Journal of Catalysis **203,** 87–93 (2001)
doi:10.1006/jcat.2001.3306, available online at http://www.idealibrary.com on IDEAL®

Role of Carbon Dioxide in the Dehydrogenation of Ethane over Gallium-Loaded Catalysts

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Received December 11, 2000; revised March 12, 2001; accepted June 11, 2001; published online August 28, 2001

The role of CO_2 in the dehydrogenation of ethane over Ga_2O_3-loaded catalysts was examined. Ga_2O_3/TiO_2 catalyst was found to be the most effective for the dehydrogenation of ethane to ethene in the presence of CO_2 at 923 K. The activity of the Ga_2O_3/TiO_2 catalyst in the presence of CO_2 increased with increases in the partial pressure of CO_2. To maintain high catalytic activity, cofeeding of CO_2 and steam was effective in the case of the Ga_2O_3/TiO_2 catalyst. Over the Ga_2O_3/TiO_2 catalyst, the presence of CO_2 markedly promoted the dehydrogenation of ethane as compared with the absence of CO_2. Using a pulsed reaction technique, the use of CO_2 in the dehydrogenation of ethane was found to reduce carbon deposition over the catalyst and to assist in the rapid desorption of the product (ethene) from the catalyst's surface. © 2001 Academic Press

Key Words: **gallium oxide; titanium oxide; carbon dioxide; oxidative dehydrogenation; ethane; pulsed reaction.**

1. INTRODUCTION

Dehydrogenation of ethane to ethene is a very important chemical process as ethene is the starting material for the production of valuable chemicals such as ethylbenzene, styrene, ethanol, acetaldehyde, acetic acid, etc. Light alkenes such as ethene, propene, and butenes are usually produced by the steam cracking process. The dehydrogenation of ethane to ethene can be carried out thermally:

$$C_2H_6 \rightleftarrows C_2H_4 + H_2 \qquad \Delta H^0_{923} = +141 \text{ kJ/mol.} \qquad [1]$$

However, the major problem involved with this reaction for ethane is the high temperature (1073–1173 K) required for favorable equilibrium. The temperature necessary for 50% conversion of ethane is about 993 K (1). Catalytic dehydrogenation at such high temperatures has a number of disadvantages. At these temperatures, undesirable side reactions are difficult to control. Another problem is a rapid coking of the catalyst (1).

An alternate method of dehydrogenation of ethane to ethene is oxidative dehydrogenation:

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O \qquad \Delta H^0_{923} = -149 \text{ kJ/mol.} \qquad [2]$$

The catalytic oxidative dehydrogenation of alkane to alkene proposes a promising alternative pyrolysis and catalytic dehydrogenation (2). This provides great advantages over the nonoxidative process in light of engineering and economic considerations. However, other problems that must be solved are the removal of the reaction heat, and the avoidance of the overoxidation of alkane and alkene to give carbon oxides, in order to obtain high alkene selectivity.

In order to reduce energy consumption in ethene production and to obtain high alkene selectivity, we have proposed the oxidative dehydrogenation of ethane with carbon dioxide (reaction 3) (3).

$$C_2H_6 + CO_2 \rightarrow C_2H_4 + CO + H_2O \qquad \Delta H^0_{923} = +135 \text{ kJ/mol.} \qquad [3]$$

Recently, several attempts have been made to use carbon dioxide as an oxidant for the dehydrogenation of ethane (3–7), propane (8, 9) or isobutane (10), ethylbenzene (11–14), and isopropylbenzene (15), and the coupling of methane (16–18). However, the roles of CO_2 in these reactions remain unclear.

We previously reported that Ga_2O_3 and Ga_2O_3/TiO_2 catalysts showed a high catalytic activity for the dehydrogenation of ethane to ethene in the presence of carbon. 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 923 K. The presence of CO_2 markedly

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0021-9517/01 $35.00

promoted the dehydrogenation of ethane over Ga_2O_3 and Ga_2O_3/TiO_2 catalysts (3, 19).

The present study deals with the dehydrogenation of ethane to ethene (reaction 3) over several gallium-loaded catalysts. It also describes the role of CO_2 in the dehydrogenation of ethane over gallium-loaded catalysts.

2. EXPERIMENTAL

2.1. *Catalysts*

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), TiO_2 (Japan Aerosil Co.), and Ga_2O_3, having a greater surface area (49.6 m^2/g), which was obtained by thermal decomposition of $Ga(NO_3)_3 \cdot 8H_2O$ (Kishida Chemicals) at 923 K for 5 h in air. Ga-loaded metal oxide catalysts containing 5 mol% Ga were prepared by impregnating an aqueous solution of $Ga(NO_3)_3 \cdot 8H_2O$ onto suspended supports, and then evaporating to dryness. Supported catalysts were calcined at 923 K for 3 h in air prior to the reaction.

