

The Role of Chemisorbed Oxygen on Diamond Surfaces for the Dehydrogenation of Ethane in the Presence of Carbon Dioxide

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Received: October 1, 2002; In Final Form: February 6, 2003

Oxidized diamond played a significant role as an efficient support for a Cr₂O₃-loaded catalyst during the dehydrogenation of C₂H₆ to C₂H₄ in the presence of carbon dioxide at 923 K, giving a 22.5% C₂H₄ yield with a 87.7% C₂H₄ selectivity. The activity of the oxidized diamond-supported Cr₂O₃ catalyst in the presence of CO₂ was about 3 times higher than that in the absence of CO₂. The activity of the oxidized diamond-supported Cr₂O₃ catalyst increased with increasing CO₂ partial pressures. XPS analyses of the fresh and the reacted catalysts in the presence and absence of CO₂ revealed that CO₂ maintained the surface Cr₂O₃ at a higher-oxidation state than the reaction in the absence of CO₂. On the other hand, bulk of Cr₂O₃ was not reduced in either atmosphere.

1. Introduction

Recently, the surface chemistry of diamond has received much attention, and several functional groups have been introduced onto the diamond surface.^{1–3} However, the limit and scope of diamond or oxidized diamond-supported catalyst have not been yet revealed. Further applications of the diamond-supported catalyst need to be explored. Diamond has long been considered an inert material. One of the present authors demonstrated that the diamond surface behaved in the manner of an organic substances.¹ In addition, the diamond surface is expected to express possible chemical reactivities as organic molecules.³ This led us to develop the novel utilization of diamond as a catalyst or catalyst–support material for chemical reactions.

Oxidized diamond has recently drawn attention as a new unique material phase as a solid carbon oxide. The diamond surface is easily oxidized by oxidative acids such as HNO₃, HClO, H₂O₂, etc. and is also oxidized with oxygen at an elevated temperature to form C–O–C ether-type structures and C=O carbonyl-type structures.¹ Until now, no carbon-oxide solid phase has been found; however, the surface of oxidized diamond

is considered to be a pseudo-carbon-oxide solid phase. The oxidized diamond surface is expected to behave as a carbon oxide for specified surface reactions such as catalytic, electrochemical reactions. Because such reactions must be controlled by the interaction between molecules and surfaces, the bulk structures of solids are less important. Silicon oxide (called silica) is widely used as a neutral support for many catalytic reactions. Silica support has very weak interactions with some metals and metal oxides and plays an important role in yielding active reaction sites due to its high surface area.

Activated carbon has been widely utilized as a support material for metal or metal oxide-loaded catalysts. Activated carbon is composed of amorphous sp² carbon atoms. Recently, carbon nanofilaments have been reported as a novel carbon material that can be used for catalytic processes.⁴ No carbon material constituted of pure sp³ carbon atoms (diamond) has been examined as a catalyst–support material. However, our recent study of oxidized diamond-supported chromium oxide (III) or nickel exhibited excellent catalytic activity for the dehydrogenation of light alkanes,^{5,6} the partial oxidation of CH₄,^{7,8} and the decomposition of CH₃OH to synthesis gas,⁹ respectively. In these reactions, weak but significant interactions between loaded metal catalysts and support surfaces seemed to play important roles in enhancing and prolonging the activity of the respective catalysts. Oxidized diamond behaved as solid carbon oxide material and presents an excellent support material for catalysts.

C₂H₄ is predominantly produced by steam cracking of naphtha, C₂H₆, or liquefied petroleum gas at high temperatures at a short residence time. To reduce the energy consumption of C₂H₄ production, oxidative dehydrogenation required by

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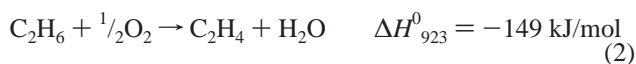
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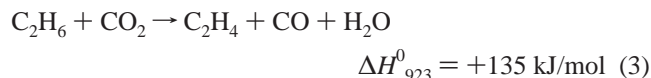
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C₂H₆ is proposed (reaction 2).



The reaction becomes exothermic and could be thermodynamically possible at a lower temperature. However, it is necessary to remove heat from the reaction and to control over-oxidation to CO_x to keep high selectivity to C₂H₄. Recently, a great variety of catalysts have been developed and tested to achieve this reaction.^{10–13} In the oxidative dehydrogenation of C₂H₆ and C₃H₈, some reports^{14,15} have pointed out that thermal noncatalytic oxidative dehydrogenation of C₂H₆ and C₃H₈ proceeded to give alkene in the same yield as compared to catalyzed runs which were operated at higher temperatures than those in noncatalyzed runs. This suggests that the catalyzed oxidative dehydrogenation of lower alkanes is not highly superior to thermal nonoxidative pyrolysis. Recently, CO₂ has been investigated as a mild oxidant for the dehydrogenation of ethylbenzene,^{16–18} C₂H₆,^{19,20} or C₃H₈,^{21,22} since many investigators have suggested that the catalyzed oxidative reactions of lower alkanes with oxygen have a lesser advantage. We first found that CO₂ markedly promoted dehydrogenation of C₂H₆ over Ga₂O₃-based catalysts^{23–25} and the oxidized diamond-supported Cr₂O₃ catalyst⁵ with high selectivity (reaction 3).



In this work, we dealt with the performance of oxidized diamond as a new support material for the Cr₂O₃-loaded catalyst in the dehydrogenation of C₂H₆ to C₂H₄ and found that the oxidized diamond-supported Cr₂O₃ catalyst markedly promoted dehydrogenation of C₂H₆ to C₂H₄ in the presence of CO₂. We applied oxidized diamond surfaces as a new catalytic support for the dehydrogenation of C₂H₆ to yield C₂H₄ and elucidated the roles of CO₂ in the dehydrogenation of C₂H₆ over the oxidized diamond-supported catalysts.

2. Experimental Section

To have a reactivity for a catalytic reaction and a hydrophobicity for impregnating metal oxides as an active material on the diamond surface, oxidized diamond was prepared by the oxidation of commercial fine-powdered diamond at 723 K for 1 h under a stream of O₂–Ar (1:4) mixed gases. Before oxidation, to eliminate impurities and activate the diamond surface, diamond powder was hydrogenated at 1173 K for 1 h. Catalysts were prepared by impregnating aqueous solutions of Fe(NO₃)₃·9H₂O, Cr(NO₃)₃·9H₂O (Wako Pure Chemical Industries Ltd.), Ga(NO₃)₃·8H₂O (Kishida Chemicals), Zn(NO₃)₂·6H₂O, Ce(NO₃)₃·6H₂O, (CH₃COO)₂Mn·4H₂O (Wako Pure Chemical Industries Ltd.), (NH₄)₄VO₃ and (NH₄)₆Mo₇O₂₄·4H₂O (Nacalai tesque, Inc.) to Al₂O₃ (JRC-ALO-4, the reference catalyst provided by the Catalyst Society of Japan), SiO₂ (Merck), activated carbon (Wako Pure Chemical Industries Ltd.), and oxidized diamond (B.E.T. surface area = 12.6 m²·g^{−1}), and they were evaporated to dryness. Supported catalysts were calcined at 723 K for 3 h in air prior to the reaction. The reaction was carried out using a fixed-bed flow-type quartz reactor (i.d. 10 mm × 350 mm) at atmospheric pressure. Using 200 mg of a catalyst, 5 mL/min C₂H₆ and 25 mL/min of CO₂ or Ar were introduced. Analyses of the C₁, C₂, and C₃ hydrocarbon gases were carried out using a Shimadzu GC14BPF gas chromatograph

