Catalysis Today 84 (2003) 149–157

www.elsevier.com/locate/cattod

Dehydrogenation of light alkanes over oxidized diamond-supported catalysts in the presence of carbon dioxide

Kiyoharu Nakagawa [a,b], Chiaki Kajita [a], Na-oki Ikenaga [a], Mikka Nishitani-Gamo [c], Toshihiro Ando [d], Toshimitsu Suzuki [a,*]

[a] Department of Chemical Engineering, Faculty of Engineering and High Technology Research Center, Kansai University, 3-3-35 Yamate, Suita, Osaka 564-8680, Japan
[b] Japan Science and Technology Corporation (JST) and National Institute for Materials Science (NIMS), 1-1, Namiki, Tsukuba, Ibaraki 305-0044, Japan
[c] Department of Applied Chemistry, Faculty of Engineering, Toyo University, 2100, Kujirai, Kawagoe, Saitama 350-8585, Japan
[d] Core Research for Evolutional Science and Technology (CREST) of Japan Science and Technology Corporation (JST) and National Institute for Materials Science (NIMS), 1-1, Namiki, Tsukuba, Ibaraki 305-0044, Japan

Abstract

Oxidized diamond demonstrated excellent support for the dehydrogenation of light alkanes to alkenes in the presence of CO_2. Oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts exhibited comparatively higher catalytic activities in the dehydrogenation of lower alkanes in the presence of CO_2. In the dehydrogenation of propane, the oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts in the presence of CO_2 afforded nearly twofold higher activities than that in the absence of CO_2. The activity of the oxidized diamond-supported V_2O_5 catalyst in the dehydrogenation of propane increased with increasing reaction temperatures. Furthermore, in the dehydrogenation of *n*-butane and *iso*-butane, a promoting effect of CO_2 on butane conversion and butenes yields was observed over the oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts, though the promotion effect was small.

UV-Vis analyses of the fresh and the reacted catalysts in the presence and absence of CO_2 revealed that CO_2 kept the surface V_2O_5 and Cr_2O_3 in a state of oxidation slightly higher than that in the absence of CO_2.

Keywords: Diamond; Carbon dioxide; Propane; Propylene; Dehydrogenation; Chromium oxide; Vanadium oxide

1. Introduction

Surface chemistry of diamond has received much recent attention [1–3]. However, diamond or oxidized diamond as a support material for catalysts has not yet been exploited. Further applications of diamond-supported catalyst need to be developed. Diamond has long been chemically considered an inert material. One of the present authors introduced the thesis that the surface of the diamond behaved as organic substances in certain chemical reactions [1]. The diamond surface is expected to have possibility of chemical reactivities as an organic substance [3]. This led us to develop novel utilization of diamond as the material of a catalyst or as a catalyst support for chemical reactions [4–6].

---

[*] Corresponding author. Tel.: +81-6-6368-0865; fax: +81-6-6388-8869.
E-mail address: tsuzuki@ipcku.kansai-u.ac.jp (T. Suzuki).

doi:10.1016/S0920-5861(03)00268-2

The diamond surface is easily oxidized by oxidative acids such as HNO_3, HClO, H_2O_2, etc., and is also oxidized with O_2 at an elevated temperature to form C–O–C ether type structures and C=O carbonyl type structures [1,2]. The oxidized diamond surface is expected to behave as a “carbon oxide” for specified surface reactions such as catalytic, electrochemical reactions. Given that such reactions are controlled via the interaction between molecules and surfaces, the bulk structure of solids is comparatively less important. The SiO_2 is widely used for many catalytic reactions as a neutral support. SiO_2 support has weak interactions with some metals and metal oxides and plays an important role in the yield of active reaction sites. The interaction of the oxidized diamond with metals/metal oxides should be weaker than that of SiO_2 and may have unique characteristics.

The catalytic dehydrogenation of alkanes has considerable industrial impact, because it represents a route by which to obtain alkenes from feedstocks of low-cost saturated hydrocarbons [7]. At present, light alkenes are obtained by steam cracking natural gas and naphtha, and fluid catalytic cracking that occurs in petroleum refining. Effective and selective conversion of lower alkanes to unsaturated hydrocarbons is a current research target of chemical industries.

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

$$C_nH_{2n+2} \rightleftarrows C_nH_{2n} + H_2 \quad (1)$$

However, the thermodynamics of this reaction involved endothermic reactions, so the equilibrium greatly favors alkanes at lower temperatures when the reaction is carried out under atmospheric pressure. The equilibrium shifts to the left side by increasing a reaction temperature with excess steam as a diluent.

