Hydrogen production by catalytic decomposition of methane over carbon black catalyst at high temperatures

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Abstract−Catalytic characteristics of carbon black for methane decomposition at high temperatures were investigated. A fixed bed reactor was made of carbon steel with 28 mm I.D and 450 mm height. The reaction was carried out under atmospheric pressure at temperature of 1,293-1,443 K. The objective was to investigate the catalytic activity of carbon black at high temperature, similar to the manufacturing process of carbon black. Almost 100% methane conversion was observed at 1,443 K, and the activation energy of the catalytic reaction over carbon black was 198 kJ/mol. The specific surface area decreased as the amount of deposited carbon increased. Since a large amount of the produced carbon was deposited on the surface, the increase of aggregates size and protrusions size of deposited carbon was larger than in the results of previous work.

Key words: Catalytic Decomposition, Methane, Hydrogen, Carbon Black, Catalyst

INTRODUCTION

Carbon black is used as reinforcing filler in tires, and the application of carbon black as a catalyst has long been studied [1,2]. Generally, carbon material is much more frequently used as a catalyst support than as a catalyst, but there are several industrial reactions, such as methane decomposition, that use carbon itself as a catalyst [3]. One attractive alternative for the production of hydrogen without CO_2 emission is catalytic decomposition of hydrocarbons since no oxidant such as steam or oxygen is used, which enables the process to be greatly simplified because the water-gas-shift and CO_2 removal stages are not required. Among the catalysts used for catalytic decomposition of methane, carbonaceous catalysts have finally attracted the attention given to metallic ones due to numerous advantages in low cost, high temperature resistance, no sulfur poisoning, and used carbon black can be recycled [4].

Carbonaceous catalyst has been reported to act as an effective catalyst for decomposition of methane. Muradov [2] investigated various carbonaceous catalysts for catalytic decomposition of methane such as activated carbon, carbon black, glassy carbon, and so on. Among these carbons, carbon black and activated carbon showed reasonable activity. Commercial carbon black exhibited stable catalytic behavior despite carbon deposition [5-8]. In contrast, activated carbon showed acceptable initial catalytic activity but was rapidly deactivated due to the pore-mouth blocking.

We investigated commercial carbon black for catalytic characteristics in methane decomposition at temperatures of 1,293-1,443 K, such as the activity, activation energy, and stability. The main objectives of this study were as follows. The first was a kinetic study of methane decomposition at high temperature, similar to carbon black into quenching process. In the commercial process, steam is employed for reducing temperature of carbon black in the quench-

ing process, and CO_x is produced. CO_x emission can be decreased by using methane instead of steam in the quenching process, and the total carbon black production can be increased since methane is decomposed over high temperature carbon black. Thus, an experiment was carried out at reaction conditions similar to the quenching process, such as reaction temperature and contact time between carbon black and methane, to confirm the kinetic behavior in quenching process.

The second objective was to investigate the effect of carbon steel reactor on the methane decomposition. The third was to analyze properties of carbon black after quenching process using methane. Properties of used carbon black such as aggregates size and specific surface area were analyzed and the morphology was observed by TEM.

EXPERIMENTAL SECTION

A sample of carbon black was obtained from a domestic manufacturer in Korea. The properties of carbon black tested in this work are presented in Table 1. The sample was dried at 473 K for 24 h in air before the reaction test. A schematic diagram of the fixed bed used in our experiment is shown in Fig. 1. The decomposition reaction was carried out in a vertical, fixed bed, 450 mm height and 28 mm I.D (60.5 mm O.D) carbon steel flow reactor heated by an electric tube furnace. Carbon steel plate with holes and cerak-wool were set up in the middle of the reactor for holding the carbon black catalyst. The electric furnace for high temperature was set up by superkanthal, which is used below 1,673 K. However, since carbon steel melts at around 1,699 K, the reaction temperature ranged from 1,293-

Table 1. Physical, chemical properties of employed carbon catalyst

Manufacturer/ supplier	Trade name	Particle diameter [nm]	Surface area [m²/g]
Rubber black	OCI Ltd.	DCC-N330	30	85