2.2. *Catalytic Activity Measurements*

The reaction was carried out with a fixed-bed flow-type quartz reactor (i.d. 10 × 350 mm) at atmospheric 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 923 K. Prior to the reaction, the catalysts were heated in Ar. The runs were conducted for 30 min and products were analyzed by using a gas chromatograph.

Analyses of the C1, C2, and C3 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 an 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 surface area of the catalyst was measured by the BET method using N_2 at 77 K 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.

Characterization of the catalyst was performed using Raman spectroscopy having a 1-μm depth resolution and employing Ar^+ laser excitation.

2.3. *Transient Response of the Pulsed Reactions*

Transient response measurement of pulsed reactions were carried out using a fixed-bed quartz reactor (i.d. 4×200 mm) which was set in a horizontal position in an electric furnace, and 100 mg of the catalyst was charged into the reactor. A pulse of C_2H_4 gas was introduced through a six-port gas sampling valve equipped with measuring tubes, under a stream of Ar carrier gas. The reaction temperature was controlled by monitoring the outside temperature of the reactor wall by using a programmable controller. The reaction system has been described elsewhere in detail (20).

Analyses of the gases during the pulsed reactions were made using an on-line quadrupole mass spectrometer (HAL201, Hiden Analytical Ltd.). The mass spectrometer scanned the parent peaks of the four compounds, H_2, C_2H_4, CO, and CO_2, within 1 s, and repeated scans were collected with a personal computer. Measured intensities were corrected for the relative sensitivities of the respective ions.

3. RESULTS AND DISCUSSION

The behavior of Ga_2O_3 and Ga_2O_3-loaded catalysts and the conversion of ethane to ethene in the presence of CO_2 have been discussed in previous papers (3, 19). The promoting effect of CO_2 on the conversion of ethane over gallium oxide catalyst is substantial. This was examined by changing the reaction conditions, and the surface areas of Ga_2O_3 and Ga_2O_3-loaded catalysts, in order to clarify the roles of CO_2.

3.1. *Effect of Carbon Dioxide Pressure on the Dehydrogenation of Ethane over Gallium-Loaded Catalysts*

Figures 1 and 2 show the effect of carbon dioxide pressure on the dehydrogenation of ethane over gallium-loaded

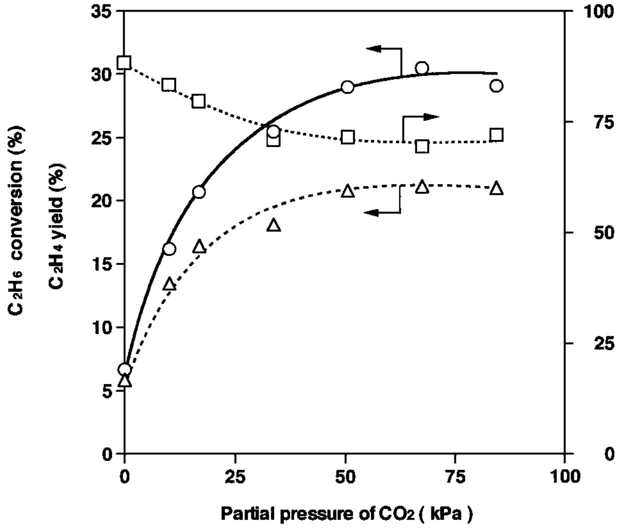

FIG. 1. Effect of partial pressure of CO_2 on the C_2H_6 conversion, C_2H_4 yield, and C_2H_4 selectivity over Ga_2O_3/TiO_2 catalyst: (○) C_2H_6 conversion, (△) C_2H_4 yield, (□) C_2H_4 selectivity. Reaction conditions: temperature, 923 K; reaction time = 0.5 h; catalyst = 200 mg; Ga : Ti = 5 : 95 (mol%); C_2H_6 = 5 mL/min; total flow rate = 30 mL/min; SV = 9,000 h^{-1} mL/g-cat.

