasing, and the present capacities are unable to meet this need. Until recently, light alkenes were obtained from steam cracking of natural gas and naphtha and from fluid catalytic cracking in petroleum refining. A potential means of lower alkane utilization of this chemical is the conversion to unsaturated hydrocarbons; the chemical industry currently has a strong dependence on the use of unsaturated hydrocarbons as starting material.

Dehydrogenation of ethane can be carried out thermally to produce molecular hydrogen as a by-product:

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \quad \Delta H^0_{298} = +137\ \text{kJ/mol} \qquad (1)$$

However, the thermodynamics of this reaction for ethane is such that the equilibrium greatly favors ethane at lower temperatures when the pressure is 1 atm. The equilibrium shifts to the left of the products as the temperature increases. The temperature needed for 50% conversion of ethane is about 720 °C [1]. In addition, the number of molecules in the products increases as compared to the number in the reactant. Thus, an operation at elevated pressures preferred in practice would shift the equilibrium conversion in the unfavorable direction. Catalytic dehydrogenation at such high temperatures has a number of disadvantages. At these temperatures, undesirable side reactions are difficult to control. Another problem is rapid coking of the catalyst [1].

Measured against other alkanes, the activation of ethane requires the highest temperature. In order to reduce the energy consumption in the ethene production, we propose the oxidative dehydrogenation of ethane:

$$C_2H_6 + (1/2)O_2 \rightarrow C_2H_4 + H_2O$$
$$\Delta H^0_{298} = -155\ \text{kJ/mol} \qquad (2)$$

The formation of water makes this reaction thermodynamically favorable. Thus in principle, practically complete conversion can be obtained even at low temperatures and high pressures. This provides great advantage over the non-oxidative process based on engineering and economic considerations. However, other problems such as the removal of the heat of reaction, control of the selectivity due to the production of undesired carbon oxides, and the flammability of the reaction mixtures causing the possibility of a runaway reaction, must be overcome. Interestingly, the best catalytic systems for oxidative dehydrogenation of ethane are not the optimal ones for higher alkanes, and vice versa. Recently, a great variety of catalysts has been developed and tested for this reaction [1–3]. However, in the oxidative dehydrogenation of propane, Burch et al. [4] pointed out that thermal non-catalytic oxidative cracking of propane proceeded to give propene in the same yield as that derived from catalyzed reactions which were operated at a 50 °C lower temperature. This suggests that catalyzed oxidative dehydrogenation of lower alkanes is not highly superior to thermal oxidative dehydrogenation.

Recently, several attempts were made to use carbon dioxide as an oxidant for coupling of methane [5–7], dehydrogenation of ethylbenzene [8–10], propane [11,12] or isobutane [13].

Hattori et al. reported the promotion of aromatization of ethane or propane over metal-loaded ZSM-5 catalysts

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[14,15]. However, the roles of CO_2 in these reactions are still not clear. In addition, the effect of CO_2 on the conversion and yield of the product was very small.

$$C_2H_6 + CO_2 \rightarrow C_2H_4 + CO + H_2O$$
$$\Delta H^0_{298} = +134 \text{ kJ/mol} \qquad (3)$$

We previously reported that gallium oxide showed a high catalytic activity 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% [16]. The present study deals with the dehydrogenation of ethane to ethene (reaction (3)) and the aromatization of ethane over several gallium-loaded catalysts. It also describes studies of markedly positive effect of CO_2 on the dehydrogenation of ethane over gallium-loaded catalysts.

