

Oxidized Diamond Supported Ni Catalyst for Synthesis Gas Formation from Methane

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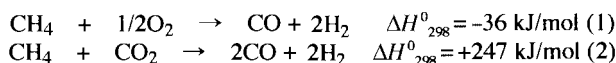
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Oxidized diamond gave the best performance among the support materials of Ni loaded catalysts for the partial oxidation of methane. Ni(5 wt%)/oxidized diamond afforded 20% conversion of methane ($\text{CH}_4/\text{O}_2 = 5$) to give CO and H_2 ratio of 2.0 at 873 K. Ni(5 wt%)/oxidized diamond also showed high catalytic activity for the CO_2 reforming of methane.

Recent studies of the surface properties of diamond have focused on the utilization of diamond as a material for use in electronic devices.¹ Diamond has been considered to be inert in relation to most chemicals. However, we were the first to describe diamond's characteristics and report its possible role as an excellent support material for the catalytic reaction.²

Synthesis gas production from methane is indispensable for the chemical utilization of natural gas. Synthesis gas is also important as for use in Fischer–Tropsch and methanol synthesis.

In view of this, partial oxidation [eq (1)] and CO_2 reforming [eq (2)] of methane have attracted much attention. Since CH_4 and CO_2 are greenhouse gases, their conversion to synthesis gas could be a method of their reduction from the environment. The transition metals of the groups 8–10 supported on metal oxides have been widely examined as catalysts for the partial oxidation and CO_2 reforming of methane to synthesis gas, and in some cases the effect of the support on the catalytic activity has been reported.^{3–5}



Ni-loaded catalysts afforded high yields of synthesis gas for both partial oxidation and CO_2 reforming of methane. However, remarkable carbon deposition occurred during the reaction over Ni-loaded catalysts.⁵ To overcome this problem, the use of catalysts containing nickel with perovskite⁶ or a nickel-magnesia solid solution catalyst⁷ have been reported. In previous papers, we have reported that Ir(5 wt%)-loaded TiO_2 catalyst afforded the highest activity for the partial oxidation of methane into CO and H_2 with a selectivity of over 80% at 873 K, without any carbon deposition. The synthesis gas production proceeded basically via a two-step path consisting of methane combustion to give CO_2 and H_2O , followed by the reforming of methane with CO_2 and H_2O .^{8–10} Since Ir is more expensive than Ni, one technical problem to be overcome in the Ir catalysts is a higher loading level of Ir.

In this letter, we focus on the partial oxidation and CO_2 reforming of methane over oxidized diamond-supported Ni, and the results are compared with those of various metal oxide sup-

ports in order to reduce carbon deposition over Ni-loaded catalysts. We have found that oxidized diamond exhibited high activity as a support material of a Ni-loaded catalyst for the partial oxidation and CO_2 reforming of methane.

The preparation of an oxidized diamond has been described previously.² Catalysts were prepared by impregnating an aqueous solution of Ni nitrate onto oxidized diamond, activated carbon, Al_2O_3 , SiO_2 , TiO_2 , MgO , and La_2O_3 . Supported catalysts were dried and calcined at 723 K for 5 h in air prior to the reaction. The reaction was carried out with a fixed-bed flow type quartz reactor (350×10 mm) at an atmospheric pressure. The conditions for partial oxidation were as follows: with 60 mg of a catalyst, 25 mL/min CH_4 and 5 mL/min O_2 were introduced at 673–873 K. For CO_2 reforming, using 100 mg of a catalyst and 300 mg of silica sand (Merck), 30 mL/min CH_4 and 30 mL/min of CO_2 were introduced. Silica sand was used as a heat buffer for a large endothermic reforming reaction. Products were analyzed by gas chromatography.

Figure 1 shows the effects of various supports at a Ni loading level of 5 wt% on the conversion of methane in the temperature ranges of 673 to 873 K. The order of catalytic activity of different supports at the reaction temperature of 873 K was Oxidized diamond > La_2O_3 > Al_2O_3 > SiO_2 > MgO > Active carbon > TiO_2 . Only the Ni/oxidized diamond catalyst afforded CO

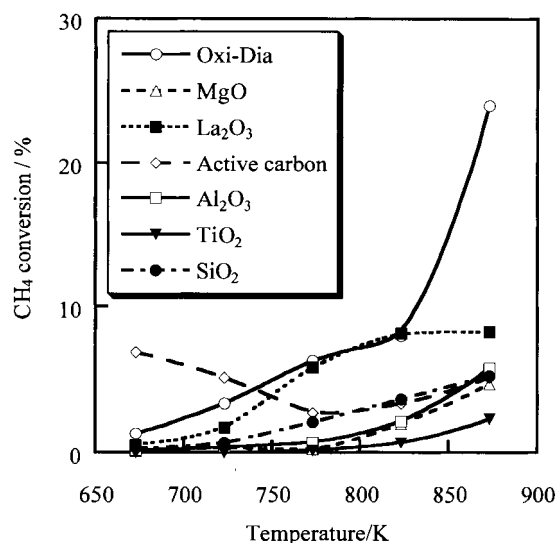


Figure 1. Effect of temperature on the CH_4 conversion over Ni-loaded catalysts. Catalyst, 0.06 g, Flow rate, 30.0 mL/min ($\text{CH}_4/\text{O}_2 = 5.0$), Ni loading level = 5 wt%.

