Production of Hydrogen and Carbon Nanofiber via Methane Decomposition

Zhi Zhang , Tao Tang , Guangda Lu , Cheng Qin , Huogen Huang , and Shaotao Zheng

Abstract—High purity hydrogen and the valuable by-product of carbon nanotubes (CNTs) can be produced by the methane catalytic decomposition. The methane conversion and the performance of CNTs were determined by the choices of catalysts and the condition of decomposition reaction. In this paper, Ni/MgO and Ni/O-D (oxidized diamond) catalysts were prepared by wetness impregnation method. The effects of reaction temperature and space velocity of methane on the methane conversion were investigated in a fixed-bed. The surface area, structure and micrography were characterized with BET, XPS, SEM, EDS technology. The results showed that the conversion of methane was above 8% within 150 min (T=500) for 33Ni/O-D catalyst and higher than 25% within 120 min (T=650) for 41Ni/MgO catalyst. The initial conversion increased with the increasing temperature of the decomposition reaction, but their catalytic activities decreased rapidly while at too higher temperature. To decrease the space velocity of methane was propitious to promote the methane conversion, but not favor of the hydrogen yields. The appearance of carbon resulted from the methane decomposition lied on the support type and the condition of catalytic reaction. It presented as fiber shape on the surface of Ni/O-D at the relatively lower temperature such as 500 and 550 , but as grain shape stacked on and overlayed on the surface of the metal nickel while at 650 . The carbon fiber can form on the Ni/MgO surface at 650 and the diameter of the carbon fiber increased with the decreasing space velocity.

Keywords—methane, catalytic decomposition,hydrogen, carbon nanofiber

I. INTRODUCTION

CATALYTIC decomposition of methane had recently received much attention as a potentially economical route for producing CO-free hydrogen that can be used directly as a fuel for H2–O2 cells[1-8]. Traditionally, hydrogen was synthesized through steam reforming or partial oxidation of methane. The CO coproduced with hydrogen was converted to CO_2 through the shift reaction with H_2O in order to obtain relatively pure hydrogen. However, 1-3% of CO was inevitably contained in the hydrogen after the shift reaction of CO. If the hydrogen was utilized as a fuel for the polymer electrolyte fuel cells (PEFC), the concentration of CO should be decreased less than 20 ppm through the selective oxidation of CO. Also carbon nanofiber or nanotubes can be produced by the decomposition of CH_4. The system of methane decomposition had been widely studied because of the conversion and

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production of methane decomposition depended on the reciprocity of catalyst carrier and active material.

Ni-based catalysts were extensively studied for methane decomposition due to their relatively higher activities and lower price compared with other transition metals .It was reported[9] that Ni/MgO were deactivated very quickly after methane contacted. The hydrogen produced amount of methane decomposing just reached to 0.75 mmol per 1 g of Ni/MgO catalyst. But Nakagawa's research indicated that methane cann't be decomposed on 5%Ni/MgO catalyst at the temperature of 600℃[10]. Recently, the surface science of diamond had attracted attention and several functional groups had been introduced onto the diamond surface[11-14]. The unique surface characteristic of diamond had attractted much interest.Oxidized diamond-supported metal oxide or metal catalysts had exhibited excellent catalytic activities for light alkane or alcohol converted to alkene, oxygenates and hydrogen.

In this paper, the oxidized diamond and MgO as catalyst support materials were examined for hydrogen production and selected Ni as active metal. The factors such as Ni contents and reaction temperature and space velocity were discussed which effected the methane conversion, catalyst lifetime and carbonfiber shape together with SEM, XPS and EDS observation.

II. EXPERIMENTAL

A. Sample preparation

The supported-Ni catalysts used in this work were prepared by impregnating the supports with aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$. The diamond and MgO were supplied from Tianjin Bodi Chemical Company(purity>99%) and Sichuan Yijing Changyun Super-hard Materials Company. In order to induce reactivity for a catalytic reaction and the hydrophilicity for impregnating metal oxides as an active material, oxidized diamond was prepared by oxidation of powdered diamond at 773 K for 2h under a stream of mixed O_2-Ar (1:4). Before the oxidation, in order to eliminate impurities and to activate the diamond surface, diamond powder was hydrogenated at 1173 K for 1 h. The catalysts were prepared by impregnating an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ onto suspended supports for 1.5h, followed by evaporation-to-dryness in automatic electric oven at 120℃. The prepared catalysts of Ni/MgO were calcined at 873 K in air prior to the reaction. To avoid a complete oxidation of diamond, the oxidation of diamond-supported catalysts were calcined at 723 K. Prior to

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the reaction, the catalysts were reduced with hydrogen at 723K for 1.5 h. The Ni loading of Ni/MgO catalyst was 41wt.% and that of Ni/O-Diamond 23wt.% and 33wt.%. Thereafter the Ni supported catalysts will be denoted as 41Ni/MgO, 23Ni/O-Diamond and 33Ni/O-Diamond respectively.