(FID detector) equipped with a 3 mm × 3 m glass column packed with Porapak Q in N₂ carrier. Analyses of CO, CO₂, and CH₄ were carried out using a Shimadzu GC8AIT gas chromatograph (TCD detector) equipped with a 3 mm × 3 m stainless steel column packed with activated carbon (30/60 mesh) using He as a carrier gas. Analyses of H₂ were carried out using a Shimadzu GC8AIT gas chromatograph (TCD detector) equipped with a 3 mm × 3 m stainless steel column packed with an activated carbon (30/60 mesh) and with N₂ carrier. The surface area of the catalyst was measured by the BET method using N₂ at 77 K using an automatic Micromeritics Gemini model 2375.

Diffuse reflectance IR spectra were recorded on an FT-IR instrument (JIR-7000, JEOL) equipped with a cooled MCT detector in the region of 400–4000 cm^{−1} at a resolution of 2 cm^{−1}. A KBr standard powder was used for the reference spectrum. Diffuse reflectance was converted into Kubelka–Munk function units. Powder X-ray diffraction (XRD) patterns were measured using a Simadzu XRD-6000 utilizing monochromatized Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) results were obtained using an X-ray photoelectron spectrometer (JPS-9000MX, JEOL) using Mg Kα radiation as the energy source. Raman spectroscopy with a 1-μm depth resolution by Ar⁺ laser excitation (NR-1800MB, Jasco) was used.

Transient response measurements of the catalyst bed temperature during the pulsed reactions were carried out using a fixed-bed quartz reactor (i.d. 4 mm × 200 mm) which was set in a horizontal position in an electric furnace. Two thin-wall sheathed thermocouples (o.d. 0.6 mm) were fixed at the front and the rear end of the catalyst bed, and 100 mg of the catalyst was charged. The reaction system has been described elsewhere in detail.²⁴ A pulse of C₂H₆ was introduced by means of a six-port gas-sampling valve equipped with measuring tubes, under a stream of CO₂ or Ar carrier gas. The reaction temperature was controlled using a programmable controller that monitored the outside temperature of the reactor wall.

3. Results and Discussion

3.1. Diffuse Reflectance FT-IR Spectroscopic Analysis of Hydrogenated and Oxidized Diamonds. Figure 1 shows the diffuse reflectance FT-IR spectra of hydrogenated and oxidized diamonds. The spectrum of hydrogenated diamond contained bands in the region of 2800–2970 cm^{−1} (Figure 1a), which were ascribed to C–H stretching vibrations (νC–H) of sp³ hybridized bonding.^{1,27,28} Oxidized diamond was obtained by the oxidation of hydrogenated diamond at 723 K for 1 h under a stream of O₂–Ar (1:4 mixture). No significant C–H stretching vibrations were observed on the oxidized diamond (Figure 1b). The spectrum of oxidized diamond contained bands in the region of 1650–1850 cm^{−1} (Figure 1b), which were ascribed to C=O stretching vibrations (νC=O), and absorptions at 1150 and 1250 cm^{−1} were assigned to C–O–C stretching vibrations (νC–O).²⁶ These results indicated that oxygen species were introduced into the diamond surface.

3.2. Dehydrogenation of C₂H₆ in the Presence of CO₂ over Oxidized Diamond-Supported Metal Oxide Catalysts. Figure 2 shows C₂H₄ yields on various oxidized diamond-supported metal oxide catalysts in the presence or absence of CO₂. Thermal dehydrogenation gave only a c.a. 2.5% of C₂H₄ yield in both CO₂ and Ar atmospheres. Equilibrium conversion of C₂H₆ to C₂H₄ is ca. 50% at 923 K at a C₂H₆–CO₂ ratio of 1:5. The order of the activity of various oxidized diamond-supported metal oxide catalysts in the presence of CO₂ at the reaction

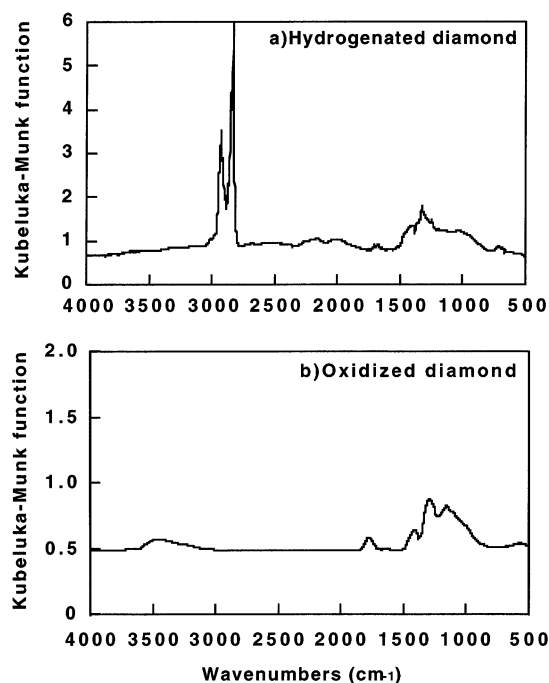


Figure 1. Diffuse reflectance FT-IR spectra of hydrogenated diamond and oxidized diamond reaction conditions: (a) Hydrogenated diamond: 1173 K for 1 h in H_2 , (b) oxidized diamond: 723 K for 1 h in air.

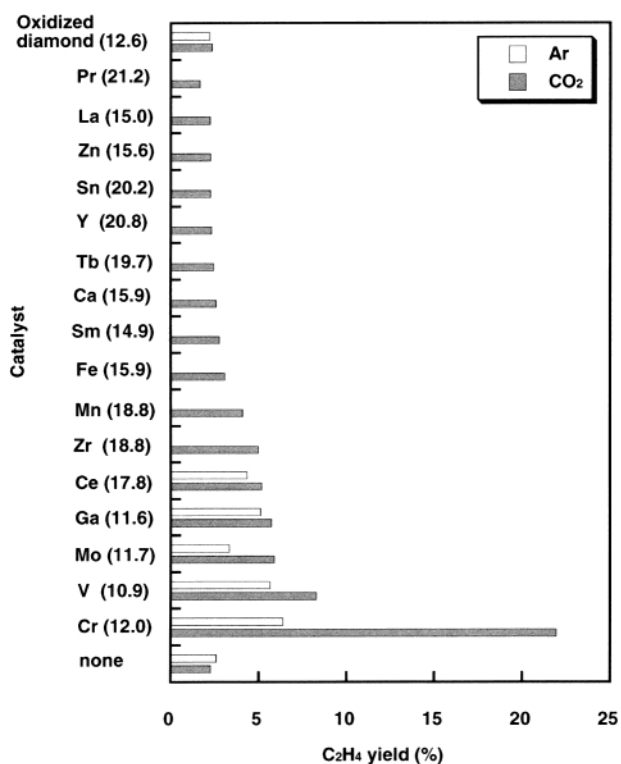


Figure 2. Dehydrogenation of C_2H_6 in the presence of CO_2 or Ar over various oxidized diamond-supported metal oxide catalysts. Reaction conditions: temperature: 923 K, reaction time: 0.5 h, $C_2H_6:CO_2$ (Ar) = 5:25 (mL/mL), catalyst = 200 mg, SV = 9000 h^{-1} mL/g-cat, numerals in parentheses: surface area (m^2/g), M:oxidized diamond = 5:95 (wt %).