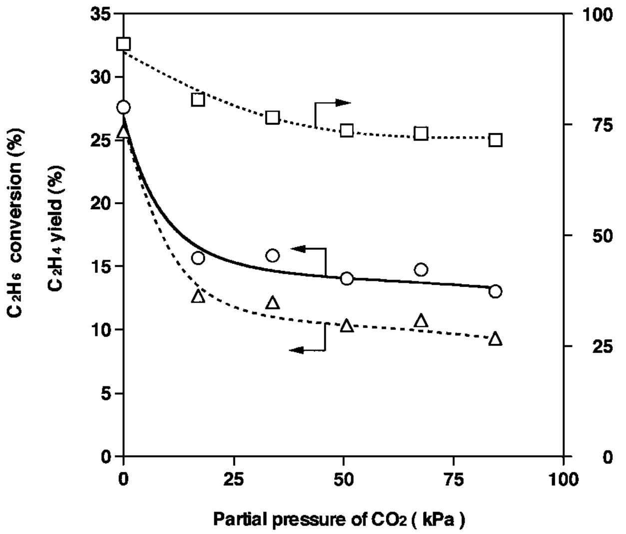

FIG. 2. Effect of partial pressure of CO_2 on the C_2H_6 conversion, C_2H_4 yield, and C_2H_4 selectivity over Ga_2O_3/Al_2O_3 catalyst: (○) C_2H_6 conversion, (△) C_2H_4 yield, (□) C_2H_4 selectivity. Reaction conditions: temperature, 923 K; reaction time = 0.5 h; catalyst = 200 mg; Ga : Al = 5 : 95 (mol%); C_2H_6 = 5 mL/min; total flow rate = 30 mL/min; SV = 9,000 h^{-1} mL/g-cat.

catalysts. In the Ga_2O_3/TiO_2 catalyst, the ethane conversion and ethene yield markedly increased when the CO_2 partial pressure was increased (Fig. 1). However, the ethene selectivity decreased only slightly with increases in the CO_2 partial pressure. These results indicate that carbon dioxide played an important role in the dehydrogenation of ethane to ethene over the Ga_2O_3/TiO_2 catalyst. On the other hand, in the Ga/Al_2O_3 catalyst, the ethane conversion and ethene yield decreased with increasing CO_2 partial pressure (Fig. 2). CO_2 did not promote dehydrogenation of ethane over the Ga_2O_3/Al_2O_3 catalyst, and moreover the yields of ethene decreased markedly with an increase in the CO_2 partial pressure.

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

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad [4]$$

$$CO_2 + C \rightleftarrows 2CO. \qquad [5]$$

In the dehydrogenation of ethane under a CO_2 atmosphere, H_2O was produced during the reaction (reaction 4). Over the Ga_2O_3/TiO_2 catalyst, the role of CO_2 could be to eliminate deposited carbon and to modify the acidity or the nature of the surface of the Ga_2O_3/TiO_2 catalyst. In contrast, ethane selectivity and the yield of the Ga_2O_3/Al_2O_3 catalyst decreased under CO_2. This result would indicate that produced H_2O (reaction 4) inhibited the dehydrogenation of ethane. Decreased ethene yield over the Ga_2O_3/Al_2O_3 catalyst might be caused by modified acidity of the surface of the Ga_2O_3/Al_2O_3 catalyst with H_2O (19).

3.2. Effect of Space Velocity on the Dehydrogenation of Ethane over Ga_2O_3/TiO_2 Catalyst

In order to obtain more information regarding the role of CO_2 in the dehydrogenation of ethane over the Ga_2O_3/TiO_2 catalyst, the space velocity was varied by increasing the feed rate at the reaction temperature of 923 K. Figure 3 shows the effect of space velocity on the dehydrogenation of ethane over Ga_2O_3/TiO_2 catalyst. Both in the presence and in the absence of CO_2, ethane conversion and ethene yield decreased with increasing space velocity. However, ethene selectivities increased. Probably, the secondary reaction, hydrocracking of ethane or ethene, was prevented. In these ranges of the space velocities examined, the activity of the Ga_2O_3/TiO_2 catalyst in the presence of CO_2 was greater than that under Ar. Especially at high

