Diamond-supported metal catalyst: a novel medium for hydrogen production from methanol decomposition

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Oxidized diamond-supported Ni catalysts gave the best performance among the oxidized diamond-supported various metal catalysts for the decomposition of methanol to synthesis gas. Ni (5 wt%)/oxidized diamond afforded 82.5% conversion of methanol to give a CO to H_2 ratio of 1.7 at 573 K.

KEY WORDS: diamond; nickel; methanol; decomposition; hydrogen; carbon monoxide.

1. Introduction

Activated carbon has been widely utilized as the support material for metal or metal oxide-loaded catalysts. Activated carbon consists of an amorphous mixture of sp^2 and sp^3 carbon atoms. Recently, carbon nanofilaments have been reported as a novel carbon material that can be used for catalytic processes [1]. No carbon material which is constituted of pure sp^3 carbon atoms (diamond) has been examined as a catalyst support material. However, our recent study of oxidized diamond-supported chromium oxide(III) [2] or nickel exhibited excellent catalytic activity for the dehydrogenation of ethane and the partial oxidation of methane [3], respectively. In these reactions, weak but significant interactions between loaded metal catalysts and support surfaces seemed to play important roles in enhancing and prolonging the activity of the respective catalysts. The oxidized diamond acts a solid carbon oxide material and presents an excellent support material for catalysts.

Recently, the surface chemistry of diamond has received much attention [4,5]. The unique characteristics, especially the surface properties, of diamond and oxidized diamond have been of much recent interest: wide band gap, optical transparency, and mechanical strength are among such properties.

Hydrogen is a desirable alternative fuel to reduce atmospheric pollution. However, great problems are involved in the storage, transformation and economic production of hydrogen. If hydrogen could be efficiently produced, it could become a major clean universal fuel. Methanol is an attractive source of hydrogen production due to its availability, high energy density, easy storage and convenient transportation. Decomposition [equation (1)] or steam reforming of methanol [equation (2)] are of current interest, due to the production of hydrogen-rich gas to a low-temperature fuel cell in moving vehicles.

$$CH_3OH \rightleftharpoons CO + 2H_2 \quad \Delta H^{o}_{298} = +90.7\,\mathrm{kJ/mol} \quad (1)$$

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2 \quad \Delta H^{o}_{298} = +49.4\,\mathrm{kJ/mol} \quad (2)$$

Many catalysts have been reported to be active in the decomposition of methanol [6–10]. Among the reported catalysts, Ni-containing catalysts have been shown to afford a high yield of synthesis gas for the decomposition of methanol. The metal particles are usually dispersed over a wide surface area of support; for example, silica is known to improve catalytic activity. The interaction of support materials and nickel particles has not been clarified.

In this study, we will consider the decomposition of methanol over oxidized diamond-supported catalysts. The results are compared with those obtained with various other metal oxide supports used to reduce reaction temperature and carbon deposition over metal-loaded catalysts. We have found that oxidized diamond performed well with high activity as a support material of Ni-loaded catalyst for the decomposition of methanol to synthesis gas.

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2. Experimental

The preparation of oxidized diamond has been described previously [4]. The catalyst supports used were oxidized diamond (BET surface area = 12.6 $m^2 g^{-1}$), Al_2O_3 (JRC-ALO-4, the reference catalyst provided by the Catalyst Society of Japan), SiO_2, activated carbon, CeO_2 (Wako Pure Chemical), MgO (Ube Industries, Ltd.) and TiO_2 and ZrO_2 (Japan Aerosil Co.). Catalysts were prepared by impregnating aqueous solutions of $RuCl_3 \cdot nH_2O$, $Pd(NO_3)_2$, $IrCl_4 \cdot H_2O$, $(NH_3)_2Pt(NO_2)_2$ (Mitsuwa Pure Chemicals), $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $RhCl_3 \cdot H_2O$ (Kishida Chemicals) onto a suspended support, followed by evaporation to dryness. Supported catalysts were dried and calcined at 723 K for 5 h in air prior to the reaction. Prior to the reaction, the catalyst was reduced with H_2 at 673 K for 1 h. The reaction was carried out with a fixed-bed flow-type quartz reactor (350 × 10 mm) at atmospheric pressure. The conditions for the decomposition of methanol were as follows: with 200 mg of a catalyst, 10 ml/min CH_3OH (gas) and 30 ml/min of Ar were introduced at 573 K. Products were analyzed by FID (Shimadzu GC14APF) and TCD (Shimadzu GC8AIT) gas chromatographs.

