Methane decomposition for hydrogen production by catalytic activity of carbon black under low flow rate conditions

Tomoharu TOKUNAGA†, Naoyuki KISHI, Kenya YAMAKAWA, Katsuhiro SASAKI and Takahisa YAMAMOTO

Quantum of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464–8603, Japan

Recently, carbon materials were reported to work as catalysts for the production of H₂ from hydrocarbons. However, the hydrogen production rate is extremely low. To broaden the scope of carbon materials as catalysts for the decomposition of hydrocarbons, a higher H₂ production rate is required. Thus, the hydrogen production rate under conditions employing a low flow rate of hydrocarbon per unit area and a large quantity of carbon materials as the catalyst should be evaluated, and the influence of these conditions on the rate of H₂ production by carbon materials should be discussed. Herein, the H₂ production rate was measured under conditions employing a low flow rate of CH₄ and a large quantity of carbon black (CB) as a catalyst. H₂ production started at 600°C and the production rate was less than 0.1%. The transmission electron microscope image of CB heated in CH₄ atmosphere demonstrated that a low flow rate of CH₄ does not affect the reaction site (i.e., graphite edges) of CB. However, the H₂ production rate was extremely low compared to that achieved with a high flow rate. It is proposed that there is an optimal flow rate for maintaining the catalytic activity at the graphite edge of CB for decomposition of CH₄.

Key-words : Carbon catalyst, Graphite, Hydrogen, Methane

1. Introduction

Numerous electrical devices are utilized in daily life. These devices operate by consuming electrical energy generated by fossil fuel combustion or nuclear reaction of fission fuel. The generated electrical energy is directly used in some devices and/or stored as charge. In the case where all the generated electrical energy is used, the issue of charge storage does not arise. However, electrical energy exceeding the requisite amount is usually generated, and the excess (redundant) electrical energy is stored by charging capacitors. The lithium ion battery (LIB) is such a capacitor that is widely utilized in mobile devices and electric vehicles.1) However, LIBs do not possess high energy density. Therefore, large volume capacitors are needed to store redundant electrical energy. Even if redundant electrical energy is stored by completely charging capacitors, the capacitors gradually self-discharge.2)–4) Thus, storage of energy, not as electrical energy but in other energy sources where the energy is easily preserved, is desirable. Fossil fuel is an energy reserve that may be used whenever electrical energy is needed. However, fossil fuel consumption is hampered by the threat of depletion of fossil fuel resources and the generation of carbon oxide gases like CO and CO₂ that lead to the human-enhanced greenhouse effect.5) Moreover, generation of electrical energy from fission fuel has the attendant danger of radioactive material release.6) Recently, H₂ as a prospective source of clean electrical energy without the concerns of the greenhouse effect and danger of radioactive materials has attracted the attention of researchers, and generation of electrical energy from H₂ has been actively studied.7)–9) Electrical decomposition of hydrocarbons is one method of producing pure H₂; however, this method requires electrical energy generated by using fossil and/or fission fuel.10) Thus, H₂ produced by the electrical decomposition method is not energy that does not generate CO and CO₂ gas. Therefore, H₂ must be produced by other methods that do not generate CO and CO₂. Generation of H₂ from hydrocarbons by thermal treatment catalyzed by noble metals is a very important H₂ production method that does not require a lot of electrical energy. Nevertheless, this method undesirably requires expensive noble metals.11)–13) Therefore, the cost of H₂ production by this method is high. Recently, it was reported that carbon materials can work as catalysts for H₂ production from hydrocarbons.14)–17) Moreover, in the case where carbon materials are used as the catalysts, CO and CO₂ are not released during H₂ production because the carbon generated by decomposition of the hydrocarbons is deposited on these carbon materials as catalysts. If carbon materials are commercially used as catalysts for production of H₂ from hydrocarbons, low cost and clean H₂ production can be achieved. In a previous study, decomposition of hydrocarbons by the catalytic activity of carbon material, including graphite, carbon black, diamond-like carbon, and fullerene, was evaluated. These studies demonstrated that graphite worked as a catalyst for decomposition of hydrocarbons and afforded a low H₂ production rate of about 1% at 850°C.19) These studies were performed by using a very high flow rate of hydrocarbon per sectional area and a low quantity of carbon materials. The flow rate of the hydrocarbon and quantity of carbon materials are expected to affect the H₂ production rate because the flow rate changes the contact time between the carbon materials and the hydrocarbon molecules and the quantity of carbon material determines the number of reaction sites. If carbon materials are used as the catalyst for a H₂ production plant, to achieve a higher H₂ production rate, a larger quantity of carbon materials and a lower flow rate of hydrocarbon per sectional area must be used compared to the conditions used