The following oxidative dehydrogenation of alkanes using oxygen as an oxidant of alkanes has been proposed as effective in decreasing reaction temperature.

$$C_nH_{2n+2} + \tfrac{1}{2}O_2 \rightarrow C_nH_{2n} + H_2O \quad (2)$$

However, several 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, which may cause a runaway reaction, must be overcome.

Among the many catalytic dehydrogenation reactions, the weak oxidation capability of CO_2 in the dehydrogenation of ethane to ethylene has been our recent focus [8–10]. Recently, several attempts were made to use carbon dioxide as an oxidant for the coupling of methane [11–13], and the dehydrogenation of ethylbenzene [14–18], *iso*-propylbenzene [19], propane [20,21], or *iso*-butane [22]. However, little discussion on the role of carbon dioxide in the dehydrogenation of alkane, as follows, has yet been published.

$$C_nH_{2n+2} + CO_2 \rightarrow C_nH_{2n} + CO + H_2O \quad (3)$$

In this report, we focus on the application of oxidized diamond as an extension of the previous dehydrogenation of ethane to the dehydrogenation of C_3–C_4 alkanes to C_3–C_4 alkenes using CO_2. We have found that the oxidized diamond-supported-Cr_2O_3 or V_2O_5 catalysts markedly promoted dehydrogenation of C_3–C_4 alkanes to C_3–C_4 alkenes under CO_2. The oxidized diamond exhibited excellent potential as a support material for catalytic dehydrogenation reactions.

2. Experimental

Commercially available fine-powdered diamond was used for this study. The diamond powder was washed with HNO_3 to remove metallic impurities, then rinsed thoroughly with distilled water. Before oxidation, to prepare homogeneous surface conditions, the diamond powder was first hydrogenated at 1173 K for 1 h under pure H_2 stream. The hydrogenated diamond powder was then oxidized at 723 K for 1 h under O_2 stream (O_2:Ar = 1:4). The oxidized diamond is known to contain oxygenated species with C–O–C and C=O structures [1,2].

Catalysts were prepared by impregnating aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, NH_4VO_3 (Wako Pure Chemical Industries), $Ga(NO_3)_3 \cdot 8H_2O$ (Kishida Chemicals), $Zn(NO_3)_2 \cdot 6H_2O$, and $(CH_3COO)_2Mn \cdot 4H_2O$ (Wako Pure Chemical Industries), to Al_2O_3 (JRC-ALO-4, the reference catalyst provided by the Catalysis Society of Japan), SiO_2 (Merck), activated carbon (Wako Pure Chemical Industries), and oxidized diamond (BET surface area $= 12.6\,m^2\,g^{-1}$), then the impregnated materials 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 with a fixed-bed flow type quartz reactor (i.d. 10 mm × 350 mm) at 1 atm pressure. Using 200 mg of a catalyst, 25–27 ml/min CO_2 (or Ar) and 5–3 ml/min of alkane (propane, *iso*-butane, or *n*-butane) were introduced at temperature ranges of 823–973 K. Prior to the reaction, the catalysts were heated in Ar. Products were analyzed by gas chromatography.

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 catalysts, treated under different conditions, were analyzed by UV-Vis diffuse reflectance spectroscopy with a JASCO (V-550) spectrophotometer.

3. Results and discussion

3.1. Dehydrogenation of propane in the presence of CO_2 over oxidized diamond-supported metal oxide catalysts

We have already reported that CO_2 markedly promoted dehydrogenation of ethane over the oxidized diamond-supported Cr_2O_3 catalyst with a high selectivity to give ethylene [4].

Fig. 1 and Table 1 show propylene yields on various oxidized diamond-supported metal oxide catalysts in the presence or absence of CO_2 at a temperature range of 873–898 K. Thermal dehydrogenation occurred to give a propylene yield of only ca. 2.5% in both CO_2 and Ar atmosphere at 898 K. Promoting effects of CO_2 on the propylene yield were observed over oxidized diamond-supported Cr, V, and Ga catalysts (Fig. 1 and Table 1). The activity of the oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts in the presence of CO_2 was two times higher than that in the absence of CO_2 at 898 K (Fig. 1). Dehydrogenation of propane in the presence of CO_2 over the oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts produced mainly propylene (C_3H_6). The promoting effect of CO_2 in the dehydrogenation of C_2H_6 on the oxidized diamond-supported Cr_2O_3 catalyst has been reported, and the ethylene yield was 22.5% with ethylene selectivity of 86.7% at 923 K [4]. In the case of the oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts, dehydrogenation of propane was also promoted in the presence of CO_2, However, secondary reactions such as decomposition to methane,