2. Experimental

The catalyst supports used were Al_2O_3, SiO_2 (JRC-ALO-4, JRC-SIO-4, the reference catalyst provided by the Catalyst Society of Japan), MgO (Ube Industries, Ltd.), TiO_2, ZrO_2 (Japan Aerosil Co.), ZnO, Y_2O_3, La_2O_3, CeO_2, Nb_2O_5, WO_3 (Nacalai tesque, Inc.), Ga_2O_3, GeO_2, Ta_2O_5 (Kishida Chemicals), and Fe_3O_4 (Wako Pure Chemical Industries, Ltd.). H-ZSM-5 (SiO_2/Al_2O_3 = 21.5) was prepared according to the literature [17,18]. Ga_2O_3, having a greater surface area, was obtained by thermal decomposition of $Ga(NO_3)_3 \cdot 8H_2O$ (Kishida Chemicals) at 650 °C for 5 h in air. Ga-loaded metal oxide catalysts containing 5 mol% Ga and Ga-loaded zeolite catalysts containing 5 wt% Ga were prepared by impregnating an aqueous solution of $Ga(NO_3)_3 \cdot 8H_2O$ (Kishida Chemicals) onto suspended supports, and then evaporating to dryness. Supported catalysts were calcined at 650 °C for 3 h in air prior to the reaction.

The reaction was carried out with a fixed-bed flow type quartz reactor (i.d. 10 × 350 mm) at 1 atm pressure. Using 150–200 mg of a catalyst, 25 ml/min CO_2 (or Ar) and 5 ml/min of C_2H_6 (or C_2H_4) were introduced at temperature ranges of 600–700 °C. Prior to the reaction, the catalysts were heated in Ar. The runs were conducted for 30 min and products were analyzed by a gas chromatograph.

Analyses of the C_1, C_2, and C_3 hydrocarbon gases were carried out with a Shimadzu GC14BPF gas chromatograph (FID detector) with a 3 mm × 3 m glass column packed with Porapack Q in a N_2 carrier. Analyses of CO, CO_2, and CH_4 were carried out with a Shimadzu GC8AIT gas chromatograph (TCD detector) with a 3 mm × 3 m stainless-steel column packed with an activated carbon (30/60 mesh) using He as a carrier gas. Analyses of H_2 were carried out with a Shimadzu GC8AIT gas chromatograph (TCD detector) with a 3 mm × 3 m stainless-steel column packed with an activated carbon (30/60 mesh) with a N_2 carrier. The liquid products (benzene and toluene) were analyzed by a gas chromatograph equipped with a Shimadzu model GC-14APF (FID detector), using a capillary column (CBP1, 0.53 mm × 25 m).

The surface area of the catalyst was measured by the BET method using N_2 at −196 °C with an automatic Micromeritics Gemini model 2375. The amount of water was determined by the Karl Fisher automatic volumetric titration method using a Hiranuma aquacounter AQV-5S.

The acidity of the Ga_2O_3-loaded catalysts was measured with the NH_3-TPD method using a BEL Japan, Inc. TPD-1-AT, and the pyridine adsorption method using FT-IR (Joel, JIR-7000).

3. Results and discussion

The behavior of several metal oxide catalysts and the conversion of ethane to ethene in the presence of CO_2 were discussed in a previous communication [16]. The promoting effect of CO_2 on the conversion of ethane over gallium oxide catalysts is substantial. This was examined by changing reaction conditions, surface area of gallium oxide and gallium-oxide-loaded catalysts, and the roles of CO_2 needs to be clarified.

3.1. Dehydrogenation of ethane in the presence of carbon dioxide over gallium oxide

Figure 1 shows the effect of the surface area of gallium oxide on the yield of ethene. In these experiments, surface areas of gallium oxides were changed by varying the decomposition temperature of gallium nitrate to gallium oxide. With increasing surface area, the ethene yield increased. A high surface area of gallium oxide was found to be effective for the dehydrogenation of ethane in the presence of carbon dioxide. Probably, the acidic site of