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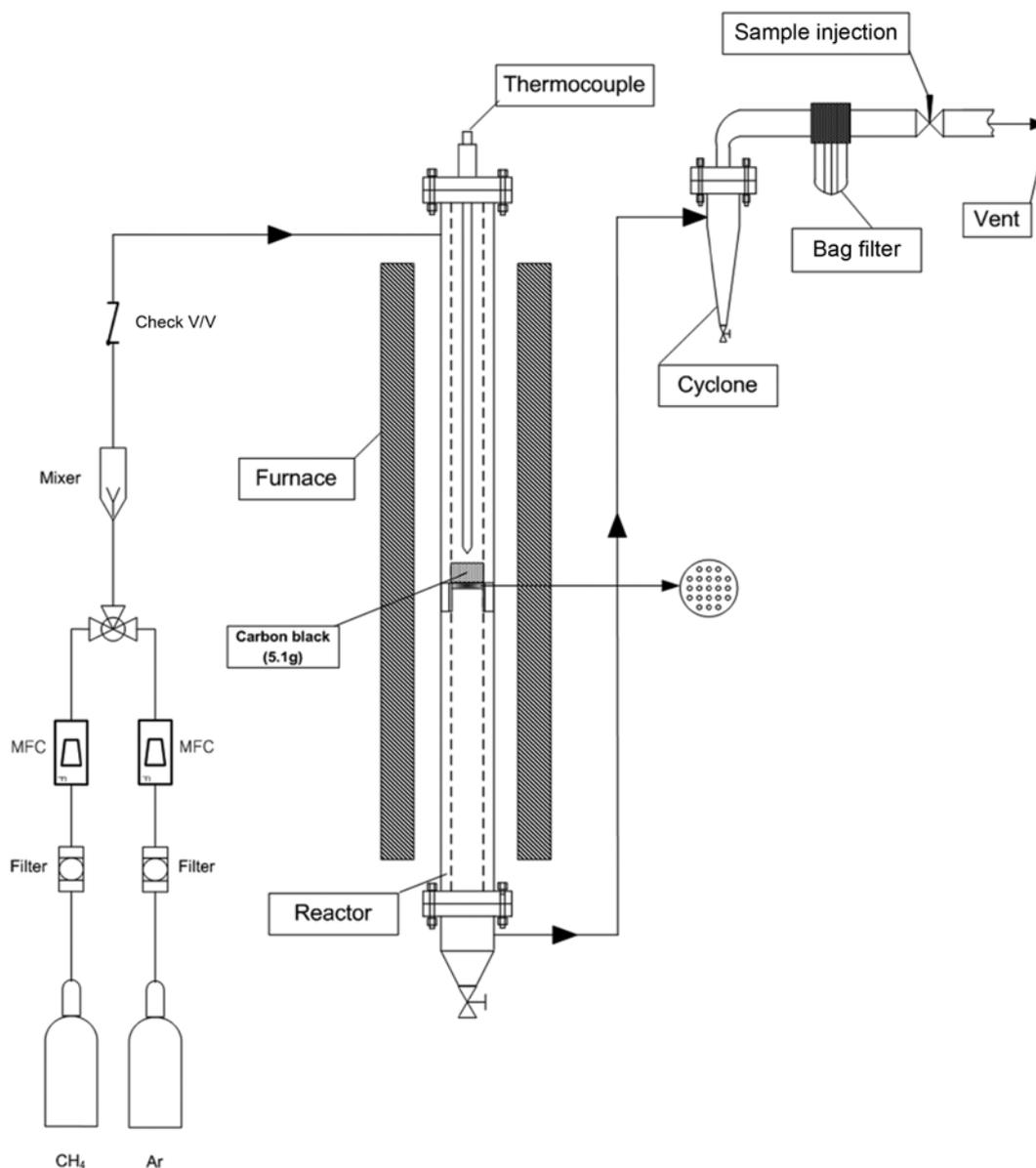
Fig. 1. Schematic diagram of fixed bed reactor system.

1,433 K. The standard reaction conditions were a catalyst charge of 5.1 g and methane flow rate of 1,268 cm^3 (STP)/min. The methane flow rate was controlled by a mass flow controller (CELERITY, TN280). A feed stream of methane entered the top of the reactor and contacted the carbon black catalyst in the reaction zone, where decomposition of methane occurred. The reaction temperature was monitored by an R-type thermocouple in the middle of the bed. Because the stainless steel sheath of the thermocouple is a good catalyst for hydrocarbon decomposition, the alumina sheath was used. To determine the effect of gas velocity, the gas velocity was changed from 3.43 cm/s to 17.15 cm/s. Hydrogen-containing gas exited from the bottom of the reactor via cyclone and a bag-filter. The exit gas from the bottom of the reactor was sampled with a gas-tight syringe through a septum. The sampling and analysis was usually done 10 min after the methane flowed, since it took some time for the reaction system to reach a steady state in order to flash the Ar gas initially present. The reaction products were analyzed by gas chromatogra-phy (Younglin, ACME 6100) using a Hayesep Q column, Ar carrier, and a thermal conductivity detector. Methane conversion was determined using calibration data.

The properties of the fresh and used carbon black samples were measured by N_2 adsorption in a Micromeritics ASAP2020 apparatus. The specific surface area of samples was calculated by applying the BET method to N_2 adsorption isotherms. A fiber-optic particle analyzer (Otsuka Electronics, FPAR-1000) was employed for measurement of aggregates size. TEM images of some samples were obtained from a high-resolution transmission electron microscope (JEOL, JEM 2100F).