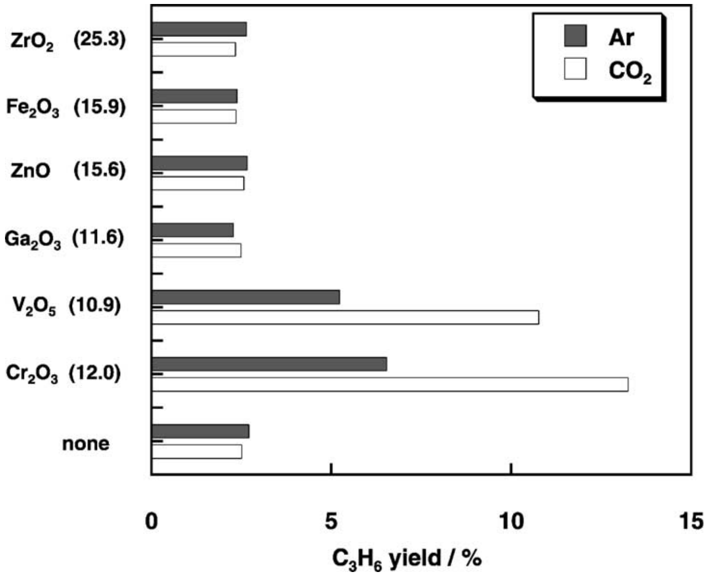

Fig. 1. Dehydrogenation of C_3H_8 in the presence of CO_2 or Ar over oxidized diamond-supported metal oxide catalysts. Temperature: 898 K; reaction time: 0.5 h; C_3H_8:CO_2(Ar) = 5:25 (ml/ml); catalyst = 400 mg; SV = 4500 h^{-1} ml/g-cat; numerals in ( ) indicate surface area (m^2/g); M:oxidized diamond = 5:95 (wt.%).

Table 1
Dehydrogenation of propane over oxidized diamond-supported catalysts[a]

Catalysts	In the presence of CO_2						In the presence of Ar						Ratio of yield (Y_{CO_2}/Y_{Ar})
	Conversion (%), C_3H_8	Yield (%), C_3H_6	Selectivity (%)				Conversion (%), C_3H_8	Yield (%), C_3H_6	Selectivity (%)				
			C_3H_6	C_1	C_2	C_4			C_3H_6	C_1	C_2	C_4	
Cr	19.7	11.8	59.9	5.4	7.3	27.4	15.0	9.8	65.5	2.5	5.6	26.4	1.2
V	13.7	8.6	62.7	3.1	7.1	27.1	11.5	6.5	56.2	2.3	7.0	34.6	1.3
Ga	9.1	3.4	37.7	3.9	13.0	45.3	8.4	3.0	36.3	3.3	9.1	51.3	1.1
Mn	9.0	2.7	29.3	7.2	17.9	45.6	8.3	2.9	35.6	4.4	12.5	47.5	0.9
Fe	6.6	1.6	23.8	4.1	13.1	59.0	5.5	0.8	14.2	3.4	11.8	70.7	2.0

[a] Reaction conditions: 873 K; SV = 9000 h^{-1} ml/g-cat. Composition of the feed gas: C_3H_8:CO_2(Ar) = 5:25.

and C_2, and dimerization to C_4 were pronounced. In the oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts, propylene yields were 13.2 and 10.8% at 898 K, respectively. One of the characteristic features of diamond support is a higher propane conversion compared with those of other metal oxides.

Fig. 2 shows the results of propylene yields at 823 K on vanadium oxide catalysts loaded on several supports, in the presence or absence of carbon dioxide. The support activity order at the reaction temperature of 823 K was oxidized diamond $>$ Al_2O_3 $>$ activated carbon $>$ SiO_2. The oxidized diamond-supported vanadium oxide catalyst afforded the highest rate of propylene production (170×10^{-4} mmol h^{-1}/m^2 unit V_2O_5) among these vanadium oxide catalysts. Propylene yield under CO_2 flow was twice as high as that under Ar flow.

The effect of loading level of vanadium oxide on the dehydrogenation of propane over the oxidized diamond-supported V_2O_5 catalyst in the presence and absence of CO_2 were examined (Table 2). The propylene yield as a function of the reaction temperature is shown in Fig. 3. Propylene yields in the non-catalytic runs did not depend upon atmosphere. In the presence