3. Results and discussion

Figures 1 and 2 show catalytic activities for the decomposition of methanol over Ni-loaded catalysts. Oxidized diamond, SiO_2, ZrO_2, activated carbon, CeO_2, TiO_2, Al_2O_3 and MgO were used as the support materials. Prior to the reaction, Ni-loaded catalysts were reduced with H_2 at 673 K for 1 h. Oxidized diamond and SiO_2-supported Ni catalysts afforded high methanol conversions of 78.9% and 78.4%, respectively. The SiO_2-supported Ni catalyst was already known to be an active catalyst [9]. In the case of SiO_2 support, carbon deposition occurred on the catalyst surface during the reaction. In contrast, oxidized diamond exhibited high activity corresponding to that of SiO_2.

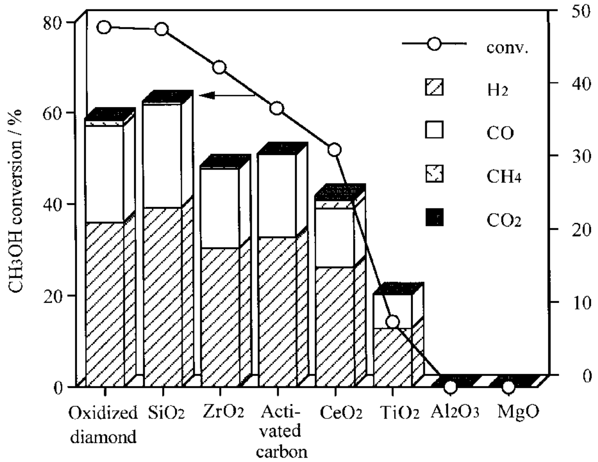

Figure 1. Effect of various supports on methanol conversion and product concentrations over Ni-loaded catalysts.

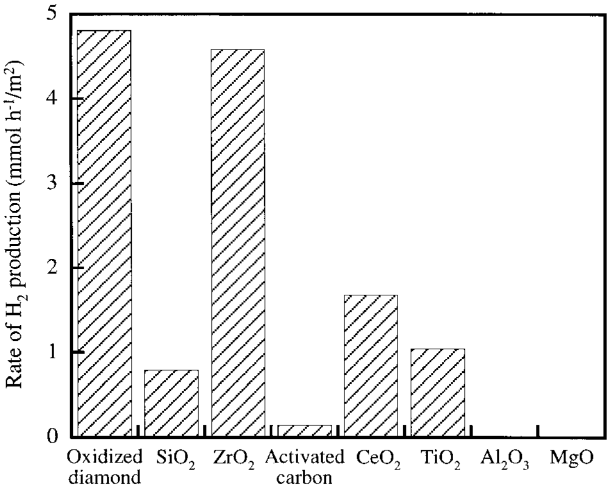

Figure 2. Rate of H_2 production in the decomposition of methanol over Ni-loaded catalysts.

Although both of these materials are composed of carbon, it is interesting that the activated carbon-supported catalyst and the oxidized diamond-supported catalyst exhibited different catalytic activities, as shown in figure 1. The higher catalytic activity was observed in the reaction with the oxidized diamond-supported catalyst. The results were similar to those in the case of activated carbon support. However, although the activated carbon had a larger specific surface area than that of oxidized diamond, activated carbon exhibited lower activity than that of the oxidized diamond, as shown in figure 2. The higher catalytic activity of the oxidized diamond-supported catalyst was therefore not due to the specific surface area of the support. The catalytic activity of a metal-loaded catalyst is also affected by the particle size of the loaded metal; if the size is smaller, the activity would be expected to increase. A larger specific surface area of a support material would yield a higher dispersion of loaded metal, namely, the metal particle size will decrease on surfaces with larger specific surface areas. Due to its larger surface area, the particle size of loaded Ni on the activated carbon would be smaller than that on the oxidized diamond. The smaller size of the loaded Ni on the activated carbon was expected to give higher activity than that observed on the oxidized diamond; however, the activity of the oxidized diamond-supported catalyst was higher. The superior catalytic activity of the oxidized diamond-supported catalyst for the decomposition of methanol was not due to either the specific surface area or the loaded metal particle size. We speculate that the excellent activity of the oxidized diamond-supported catalyst originated from the chemical interaction