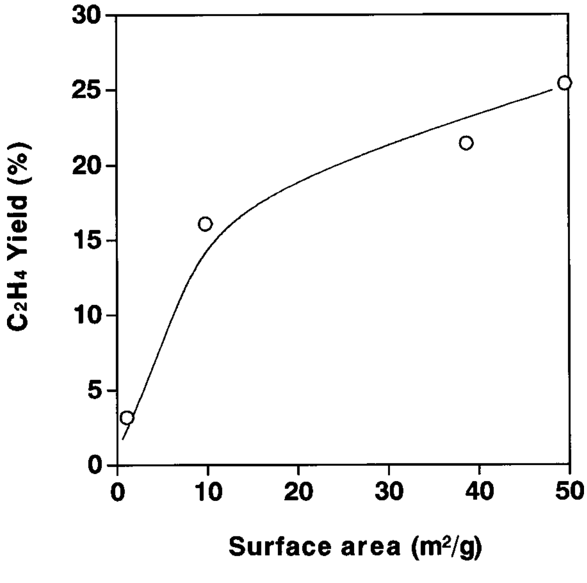

Figure 1. Effect of surface area of Ga_2O_3 on the dehydrogenation of ethane. Reaction conditions: temperature 650 °C, reaction time = 0.5 h, $C_2H_6:CO_2$ = 5 : 25 (ml/ml), catalyst = 200 mg, SV = 9,000 ml/(g-cat h).

gallium oxide was the active site of the dehydrogenation of ethane. A weakly acidic character of the gallium oxide catalyst was detected by the NH_3-TPD method. The desorption of NH_3 over a gallium oxide surface exhibited a large desorption at about 182.4 °C and only a small desorption at 565.0 °C. The pyridine adsorption method by FT-IR exhibited weak absorption at about 1450 cm^{-1} after evacuation, indicating the existence of a Lewis acid site.

The effect of reaction temperature on the dehydrogenation of ethane over gallium oxide (SA 9.8 m^2/g) in the presence or the absence of carbon dioxide was examined. The ethene yield as a function of reaction temperature is shown in figure 2.

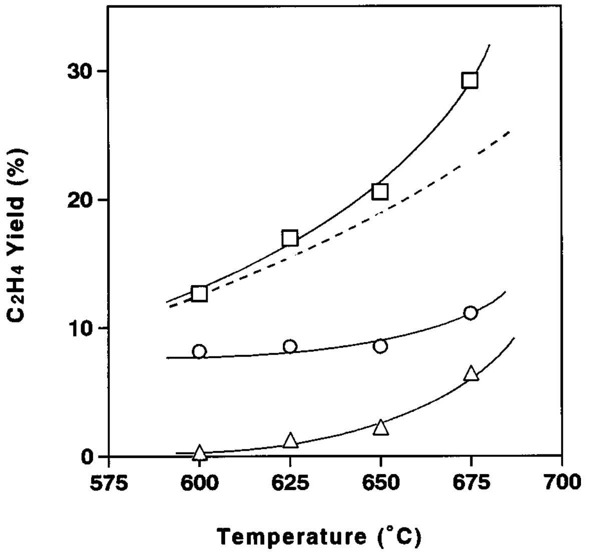

Figure 2. Effect of reaction temperature on ethene yield over Ga_2O_3 catalyst: (☐) Ga_2O_3 under CO_2, (○) Ga_2O_3 under Ar, and (△) without catalyst under CO_2, (- - -) (Ga_2O_3 under CO_2) – (without catalyst under CO_2). Reaction conditions: reaction time = 0.5 h, $C_2H_6 : CO_2$ (or Ar) = 5 : 25 (ml/ml); catalyst = 200 mg, SV = 9,000 ml/(g-cat h).

In the presence of carbon dioxide, the ethene yield markedly increased with increasing the reaction temperature. However, in the absence of carbon dioxide, the ethene yield only slightly increased with increasing reaction temperature. These results indicate that carbon dioxide played an important role in the dehydrogenation of ethane to ethene at a higher temperature.