† Corresponding author: T. Tokunaga; E-mail: t.tokunaga@numse.nagoya-u.ac.jp
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in the past studies. However, the effect of a low hydrocarbon flow rate per sectional area and large quantity of carbon materials on the H2 production rate and catalytic activity of the carbon materials has not yet been clarified. In this study, the H2 production rate achieved by using carbon materials as the catalyst is measured, and the catalytic activity of the carbon materials is evaluated under conditions employing a low flow rate of hydrocarbon per sectional area and large quantity of carbon materials.

2. Experimental procedures

A gas mixture comprising Ar and 10% CH4 was used as the feed gas. Powdered carbon black (CB, DENKA BLACK, Denka Company Limited, Japan; 10 g) was used as the catalyst. The quantity of 10 g is significantly larger than that of the few milligrams generally used in previous studies. The CB used herein has a high specific surface of 68 m2·g⁻¹, which is almost equal to that of CB used in prior reports. The rate of H2 production from CH4 by using CB as a catalyst was measured by using a gas reaction system. A schematic of the gas reaction system is presented in Fig. 1. This system comprises a gas feed component, the reactor, and the gas chromatograph (GC, GC-2014, SHIMADZU, Japan). Feed gas flowed to the reactor from a cylinder, and the reacted gas in the reactor exited through the outlet of the reactor to the GC. The reacted gas was analyzed by GC at various intervals. The reactor had an inner diameter of 50 mm and height of 500 mm; thus, even if the reaction between CH4 and CBs was very weak, there was enough reacted gas from 50 mm and height of 500 mm; thus, even if the reaction between CH4 and CBs was possible.

The gas reaction system was operated according to the following sequence. CB was introduced into the reactor and Ar gas (99.9999%; 100 sccm) controlled by a mass flow controller (MFC) was introduced into the reactor to purge the atmospheric air. The CB was then heated to 500°C to remove sorbed gas on CB and on the inside wall of the reactor. Ar was used as a carrier gas for the feed to the GC equipped with a thermal conductivity detector; Ar included in the feed gas was not detected in this system. After purging the sorbed gas, as confirmed by GC, heating was stopped and the reactor was naturally cooled to room temperature with flowing Ar. When the reactor was cooled to room temperature, Ar gas inside the feed gas line and MFC was evacuated by a diaphragm pump. Feed gas (100 sccm) was then introduced into the reactor under the control of the MFC. The flow rate of CH4 per sectional area of the reactor was 0.0051 sccm·mm⁻², which is about one hundredth of the flow rate per sectional area used in prior reports. The reactor was then heated to 500–1100°C, and the reaction between CH4 and CBs was started. The reacted gas was analyzed to identify the generated gases and evaluate the temperature-dependence of the gas generated via GC.

The reacted CB was recovered from the reactor and the nanostructures of the reacted and unreacted CB samples were observed to reveal the differences using a transmission electron microscope (TEM, JEM-2010F, JEOL, Japan).

3. Results and discussion

The gas chromatographic analysis of the reacted gas at each temperature after 1 h of heating is summarized in Fig. 2. Only two peaks appearing at 1.9 and 10.5 min were observed in Fig. 2, and the identity of these two peaks was estimated from analysis of various pure gases, indicating that the peaks respectively corresponded to H2 and CH4. No other gases were detected. The intensity of the H2 peaks increased and that of the CH4 peaks decreased with increasing heating temperature, indicating decomposition of CH4 at higher temperature. Enhanced CH4 decomposition was not observed in the absence of CB, confirming that CB worked as a catalyst for CH4 decomposition. At 500°C, no signals of H2 were observed. However, generation of H2 at 600°C was confirmed (inset of Fig. 2), and it was clear that decomposition due to the catalytic activity of CB was initiated above 600°C under the present conditions.