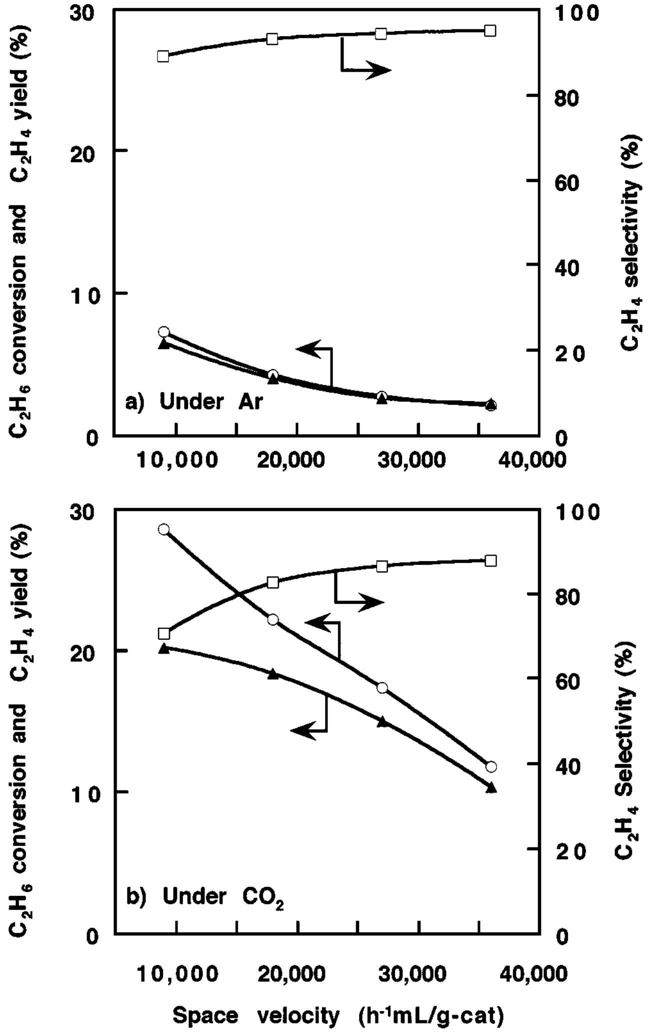

FIG. 3. Effect of space velocity on the C_2H_6 conversion, C_2H_4 yield, and C_2H_4 selectivity over Ga_2O_3/TiO_2 catalyst: (○) C_2H_6 conversion, (▲) C_2H_4 yield, (□) C_2H_4 selectivity, Reaction conditions: temperature, 923 K; reaction time = 0.5 h; catalyst = 200 mg; Ga : Ti = 5 : 95 (mol%); $C_2H_6 : CO_2$ (or Ar) = 1 : 5.

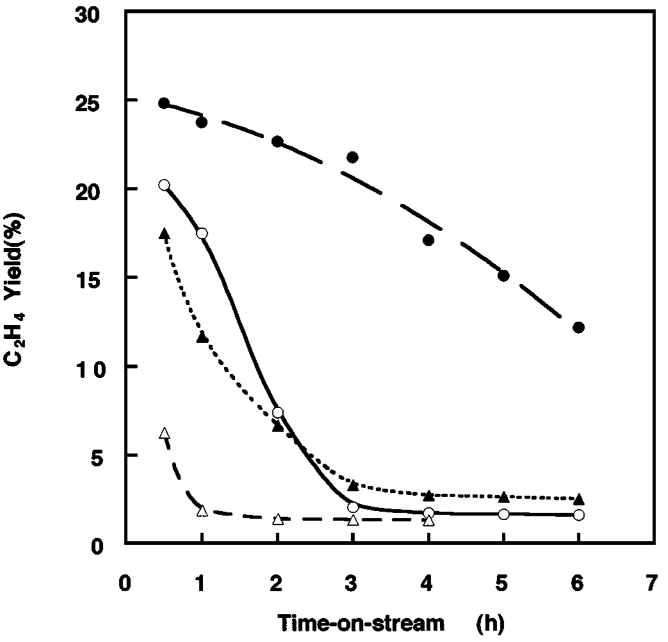

FIG. 4. Effect of time-on-stream on the C_2H_4 yield over Ga_2O_3/TiO_2 catalyst: (○) CO_2, (●) $CO_2 + H_2O$, (△) Ar, (▲) Ar + H_2O. Reaction conditions: temperature, 923 K; catalyst = 200 mg; Ga : Ti = 5 : 95 (mol%); $C_2H_6 : CO_2$ (or Ar) = 5 : 25 (mL/mL); $C_2H_6 : H_2O : CO_2$ (or Ar) = 1 : 1 : 5; total flow rate = 30 mL/min.

space velocities, the activity of the Ga_2O_3/TiO_2 catalyst in the presence of CO_2 was about 5 times greater than that in the absence of CO_2. Under an Ar atmosphere, ethene yield decreased with increasing space velocity, and above 27,000 h^{-1} mL/g-catalyst, the same yield as that of the uncatalyzed run was obtained. Under a CO_2 atmosphere, the catalytic activity of the Ga_2O_3/TiO_2 catalyst was maintained despite high space velocities.

However, the dehydrogenation of ethane proceeded over the Ga_2O_3/TiO_2 catalyst even at high space velocity under CO_2 flow. From these findings CO_2 seemed to positively promote the dehydrogenation of ethane over the Ga_2O_3/TiO_2 catalyst.

3.3. *Effect of Time-on-Stream on the Dehydrogenation of Ethane over the Ga_2O_3/TiO_2 Catalyst*

Figure 4 shows the effect of time-on-stream on the dehydrogenation of ethane over the Ga_2O_3/TiO_2 catalyst. Both in the presence and in the absence of CO_2 over Ga_2O_3/TiO_2, ethene yields decreased remarkably with increasing reaction times, due to carbon deposition.