In the dehydrogenation under CO_2 atmosphere, the roles of CO_2 would be considered as follows:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{4}$$

$$CO_2 + C \rightleftharpoons 2CO \tag{5}$$

The promoting effect of CO_2 in the dehydrogenation of propane with Cr_2O_3/SiO_2 has been reported [10], but the increase in the propene yield was only 2.6% of the total yield of 9.1% at 550 °C. CO_2 promoted the dehydrogenation of ethane exclusively over the Ga_2O_3 catalyst. To the best of our knowledge, such marked enhancement by CO_2 in a hydrocarbon conversion process has not been previously observed. The role of CO_2 in the dehydrogenation of ethane over Ga_2O_3 is as yet unclear. In the CO_2, considerable amounts of CO and H_2O were formed during the reaction, indicating the occurrence of a reaction between CO_2 and H_2 (reaction (4)). Removal of carbon deposits through the Boudouard reaction (reaction (5)) is another plausible cause (see section 3.3).

3.2. Effect of support on the dehydrogenation of ethane in the presence of carbon dioxide over supported gallium oxide catalysts

Table 1 lists ethene yields over Ga_2O_3 and gallium-loaded TiO_2, ZrO_2, ZnO, Al_2O_3, and SiO_2 catalysts in the

Table 1
Dehydrogenation of ethane over gallium-loaded catalysts in the presence of carbon dioxide.[a]

Catalyst	Surface area (m^2/g)	C_2H_6 conv. (%)	C_2H_4 yield (%)	Selectivity (%)		
				C_2H_4	CH_4	C_3
TiO_2 (CO_2)	50.2	28.6	20.2	70.8	28.2	0.9
TiO_2 (Ar)	50.2	6.7	5.9	88.3	11.1	0.5
ZrO_2 (CO_2)	20.1	14.8	10.8	72.6	25.1	1.7
ZrO_2 (Ar)	20.1	5.2	4.7	90.2	6.9	1.2
ZnO (CO_2)	5.1	11.1	10.0	89.8	9.6	0.6
ZnO (Ar)	5.1	4.1	3.8	91.3	6.8	1.9
Al_2O_3 (CO_2)	149	13.1	9.4	71.6	26.2	2.1
Al_2O_3 (Ar)	149	27.6	25.7	93.1	6.9	–
SiO_2 (CO_2)	421	9.5	9.3	97.9	1.1	1.0
SiO_2 (Ar)	421	10.2	9.9	97.0	2.2	0.6
Ga_2O_3 (CO_2)[b]	9.8	19.6	18.6	95.0	3.8	1.0
Ga_2O_3 (Ar)[b]	9.8	9.6	9.0	94.0	5.0	0.7
Ga_2O_3 (CO_2)	49.6	29.2	25.4	87.0	12.3	0.7
Ga_2O_3 (Ar)	49.6	9.8	8.8	89.6	10.4	–
None (CO_2)	–	2.4	2.3	95.6	1.3	2.9
None (Ar)	–	2.7	2.6	95.9	1.3	2.8

[a] Reaction conditions: 650 °C, SV = 9,000 ml/(g-cat h), composition of the feed gas $C_2H_6 : CO_2$ (Ar) = 5 : 25 (ml/ml).
[b] [16].

Table 2

Effect of Ga content on the dehydrogenation of ethane over Ga/TiO_2 in the presence of carbon dioxide.[a]

Ga content (mol%)	C_2H_6 conv. (%)	C_2H_4 yield (%)	Selectivity (%) C_2H_4	CH_4	C_3
1.0	18.3	14.1	77.2	21.9	0.9
5.0	28.6	20.2	70.8	28.2	0.9
10.0	31.3	23.1	74.2	24.9	1.0

[a] Reaction conditions: 650 °C, SV = 9,000 ml/(g-cat h), composition of the feed gas $C_2H_6 : CO_2 = 5 : 25$ (ml/ml).