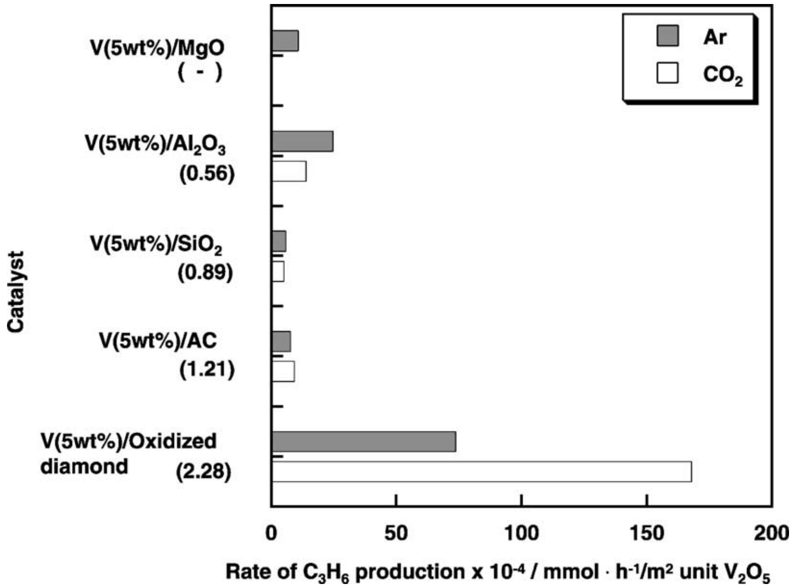

Fig. 2. Dehydrogenation of C_3H_8 in the presence of CO_2 or Ar over various catalysts. Temperature: 823 K; reaction time: 0.5 h; C_3H_8:CO_2(Ar) = 3:27 (ml/ml); catalyst = 200 mg; SV = 9000 h^{-1} ml/g-cat; numerals in ( ) indicate C_3H_6 yield under CO_2 flow/C_3H_6 yield under Ar flow.

Table 2
Effect of V content on the dehydrogenation of propane over oxidized diamond-supported vanadium oxide catalyst[a]

V catalysts (wt.%)	In the presence of CO_2						In the presence of Ar						Ratio of yield (Y_{CO_2}/Y_{Ar})
	Conversion (%), C_3H_8	Yield (%), C_3H_6	Selectivity (%)				Conversion (%), C_3H_8	Yield (%), C_3H_6	Selectivity (%)				
			C_3H_6	CH_4	C_2H_4	C_2H_6			C_3H_6	CH_4	C_2H_4	C_2H_6	
No catalyst	0.9	0.5	57.8	0.0	7.0	35.2	0.9	0.5	59.1	0.0	0.0	40.9	1.0
1	1.6	0.9	53.9	20.9	4.7	20.5	3.3	3.0	90.8	0.0	2.3	6.9	0.3
3	4.2	3.1	73.3	17.6	2.3	6.8	2.4	2.0	83.0	0.0	3.5	13.5	1.6
5	4.0	3.5	86.8	2.5	2.9	7.8	2.8	2.2	78.0	4.4	3.5	14.1	1.6
10	5.9	3.7	63.0	30.0	2.1	4.9	3.5	2.9	83.7	1.5	4.1	10.7	1.3

[a] Reaction conditions: 823 K; SV = 9000 h^{-1} ml/g-cat. Composition of the feed gas: C_3H_8:CO_2(Ar) = 3:27.

of carbon dioxide over oxidized diamond-supported vanadium oxide catalyst, propylene yields remarkably increased with increasing reaction temperature, and 13.8% of propylene yield was obtained at 923 K. In addition, CO was formed during the temperature-programmed reaction with CO_2 after the dehydrogenation of propane in the presence of CO_2 over the oxidized diamond-supported V_2O_5 catalyst. In the dehydrogenation of alkane, carbon deposition is one of the serious problems. In the dehydrogenation of alkane over the oxidized diamond-supported catalysts, carbon deposition was observed. Notably, the carbon deposition in the presence of CO_2 was less than that in the absence of CO_2.

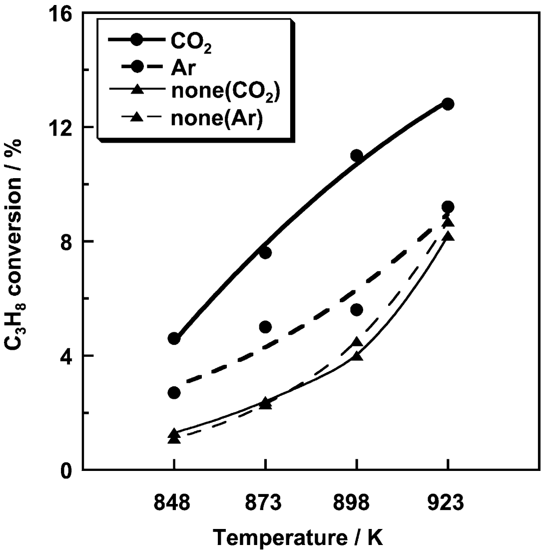

Fig. 3. Effect of temperature on the conversion of C_3H_8 over V (5 wt.%)/oxidized diamond catalyst. Reaction time: 0.5 h; C_3H_8:CO_2(Ar) = 3:27 (ml/ml); catalyst = 200 mg; SV = 9000 h^{-1} ml/g-cat.