Carbon deposition is one of the major problems involved in the dehydrogenation of ethane. A role of water in the dehydrogenation of ethane would be considered as follows (19):

$$H_2O + C \rightarrow CO, CO_2, H_2. \qquad [6]$$

To improve the stability of the catalyst, steam was introduced in the dehydrogenation of ethane over the Ga_2O_3/TiO_2 catalyst in the presence and in the absence of CO_2. With the Ga_2O_3/TiO_2 catalyst, deactivation of the catalyst in the presence and in the absence of CO_2 without steam occurred, and conversion of ethane decreased from 20.2% to 2% and from 6.2% to 1.4% within 3 h, respectively. In contrast, the ethene yield markedly increased by introducing steam both in the presence and in the absence of CO_2 in the runs for 6 h. These results suggest that steam might also have promoted the dehydrogenation of ethane over the Ga_2O_3/TiO_2 catalyst. In this reaction, COx was detected. Therefore, the addition of steam could eliminate deposited carbon on the surface of the Ga_2O_3/TiO_2 catalyst.

3.4. *Comparison between Deposited Carbons on the Dehydrogenation of Ethane in the Presence of CO_2 and in the Absence of CO_2*

To investigate the amounts of and types of deposited carbons on the dehydrogenation of ethane in the presence and in the absence of CO_2 over a Ga_2O_3/TiO_2 catalyst, the catalysts used were examined by means of Raman spectroscopy. The Raman spectra of the Ga_2O_3/TiO_2 catalysts used in the presence and in the absence of CO_2 are shown in Fig. 5. Two peaks were observed for the spectra of

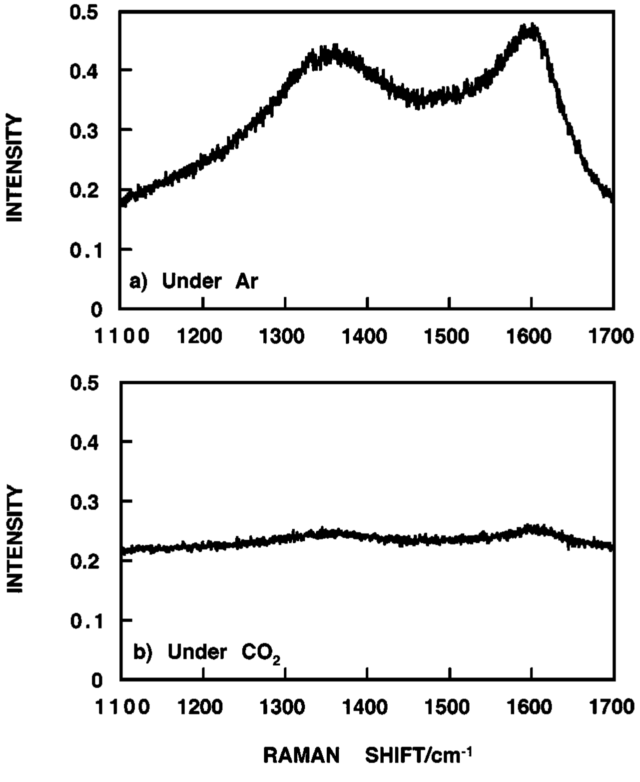

FIG. 5. Raman spectrum of Ga_2O_3/TiO_2 catalysts used in the presence and absence of CO_2. (a) Catalyst was reacted with ethane under Ar, 4 h, 923 K. (b) Catalyst was reacted with ethane under CO_2, 6 h, 923 K.