presence or absence of CO_2 at 650 °C. The greater the surface area of Ga_2O_3, the more effective is the dehydrogenation of ethane. The activity of the Ga_2O_3/TiO_2 catalyst in the presence of CO_2 was four times as great as that in the absence of CO_2. The activity of the Ga_2O_3/ZrO_2 and Ga_2O_3/ZnO catalysts in the presence of CO_2 was three times greater than that in the absence of CO_2. The activity order was related to the surface area of support materials such as TiO_2, ZrO_2, and ZnO, which are amphoteric oxides. In contrast, with a Ga_2O_3/Al_2O_3 catalyst the activity in the presence of CO_2 decreased to a half of that in the absence of CO_2 at 650 °C. However, at 700 °C, ethene conversions were almost the same values both in the presence and absence of CO_2 (see section 3.3, figure 4). CO_2 did not affect the Ga_2O_3/SiO_2 catalyst. The dehydrogenation activity of ethane in the presence of CO_2 with Ga_2O_3-loaded catalysts was strongly affected by the characteristics of support oxides. Dehydrogenation of C_2H_6 was strongly inhibited when Ga_2O_3 was impregnated onto basic oxides such as MgO or La_2O_3. From these findings the role of CO_2 seemed to be as follows: slightly acidic CO_2 may be strongly adsorbed onto the basic site of gallium oxide, and as a result, the acidity of Ga_2O_3 would be enhanced. Dehydrogenation of ethane seemed to be catalyzed by acid sites on Ga_2O_3. A weakly acidic nature of the Ga_2O_3/TiO_2 catalyst was detected by the NH_3-TPD method (NH_3 desorption at about 207.4 and 599.8 °C).

Solymosi et al. reported that the decomposition of adsorbed CH_3 species was accelerated by CO_2 over TiO_2 [19]. In the presence of CO_2, H_2O was detected and methane selectivity increased over Ga_2O_3/TiO_2, ZrO_2, ZnO, and Al_2O_3 catalysts. This seems to indicate that hydrocracking of ethane occurred. Therefore, the effect of CO_2 would be to modify the acidity of the surface of the Ga_2O_3/TiO_2 catalyst.

Table 2 illustrates the effects of the Ga loading level on the conversion of ethane and on the selectivity and yield of ethene. Ethane conversion and ethene yield increased with increasing gallium content. The conversion of ethane (18.3%) was obtained with as small an amount as 1 mol% gallium, and the selectivity to ethene remained constant over the gallium oxide loading level of 1–10 mol%, at the reaction temperature of 650 °C.

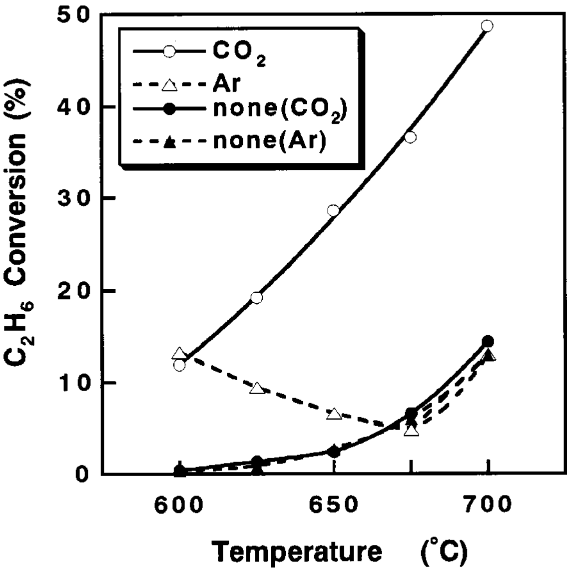

Figure 3. Effect of reaction temperature on the conversion of C_2H_6 over Ga(5 mol%)/TiO_2 catalyst: (○) CO_2, (△) Ar, (●) none (CO_2), and (▲) none (Ar). Reaction conditions: reaction time = 0.5 h, $C_2H_6 : CO_2$ (or Ar) = 5 : 25 (ml/ml); catalyst = 200 mg, SV = 9,000 ml/(g-cat h).

