Novel Selective Oxidation of Light Alkanes Using Carbon Dioxide. Oxidized Diamond as a Novel Catalytic Medium

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Carbon dioxide is an effective oxidant for the conversion of alkanes to chemical feedstocks. Oxidized diamond is useful as a novel catalytic support material. Oxidized diamond provided catalytic sites for the activation of alkanes under CO_2 atmosphere. The present findings also suggest that the surface-properties of oxidized diamond may facilitate unique catalytic reactions, such as alkanes conversion in the presence of CO_2.

The effective chemical utilization of carbon dioxide may be an important tool for the prevention of global warning.[1] Natural gas components methane and ethane are also greenhouse gases, and effective utilization or conversion of natural gas is needed as an oil-alternate fuel and chemical feedstock.[2]

Several attempts have been made to use CO_2 as a solvent,[3] in catalytic reactions,[4] as an oxidant,[5] etc. However, the role of CO_2 in these reactions is still unclear. Furthermore, CO_2 has produced no significant improvement in product yields. Recently we discovered that CO_2 markedly promoted the dehydrogenation of alkanes with high alkenes selectivity.[6] A unique property of CO_2 (the ability to oxidize metal oxides) plays an important role in alkane dehydrogenation.[6] This leads us to a novel utilization of diamond. Oxidized diamond exhibits novel and unique catalytic properties applicable to alkane conversion chemistry,[7] and is useful in electrodes.[8] Oxygen species on the diamond surface play an important role in its catalytic activity in activating light alkane reactions.

The direct production of oxygenates from light alkanes such as methane and ethane using an oxidant is one of the great challenges in catalysis research. The direct conversion of alkanes to oxygenates is a significant challenge in catalysis technology, and would simplify industrial processes and decrease production costs by allowing the innovative utilization of natural gas. The selective oxidation of alkanes to oxygenates has been performed using oxygen as an oxidant over various catalysts. The oxidative conversion of light alkanes is exothermic, so the reaction is thermodynamically possible at a lower temperature.

However, it is necessary to remove heat from the reaction and to control over-oxidation to CO_2 in order to attain high selectivity for the useful products. No reports have addressed the possibility of direct conversion of light alkanes to alcohols or aldehydes using CO_2 as an oxidant and a generic plug flow reactor at atmospheric pressure, due to the difficulty of transferring the oxygen of carbon dioxide into organic compounds.

In the present study, we report the novel selective oxidation of alkanes using CO_2 as an oxidant over oxidized diamond-supported catalysts, and the extension of the oxidation capability of CO_2 to selective oxidation of light alkanes to oxygenates.

$$CH_4 + 2CO_2 \rightleftarrows HCHO + 2CO + H_2O$$
$$\Delta H^\circ_{298} = +246\,\text{kJ/mol.} \quad (1)$$
$$C_2H_6 + 2CO_2 \rightleftarrows CH_3CHO + 2CO + H_2O$$
$$\Delta H^\circ_{298} = +198\,\text{kJ/mol.} \quad (2)$$

In order to induce the reactivity for a catalytic reaction and the hydrophilicity to be impregnated with metal oxides as an active material, oxidized diamond was prepared by oxidation of commercial finely-powdered diamond at 723 K for 1 h under a stream of O_2–Ar (1:4). Before oxidation, in order to eliminate impurities and activate the diamond surface, the diamond powder was hydrogenated at 1173 K for 1 h. V_2O_5-loaded catalysts (containing 2, 3 wt % of V_2O_5) was prepared by soaking oxidized diamond (BET surface area $= 12.6\,m^2/g$) in an aqueous solutions of NH_4VO_3 and, evaporating to dryness. Supported catalysts were calcined at 723 K for 3 h in air prior to use. The catalyzed reaction was carried out using a fixed-bed flow type quartz reactor under atmospheric pressure. Using 100 mg of a catalyst, 15 mL/min C_2H_6 and 15 mL/min of CO_2 were introduced. The C1, C2, and C3 hydrocarbon gases and products were analyzed with a gas chromatograph (TCD, FID) and by FT-IR. The catalyst was analyzed by UV–vis diffuse reflectance spectroscopy.

Table 1 shows the results of selective oxidation of ethane using CO_2 over the V_2O_5-loaded catalysts. Oxygenates (acetaldehyde and formaldehyde) were not formed either in the uncatalyzed reaction or under an Ar atmosphere. Oxygenate was formed, however, when the oxide of the 4B group was used for the catalyst support. The V_2O_5/oxidized diamond catalyst gave the highest CH_3CHO yield, and continued to form oxygenates over 5 h. When SiO_2, GeO_2, and TiO_2 were used as support materials, oxygenates were also formed. With the other support, C_2H_4 was main product. Though oxygenate yields were still low, it became clear that CO_2 played the role of an oxidant for the selective oxidation of light alkanes. Oxygenate yield increased with increasing reaction temperature over the V_2O_5/oxidized diamond catalyst. In the selective oxidation of alkanes, both the structure and reactivity of the oxygen species on the catalyst surface are important in the formation of oxygenates. A detailed investigation of the reaction mechanism is currently underway. It seems that the surface oxygen species on an oxidized diamond support plays an important role in the formation of oxygenates. The active species is a high oxidation state of vanadium oxides, and CO_2 seems to be concerned in the redox for the vanadium. No reports have described the direct formation of oxygenates in