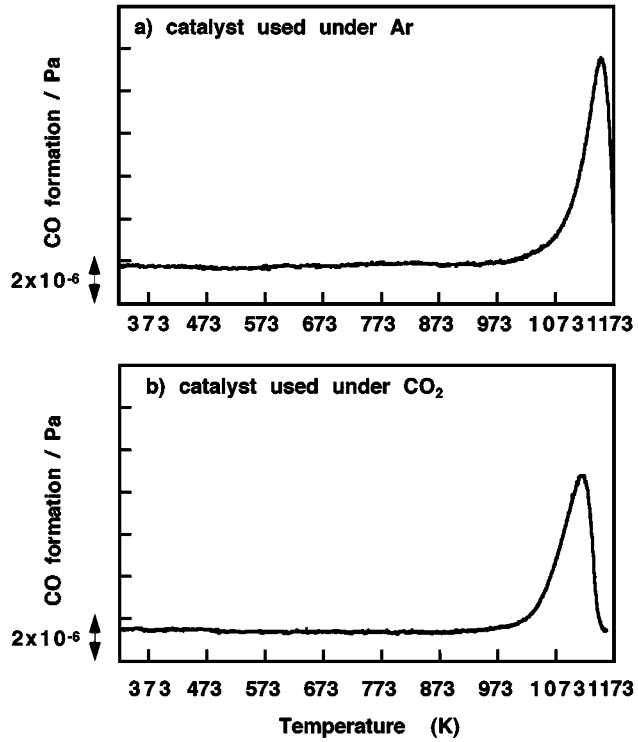

FIG. 6. Temperature-programmed reaction (oxidation with CO_2) of deposited carbon on Ga_2O_3/TiO_2 catalysts used. (a) Catalyst was reacted with ethane under Ar, 4 h, 923 K. (b) Catalyst was reacted with ethane under CO_2, 6 h, 923 K. Reaction conditions: sample = 100 mg; Ga : Ti = 5 : 95 (mol%); CO_2 flow rate = 10 mL/min; heating rate = 20 K/min.

deposited carbon both in the presence and in the absence of CO_2: one appeared at around 1350 cm^{-1} and the other at 1600 cm^{-1}. The intensities of these absorptions in the spectrum obtained in the absence of CO_2 were much larger than those in the presence of CO_2. This indicates that the amounts of deposited carbon in the absence of CO_2 were larger than those in the presence of CO_2.

Temperature-programmed reactions (oxidation) with CO_2 were carried out in order to investigate the reactivity of deposited carbon species on the Ga_2O_3/TiO_2 catalyst in the presence and in the absence of CO_2 (Fig. 6). Samples were reacted with ethane at 923 K for 6 h in the presence of CO_2 and for 4 h in the absence of CO_2. In the temperature-programmed reactions (oxidation) with CO_2 over the Ga_2O_3/TiO_2 catalyst dehydrogenated in the absence of CO_2, a large amount of CO (*m*/*z* 28) was detected above 1023 K, and CO continued to be detected after reaching 1173 K. The maximum rate of CO desorption appeared at 1150 K. In contrast, over the Ga_2O_3/TiO_2 catalyst dehydrogenated in the presence of CO_2, the amount of CO was much smaller than that in the absence CO_2. Note that in the presence of CO_2, a large amount of ethane was dehydrogenated. The maximum rate of CO desorption appeared at 1120 K, and all the carbon was completely removed below 1173 K.

In addition, the formation of CO was observed at a lower temperature in the dehydrogenation under CO_2. After temperature-programmed reactions (oxidation) with CO_2, deposited carbon remained over Ga_2O_3/TiO_2 catalyst in the dehydrogenation under Ar. In contrast, in the case of the dehydrogenation under CO_2, deposited carbon was fully removed by the reaction with CO_2 during the temperature-programmed reaction.

These results indicate that the amount of deposited carbon over the Ga_2O_3 catalyst in the presence of CO_2 was smaller and had a higher reactivity than that formed under Ar. Therefore, one possible reason for the increased dehydrogenation in the presence of CO_2 is elimination of deposited carbon (reaction 5).

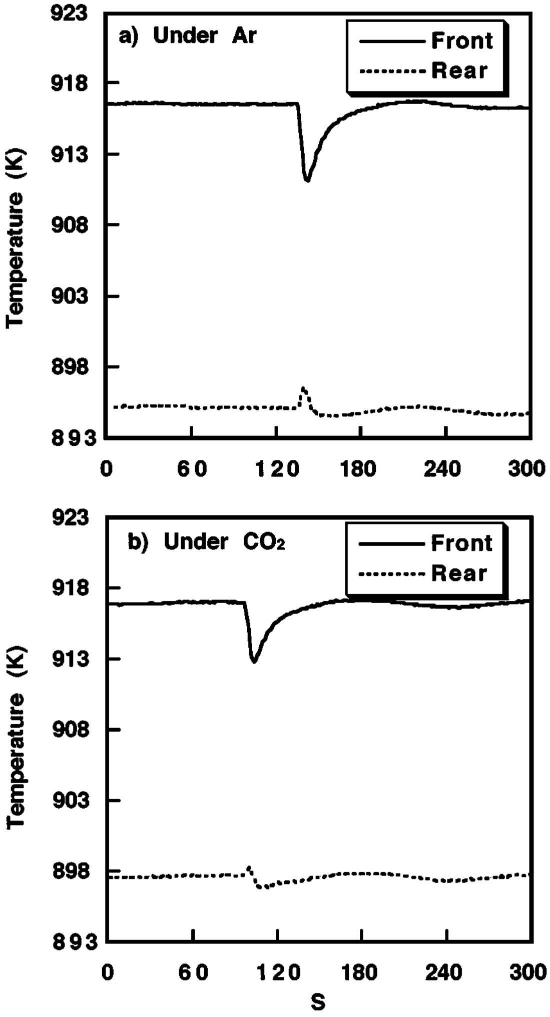

FIG. 7. Temperature profile at front and rear edge of the catalyst bed over Ga_2O_3/TiO_2 catalysts. Reaction conditions: catalyst = 100 mg; Ga : Ti = 5 : 95 (mol%); Ar or CO_2 carrier = 30 mL/min; C_2H_6 pulse = 1 mL; furnace temperature, 923 K.