3.3. Effect of temperature on the dehydrogenation of ethane in the presence and absence of carbon dioxide over gallium-oxide-loaded catalysts

Figure 3 shows the temperature dependence of the catalytic activity of the Ga(5 mol%)/TiO_2 catalyst in the presence or the absence of CO_2. Ethene yields in the non-catalytic runs did not depend upon atmosphere. In the presence of CO_2 over Ga_2O_3/TiO_2, ethene yields increased remarkably with increasing reaction temperature, and 27.4% of ethene yield was obtained at 700 °C. In contrast, the ethene yield in the absence of CO_2 decreased with increasing reaction temperature, and above 675 °C the same yield as that of the uncatalyzed run was obtained. Probably, this inverse relation to a rise in temperature is caused by rapid carbon deposition. CO was detected over Ga_2O_3-loaded catalysts during dehydrogenation of ethane in the presence of CO_2. In addition, CO was formed during the temperature-programmed reaction with CO_2 after dehydrogenation of ethane in the presence of CO_2 over Ga_2O_3/TiO_2. Therefore, one possible cause of the increased dehydrogenation in the presence of CO_2 is the elimination of deposited carbon (reaction (5)). Similar results were obtained

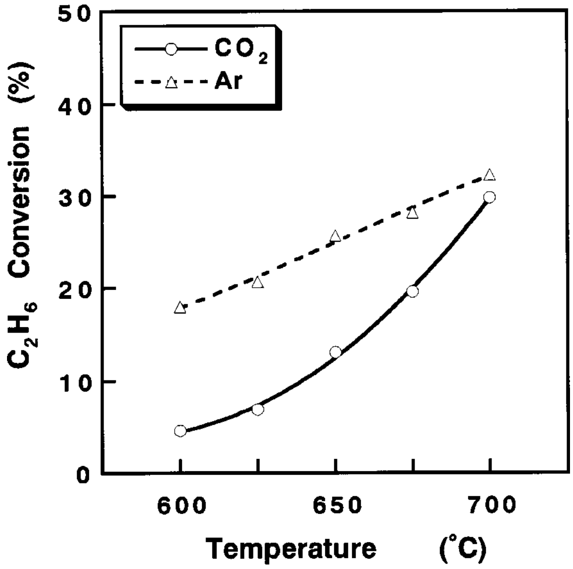

Figure 4. Effect of reaction temperature on the conversion of C_2H_6 over Ga(5 mol%)/Al_2O_2 catalyst: (○) CO_2 and (△) Ar. Reaction conditions: reaction time = 0.5 h, $C_2H_6 : CO_2$ (or Ar) = 5 : 25 (ml/ml); catalyst = 200 mg, SV = 9,000 ml/(g-cat h).

using ZrO_2 and ZnO supports. Dehydrogenation of ethane in the presence of CO_2 using TiO_2, ZrO_2, and ZnO supports was noticeably promoted by increasing the reaction temperature. In contrast, the Ga_2O_3/Al_2O_3 catalyst did not promote dehydrogenation of ethane in the presence of CO_2, and the yields of ethene exhibited low values at temperature ranges of 600–700 °C (figure 4) as compared to the run in the absence of CO_2. Detailed studies of the positive and negative effect on the dehydrogenation of ethane in the presence of CO_2 over Ga_2O_3/TiO_2 and Ga_2O_3/Al_2O_3 are described below.

