Oxidized Diamond: A Novel Support for Catalytic Dehydrogenation

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We found that oxidized diamond played a significant role to improve catalyst performance of Cr_2O_3 catalyst during the dehydrogenation of C_2H_6 to C_2H_4 in the presence of CO_2.

Oxidized diamond surface is recently focused to be a new unique material phase as a carbon–oxide solid. Diamond surface is easily oxidized by oxidative acids such as HNO_3, HClO, H_2O_2 etc. and 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] Till now, no carbon–oxide solid phase was found, however, the oxidized diamond near surface is considered to be a pseudo-carbon–oxide solid. The oxidized diamond surface is expected to behave itself as a carbon–oxide for specified surface reactions such as catalytic, electrochemical reactions. Since such reactions must be controlled by the interaction between molecules and surfaces, the bulk structures of solids are less important. 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 to yield 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.

Among many catalytic reactions, we are recently interested in the weak oxidation capability of CO_2 in the dehydrogenation of alkane to alkene.[3,4] Recently, CO_2 has been investigated as a mild oxidant for dehydrogenation of hydrocarbons.[5–7] The dehydrogenation process using CO_2 could be an energy-saving process as compared with a present commercial process using steam. We have first found that CO_2 markedly promoted dehydrogenation of C_2H_6 over Ga_2O_3 catalyst with high selectivity to give C_2H_4 (reaction 1).[3,4]

$$C_2H_6 + CO_2 \rightarrow C_2H_4 + CO + H_2O \quad \Delta H_{923} = +135\ \mathrm{kJ/mol} \quad (1)$$

In this report, we first focus to apply the oxidized diamond as a novel catalyst support for the dehydrogenation of C_2H_6 to C_2H_4 with CO_2. We have found that the oxidized diamond supported-Cr_2O_3 catalyst markedly promoted dehydrogenation of C_2H_6 to C_2H_4 with CO_2 and the oxidized diamond exhibited an excellent potential as a support material for catalytic reactions.

Commercially available fine-powdered diamond was used for the study. The diamond powder was washed with HNO_3 to remove metallic impurities and then rinsed with distilled water thoroughly. 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 have oxygenated species with C–O–C and C=O structures.[1,2] The oxidized diamond powder has a specific surface area of 12.6 $m^2 \cdot g^{-1}$. Catalysts were prepared by impregnating metal salts to oxidized diamond. Supported catalysts were dried and 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 at an atmospheric pressure. Products were analyzed by a gas chromatograph.

Figure 1a shows the results of ethene yields at 923 K on oxidized diamond supported various metal oxide catalysts in the presence of CO_2. Thermal dehydrogenation occurred to give only ca. 2.5% of C_2H_4 yield in the presence of CO_2. Equilibrium conversion of C_2H_6 to C_2H_4 is ca. 50% at 923 K at a C_2H_6–CO_2 ratio of 1:5. The order of the activity of oxidized diamond supported various metal oxide catalysts in the presence of CO_2 at 923 K was as follows: $Cr_2O_3 > V_2O_5 > MoO_3 > Ga_2O_3 > CeO_2 > Mn_3O_4 > Fe_2O_3 > ZnO$. The C_2H_4 selectivities in all the metal oxide catalysts were higher than 85% in the dehydrogenation of C_2H_6 in the presence of CO_2. The oxidized diamond alone did not show catalytic activity by itself. Oxidized diamond-supported Fe, Mn, Ce, Ga, and Mo oxide catalysts exhibited slight catalytic activity. These catalysts were known to be active catalysts for dehydrogenation of alkane. The oxidized diamond-supported Cr_2O_3 catalyst afforded the highest C_2H_4 yield (22.5%) among various oxidized diamond-supported metal oxide catalysts.

To compare oxidized diamond-supported metal oxide catalysts with unsupported metal oxide catalysts, Figure 1b shows C_2H_4 yields over unsupported metal oxides (bulk oxides) catalysts. All of the bulk metal oxide catalysts exhibited only weak catalytic activities. The order of the activity of bulk metal oxides at 923 K was as follows: $Ga_2O_3 > Cr_2O_3 > V_2O_5 > Mn_3O_4 > ZnO > CeO_2 > Fe_2O_3 > MoO_3$. These results clearly indicated that the oxidized diamond support has a significant role for the metal oxide catalysts. Catalytic activities of some metal oxide catalysts were enhanced with the oxidized diamond. Particularly, the oxidized diamond supported-Cr_2O_3 acts an excellent catalyst. The activity order of metal oxide catalysts did not agree with that of oxidized diamond supported catalysts. This seems to indicate that weak interaction between metal oxides and support played an important role in the dehydrogenation activity. The oxidized diamond surface has moderately strong dipoles and was polarized. The interaction between the diamond surface and metal/metal oxides should be increased by the oxidation as compared with the hydrogenated and clean diamond surfaces.

Table 1. Dehydrogenation of ethane over oxidized diamond supported catalysts

		In the presence of CO_2				In the presence of Ar				Ratio of Yield
	Surface area	Conv./ %	Yield/ %	Selectivity/ %		Conv./ %	Yield/ %	Selectivity/ %		Y_{CO_2}/Y_{Ar}
Catalysts	m^2/g	C_2H_6	C_2H_4	C_2H_4	CH_4	C_2H_6	C_2H_4	C_2H_4	CH_4	
Cr_2O_3	12.0	27.4	23.8	86.7	13.3	7.0	6.8	97.1	2.9	3.5
V_2O_5	10.9	9.3	8.3	89.2	10.8	5.9	5.7	96.0	4.0	1.5
MoO_3	11.7	6.8	5.9	87.4	5.7	7.9	3.3	57.9	42.1	1.8
Ga_2O_3	11.6	5.8	5.7	99.7	0.3	5.2	5.1	99.6	0.4	1.1

Catalyst: 200 mg, reaction temperature: 923 K, SV=9000 h^{-1}mL/g-cat, composition of the feed gas: $C_2H_6/CO_2(Ar)=5/25$.

