

Oxidized diamond as a novel catalyst medium: Dehydrogenation of light alkane using carbon dioxide

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The near surface of the oxidized diamond is considered to be a pseudo-carbon-oxide solid (1). 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. This led us to employ diamond in a novel way. Oxidized diamond exhibited novel and unique catalytic properties for alkane conversion chemistry in the presence of CO₂ (2).

In this study, we will describe the novel oxidation of alkanes using CO₂ as an oxidant over oxidized diamond-supported catalysts, and show that CO₂ markedly promoted the activation of light alkanes.

Catalysts were prepared by impregnating aqueous solutions of metal nitrates into oxidized diamond, and they were then 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 under atmospheric pressure.

Dehydrogenation of light alkanes in the presence of CO₂ over the oxidized diamond-supported metal oxide catalysts.



Table 1 shows the alkene yields on oxidized diamond-supported Cr₂O₃ and V₂O₅ catalysts in the presence and absence of CO₂. The activity of oxidized diamond-supported Cr₂O₃ and V₂O₅ catalysts in the presence of CO₂ was twice that of catalysts without CO₂. Dehydrogenation of light alkanes in the presence of CO₂ over oxidized diamond-supported Cr₂O₃ and V₂O₅ catalysts produced mainly alkene, CH₄, CO, H₂, and H₂O. The alkene yield with the oxidized diamond-supported Cr₂O₃ and V₂O₅ catalysts in the presence of CO₂ was slightly higher as compared to the run in Ar. The promoting effect of CO₂ in the dehydrogenation of light alkanes on oxidized diamond-supported Cr₂O₃ and V₂O₅ catalysts was observed. CO₂ promoted the dehydrogenation of ethane exclusively over oxidized diamond-supported Cr₂O₃ and V₂O₅ catalysts. Dehydrogenation of C₂H₆ was strongly promoted when Cr₂O₃ was the active species. Based on these findings, the role of CO₂ could be explained as follows; slightly acidic CO₂ might have been strongly adsorbed onto the basic site of catalyst surface, and as a result, the acidic properties of Cr₂O₃ and V₂O₅ would be enhanced. Such a possibility was supported by the result in which following dehydrogenation a certain amount of carbon was formed onto the catalyst (Cr₂O₃ and V₂O₅).

1) T. Ando. *et al.*, *J. Chem. Soc. Faraday Trans.*, **1993**, 89, 749.

2) K. Nakagawa. *et al.*, *Chem. Lett.*, **2000**, 1100.

Table 1 Dehydrogenation of light alkane over oxidized diamond supported catalysts.

Catalysts	alkane	Product alkene	In the presence of CO ₂			In the presence of Ar			Ratio of Yield Y _{CO₂/Ar}
			Conv., %	Yield, %	Sele., %	Conv., %	Yield, %	Sele., %	
			Alkane	Alkene	Alkene	Alkane	Alkene	Alkene	
Cr ₂ O ₃	C ₂ H ₆	C ₂ H ₄	27.4	23.8	86.7	7.0	6.8	97.1	3.5
V ₂ O ₅	T=923 K		9.3	8.3	89.2	5.9	5.7	96.0	1.5
none			2.4	2.3	95.6	2.7	2.6	95.9	0.9
Cr ₂ O ₃	C ₃ H ₈	C ₃ H ₆	19.7	11.8	59.9	15.0	9.8	65.5	1.2
V ₂ O ₅	T=873 K		13.7	8.6	62.7	11.5	6.5	56.2	1.3
none			2.4	1.4	59.9	2.3	1.2	52.7	1.2
Cr ₂ O ₃	n-C ₄ H ₁₀	Butenes	18.9	11.3	60.0	16.8	11.6	69.5	1.0
V ₂ O ₅	T=873 K		20.1	12.2	60.9	14.1	8.2	58.3	1.5
Cr ₂ O ₃	i-C ₄ H ₁₀	i-C ₄ H ₈	22.7	17.5	77.3	18.6	16.0	86.0	1.1
V ₂ O ₅	T=893 K		25.3	21.0	82.9	19.0	15.3	80.3	1.4

Reaction conditions: , SV=9000 mL/g-cat

Composition of the feed gas: Alkane/CO₂/Ar=5/25