temperature of 923 K was as follows: $Cr_2O_3 > V_2O_5 > MoO_3 > Ga_2O_3 > CeO_2 > Mn_3O_4 > Fe_2O_3 > Sm_2O_3 > CaO > Tb_4O_6 > Y_2O_3 > SnO_2 > ZnO > La_2O_3 > Pr_6O_{11}$. The C_2H_4 selectivities in all the metal oxide catalysts were higher than 85% in the dehydrogenation under CO_2 atmosphere. Oxidized

TABLE 1: Dehydrogenation of Ethane over Oxidized Diamond-Supported Catalysts^a

catalysts	surface area m^2/g	conv., % C_2H_6	yield, % C_2H_4	selectivity, %	
				C_2H_4	CH_4
$Cr_2O_3(CO_2)$	12.0	27.4	23.8	86.7	13.3
$Cr_2O_3(Ar)$	12.0	7.0	6.8	97.1	2.9
$V_2O_5(CO_2)$	10.9	9.3	8.3	89.2	10.8
$V_2O_5(Ar)$	10.9	5.9	5.7	96.0	4.0
$MoO_3(CO_2)$	11.7	6.8	5.9	87.4	5.7
$MoO_3(Ar)$	11.7	7.9	3.3	57.9	42.1
$Ga_2O_3(CO_2)$	11.6	5.8	5.7	99.7	0.3
$Ga_2O_3(Ar)$	11.6	5.2	5.1	99.6	0.4

^a Reaction conditions: 923 K, SV = 9000 h^{-1} mL/g-cat. Composition of the feed gas: $C_2H_6/CO_2(Ar)$ = 5/25.

diamond alone and Sm-, Ca-, Tb-, Y-, Sn-, Zn-, La-, and Pr-loaded on oxidized diamond catalysts did not show catalytic activity. Oxidized diamond-supported Mo, Ga, Ce, Zr, Mn, and Fe oxide catalysts exhibited slight catalytic activity. Mo-, Ga-, Ce-, and Fe-containing catalysts were known to be active catalysts for the dehydrogenation of alkane in the presence of O_2 or steam. The oxidized diamond-supported Cr_2O_3 catalyst afforded the highest yield of C_2H_4 (22.5%) among various oxidized diamond-supported metal oxide catalysts.

The promoting effects of CO_2 on C_2H_4 yield were observed over oxidized diamond-supported Cr, V, Mo, Ga, and Ce catalysts (Table 1). In particular, the activity of the oxidized diamond-supported Cr_2O_3 catalyst in the presence of CO_2 was 3 times higher than that in the absence of CO_2 . Dehydrogenation of C_2H_6 in the presence of CO_2 over the oxidized diamond-supported Cr_2O_3 catalyst produced mainly C_2H_4 , CO, H_2 , and H_2O . The promoting effect of CO_2 in the dehydrogenation of C_2H_6 on the Ga_2O_3 was twice that under Ar atmosphere.²³ In the case of Ga_2O_3/TiO_2 , the conversion of C_2H_6 in the presence of CO_2 increased twice that in the presence of Ar; however, a secondary reaction such as the decomposition of C_2H_6 or C_2H_4 occurred to give CH_4 decreasing C_2H_4 selectivity.^{24,25} In the oxidized diamond-supported Cr_2O_3 catalyst, the increase in C_2H_4 yield was about 17% in the presence of CO_2 . One of the characteristic features of diamond support is a higher C_2H_4 selectivity. By using this support, the absence of secondary reactions with reactants or products could probably be prevented.

3.3. Effect of Support on the Dehydrogenation of C_2H_6 over Cr_2O_3 -Loaded Catalysts. Oxidized diamond-supported metal oxide catalysts were compared to unsupported metal oxide or Cr_2O_3 -loaded catalysts on various support materials. Figure 3 shows C_2H_4 yields on bulk metal oxide and Cr_2O_3 -loaded on various support materials. The order of the activity compared by unit Cr and by unit surface area at a reaction temperature of 923 K was as follows: Oxidized diamond > unsupported Cr_2O_3 > Al_2O_3 > SiO_2 > activated carbon. The C_2H_4 selectivities in all the metal oxide catalysts were higher than 90% in the dehydrogenation of C_2H_6 in the presence of CO_2 . However, the unsupported Cr_2O_3 catalyst showed a lower C_2H_4 yield than did the oxidized diamond-supported Cr_2O_3 catalyst. This indicated that oxidized diamond significantly supported the Cr_2O_3 -loaded catalyst in the dehydrogenation of C_2H_6 to C_2H_4 in the presence of CO_2 .

3.4. Effect of Temperature on the Dehydrogenation of C_2H_6 in the Presence and Absence of CO_2 over Oxidized Diamond-Supported Cr_2O_3 Catalyst. Figure 4 shows the temperature dependence of catalytic activity of the oxidized diamond-supported Cr_2O_3 catalyst in the presence and the absence of CO_2 . C_2H_4 yields in the noncatalytic runs did not

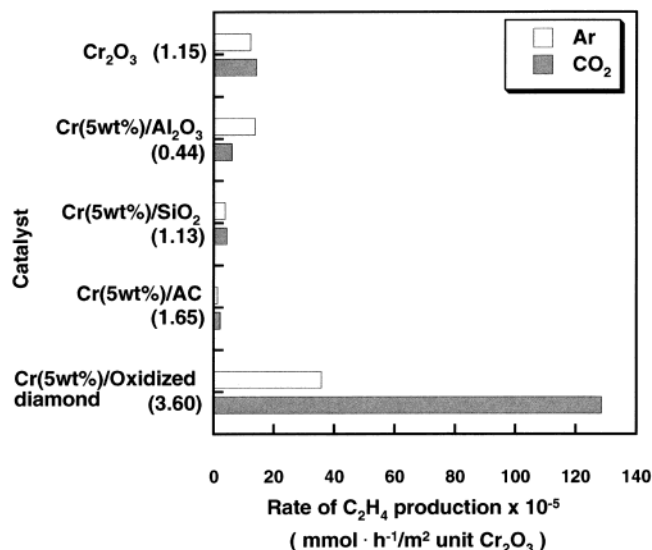


Figure 3. Dehydrogenation of C₂H₆ in the presence of CO₂ or Ar over various Cr₂O₃-loaded catalysts. Reaction conditions are the same as those shown in Figure 2: C₂H₄ yield under CO₂ flow/C₂H₄ yield under Ar flow.