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

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad (4)$$

$$CO_2 + C \rightleftarrows 2CO \qquad (5)$$

Therefore, two possible explanations for the increased conversion of dehydrogenation reaction in the presence of CO_2 are plausible. One is that the removal of hydrogen from products shifts equilibrium (reaction (4)), and the other is that elimination of deposited carbon (reaction (5)) occurs. Similar tendencies were observed with Cr_2O_3 and V_2O_5-loaded catalysts. Dehydrogenation of propane in the presence of CO_2 using the oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts was noticeably promoted by increasing the reaction temperature. Under Ar atmosphere at 923 K, C_3H_8 conversion showed the same value as that of thermal reaction.

At 823 K no significant effect of loading level of V_2O_5 was observed on the propane conversion and propylene yield.

In the dehydrogenation of propane under CO_2, oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts afforded higher C_3H_6 conversions. It is considered that the CO_2 played a role in the shift of equilibrium and in the elimination of deposited carbon.

3.2. Dehydrogenation of n-butane and iso-butane in the presence of CO_2 over oxidized diamond-supported metal oxide catalysts

Fig. 4 shows the results of *n*-butane conversion over various oxidized diamond-supported metal

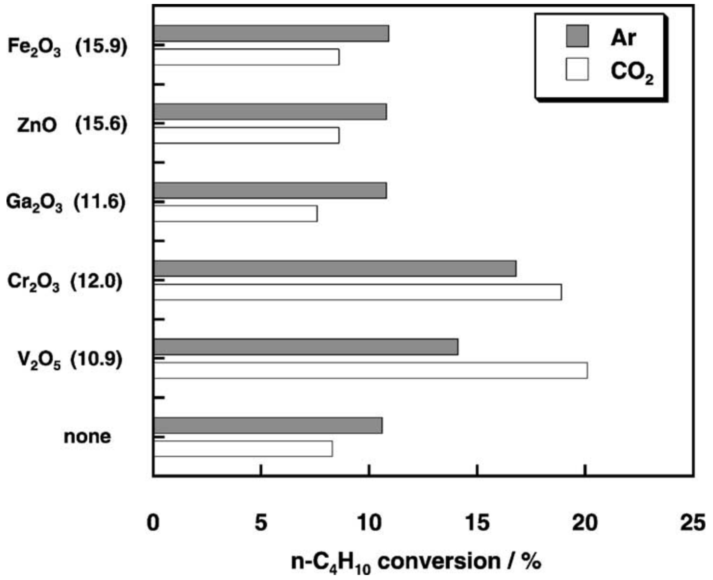

Fig. 4. Dehydrogenation of n-C_4H_{10} in the presence of CO_2 or Ar over oxidized diamond-supported metal oxide catalysts. Temperature: 873 K; reaction time: 0.5 h; C_4H_{10}:CO_2(Ar) = 5:25 (ml/ml); catalyst = 400 mg; SV = 4500 h^{-1} ml/g-cat; numerals in ( ) indicate surface area (m^2/g); M:oxidized diamond = 5:95 (wt.%).

oxide catalysts in the presence or absence of CO_2 at 873 K. Small promoting effects of CO_2 on the n-butane conversion were observed upon the oxidized diamond-supported V_2O_5 and Cr_2O_3 catalysts. Dehydrogenation of n-butane in the presence CO_2 over the oxidized diamond-supported V_2O_5 catalyst produced mainly *trans*-2-butene, CO, and H_2.

Fig. 5 shows the results of the *iso*-butene yield at 873 K in the dehydrogenation of *iso*-butane on various oxidized diamond-supported metal oxide catalysts in the presence or absence of CO_2. The order of activity of various oxidized diamond-supported metal oxide catalysts in the presence of CO_2 at 873 K was as follows: $V_2O_5 = Cr_2O_3 > Ga_2O_3 > ZnO > ZrO_2 > Fe_2O_3$. A very small promoting effect of CO_2 on the *iso*-butane conversion was observed upon the oxidized diamond-supported V_2O_5 catalyst.