3.5. *Transient Response of Catalyst Bed Temperature in the Pulsed Reaction of Dehydrogenation of Ethane in the Presence and Absence of CO_2*

In order to investigate the promoting effect of CO_2 on the dehydrogenation of ethane in the presence of CO_2 over a Ga_2O_3/TiO_2 catalyst, a pulsed reaction technique was employed to measure transient temperature changes in the catalyst beds.

Figure 7 shows the transient temperature responses of the Ga_2O_3/TiO_2 catalyst against a pulsed injection of C_2H_6 in the presence and in the absence of CO_2. The temperature at the front edge decreased with the introduction of the C_2H_6 pulse both in the presence and in the absence of CO_2. In the absence of CO_2, a large decrease in the temperature of the front edge of the catalyst bed was observed as compared with the temperature drop in the presence of CO_2. Both reactions [1] and [3] are endothermic reactions. Observation of the catalyst bed temperature by means of injecting a pulse of reactants may provide information regarding the reaction taking place on the catalyst bed. Since reaction [1] is more endothermic than reaction [3], this result may indicate that the advantage of thermodynamics in the dehydrogenation of ethane in the presence of CO_2 is much larger than that in the absence of CO_2.

In the dehydrogenation of ethylbenzene to styrene under CO_2, thermodynamic considerations indicated that the equilibrium yield of styrene under CO_2 was much higher than that under steam (without CO_2) (13). In the dehydrogenation of ethane to ethene, the advantages of using CO_2 instead of Ar (without CO_2) would be given on the basis of thermodynamic considerations.

TABLE 1

C_2H_4 Area Ratio Against Responses to C_2H_4 Pulse over Ga_2O_3-Loaded Catalysts under CO_2 or Ar Steady Flow

Catalyst	Surface area (m^2/g)	C_2H_4 area ratio under CO_2/under Ar
None	—	1.08
TiO_2	52.5	1.02
Ga_2O_3	49.6	1.44
Ga_2O_3/TiO_2	50.2	2.16
Ga_2O_3/Al_2O_3	149	1.47
Ga_2O_3/SiO_2	421	0.93

Catalyst, 200 mg; reaction temperature, 923 K.

3.6. *Transient Response of Ethene Desorption in the Pulsed Reaction over Ga_2O_3-Loaded Catalysts in the Presence and Absence of CO_2*

To obtain more information regarding the dehydrogenation of ethane in the presence of CO_2 over Ga_2O_3-loaded catalysts, a pulsed reaction technique was employed to measure the amount of ethene adsorption over the catalyst.

Transient response of ethene adsorption was measured by introducing the same amount of ethene pulse under a CO_2 or Ar steady flow. Table 1 and Fig. 8 show the transient response of ethene adsorption over various Ga_2O_3-loaded catalysts against a pulsed introduction of ethene at 923 K under a steady flow of CO_2 or Ar. When as blank runs noncatalyst, TiO_2, and Ga_2O_3/SiO_2 catalysts were examined, the same responses of ethene and similar ethene area ratios, 1.08, 1.02, and 0.93, were observed for both