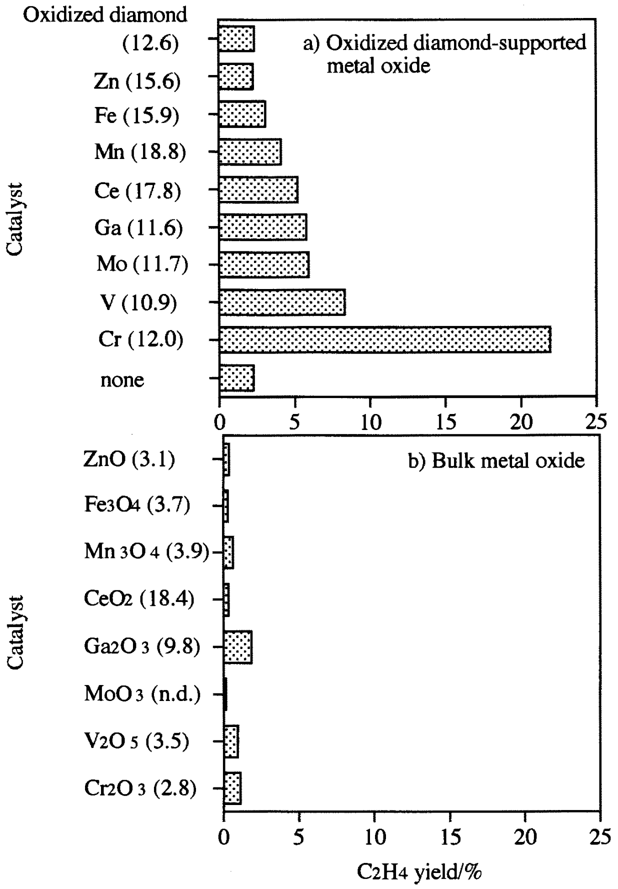

Figure 1. Dehydrogenation of C_2H_6 in the presence of CO_2 over oxidized diamond-supported metal oxide catalysts and unsupportedmetal oxide catalysts. Temperature: 923 K, Reaction time: 0.5 h,C_2H_6 : CO_2 = 5 : 25 (mL/mL), metal oxide=20 mg, SV=9000 h^{-1}mL/g-cat, (): surface area (m^2/g)

Table 1 lists the results of the dehydrogenation of C_2H_6 over oxidized diamond supported-Cr_2O_3, V_2O_5, MoO_3, and Ga_2O_3 catalysts as compared with the presence of and the absence of CO_2. The activity of the oxidized diamond supported-Cr_2O_3 catalyst in the presence of CO_2 was three times as much higher than that without CO_2. Promoting effects of CO_2 on the C_2H_4 yields were observed on all the catalyst. 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 yield of C_2H_4 with the other catalysts in the presence of CO_2 was slightly higher as compared to the run in the absence of CO_2. One of characteristic features of the oxidized diamond as a support for catalyst is a higher C_2H_4 selectivity (Ga_2O_3/TiO_2 70.8%).[4] Probably, an absence of secondary reaction with reactants or products would be one of the important roles of the oxidized diamond support. Roles of CO_2 for the dehydrogenation of C_2H_6 over the oxidized diamond supported-Cr_2O_3 catalyst are still not clear. Carbon dioxide slightly oxidized diamond surface at above 873 K to give CO and this kept oxidized diamond phase as evidenced by FT-IR adsorption at 1750 cm^{-1}. Oxygen transfer from diamond surface to the active metal oxide seems to promote dehydrogenation of C_2H_6. In the Ga_2O_3 catalyst, apparent carbon deposition occurred (color changed to black), however, no significant carbon deposition was observed over the oxidized diamond supported-Cr_2O_3 catalyst (no color change). CO was detected about twice as much amount of C_2H_4 over the oxidized diamond supported-Cr_2O_3 catalyst during dehydrogenation of C_2H_6 in the presence of CO_2. One possible reason for the increased yield of C_2H_4 in the presence of CO_2 would be oxidative dehydrogenation of C_2H_6 with CO_2. Another possibility is an elimination of deposited carbon. In addition, X-ray photoelectron spectroscopic (XPS) analysis indicated that CO_2 kept chromium oxide on the oxidized diamond to be higher oxidation state. The XPS peak of chromium species of the oxidized diamond supported-Cr_2O_3 catalyst slightly shifted to higher binding energy after the reaction at 923 K in the presence of CO_2 as compared with that of the fresh one and/or after the reaction in the absence of CO_2. This result suggests that CO_2 could maintain chromium oxide in higher oxidation states.

Both carbon oxides, oxidized diamond and carbon dioxide, play important roles to yield active catalytic sites for the dehydrogenation of C_2H_6. This is the first report that oxidized diamond is proposed to be useful as a novel catalytic medium, and suggesting that the surface property of oxidized diamond has a potential possibility for producing unique reaction fields in the catalytic activation of hydrocarbon chemistry.

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