In the dehydrogenation of ethane under CO_2 atmosphere, a large promoting effect on the ethylene yield was observed over the oxidized diamond-supported Cr_2O_3 catalyst [4]. However, the promoting effect of carbon dioxide in the dehydrogenation of C_3 and C_4 alkanes under a CO_2 atmosphere was small compared with that in the dehydrogenation of ethane. The weak promoting effect of CO_2 atmosphere in the cases of C_3 and C_4 alkanes might be ascribed to the fact that lower reaction temperatures were applied in order to obtain considerable conversions, since the bond dissociation energy of CH_2 or CH groups in propane, butane, and *iso*-butane are lower than that of CH_3 in ethane. In the dehydrogenation of a higher alkane, the produced alkenes contains allylic hydrogen, which has much lower bond dissociation energy than that of starting alkanes. Thus, abstraction of hydrogen from the allylic position may proceed more rapidly to give coke precursors. Deactivation of the catalyst could not be avoided, consequently giving decreases in alkene yields.

3.3. UV-Vis characterization of oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts

In order to understand the role that CO_2 plays in relation to the catalyst surface or oxidation states of catalysts in the dehydrogenation reactions, UV-Vis measurements were carried out. Fig. 6 shows the UV-Vis diffuse reflectance spectra of the oxidized diamond-supported Cr (5 wt.%) catalyst. For the fresh catalyst, four peaks appeared, one each at about 275, 370, 460, and 600 nm. The peaks of 275 and 370 nm

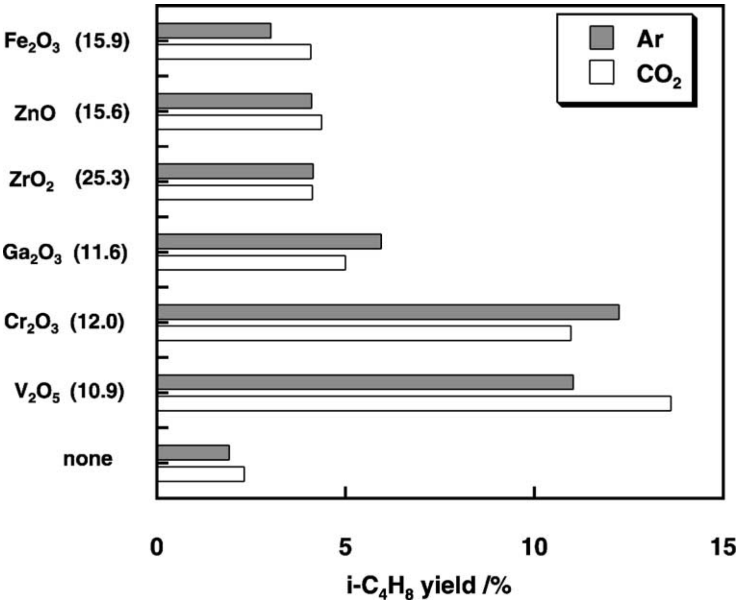

Fig. 5. Dehydrogenation of i-C_4H_{10} in the presence of CO_2 or Ar over oxidized diamond-supported metal oxide catalysts. Temperature: 873 K; reaction time: 0.5 h; i-C_4H_{10}:CO_2(Ar) = 5:25 (ml/ml); catalyst = 400 mg; SV = 4500 h^{-1} ml/g-cat; numerals in ( ) indicate surface area (m^2/g); M:oxidized diamond = 5:95 (wt.%).

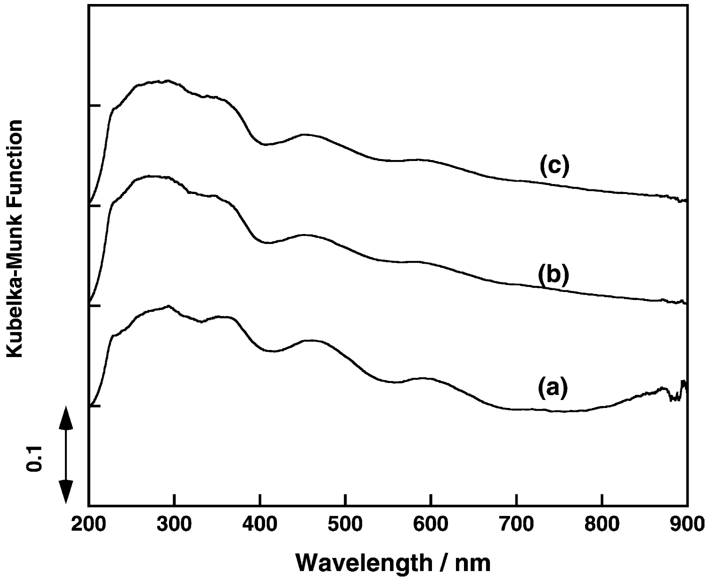

Fig. 6. UV spectra of Cr (5 wt.%)/oxidized diamond catalysts before and after dehydrogenation of propane: (a) fresh; (b) after reaction with CO_2 flow; (c) after reaction with Ar flow.

corresponded to Cr^{6+}, and the peaks of 460 and 600 nm to Cr^{3+} [23,24]. From these results, the fresh catalyst had both valency states of Cr^{6+} and Cr^{3+}. The peak of Cr^{6+} after dehydrogenation of propane in the presence of CO_2 slightly strengthened as compared to that reacted in the presence of Ar. This result indicates that the chromium oxide could sustain a higher oxidation state. Wang reported on the dehydrogenation of ethane in the presence of CO_2 over Cr_2O_3/SiO_2 catalyst and found that Cr^{3+} and Cr^{6+} coexist on the surface of the catalyst. They proposed that the redox property played an important role in the dehydrogenation of alkane under a CO_2 atmosphere [25].