B. Characterization methods

During the reaction, a part of the gases in the stream out of the catalyst-bed was analyzed using by TCD gas chromatographs (Shimadzu GC-14C). In fact, hydrogen only was detected as a gaseous product.The carbon formed on the catalysts after the CH_4 decomposition was studied by scanning electron microscopy(SEM, Sirion-200).X-ray Photoelectron Spectroscopy(XPS) was used to analyse oxidized diamond near surface. The surface area of catalyst and supports were measured by using adsorption method of liquid nitrogen circumstance at 77K according BET method. The values of MgO, 41Ni/MgO, O-Diamond and 33Ni/O-Diamond were $13.56m^2/g$,$21.11m^2/g$,$0.2618m^2/g$,$5.36m^2/g$ respectively. The decomposition of methane was carried out using a fixed-bed flow-type quartz reactor (300×Ø10mm) at atmospheric pressure.

III. RESULTS AND DISCUSSION

A. XPS analysis of oxidized diamond

Diamond was one of the most important, interesting, unique, and stable forms of carbonaceous materials. Especially, oxidized diamond solid was recently focused to be a novel unique material phase as a carbon oxide. Till now, no carbon-oxide solid phase was found, however, the oxidized diamond near surface was considered to be a pseudo-carbon-oxide solid[10]. Fig. 1 shows the XPS spectrum of oxidized diamond. The C1s binding energy of original diamond was about 284.2eV. The O1s peak also can been gained because of adsorptive O2 or CO2 on the surface of diamond. The peak intensity was weak and its binding energy was about 532.6eV. But the C1s peak position of oxidized diamond changed obviously and the binding energy increased 4eV. From the C1s fit curve it was shown that there were two C1s peaks at about 286eV and 288eV except for 284.2eV. And the intensity of O1s peak increased greatly. The results indicated that the diamond surface has been oxidized. It was in accord with Nakagawa[10] investigation using the diffuse reflectance FT-IR spectra of oxidized diamond. Perhaps the interaction between loaded-Ni and oxygen species on the diamond surface will play some important roles on catalytic activity of the Ni/oxidized diamond catalyst.
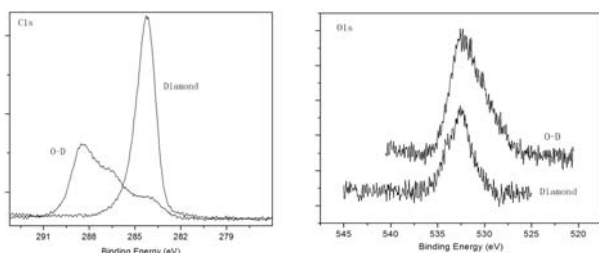

Fig. 1 C1s and O1s regions for diamond and oxidized diamond

B. Effects of reaction temperature on the decomposition of CH_4

Fig. 2 shows the effects of reaction temperature on CH_4 conversion over the 33Ni/O-Diamond and 41Ni/MgO (100mg) catalysts using a fixed-bed flow-type reactor. The initial conversion of methane (C0)increased from 2.5% to 18% with increasing the reaction temperature to the range of 723 to 823 K over the 33Ni/O-Diamond. The initial conversion of methane for 33Ni/O-Diamond catalyst was 24% at 923 K. As the temperature increased, the initial activity increased but the deactivation occurred more rapidly. The conversion of methane(C) changed unconspicuous at 723 K. However, the conversion of methane(C) decreased rapidly at 923 K and maintained between 4%-7%.There was a funny phenomenon that the conversion of methane not only keeped fixedness but also increased a little after 20 minutes at the temperature of 450 ℃,500℃,650℃, while decreased continually at 550℃. The reason for this was not clear at present. The effects of reaction temperature on CH_4 conversion over the 41Ni/MgO accorded with 33Ni/O-Diamond. It can been seem that the catalytic activity of 41Ni/MgO was higher than that of 33Ni/O-Diamond. But the lifetime of 33Ni/O-Diamond catalyst was longer than 41Ni/MgO. So the Ni/O-Diamond catalyst will have a good application foreground.
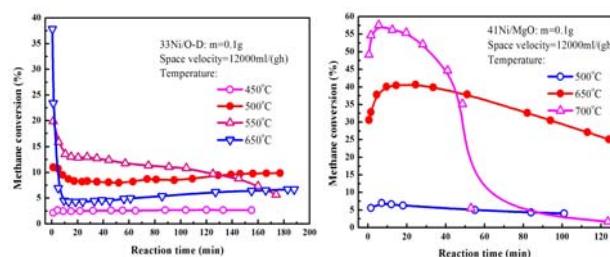