Table.1 Effect of reaction temperature on the CO₂ reforming of methane with oxidized diamond-supported Ni catalyst

Temperature K	Conversion		Yield		H ₂ /CO (ratio)
	CH ₄ %	CO ₂ %	H ₂ %	CO %	
673	0.8	2.7	0.9	2.7	0.32
773	8.9	13.0	6.8	10.9	0.59
873	26.8	33.0	23.6	29.9	0.79
973	48.1	69.0	37.5	58.5	0.64
1073	85.1	92.7	68.2	93.2	0.73

Catalyst, 0.10 g; Silica sand, 0.3 g; Ni loading level, 5 wt%; Flow rate, 60.0 mL/min(CH₄/CO₂=1.0);

Reaction time, 0.5 h; Space velocity=36000 mL/h·g-catalyst.

and H₂ at 873 K with a small amount of carbon deposition. The other supported Ni catalysts yielded CO₂ and H₂O via complete oxidation of methane. To give high activity for partial oxidation of methane, metallic Ni species is required.⁵ On basic metal oxides or Al₂O₃, nickel oxide was stabilized and could be reduced to metallic nickel at lower temperatures only with great difficulty.^{5,11} These findings suggest that active species of the Ni catalyst for partial oxidation seems to be metallic nickel. NiO on the oxidized diamond might be easily reduced to metallic Ni, due to a weak interaction between the support and loaded NiO. In the fresh catalyst, the oxidic nickel species, stabilized on TiO₂, Al₂O₃, MgO, La₂O₃, and SiO₂ surface, did not exhibit catalytic activity until it was reduced to metallic form at 923 K.

Figure 2 shows the temperature dependence of the catalytic activity of a Ni/oxidized diamond catalyst for the partial oxidation of methane. When the temperature was increased from 673 to 973 K, synthesis gas was formed above 873 K. Below 823 K, only the complete oxidation of methane occurred. The Ni/oxidized diamond catalyst was activated and produced synthesis gas above temperature of 823 K. Furthermore, carbon deposition was not observed for Ni/Oxidized diamond catalyst at the reaction temperature of 973 K. Carbon deposition on the Ni/oxidized diamond catalyst was measured under an isothermal reaction at 973 K with a thermobalance. These results seem to indicate that the synthesis gas production via the partial oxidation of methane proceeded basically by means of a two-step path consisting first

of methane combustion to give CO₂ and H₂O, followed by the methane reforming with both CO₂ and H₂O.

The effect of supports on the partial oxidation of methane seemed to be related to the catalytic activity of the CO₂ reforming reaction.⁹ CO₂ reforming was carried out with oxidized diamond-supported nickel catalysts, and the relation between the activity in the partial oxidation and the CO₂ reforming was compared. Prior to the reaction, catalysts were reduced with H₂ at 873 K for 1 h. Table 1 illustrates the results of the CO₂ reforming of methane with a Ni/oxidized diamond catalyst. CH₄ and CO₂ conversions were greatly affected by the support of nickel. In all the cases, the CO₂ conversion was higher than that of CH₄. The synthesis gas yields increased with increasing reaction temperatures from 673 to 1073 K. Oxidized diamond support exhibited significant catalytic activity with a small amount of carbon deposition. In the dehydrogenation of ethane over the Cr₂O₃/oxidized catalyst, the catalytic dehydrogenation of ethane was promoted in the presence of CO₂, as compared with the absence of CO₂.² The significant effect of the support might be ascribed to the activation of CO₂ with metal oxides used as supports. These results indicate that oxidized diamond is useful as a novel support of catalyst, and suggesting that the surface properties of oxidized diamond have a potential possibility for producing unique reaction fields in the catalytic activation of methane to synthesis gas.

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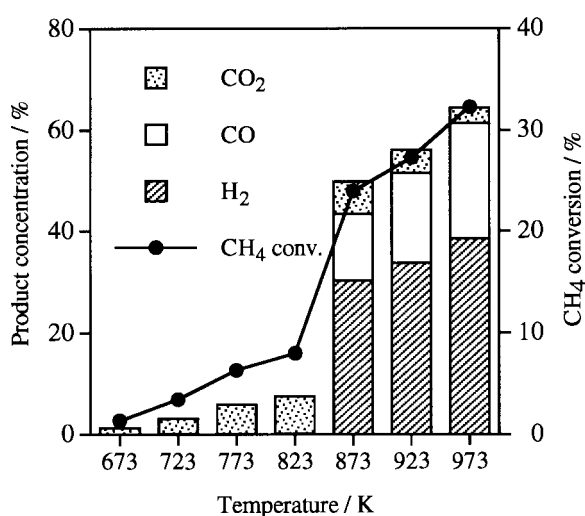


Figure 2. Effect of temperature on the products concentration over Ni (5 wt%) Oxidized diamond catalyst. Flow rate, 30 mL / min (CH₄ / O₂ = 5.0), Space velocity = 30000 mL / h · g-catalyst.

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