Fig. 7 shows the UV-Vis diffuse reflectance spectra of the oxidized diamond-supported V (5 wt.%) catalyst. Fresh catalyst exhibited absorptions at around 270 and 400 nm. The peaks of 270 and 400 nm indicated the presence of tetrahedral V^{5+} species [18,26]. Both of the catalysts used in the presence and absence of CO_2 exhibited absorptions at 270 and 400 nm, and in addition to these, a very broad new peak at around 600 nm appeared. This peak corresponded to V^{4+} [18,26]. It is obvious that the reduction of the vanadium species during dehydrogenation of propane occurred in both the presence and absence of CO_2. However, the V^{5+} peak of 400 nm in the presence of Ar was slightly weaker than that in the presence of CO_2. This result indicated that CO_2 slightly oxidized vanadium species during the reaction in the presence of CO_2.

The oxidized diamond-supported V (5 wt.%) catalyst did not afford a high ethylene yield in the dehydrogenation of ethane [4]. However, it exhibited high catalytic activities for the dehydrogenation of C_3 and C_4 alkanes. In general, it seems to be difficult to maintain a high valency state of vanadium oxides at higher temperatures under a low oxygen partial pressure. Dehydrogenation of ethane over the oxidized diamond-supported V_2O_5 catalyst was carried out above 923 K [4]. In contrast, dehydrogenation of C_3 and C_4 alkanes over the oxidized diamond-supported catalysts was mainly carried out under 893 K. Therefore, the vanadium oxide in the high oxidation states was maintained due to lower reaction temperatures, and the oxidized diamond-supported V_2O_5 catalyst could produce high catalytic activities.

We propose that maintenance of the higher oxidation state of chromium and vanadium species might be one of the important factors for high catalytic

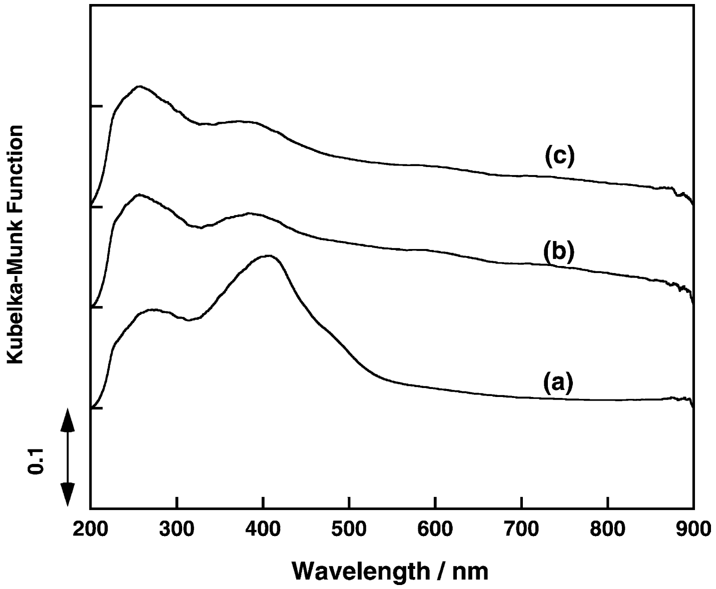

Fig. 7. UV spectra of V (5 wt.%)/oxidized diamond catalysts before and after dehydrogenation of propane: (a) fresh; (b) after reaction with CO_2 flow; (c) after reaction with Ar flow.

activities in the dehydrogenation of alkane in the presence of CO_2.

4. Conclusion

Among oxidized diamond-supported metal oxide catalysts, the oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts exhibited the highest alkene yield for the dehydrogenation of C_3–C_4 alkanes in the presence of CO_2. A support effect of oxidized diamond for Cr_2O_3- and V_2O_5-loaded catalysts was observed in the presence of CO_2. Propylene yields over oxidized diamond-supported V_2O_5 catalyst were increased with increasing reaction temperature.

The role of CO_2 in the dehydrogenation of lower alkanes over the oxidized diamond-supported Cr_2O_3 and V_2O_5 catalysts might be to maintain a higher oxidation state of chromium and vanadium species.