Table 1
Effect of reduction temperature on the catalytic activity over oxidized diamond-supported Ni catalyst

Temperature (K)	Conversion (%)	Product (mmol)				H_2/CO (ratio)
		H_2	CO	CH_4	CO_2	
673	72.5	10.6	7.0	0.2	–	1.5
773	82.5	13.2	7.7	0.3	–	1.7
873	68.8	10.6	6.2	0.3	–	1.7

Note: Catalyst, 0.20 g; Ni loading level, 5 wt%; temperature, 573 K; reaction time, 0.5 h; flow rate = 40 ml/min ($Ar/CH_3OH = 3$).

between the loaded Ni and the oxidized diamond support surface.

Matsumura *et al.* [9] reported that the catalytic activity over a SiO_2-supported Ni catalyst was not simply related to the nickel surface area, and they also noted that small nickel particles were disadvantageous for the decomposition of methanol. In the case of synthesis gas formation from methane with partial oxidation and CO_2 reforming, the oxidized diamond-supported Ni catalyst has afforded high catalytic activity [5]. Oxygen transfer between both the carbon–oxygen bond on the diamond surface to loaded metal and the reverse of this reaction seems to play an important role in the catalytic activity of the oxidized diamond-supported catalyst. However, the significant effect between oxidized diamond and Ni is, as of yet, unclear; the size of nickel particles, as well as the weak interaction between the oxidized diamond (as a support material) and loaded Ni species, may be important factors.

In the decomposition of methanol, the stoichiometric ratio of produced H_2/CO is equal to 2. However, the ratios of H_2/CO in the present study were always less than 2. The reason for this seems to be a methanation [equation (3)] and a water–gas shift reaction [equation (4)].

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta H^\circ_{298} = -206\,\mathrm{kJ/mol} \tag{3}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H^\circ_{298} = -41\,\mathrm{kJ/mol} \tag{4}$$

Nickel oxide did not show high activity as regards the decomposition of methanol. Table 1 illustrates the effects of the H_2 reduction temperature and Ni/oxidized diamond catalyst on the conversion of methanol. At the H_2 reduction temperature of 773 K, the highest methanol conversion was obtained. Figure 3 shows the effect of the reaction temperature on catalytic activity. When the temperature was increased from 523 to 643 K, the conversion of methanol increased with increasing reaction temperatures, and conversions of methanol reached nearly 100% at the temperature of 598 K. In contrast, CO selectivities decreased with increasing reaction temperature, due to side reactions [equations (3) and (4)].

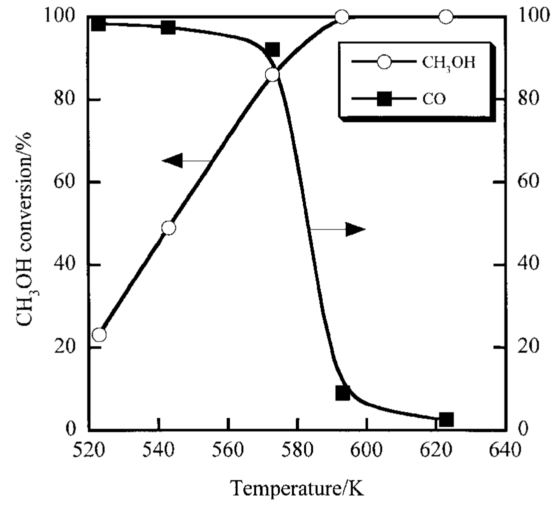

Figure 3. Effect of reaction temperature of oxidized diamond-supported Ni catalyst on methanol conversion and CO selectivity.