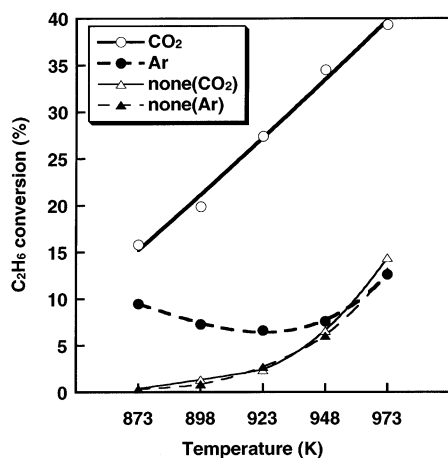


Figure 4. Effect of temperature on the conversion of C₂H₆ over oxidized diamond-supported Cr₂O₃ catalyst. Reaction conditions: the same as those shown in Figure 2, except for temperature.

depend on atmosphere. In the presence of CO₂ over the oxidized diamond-supported Cr₂O₃ catalyst, C₂H₄ yields increased remarkably with increasing reaction temperature, and a 27.4% C₂H₄ yield was obtained at 973 K. In contrast, C₂H₄ yield in the absence of CO₂ decreased with increasing reaction temperature, and above 948 K the same yield as that of the uncatalyzed run was obtained. In the absence of CO₂, this inverse relation, i.e., the decrease the C₂H₄ yield with an increase in the reaction temperature, is probably caused by rapid carbon deposition on the catalyst surface. CO was detected over the catalyst during dehydrogenation of C₂H₆ in the presence of CO₂. In addition, CO was formed during the reaction between CO₂ and used catalyst (oxidized diamond-supported Cr₂O₃ catalyst) after the dehydrogenation of C₂H₆ in the absence of CO₂. Therefore, in the presence of CO₂, the elimination of deposited carbon (reaction 5) may be a possible case of the promoting effects on the dehydrogenation of C₂H₆.

Figure 5 shows effect of the Cr₂O₃-loading level on C₂H₄ yield in the dehydrogenation of C₂H₆ under CO₂ atmosphere. The highest C₂H₄ yield (23.8%) was obtained at 2.5 wt % Cr₂O₃, and C₂H₄ yield remained constant over a Cr₂O₃-loading level of 1.0–7.5 wt %, at a reaction temperature of 923 K.

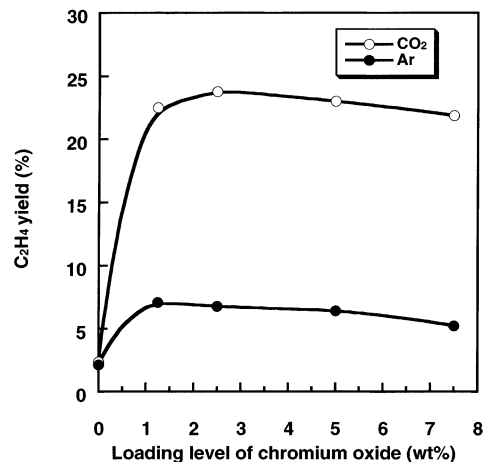


Figure 5. Effect of loading level of oxidized diamond-supported chromium oxide on C₂H₄ yield in the presence of CO₂ or Ar. Reaction conditions: temperature: 923 K, reaction time: 0.5 h, C₂H₆:CO₂ (Ar) = 5:25 (mL/mL), catalyst = 200 mg, SV = 9000 h⁻¹ mL/g-cat.

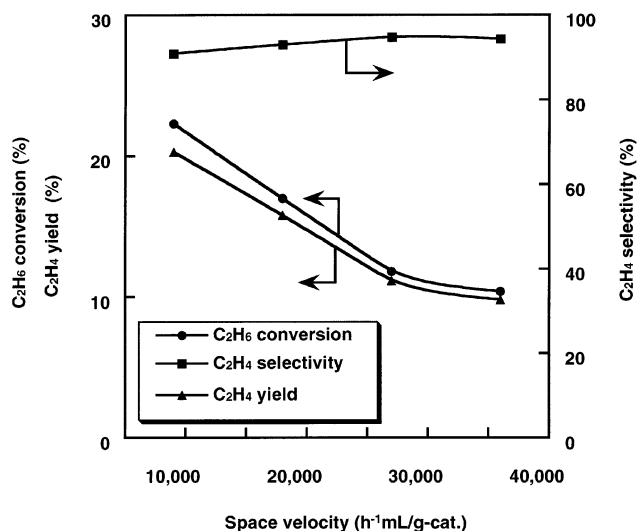


Figure 6. Effect of space velocity on the C₂H₆ conversion, and C₂H₄ yield and selectivity over oxidized diamond-supported Cr₂O₃ catalyst. Reaction conditions: temperature: 923 K, catalyst = 200 mg, loading level of Cr = 2.5 wt %, C₂H₆:CO₂ = 1:5.

3.5. Effect of Space Velocity on the Dehydrogenation of C₂H₆ over Oxidized Diamond-Supported Cr₂O₃ Catalyst. To obtain more detailed information regarding the role of CO₂ on the dehydrogenation of C₂H₆ over the oxidized diamond-supported Cr₂O₃ catalyst, the space velocity was varied by increasing the feed rate at a reaction temperature of 923 K. Figure 6 shows the effect of space velocity on the dehydrogenation of C₂H₆ over the oxidized diamond-supported Cr₂O₃ catalyst. In the presence of CO₂, C₂H₆ conversion and C₂H₄ yield decreased with increasing space velocity. In contrast, C₂H₄ selectivity increased. Selectivity of CH₄ which was produced by hydrocracking of C₂H₆ and C₂H₄ decreased with increasing space velocity. Probably a secondary reaction of C₂H₆ or C₂H₄, such as hydrocracking, decreased. Under a CO₂ atmosphere, the yield of C₂H₄ on the oxidized diamond-supported Cr₂O₃ catalyst did not significantly decrease even at a high space velocity.

Figure 7 shows the effect of apparent contact time (1/SV) on C₂H₆ conversion over the oxidized diamond-supported Cr₂O₃ catalyst. Instead of reaction rates, C₂H₆ conversion at the initial stage was used to evaluate reaction rates. The good linear relation between the natural logarithms of conversion against

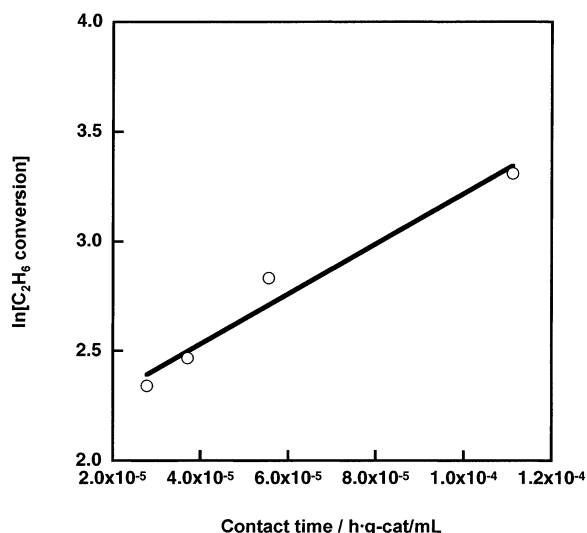


Figure 7. Effect of contact time on C_2H_6 conversion over oxidized diamond-supported Cr_2O_3 catalyst.