Acknowledgements

This work was supported by the grant-in-aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture Japan (no. 10555283), and a grant from the Japan Society for the Promotion of Science (no. 14350429).

K. Nakagawa is grateful for a fellowship from the Japan Society for the Promotion of Science (JSPS) for Young Scientists.

References

[1] T. Ando, K. Yamamoto, M. Ishii, M. Kamo, Y. Sato, J. Chem. Soc., Faraday Trans. 89 (1993) 3635.
[2] M.P. D'Evelyn, in: M.A. Prelas, G. Popovici, L.K. Bigelow (Eds.), Surface Properties of Diamond in Handbook of Industrial Diamonds and Diamond Film, Marcel Dekker, New York, 1994, Chapter 4, pp. 89–146.
[3] J.M. Buriak, Angew. Chem. Int. Ed. 40 (2001) 532.
[4] K. Nakagawa, C. Kajita, N. Ikenaga, T. Kobayashi, M.N. Gamo, T. Ando, T. Suzuki, Chem. Lett. (2000) 1100.
[5] K. Nakagawa, H. Nishimoto, Y. Enoki, S. Egashira, N. Ikenaga, T. Kobayashi, M.N. Gamo, T. Ando, T. Suzuki, Chem. Lett. (2001) 460.
[6] K. Nakagawa, T. Hashida, C. Kajita, N. Ikenaga, T. Kobayashi, M.N. Gamo, T. Suzuki, T. Ando, Catal. Lett. 80 (2002) 161.
[7] B.M. Weckhuysen, I.E. Wachs, R.A. Schoonheydt, Chem. Rev. 96 (1996) 3327.
[8] K. Nakagawa, M. Okamura, N. Ikenaga, T. Suzuki, T. Kobayashi, Chem. Commun. (1998) 1025.
[9] K. Nakagawa, C. Kajita, Y. Ide, M. Okamura, S. Kato, H. Kasuya, N. Ikenaga, T. Kobayashi, T. Suzuki, Catal. Lett. 64 (2000) 215.
[10] K. Nakagawa, C. Kajita, K. Okumura, N. Ikenaga, M.N. Gamo, T. Ando, T. Kobayashi, T. Suzuki, J. Catal. 203 (2001) 87.
[11] T. Nishiyama, K. Aika, J. Catal. 122 (1990) 346.
[12] K. Asami, K. Kusakabe, N. Ashi, Y. Ohtsyka, Appl. Catal. A 156 (1997) 245.
[13] Y. Wang, Q. Zhuang, Y. Takahashi, Y. Ohtsuka, Catal. Lett. 56 (1998) 203.
[14] S. Sato, M. Ohhara, T. Sodesawa, F. Nozaki, Appl. Catal. 37 (1988) 207.
[15] M. Sugino, H. Shimada, T. Turuda, H. Miura, N. Ikenaga, T. Suzuki, Appl. Catal. A 121 (1995) 125.
[16] N. Mimura, I. Takahara, M. Saito, T. Hattori, K. Ohkuma, M. Ando, Catal. Today 45 (1998) 61.
[17] Y. Sakurai, T. Suzaki, K. Nakagawa, N. Ikenaga, H. Aota, T. Suzuki, Chem. Lett. (2000) 526.
[18] Y. Sakurai, T. Suzaki, K. Nakagawa, N. Ikenaga, H. Aota, T. Suzuki, J. Catal. 209 (2002) 16.
[19] Y. Sakurai, T. Suzaki, K. Nakagawa, N. Ikenaga, T. Suzuki, Catal. Lett. 69 (2000) 59.
[20] I. Takahara, M. Saito, Chem. Lett. (1996) 973.
[21] T. Hattori, M. Komai, A. Satsuma, Y. Murakami, Nippon Kagaku Kaishi (in Japanese), 1991, p. 648.
[22] H. Shimada, T. Akazawa, N. Ikenaga, T. Suzuki, Appl. Catal. A 168 (1998) 243.
[23] F. Cavani, K. Koutyrev, F. Trifiró, A. Bartolini, D. Ghisletti, R. Lezzi, A. Santucci, G. Del Piero, J. Catal. 158 (1996) 236.
[24] M. Cherian, M.S. Rao, W.T. Yang, J.M. Jehng, A.M. Hirt, G. Deo, Appl. Catal. A 233 (2002) 21.
[25] S. Wang, K. Murata, T. Hayakawa, S. Hamakawa, K. Sukuki, Appl. Catal. A 196 (2000) 1.
[26] Z. Zhao, Y. Yamada, Y. Teng, A. Ueda, K. Nakagawa, T. Kobayashi, J. Catal. 190 (2000) 215.