Fig 2 Effects of temperature on CH4 conversion

It was well known that the catalytic activities of the methane decomposition over the Ni-loaded catalysts depended strongly upon the support materials. Generally in order to improve the catalytic activities, we will select the materials with bigger surface area because it can ameliorate active metal dispersion on support materials. In this paper, we used MgO and O-Diamond with lower surface area as the support materials. The surface areas of MgO, O-Diamond, 41Ni/MgO and 33 Ni/O-Diamond were $13.56m^2/g$, $0.26m^2/g$, $21.11m^2/g$ and $5.36m^2/g$ respectively. The initial conversion of methane for Ni/ MgO catalyst was more than 30% at space velocity of 12000 $ml \cdot g^{-1} \cdot h^{-1}$ at 650℃. The conversion of methane for Ni/O-Diamond catalyst can maintain above 8% for 150min at space velocity of 12000 $ml \cdot g^{-1} \cdot h^{-1}$ at 500℃. In our system, it was notable that the catalyst with lower surface area showed higher activities. The reason for the high catalytic activity of the catalysts was not clear yet. However, the interaction between loaded-Ni and support material perhaps plays some important roles.

Many researchers thought that the carbon deposited on the catalyst surface was the main reason for inactivation because it covered the active site. It was shown that the quantity of carbon

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at 550℃ was higher than at 650℃ from figure 2(a). However the catalyst deactivated more rapidly at 650℃ than at 550℃. Presently the mechanism of carbon growth can explain the phenomenon of the catalyst deactivation. It makes against maintaining the catalyst activity in condition of too high or too low temperature. Too low temperature will result in little solubility of carbon in metal Ni. If the temperature was too high, the velocity of produced carbon was higher than that of body pervasion and surface transference in metal Ni. In the end carbon produced by methane decomposition must enrich on the catalyst surface and induce deactivation.

C. Effects of space velocity on the decomposition of CH₄

Fig. 3 shows the effects of space velocity on CH_4 conversion over the 23Ni/O-Diamond and 41Ni/MgO catalysts at the temperature of 550℃ and 650℃ respectively. The initial activity decreased along with the space velocity increasing. If the space velocity was high, the time contacted between methane and catalyst surface was short. Thus low CH_4 conversion will be achieved. The CH_4 conversion was about 50% at space velocity of 6000 $ml·g^{-1}·h^{-1}$ shown in Fig.3. Although low space velocity can improve the CH_4 conversion, it has no benefit to increase the hydrogen yields.
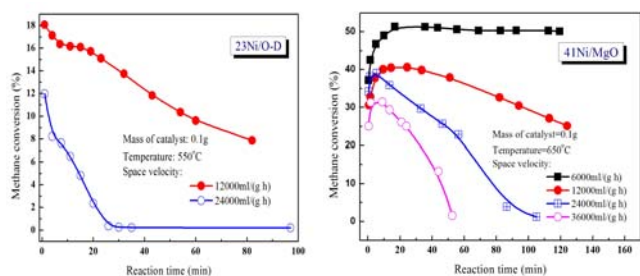

Fig.3 Effect of space velocity on the catalytic activity for methane decomposition

D. Formation of deposited carbon

Fig.4 and Fig.5 showed SEM images of Ni/ MgO and Ni/O-Diamond catalysts after methane decomposition. It was shown that the catalyst kinds and reaction conditions influenced not only the CH_4 conversion but also microcosmic morphology of carbon. SEM images in Figs.4 showed formation of fibrous carbons on the surface of 23Ni/O-Diamond and 33Ni/O-Diamond at the relatively lower temperature such as 500℃ and 550℃, but grain shape stacked on and overlayed on the surface of the metal nickel while at 650 ℃(Figs.4(a) and Figs.4(c)). So the carbon shape had relation with the catalytic reaction temperature. The deactivation occurred very rapidly as the temperature increased shown in the present study. The carbon shape in Figs.4(b) and Figs.4(d) resulted in the rapid deactivation of Ni/O- Diamond.