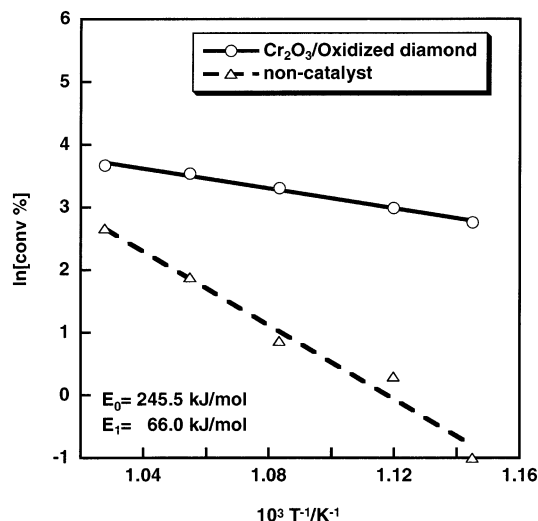


Figure 8. Arrhenius plots showing the dehydrogenation of ethane in the presence of CO_2 over oxidized diamond-supported Cr_2O_3 catalyst.

the inverse of SV clearly shows that the reaction is approximately first-order to C_2H_6 . In this relation CO_2 , contact time was changed simultaneously; thus, the reaction rate evaluated involves the effect of reaction order against CO_2 . Since the reaction was carried out in excess CO_2 ($CO_2/C_2H_6 = 5$), the effect of CO_2 on the reaction rates was not seen, indicating that reaction order to CO_2 is nearly zero.

Figure 8 shows Arrhenius plots of the dehydrogenation of ethane in the presence of CO_2 . The apparent activation energy over the oxidized diamond-supported Cr_2O_3 catalyst is ca. 66 kJ/mol and is much lower than that of the thermal reaction of 246 kJ/mol. The large advantage of catalytic dehydrogenation was semiquantitatively clarified. As shown in Figure 4, however, due to the rapid deactivation of the dehydrogenation of C_2H_6 under an Ar atmosphere, a comparison of activation energy between the run in CO_2 and Ar could not be performed.

3.6. Effect of CO_2 and Steam Pressure on the Dehydrogenation of C_2H_6 over Oxidized Diamond-Supported Cr_2O_3 Catalyst. Figure 9 shows the effect of CO_2 partial pressure on the dehydrogenation of C_2H_6 over the oxidized diamond-supported Cr_2O_3 catalyst. C_2H_6 conversion and C_2H_4 yield markedly increased with the addition of a small portion of CO_2 and increased gradually with further increases in the CO_2 partial

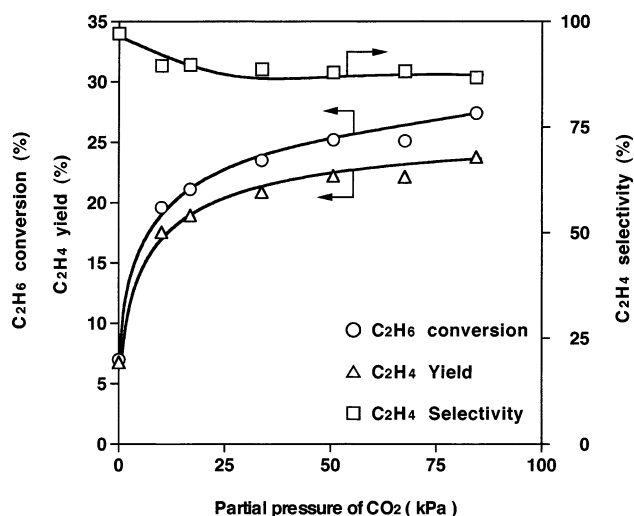


Figure 9. Effect of partial pressure of CO_2 on C_2H_6 conversion, and C_2H_4 yield and selectivity over oxidized diamond-supported Cr_2O_3 catalyst. Reaction conditions: temperature: 923 K, reaction time: 0.5 h, catalyst = 200 mg, loading level of Cr = 2.5 wt %, SV = 9000 h^{-1} mL/g-cat, C_2H_6 : 5 mL/min, total flow rate = 30 mL/min.

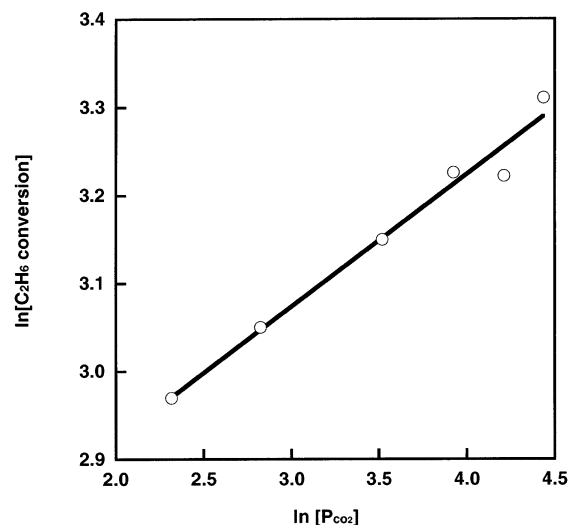


Figure 10. The relationship between $\ln[C_2H_6 \text{ conversion}]$ and $\ln[CO_2 \text{ partial pressure}]$ over oxidized diamond-supported Cr_2O_3 catalyst. Reaction conditions: temperature: 923 K, reaction time: 0.5 h, catalyst: 200 mg, loading level of Cr = 2.5 wt %, SV = 9000 h^{-1} mL/g-cat, C_2H_6 : 5 mL/min, total flow rate = 30 mL/min.

pressure. The C_2H_4 selectivity only slightly decreased with increases in the CO_2 partial pressure. These results indicate that only a small amount of CO_2 played an important role in increasing C_2H_4 yield over the oxidized diamond-supported Cr_2O_3 catalyst. Figure 10 shows relationship between $\ln[C_2H_6 \text{ conversion}]$ and $\ln[\text{partial pressure of } CO_2]$ over the oxidized diamond-supported Cr_2O_3 catalyst. The good linear relation between $\ln[C_2H_6 \text{ conversion}]$ and $\ln[\text{partial pressure of } CO_2]$ was obtained. It was indicated that C_2H_6 conversion strongly depended upon partial pressure of CO_2 .