Table 1. Effect of supported V_2O_5 catalyst on the selective oxidation of C_2H_6 using CO_2

Support	Temperature /K	Conv., %	Yield, μmol/h			
		C_2H_6	CH_3CHO	HCHO	C_2H_4	CO
Oxidized Diamond	923	9.9	14.1	1.6	175	1255
SiO_2	973	22.3	5.6	0.0	1930	1880
GeO_2	773	0.1	1.6	0.0	0	35
TiO_2	873	3.6	0.7	0.0	19	576
Al_2O_3	973	38.2	0.0	0.0	2500	3690
MgO	973	25.6	0.0	0.0	1400	3863
Blank	923	0.0	0.0	0.0	0	0

V_2O_5 loading level: 3 wt %, Catalyst: 100 mg, SV: 18000 h^{-1}·mL/g-cat. Reaction time: 1 h, Total flow rate: 30 mL/min, C_2H_6:CO_2 = 15:15 mL/mL.

Table 2. Effect of supported V_2O_5 catalyst on the selective oxidation of CH_4 using CO_2

Support	Temperature /K	Yield, μmol/h	
		HCHO	CO
SiO_2*	973	14.2	287
Oxidized Diamond*	973	6.6	618
GeO_2	873	2.7	39
TiO_2	973	1.5	1157
Al_2O_3	973	0.0	1287
Blank	973	0.0	0.0

V_2O_5 loading level: 2 wt %, Catalyst: 100 mg, SV: 18000 h^{-1}·mL/g-cat. Total flow rate: 30 mL/min, CH_4:CO_2 = 10:20 mL/mL. Reaction time: 1 h, *Catalyst: 50 mg, SV: 36000 h^{-1}·mL/g-cat.

the selective oxidation of alkane using CO_2. Therefore, this is a very significant new utilization of CO_2.

In the second reaction, methane was used to explore the selective oxidation of light alkanes using CO_2. Table 2 shows the results of selective oxidation of methane over the V_2O_5-loaded catalysts. Formaldehyde was formed over V_2O_5 loaded SiO_2, oxidized diamond, GeO_2, and TiO_2. It was confirmed that CO_2 could be used as an oxidant in the selective oxidation of methane which has low reactivity.

In the oxidation of C_2H_6 and CH_4 with CO_2 using V_2O_5-loaded oxidized diamond catalyst, CO was formed in addition to other oxygenates. This means that CO_2 reforming of CH_4, C_2H_6, or decomposition of HCHO, CH_3CHO to CO and H_2 seemed to take place concurrently.

Figure 1 shows UV–vis diffuse reflectance spectra of the oxidized diamond-supported V_2O_5 (3 wt %) catalyst. Fresh catalyst exhibited absorptions at around 270 nm and 400 nm, indicating the presence of tetrahedral V^{5+} species.[10] Used catalyst in the presence of CO_2 also exhibited absorptions at 270 nm and 400 nm, and in addition to these, a very broad new peak at around 600 nm appeared. This peak correspond to V^{4+}.[10] It is obvious that reduction of the vanadium species occurred during oxidation of ethane. However, peaks at 270 and 400 nm remained after reaction. This indicates that CO_2 slightly oxidized the vanadium species during the reaction in the presence of CO_2.

In order to obtain oxygenates in the selective oxidation of light alkanes using CO_2, V_2O_5, or the higher oxidation state of vanadium oxides are required. If the vanadium oxides are dispersed on the oxidized diamond surface, the vanadium oxides might be stabilized and not easily to be reduced. Even if the vanadium oxides were reduced by alkenes, oxygenates or H_2, they would nonetheless be oxidized by CO_2 or oxygen species on the diamond surface, which might be supplied by CO_2. Such mutual promotion is believed to take place during the phase formation of vanadium oxides, and to be the reason for the observed apparent synergism or promoting effect of CO_2 for the activation of light alkanes.

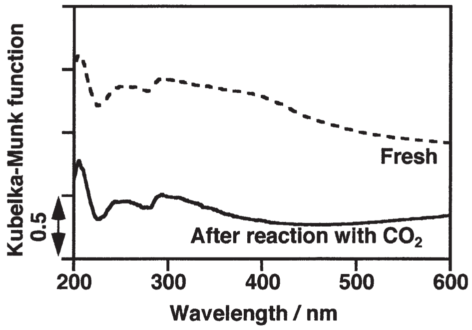

Figure 1. UV–vis spectra of fresh and reacted V_2O_5/oxidized diamond catalysts. Reacted V_2O_5/oxidized diamond catalyst; Temperature: 923 K, Reaction time: 1 h, Catalyst = 100 mg, C_2H_6:CO_2 = 15:15 (mL/min), SV = 18000 h^{-1}·mL/g-cat.

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