The data in Fig. 2 were converted to the H2 production rate at each temperature and summarized in an Arrhenius plot (Black filled circle in Fig. 3). From inset of Fig. 3, comparing H2 production between existence and non existence of CB indicated that CH4 was not decomposed at the surface of the reactor. Moreover inset shows that production comparing the linear relationship between the H2 production rate and temperature. Then the H2 production rate was 0.005–0.1% at 600–800°C. Above 900°C, the H2 production rate increased drastically, and reached 14.7%. It is thought that this drastic change of the H2 production rate originated from direct CH4 decomposition by heating. The objective of this study is to discuss CH4 decomposition by the catalytic activity of CB, and the contribution due to thermal decomposi-

![Fig. 1. Schematic of a gas reaction system.](image)

![Fig. 2. Relationship between detection time and gas chromatograph intensity in each heating temperature. Inset means gas chromatograph intensity around H2 at 600°C.](image)
tion must be separated. The gradient of the Arrhenius plot Fig. 3 changed around 900°C, indicating that the activation energy for CH₄ decomposition changed. CH₄ is generally decomposed at high temperatures around 1000°C.²⁰ A low gradient temperature profile was observed over 900°C in Fig. 3, and CH₄ was decomposed mainly by heating in that temperature range. In other words, the steep gradient profile in the low temperature regime below 900°C corresponds to CH₄ decomposition, not by heating, but mainly by the catalytic activity of CB. The catalytic activity of graphite, mesoporous carbon, and activated carbons (such as CB) has been evaluated by various researchers. Muradov showed that activated carbon worked as a catalyst for CH₄ decomposition above 850°C,¹⁸ and Lee et al. revealed that the surface of CB had a catalytic effect over 750°C.¹⁵ Moreover Serrano et al. reported that the catalytic effect of mesoporous carbon for CH₄ decomposition was activated above 740°C.²⁰ However, the present decomposition temperature of 600°C is lower than those in prior reports. The present setup can tolerate a large quantity of CB; thus, even if the rate of CH₄ decomposition in the presence of CB is extremely low, a sufficient volume of H₂ was generated for GC analysis. The present results revealed that CH₄ was decomposed at 600–800°C due to the catalytic activity of CB. Thus, GC analysis could be used to monitor the H₂ production rate at various intervals during heating at 800°C, where the rate of H₂ production in CH₄ atmosphere was high.

The relationship between the H₂ production rate at 800°C and the heating time up to 180 h is shown in Fig. 4. The initial H₂ production rate was 0.07%; however, this rate gradually increased with longer heating time and finally reached 0.14% after 180 h. After CH₄ was decomposed, H₂ and carbon were generated on the surface of CB; H₂ was then rapidly dispersed into the atmosphere and detected by GC. The generated carbon was expected to be deposited and to form some structures on the surface of CB. The generated carbon was deposited and covered the surface of CB, thereby reducing the surface area of CB. Although it is generally thought that the surface of CB works as the catalyst for CH₄ decomposition, the H₂ production rate gradually increased although the original surface area decreased.

To reveal to origin of the catalytic activity of CB at a low flow rate of CH₄, the morphology of non-heated CB was compared with that of the sample heated for 1 h by using TEM. TEM images of the non-heated and heated CB are shown in Fig. 5. The low magnification image of the non-heated CB in the inset of Fig. 5 shows that the non-heated CB had a spherical shape and some of the CB particles were connected to each other. Figure 5(a) shows that the surface of the non-heated CB was smooth and that the structure was constructed from curved graphite walls with interruption, and it was clear that the crystallinity of CB was low. The TEM image of heated CB is shown in Fig. 5(b). Tip structures, which were not observed on the surface of non-heated CB,
appeared on the surface of heated CB. This tip structure was formed on the interruption point of the curved graphite wall; thus, these interruption points are expected to work as the catalytic sites for CH₄ decomposition. These interruption points correspond to graphite wall edges; thus, these results mean that the graphite edge works as a catalytic site for CH₄ decomposition, and the tip structure appeared at the interruption points. To evaluate the structure and morphology of CB after long-term heating, CB was heated for 180 h and subjected to TEM observation. The low magnification image of CB heated for 180 h is presented in the inset of Fig. 6. The connected sphere structure of CB was not drastically changed by heating for 180 h. However, CB heated for 180 h had a shape that was not observed for CB heated for 1 h, and a thin graphite wall-like structure, marked by a black arrow, was present on the surface of CB. The thin, graphite wall-like structure was seen to grow from the surface of CB. Figures 5 and 6 show that CH₄ was decomposed on the interruption points on the surface of CB, and carbon having a graphitic structure was generated and constructed the thin graphite wall-like structure.