In the dehydrogenation of C_2H_6 under a CO_2 atmosphere, the roles of CO_2 would be considered as follows:



In the dehydrogenation of C_2H_6 under a CO_2 atmosphere, H_2O was produced during the reaction (reaction 4). Cr_2O_3 has

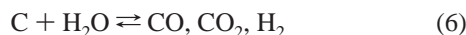
TABLE 2: Effect of Steam on the Products Yield in the Dehydrogenation of Ethane^a

atmosphere	steam pressure (Pa)	C ₂ H ₆ conv. (%)	yield (%)	
			C ₂ H ₄	CH ₄
CO ₂	0	27.4	23.8	3.6
	6	25.4	21.7	3.7
	106	20.3	18.0	2.3
Ar	0	7.0	6.8	0.2
	6	14.9	13.8	1.2
	106	15.5	16.1	1.5

^a Reaction conditions: 923 K, Cr₂O₃ loading level = 2.5 wt.%, catalyst = 200 mg SV = 9000 h⁻¹ mL/g-cat, ratio of C₂H₆/CO₂ (or AR) = 1/5, flow rate = 30 mL/min.

been reported to be a solid acid catalyst.²⁹ Therefore, there is the possibility of carbon deposition on the Cr₂O₃-loaded catalyst in the dehydrogenation of ethane. As mentioned above over the oxidized diamond-supported Cr₂O₃ catalyst, CO₂ acts to eliminate deposited carbon and to remove H₂ from the reaction site, thus shifting the equilibrium favorably to the product side. Another possibility of the role of CO₂ and formed H₂O might be the modification the acidity or the chemical structure of the surface of the oxidized diamond-supported Cr₂O₃ catalysts. A similar result was obtained using Ga₂O₃-loaded catalysts.^{24,25}

In the dehydrogenation of C₂H₆ under CO₂, water was produced during the reaction (reaction 3). Carbon deposition is one of major problems in the dehydrogenation of C₂H₆. The role of water in the dehydrogenation of ethane under CO₂ would be considered as follows:



To obtain information regarding the effect of steam on the dehydrogenation of C₂H₆, steam was introduced in the dehydrogenation of C₂H₆ over the oxidized diamond-supported Cr₂O₃ catalyst in the presence and in the absence of CO₂. Using the oxidized diamond-supported Cr₂O₃ catalyst, C₂H₄ yield in the absence of CO₂ was about 5.9%. C₂H₄ yield was markedly increased by the introduction of steam, and a product distribution similar to that in the run under CO₂ was obtained (Table 2). These results suggest that steam produced in the presence of CO₂ might also have promoted the dehydrogenation of C₂H₆. In this reaction, CO_x was detected and CH₄ selectivity increased. Therefore, steam could eliminate deposited carbon on the catalyst's surface.

3.7. Effect of Time-on-Stream on the Dehydrogenation of C₂H₆ over Oxidized Diamond-Supported Cr₂O₃ Catalyst. Figure 11 shows effect of time-on-stream on the dehydrogenation of C₂H₆ over the oxidized diamond-supported Cr₂O₃ catalyst. Both in the presence and in the absence of CO₂ over this catalyst, C₂H₄ yields decreased markedly with increasing reaction time, due to carbon deposition. Using the oxidized diamond-supported Cr₂O₃ catalyst, deactivation of the catalyst in the presence and absence of CO₂ without steam decreased from 22.5 to 11.5% and from 7.4 to 2.7% within 3 h, respectively.

To improve the stability of the catalyst's activity, steam was introduced in the dehydrogenation of C₂H₆ over the oxidized diamond-supported Cr₂O₃ catalyst in the presence and in the absence of CO₂. As described above, the introduction of steam together with CO₂ improved the catalyst's stability over a long run.

3.8. Role of Oxidized Diamond and CO₂ in the Dehydrogenation of C₂H₆ over Cr₂O₃-Loaded Catalyst. To examine the promoting effect of CO₂ on the dehydrogenation of C₂H₆

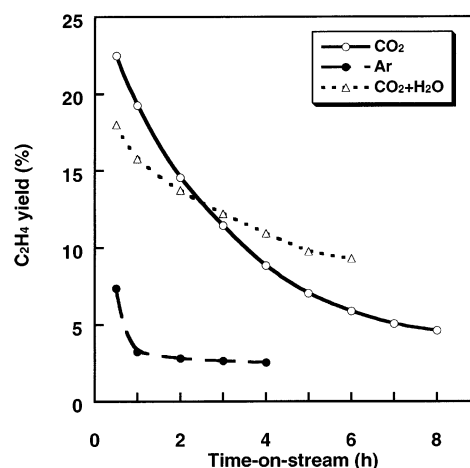


Figure 11. Effect of time on stream on C₂H₄ yield over oxidized diamond-supported Cr₂O₃ catalyst. Reaction conditions: temperature: 923 K, C₂H₆:CO₂ (Ar) = 5:25 (mL/min), catalyst = 200 mg, loading level of Cr = 2.5 wt %, SV = 9000 h⁻¹ mL/g-cat, C₂H₆: H₂O:CO₂ = 1:1:5, total flow rate = 30 mL/min.

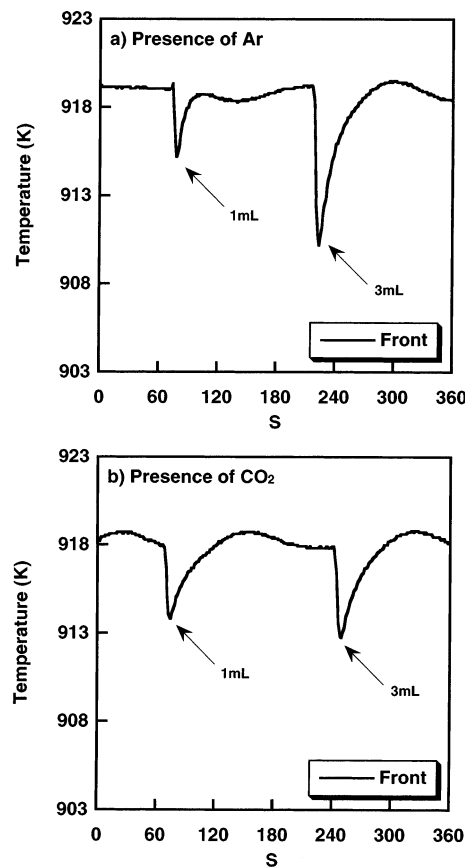


Figure 12. Temperature profile at the front edges of the catalyst bed and response to pulse over oxidized diamond-supported Cr₂O₃ catalyst. Reaction conditions: Ar or CO₂ carrier = 30 mL/min, mixed gas, C₂H₆ = 1 mL, furnace temperature, 923 K.

over the oxidized diamond-supported Cr₂O₃ catalyst, a pulsed reaction technique^{25,26} was employed to measure transient temperature changes in the catalyst beds.

Figure 12 shows the transient temperature responses of the oxidized diamond-supported Cr₂O₃ catalyst against a pulsed injection of C₂H₆ in the presence and the absence of CO₂. The temperature at the front edge of the catalyst bed decreased with the introduction of the C₂H₆ pulse both in the presence and absence of CO₂ at 923 K. In the absence of CO₂, a large decrease in the temperature (c.a. 10 K: 3 mL pulse) of the front edge of