3.4. Effect of steam on the dehydrogenation of ethane over Ga_2O_3/TiO_2 and Ga_2O_3/Al_2O_3 catalysts

In the dehydrogenation of ethane in CO_2, water was produced during the reaction (reaction (3)). Carbon deposition is one of the major problems in the dehydrogenation of ethane. The role of water in the dehydrogenation of ethane would be considered as follows:

$$H_2O + C \rightarrow CO, CO_2, H_2 \qquad (6)$$

In order to obtain information about the effect of steam on the dehydrogenation of ethane, steam was introduced in the dehydrogenation of ethane over Ga_2O_3/TiO_2 and Ga_2O_3/Al_2O_3 catalysts in the absence of CO_2. With the Ga_2O_3/TiO_2 catalyst, the ethene yield in the absence of CO_2 was about 5.9%. The ethene yield was markedly increased by introducing steam, and a products distribution similar to the run under CO_2 was obtained (table 3). These results suggest that steam produced in the presence of CO_2 might also have promoted the dehydrogenation of ethane over the Ga_2O_3/TiO_2 catalyst. In this reaction, CO_x was detected and methane selectivity increased. Therefore, the effect of steam could be to eliminate deposited carbon and to modify the acidity of the surface of the Ga_2O_3/TiO_2 catalyst. Ethane yields over Ga_2O_3/Al_2O_3 decreased with increasing steam partial pressure (table 3). This result indicated that produced H_2O (reaction (4)) inhibited the dehydrogenation of ethane in the presence of CO_2. The decreasing ethene yield over Ga_2O_3/Al_2O_3 might be caused by modified acidity of the surface of the Ga_2O_3/Al_2O_3 catalyst.

3.5. Effect of carbon dioxide on the aromatization of ethane over Ga-loaded zeolite catalysts

Ga_2O_3 catalyst afforded a higher ethene yield in the presence of CO_2 above 650 °C. In view of the conversion of produced ethene to benzene, we investigated one-step aromatization of ethane to benzene over Ga_2O_3-containing catalysts in the presence of CO_2.

Benzene formation via aromatization of ethane proceeds as follows:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad (1)$$

$$3C_2H_4 \rightarrow C_6H_6 + 3H_2 \qquad (7)$$

Metal (Ga, Pt, etc.)-loaded H/ZSM-5 catalysts are known to be most effective for the aromatization of ethane [20–24]. Since the above mentioned Ga_2O_3 afforded greater catalytic

Table 3
Effect of stream on the product yields in the dehydrogenation of ethane in the presence of Ar over Ga(5 mol%)/TiO_2 and Ga(5 mol%)/Al_2O_3 catalysts.

Support	Steam pressure (mm Hg)	C_2H_6 conv. (%)	C_2H_4 yield (%)	Selectivity (%)		
				C_2H_4	CH_4	C_3
TiO_2 (CO_2)	–	28.6	20.2	70.8	28.2	0.9
TiO_2 (Ar)	–	6.7	5.9	88.3	11.1	0.5
TiO_2 (Ar)	4.6	14.8	12.7	86.1	13.9	–
TiO_2 (Ar)	79.6	24.1	17.5	72.7	27.3	–
Al_2O_3 (CO_2)	–	13.1	9.4	71.6	26.2	2.1
Al_2O_3 (Ar)	–	27.6	25.7	93.1	6.9	–
Al_2O_3 (Ar)	4.6	27.7	24.7	89.1	10.9	–
Al_2O_3 (Ar)	79.6	21.8	16.5	75.8	24.2	–

[a] Reaction conditions: 650 °C, catalyst = 200 mg, SV = 9,000 ml/(g-cat h), composition of the feed gas $C_2H_6 : CO_2$ (Ar) = 5 : 25 (ml/ml), flow rate = 30 ml/min.

Table 4
Product yields on the aromatization of ethane and ethene over gallium + ZSM-5 catalysts in the presence and absence of carbon dioxide.[a]

Feed (temperature (°C))	Catalyst	Yield in the presence of CO_2 (%)			Yield in the absence of CO_2 (%)		
		Benzene	Toluene	C_2H_4	Benzene	Toluene	C_2H_4
Ethane (675 °C)	HZSM-5	0.9	–	2.3	0.8	–	2.3
	Ga_2O_3 + HZSM-5[b] (physical mixture)	3.6	0.3	2.3	2.0	0.4	2.8
	Ga(5 wt%)/HZSM-5[c] (impregnation)	5.8	0.6	2.2	3.7	1.0	3.7
Ethene (650 °C)	Ga_2O_3 + HZSM-5[d] (physical mixture)	20.3	7.0	–	13.2	8.4	–