The above results demonstrate that CB functions as a catalyst for CH₄ decomposition above 600°C at a low flow rate of CH₄, and carbon generated via CH₄ decomposition is deposited on the interruption points of the graphite layer of CB. Moreover, the deposited carbon formed a thin wall-like structure after long-term heating. Lee et al. reported that CH₄ reacted with the surface of CB to generate pillar- and cone-shaped structures on the surface of CB. Moreover, Kameya et al. reported formation of a graphite sheet from the surface of CB. The respective groups reported that CH₄ reacted with the carbon surface. Although these studies were performed using a high flow rate of CH₄, the structure of heated CB observed in this study is largely similar to that of CB reported previously. The reaction site between CH₄ and graphite has been discussed based on calculation, and Huang et al. showed that the graphite edge has dangling-bonds and is not stable, and the graphite edge is thus highly reactive. The thin graphite wall-like structure generated after 180 h of heating had more graphite edges than CB heated for 1 h; thus, the H₂ production rate was expected to increase gradually. It is proposed that the interruption points on the surface of CB work as catalytic sites for CH₄ decomposition, and new reaction sites for CH₄ decomposition are formed even at a low flow rate of CH₄.

The lowest temperature for activation of CB of 600°C achieved herein is attributed to the ability of the present set-up to treat an extremely large quantity of CB relative to that employed in previous reports, as one important reason. However, the shape and structure of the CBs used in this study represent another possible source of this relatively low-temperature activation of CB. The electronic density of states (DOS) around the surface generally affects the catalytic activity, and the material structure is governed by the DOS. In other words, the surface structure of a material must be evaluated to discuss the catalytic activity. Each carbon material has a different DOS, and it is expected that the variation of the DOS depending on the structure of the carbon materials affects the temperature of the reaction between CH₄ and the carbon materials. The relationship between the detailed structures of the carbon materials and the reaction temperature should be clarified to assess this expectation.

Moreover, an extremely high H₂ production rate was anticipated because the present set-up treats a large quantity of CB and uses a low flow rate of CH₄. However, the production rate of about 0.1% at 800°C obtained herein is extremely low compared to that of about 1% obtained in previous studies, despite the use of a large quantity of CB. Thus, it is deduced that the catalytic activity of CB depends on the flow rate. The flow rate changes the contact time between the surface of CB and the CH₄ molecule. In the case of a higher flow rate, the contact time decreases. Although a long contact time between CH₄ and CB was expected to induce a high H₂ production rate under catalysis by CB, the H₂ production rate declined at the low flow rate used herein. During crystal growth, a structure having high crystallinity is constructed when the feed of atoms to the crystal is slow, and a structure having dislocations and defects is constructed when the feed of atoms is fast. The quantity of carbon generated via CH₄ decomposition is very low, and the graphite edges plausibly could not maintain the dangling-bond having high reactivity; thus, closed graphite structures, such as five- and seven-membered rings having lower reactivity than the dangling-bond, were expected to be formed at the edge of graphite. The detailed structure of the graphite edge was not observed in this research; the detailed structure at the edge of carbon during CH₄ decomposition should be observed to substantiate this hypothesis via methods such as in-situ atomic level observations.

4. Conclusions

In this study, the rate of production of H₂ was measured by GC at various temperatures using a low flow rate of CH₄ per unit area and a large quantity of CBs as the catalyst. H₂ production was confirmed at temperatures above 600°C and CH₄ was decomposed under the catalytic activity of CB at temperatures between 600 and 800°C. However, the rate of production of H₂ was extremely low. The H₂ production rate increased gradually at longer times. Carbon generated from CH₄ decomposition was deposited at the interruptions of the carbon wall on the surface of CB. Tips and thin, wall-like structures were generated at the interruptions in the graphite wall. As these new carbon structures act as CH₄ decomposition sites, it was expected that the rate of production of H₂ would gradually increase. Although CH₄ reacted at the interruption points on the surface of CB in the presence of a large quantity of carbon materials and with a low flow rate of hydrocarbon per sectional area, a high production rate was not obtained. The structure at the edge of graphite is thought to affect the reactivity of CB.
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