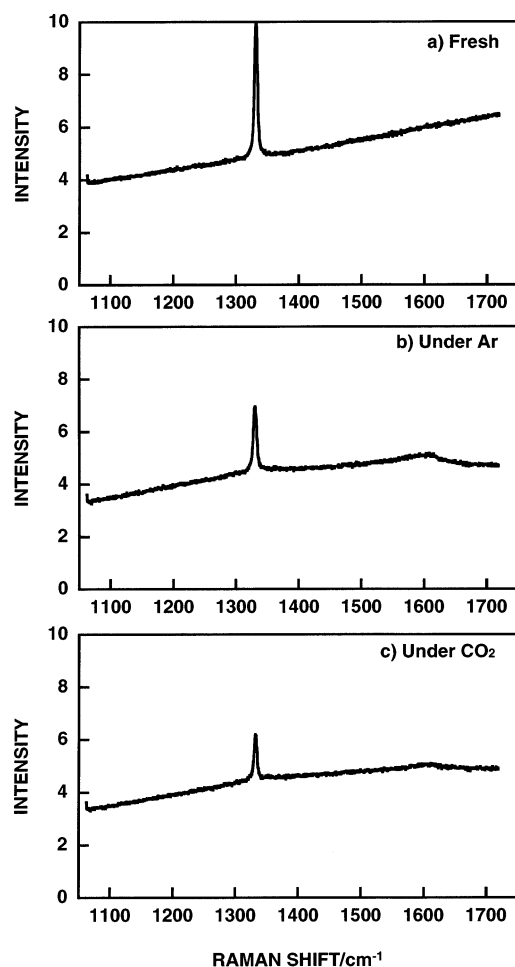


Figure 13. Raman spectra of oxidized diamond-supported Cr_2O_3 catalyst. Reaction conditions: temperature: 923 K, reaction time: 0.5 h, $\text{C}_2\text{H}_6/\text{CO}_2$ (Ar)=5:25 (mL/mL), Catalyst=200 mg, Loading level of Cr = 5 wt %, SV = 9000 h^{-1} mL/g-cat.

the catalyst bed was observed as compared to the temperature drop in the presence of CO_2 . Observation of the catalyst-bed temperature by means of injecting a pulse of reactants might provide detailed information regarding the reaction being taking place on the catalyst's surface. Both reactions 1 and 3 are endothermic reactions, the value of ΔH of both reactions are also almost the same. Reaction 1 is more endothermic than reaction 3. The temperature drop in the catalyst bed might have indicated that the advantage of the dehydrogenation of C_2H_6 in the presence of CO_2 is much larger than that in the absence of CO_2 . In the dehydrogenation of C_2H_6 to C_2H_4 , the advantages in using CO_2 instead of Ar (without CO_2) would be expressed on the basis of thermodynamic considerations.

To determine the types of deposited carbons during the dehydrogenation of C_2H_6 in the presence and absence of CO_2 over the oxidized diamond-supported Cr_2O_3 catalyst, used catalysts were examined using Raman spectroscopy. The Raman spectra of the used oxidized diamond-supported Cr_2O_3 catalysts in the presence and the absence of CO_2 are shown in Figure 13. Two peaks were observed for the spectra of deposited carbon both in the presence and the absence of CO_2 : one appears around 1330 cm^{-1} and the other, at 1600 cm^{-1} . The peak at 1330 cm^{-1} is ascribed to diamond. In addition, the peak at 1600 cm^{-1} was assigned to the in-plane carbon-carbon stretching vibration of graphite layers.³⁰ It is considered that deposited carbons both in the presence and absence of CO_2 might be same types.

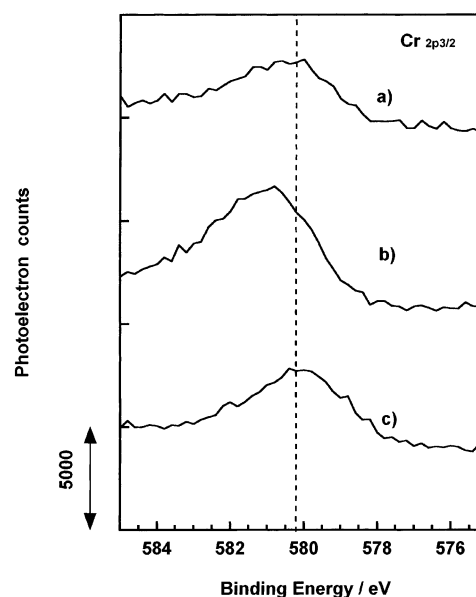


Figure 14. X-ray photoelectron spectra of oxidized diamond-supported Cr_2O_3 catalyst. Reaction conditions: loading level of Cr = 7.5 wt %, (a) fresh, (b) after reaction with CO_2 flow, (c) after reaction with Ar flow.

The role of CO_2 in the dehydrogenation of C_2H_6 over the oxidized diamond-supported Cr_2O_3 catalyst might be considered as follows: in the Ga_2O_3 catalyst, a visible amount of carbon was deposited;²⁵ however, visible carbon deposition was not observed over the oxidized diamond-supported Cr_2O_3 catalyst. CO was detected at nearly twice the amount of C_2H_4 over the oxidized diamond-supported Cr_2O_3 catalyst during the dehydrogenation of C_2H_6 in the presence of CO_2 . One possible cause of this increased dehydrogenation in the presence of CO_2 might be a utilization of CO_2 as oxidant for the dehydrogenation of C_2H_6 . A second possibility would be the elimination of deposited carbon.

In the XRD patterns of the oxidized diamond-supported Cr_2O_3 catalyst, Cr_2O_3 was observed both in the presence and absence of CO_2 for the fresh and used catalysts. However, XPS analyses revealed that the binding energy of the chromium species of the oxidized diamond-supported Cr_2O_3 catalyst reacted at 923 K in the presence of CO_2 shifted to a slightly higher binding energy than that of fresh catalyst or that reacted at 923 K in the presence of Ar (Figure 14). This result could show the oxidation of chromium oxide to maintain a higher-oxidation state. Wang et al. investigated the dehydrogenation of C_2H_6 in the presence of CO_2 over a $\text{Cr}_2\text{O}_3/\text{SiO}_2$ catalyst and, on the basis of the results of XPS analyses, found Cr^{3+} and Cr^{6+} coexist on the catalyst's surface. They proposed that the redox property played an important role in dehydrogenation in the presence of the CO_2 .¹⁹ We consider that maintaining a higher-oxidation state of the chromium species might be an important factor indicating high catalytic activities for the dehydrogenation of C_2H_6 in the presence of CO_2 .

Figure 15 shows diffuse reflectance FT-IR spectra of the oxidized diamond-supported Cr_2O_3 catalyst. After the reaction in the absence of CO_2 , the spectra from 1650 to 1850 cm^{-1} and at 1150 – 1250 cm^{-1} which were ascribed to $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ stretching vibrations decreased compared with those in the presence of CO_2 . From these results, it is suggested that CO_2 also played an important role in maintaining the oxygen species on the diamond surface. To obtain a high C_2H_4 yield in the dehydrogenation of C_2H_6 , it would be necessary to keep