[a] Composition of the feed gas C_2H_6 (C_2H_4) : CO_2 (Ar) = 5 : 25 (ml/ml).
[b] Ga_2O_3 = 200 mg, HZSM-5 = 150 mg.
[c] Ga(5 wt%)/HZSM-5 = 200 mg.
[d] Ga_2O_3 = 200 mg, HZSM-5 = 200 mg.

activity for the dehydrogenation of ethane, we examined the use of the Ga_2O_3 + HZSM-5 catalyst system for the aromatization of C_2H_6 in the presence of CO_2.

Table 4 lists the aromatics yield over a combination of Ga_2O_3 and H/ZSM-5 catalysts in the reaction of ethane in the presence or the absence of CO_2. The aromatics yield with HZSM-5 did not depend on the presence of CO_2. The Ga/HZSM-5 (impregnation) catalyst afforded the highest aromatics yield both in the presence and in the absence of CO_2 at 675 °C. Admixed Ga_2O_3 + H/ZSM-5 exhibited a small promoting effect in the aromatization of ethane in the presence of CO_2. In the cases of admixed Ga_2O_3 + H/ZSM-5, aromatics and ethene yields in the presence of CO_2 were higher than those in the absence of CO_2. Therefore, the promoting effect of CO_2 for the aromatization of ethane seemed to appear in the dehydrogenation of ethane to ethene over Ga_2O_3 + H/ZSM-5 systems.

To obtain detailed information about the promoting effect of CO_2 on the aromatization of ethane, the aromatization of ethene over a Ga_2O_3 + H/ZSM-5 (physical mixture) catalyst in the presence or the absence of CO_2 was examined (table 4). In the aromatization of ethene, the aromatics yield in the presence of CO_2 was much higher than that in absence of CO_2. This result seems to indicate that the formation of alkene through dehydrogenation of ethane is the first step of the aromatization of ethane, as reported previously [22,25]. The aromatics yield in the presence of CO_2 was higher than that in the absence of CO_2. In the presence of CO_2, the aromatization of ethene over the Ga_2O_3 + H/ZSM-5 catalyst was also promoted. In addition, CO and H_2O were formed. The promoting effect of CO_2 on the aromatization of ethane over Ga_2O_3 + H/ZSM-5 was observed in both the dehydrogenation of ethane to ethene and the aromatization of ethene to aromatics. Hattori et al. also reported similar results using a Ga/ZSM-5 catalyst [14]. The role of CO_2 in the aromatization of ethane is considered to be the following: consumption of formed H_2 via reverse water–gas shift reaction (reaction (4)) and elimination of deposited carbon via Boudouard reaction (reaction (5)) proceeded to the reactions favorable side. A unique promoting effect of CO_2 on the dehydrogenation and aromatization of ethane over Ga_2O_3-loaded and Ga_2O_3-containing catalysts was observed.

4. Conclusion

Ga_2O_3 and Ga_2O_3/TiO_2 catalysts exhibited a high ethene yield in the presence of carbon dioxide. Ga_2O_3 which has a higher surface area was found to be an effective catalyst for the dehydrogenation of ethane to ethene in the presence of carbon dioxide at 650 °C. The reaction seemed to proceed on the acid site of the catalyst, since Ga_2O_3 loaded on the basic support did not exhibit dehydrogenation activity. Steam which was produced in the presence of CO_2 also played an important role in the dehydrogenation of ethane over the Ga_2O_3/TiO_2 catalyst. Furthermore, the promoting effect of CO_2 was observed in the aromatization of ethane and ethene over the Ga_2O_3 + H/ZSM-5 (physical mixture) catalyst.

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