Fig.5 showed that the carbon fiber also can form on the Ni/MgO surface at 650℃. So the catalyst kinds influenced the carbon form deposited on the catalyst surface except for the catalytic reaction temperature. SEM images showed that the
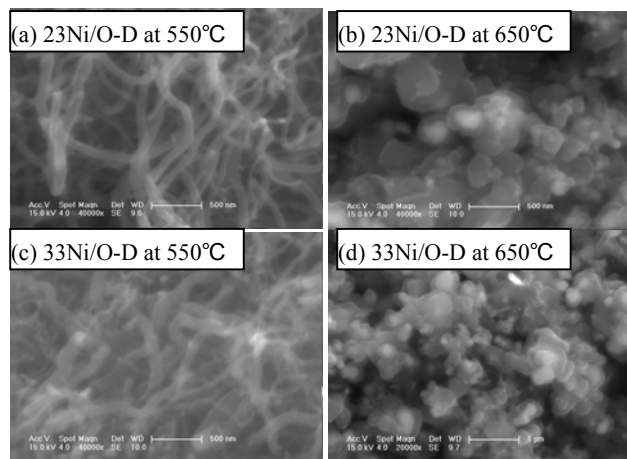

Fig.4 SEM micrograph of Ni/O-D after methane decomposition (space velocity=12000 ml/(h·g))

carbon nanofiber had a difference in diameter for methane decomposition at different space velocity. The lower the space velocity was, the thicker the carbon deposited on the catalyst surface was. The produced carbon yields were little relatively at lower space velocity just because of less methane touching with the catalyst. So the produced carbon can stack orderly on the catalyst surface and come into being thick carbon nanofiber.
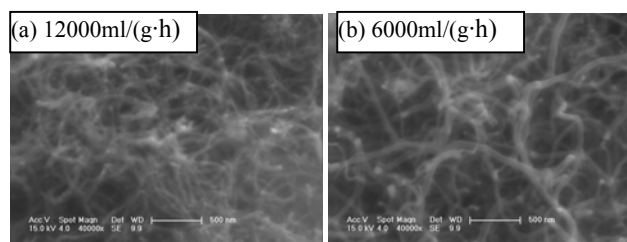

Fig. 5 SEM micrograph of 41.2Ni/MgO after methane decomposition at 650℃

Generally four steps can explain the mechanism of methane decompositing. Firstly, adsorption and decomposition reactions occurred for methane on the catalyst surface. Secondly, carbon species dissolved and separated from the catalyst surface. Thirdly, carbon species diffused into the catalyst inside and transferred in body. Finally, carbon species growthed on the catalyst surface. The pervasion rate of carbon in metal was the rate-determining step during carbon nanofibre growing. If the temperature was too high, the carbon produced velocity was higher than its diffusing and transferring speed. So the catalyst deactivated very rapidly before the carbon began growthing. The morphology of carbon was just like that shown in Fig.4(a) and Fig.4 (c).

It was concerned about selecting the reaction conditions to produce carbon nanofiber or nanotube. It was reported[19-21] that the factors such as reaction temperature, time, space velocity effected the form of produced carbon. The same time the structure and property of supported materials play an important role in methane decomposition as well as the interaction between carrier and active metal. In order to understanding the catalytic action of the supported materials, energy-dispersive spectra (EDS) for some wee spots on 33Ni/O- Diamond were measured at the same time as the SEM

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images as shown in Fig.6. No.1 area represented existing carbon and No.2 had no carbon. The result showed that there were C and Ni elements in No.1 area. The C elements consisted of diamond and produced carbon from decomposition of the methane. The ratio of C/Ni was 12:1. There was only one C element represented diamond in No.2 area. This indicated that the produced carbon only gathered around the Ni metal. There was no carbon produced on the place of no active metal. The Ni reacted the main effect on methane decomposition and the supported materials had no catalysis.
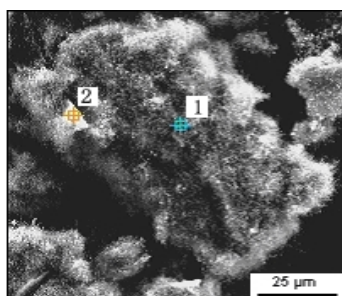

Fig. 6 SEM micrograph of 33Ni/O-D surface after methane decomposition（×1000）

IV. CONCLUSIONS

The conclusions were as follows from the results described above. O-Diamond and MgO were the effective supports of Ni-supported catalysts for methane decomposition to hydrogen. As the temperature increased, the initial activity increased but the deactivation occurred more rapidly. The effects of reaction temperature on CH4 conversion over the 41Ni/MgO accorded with 33Ni/O-Diamond. The catalytic activity of 41Ni/MgO was higher than that of 33Ni/O-Diamond and the lifetime of 33Ni/O-Diamond catalyst was longer than 41Ni/MgO.

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