Figure 4 shows the conversion of methanol and product distributions over oxidized diamond-supported metal (5 wt%) catalysts. Prior to the reaction, all of the catalysts were reduced with H_2 at 773 K for 1 h. The order of catalytic activity of metal species at the reaction temperature of 573 K was Ni > Co > Pd > Rh > Ir > Cu > Pt > Ru. The oxidized diamond-supported Ni catalyst afforded the highest conversion of methanol, and CO and H_2 yield, among the oxidized diamond-supported metal catalysts. The oxidized diamond-supported Cu catalyst did not show a high rate of methanol conversion. CuO-containing catalysts were reported to be an active species for the decomposition of methanol [6,7]. Pd-loaded CeO_2 and ZrO_2 were known to be the most highly active catalysts for this reaction [8]. However, the oxidized diamond-supported Pd catalyst did not afford high catalytic activity. To achieve a high methanol conversion using a Pd-loaded catalyst, it was essential to use small particles of Pd on the

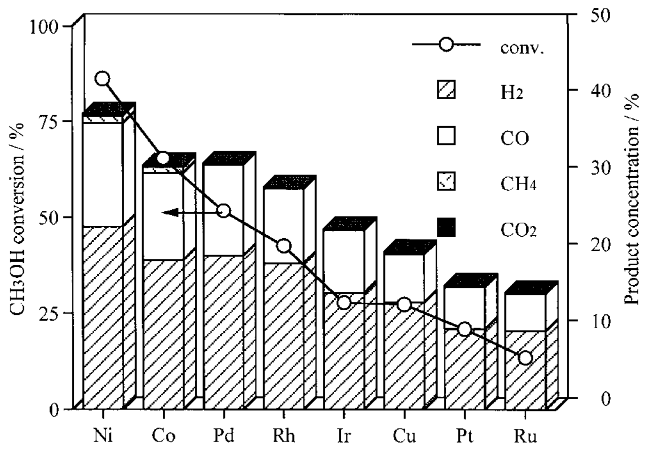

Figure 4. Effect of transition metals on methanol conversion and product concentrations over oxidized diamond-supported catalysts.

support material [8]. Therefore, larger particles would be loaded on the oxidized diamond-supported catalyst, due to the small specific surface area of oxidized diamond ($12.6\,m^2\,g^{-1}$).

These results indicate that oxidized diamond is useful as a novel catalytic support material. The present findings also suggest that the surface properties of oxidized diamond have the potential to produce unique catalytic reactions, such as hydrogen production from methanol and hydrocarbons.

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References

[1] G. Mestl, N.I. Maksimova, N. Keller, V.V. Roddatis and R. Schlögl, Angew. Chem. Int. Ed. 40 (2001) 2066.

[2] K. Nakagawa, C. Kajita, N. Ikenaga, T. Kobayashi, M. Nishitani-Gamo, T. Ando and T. Suzuki, Chem. Lett. (2000) 1100.

[3] K. Nakagawa, H. Nishimoto, Y. Enoki, S. Egashira, N. Ikenaga, T. Kobayashi, M. Nishitani-Gamo, T. Ando and T. Suzuki, Chem. Lett. (2001) 460.

[4] T. Ando, K. Yamamoto, M. Ishii, M. Kamo and Y. Sato, J. Chem. Soc., Faraday Trans. 89 (1993) 3635.

[5] J.M. Buriak, Angew. Chem. Int. Ed. 40 (2001) 532.

[6] W.H. Cheng, S. khter and H.H. Kung, J. Catal. 82 (1983) 341.

[7] J.F. Edwards and G.L. Schrader, J. Phys. Chem. 89 (1985) 782.

[8] Y. Usami, K. Kagawa, M. Kawazoe, Y. Matsumura, H. Sakurai and M. Haruta, Appl. Catal. A. 171 (1998) 123.

[9] Y. Matsumura, K. Kuraoka, T. Yazawa and M. Haruta, Catal. Today. 45 (1998) 191.

[10] S. Imamura, T. Higashihara, Y. Saito, H. Aritani, H. Kanai, Y. Matsumura and N. Tsuda, Catal. Today. 50 (1999) 369.