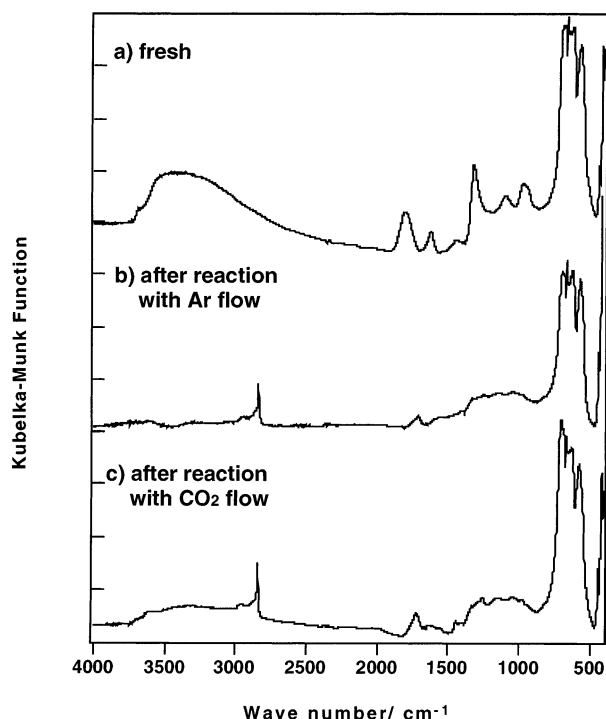
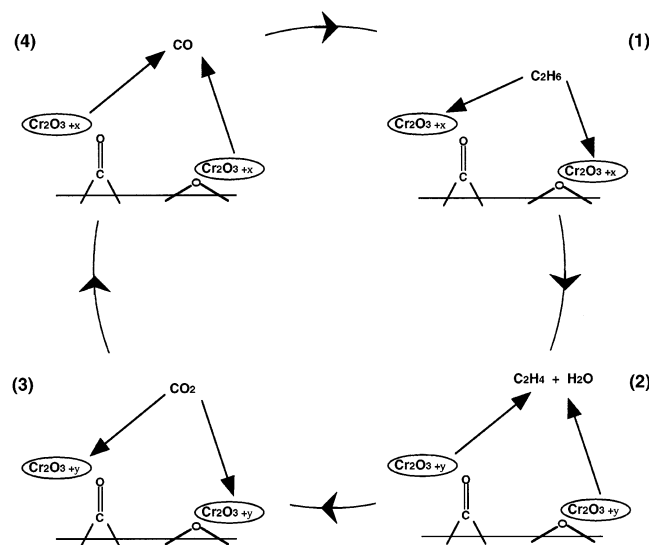


Figure 15. Diffuse reflectance FT-IR spectra of oxidized diamond-supported Cr_2O_3 catalyst. Reaction conditions: temperature: 923 K, $\text{C}_2\text{H}_6:\text{CO}_2$ (Ar) = 5:25 (mL/min), catalyst = 200 mg, loading level of Cr = 7.5 wt %, SV = 9000 h^{-1} mL/g-cat.

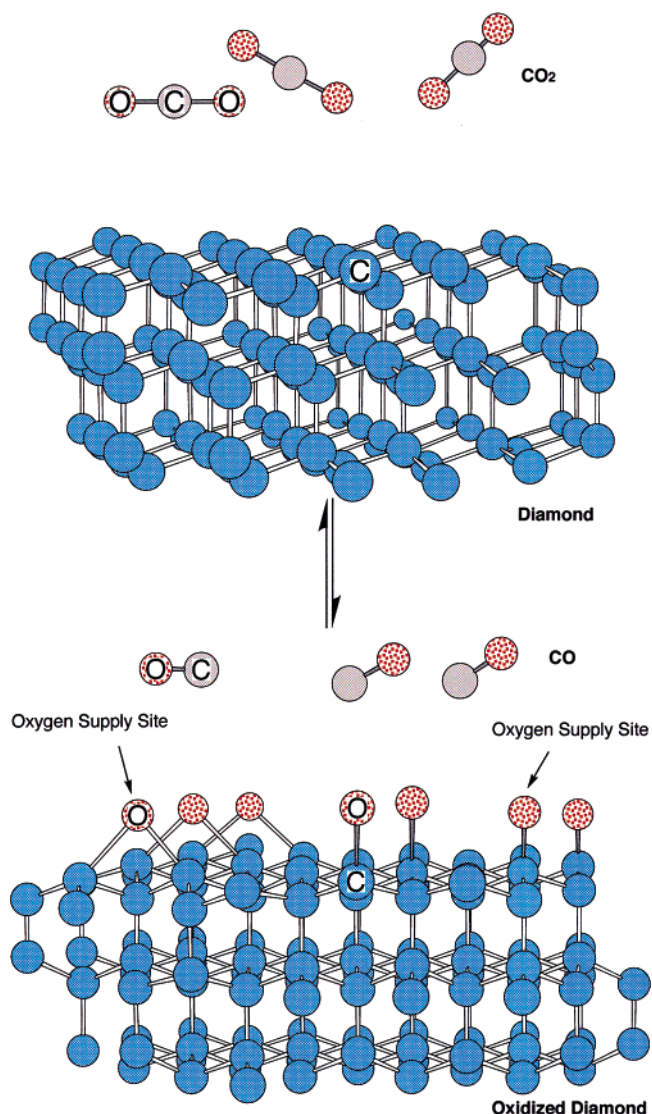
SCHEME 1: Proposed Reaction Pathway for the Dehydrogenation of Ethane over the Oxidized Diamond-Supported Cr_2O_3 Catalyst in the Presence of CO_2



both the highly oxidized state of chromium species and the presence of oxygen species on diamond surface.

Scheme 1 shows the most plausible interpretation of such a synergism between Cr_2O_3 and oxidized diamond regarding the dehydrogenation of C_2H_6 in the presence of CO_2 . To produce C_2H_4 , Cr_2O_3 or a higher-oxidation state of chromium oxides are required. If chromium oxides are dispersed on the oxidized diamond surface, the chromium oxides might stabilize and become difficult to reduce. Even if the chromium oxides are reduced with C_2H_6 or H_2 , they will be oxidized by CO_2 or oxygen species of the diamond surface. The threshold loading level of Cr_2O_3 on oxidized diamond might be ca. 1.25–2.5 wt %. In the case of the oxidized diamond-supported Cr_2O_3 catalyst,

SCHEME 2: Proposed Oxidation of Diamond Surface by CO_2



the threshold level would be considered based on the total amount of oxygen species on the diamond surface. The oxygen species on the oxidized diamond surface were supplied from CO_2 (Scheme 2). Such a mutual promotion effect on chromium oxide phase formation is believed to be the reason for the observed apparent synergism or promoting effect of CO_2 on the dehydrogenation of C_2H_6 .

4. Conclusions

Among Cr_2O_3 loaded-catalysts, the oxidized diamond-supported Cr_2O_3 catalyst exhibited the highest C_2H_4 yield for the dehydrogenation of C_2H_6 in the presence of CO_2 . C_2H_4 yields over this catalyst increased with increasing CO_2 partial pressure. To maintain catalytic activity, steam which was produced in the presence of CO_2 also played an important role in the dehydrogenation of C_2H_6 over the catalyst.

From the results of XRD and XPS, to obtain a high C_2H_4 yield in the dehydrogenation of C_2H_6 , it was suggested that a higher-oxidation state of chromium species might be required. From the result of FT-IR, the presence of oxygen species on the diamond surface would also play the important role for the dehydrogenation of C_2H_6 to C_2H_4 in the presence of CO_2 using Cr_2O_3 -loaded oxidized diamond catalyst.

The role of CO₂ for the dehydrogenation of C₂H₆ on the oxidized diamond-supported Cr₂O₃ catalyst might be to eliminate deposited carbon of catalyst surface. Furthermore, to maintain the higher-oxidation state of the chromium species and oxygen species on the diamond surface, CO₂ would be necessary.

Acknowledgment. K.N. is grateful to the Japan Society for the Promotion of Science (JSPS) for his young scientist fellowship.

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