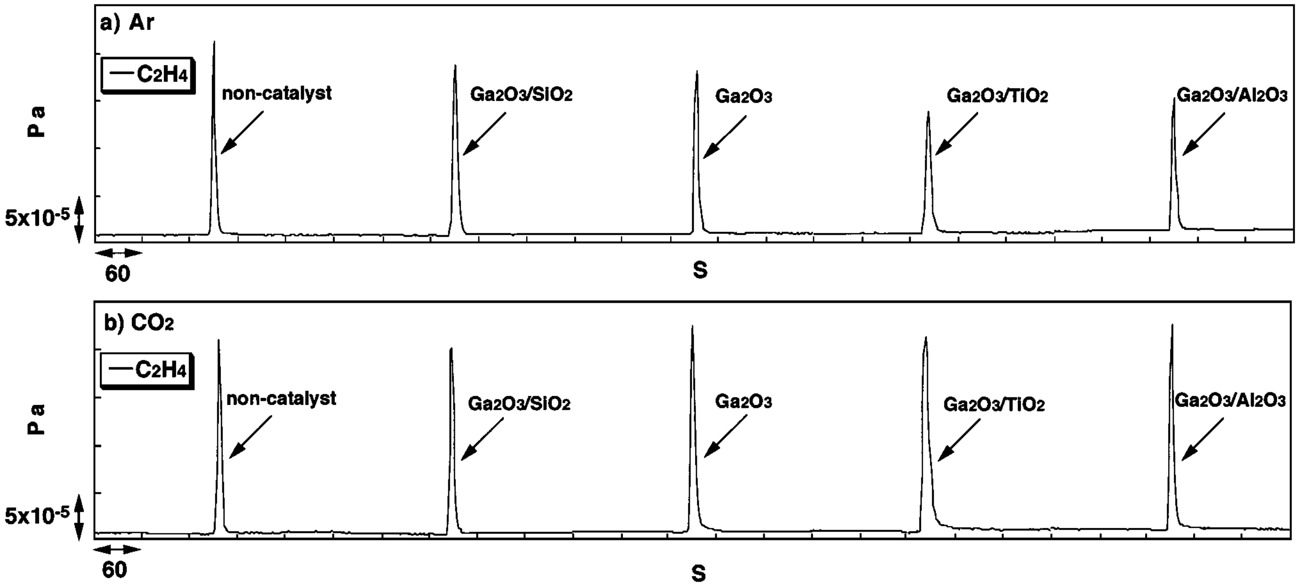

FIG. 8. Transient responses of C_2H_4 adsorption over gallium-loaded catalysts against a pulsed introduction of C_2H_4 under steady flow of Ar or CO_2. Reaction conditions: catalyst = 100 mg; Ga : M = 5 : 95 (mol%); Ar or CO_2 carrier = 30 mL/min; C_2H_4 pulse = 1 mL; furnace temperature, 923 K.

responses against CO_2 and Ar flows (Table 1 and Fig. 8). However, when Ga_2O_3, Ga_2O_3/TiO_2, and Ga_2O_3/Al_2O_3 catalysts were used (Table 1 and Fig. 8), the response of ethene under Ar was smaller than that under CO_2, and ratios of ethene area under CO_2 against under Ar were about 1.4–2.0. In addition, under Ar steady flow, carbon depositions were observed. Deference of catalyst's surface area did not strongly affect ethene adsorption.

Several roles of CO_2 could be considered: (1) inhibition of ethene adsorption on the catalyst surface; (2) control of carbon deposition from ethene; (3) promotion of desorption of ethene from the catalyst surface. Especially regarding the desorption of ethene, ethene which seemed to be a basic product would be easily adsorbed on the acidic site of the catalysts. Therefore, these results seem to indicate that, under Ar steady flow, ethene was strongly adsorbed on the surface of the catalysts and carbon deposition was induced. Ga_2O_3 and Ga_2O_3/TiO_2 catalysts, but not the Ga_2O_3/Al_2O_3 catalyst, were found to be effective agents for the dehydrogenation of ethane to ethene in the presence of CO_2. Furthermore, the acidic site of the Ga_2O_3-loaded catalysts would be the active site of the dehydrogenation of ethane (19). Another role of CO_2 in the dehydrogenation of ethane might be to promote rapid desorption of product (ethene) from the surface of the catalyst. Such assistance by CO_2 for the desorption of ethene from the catalyst seems to be necessary for dehydrogenation activity and anticoking.

4. CONCLUSION

Ga_2O_3/TiO_2 catalyst exhibited a high ethene yield in the presence of carbon dioxide. Increasing CO_2 partial pressure was found to be an effective catalyst for the dehydrogenation of ethane to ethene over a Ga_2O_3/TiO_2 catalyst at 923 K. Over the Ga_2O_3/TiO_2 catalyst, the deposited carbon in the absence of CO_2 seemed to be larger and less reactive than that in the presence of CO_2. Both CO_2 and steam played important roles in the maintenance of catalytic activity in the dehydrogenation of ethane over the Ga_2O_3/TiO_2 catalyst. For carbon deposition during the reaction, Raman spectra and temperature-programmed reaction with CO_2 also indicated the validity of the dehydrogenation of ethane in the presence of CO_2. Furthermore, in terms of the transient response to a certain amount of ethene adsorption in the pulsed reaction over Ga_2O_3-loaded catalysts in the presence and in the absence of CO_2, the promoting effect of CO_2 was observed in the rapid desorption of ethene from the catalyst surface.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research (B) 10555283, (C) No. 09650864, and (C) No. 11650811 from the Ministry of Education, Science, Sports, and Culture of Japan. K.N. is grateful for his research fellowship from the Japan Society for the Promotion of Science (JSPS) for Young Scientists.

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