RESULTS AND DISCUSSION

1. Non-catalytic Decomposition of Methane at High Temperature

Non-catalytic thermal decomposition of methane may occur when
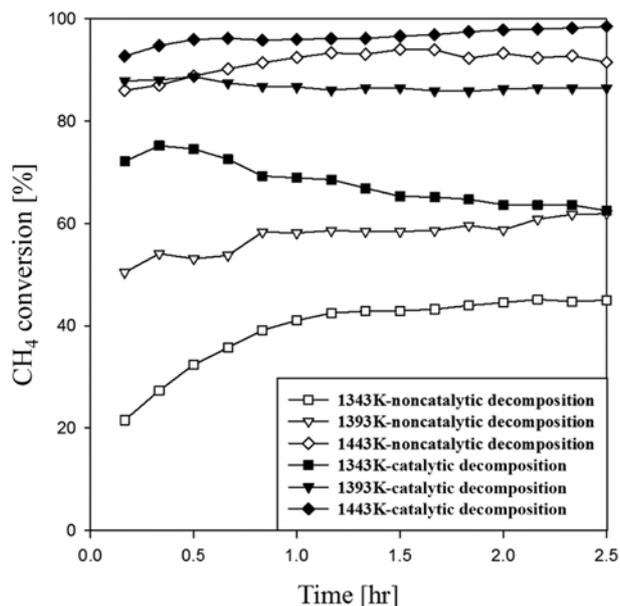
Fig. 2. CH₄ conversion vs. time in the absence of carbon black and over carbon black.

Fig. 3. Arrhenius plot for non-catalytic and catalytic decomposition of methane over carbon black.

the reaction temperature is high. This phenomenon was observed in a previous study [8]. To compare the catalytic decomposition results, homogeneous thermal (non-catalytic) decomposition experiments were first performed in the temperature range of 1,293-1,443 K.

The catalytic activities of various reaction temperatures were compared, and representative results are shown in Fig. 2. No gaseous products other than hydrogen were detected. This has been confirmed to be true by thermodynamic analysis [9]. It was confirmed that non-catalytic decomposition of methane was significant at high temperature, and the methane conversion exhibited stable or quasi-state activity. Large difference was observed between different reaction temperatures. As shown in Fig. 2, at high temperature the methane conversions were considerably high when considering the result from a previous study [8]. One possible explanation for this may be given as follows by taking into account the catalytic action of the carbon steel reactor. A produced film in the carbon steel reactor after reaction was analyzed by EDAX, and carbon was detected. Since the carbon steel reactor acted as a catalyst, the produced carbon from the decomposition of methane was deposited on the walls of the carbon steel reactor. Thus, methane conversion was higher than the results of the earlier study, and methane conversion increased slowly due to carbon film in an inside wall of the carbon steel reactor (Fig. 2). Another reason for higher methane conversion is the difference of gas velocity. The gas velocity of methane was 3.43 cm/sec in this study and approximately 4.17 cm/sec in previous work [8]. Because the residence time of methane in the heating zone decreased as gas velocity of methane increased, the methane conversion with slow gas velocity in this study was higher than in earlier work.

As shown in Fig. 2, methane conversion increased slightly at 1,343 K and 1,393 K. The reason for this is the increase of deposited carbon on the reactor wall. Since it acted as catalyst, methane conversion increased slightly.

The activation energy for non-catalytic decomposition of methane was determined from the Arrhenius plot, as shown in Fig. 3.
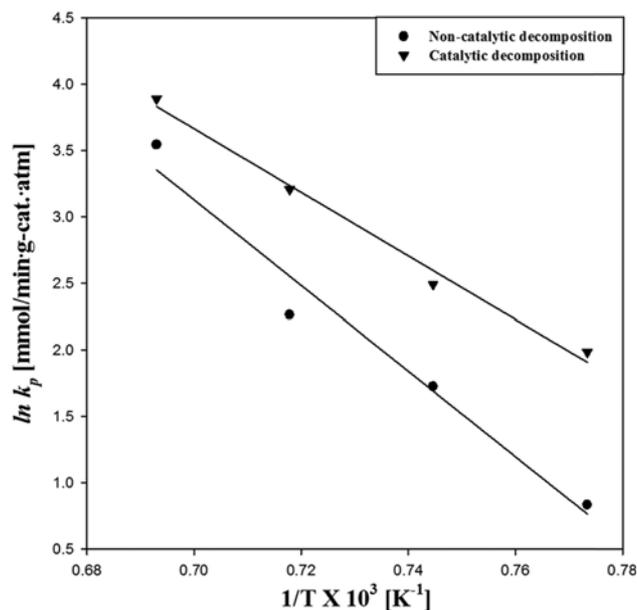
The rate constant was calculated by Eq. (1) for the first-order reaction in the integral reactor [10].

$$k_p = (F_A/g_{CB} P_{A,O})[-2\ln(1-x_{Af})-x_{Af}] \tag{1}$$

The methane conversion was calculated from the average conversion after 30 min time on stream. The activation energy of non-catalytic decomposition was 268 kJ/mol. Muradov [2] reported that the activation energy of the carbon nuclei formation during thermal decomposition of methane is 316.8 kJ/mol, that of the carbon crystallite growth is 227.1 kJ/mol, and that the C-H bond energy in CH₄ is 439 kJ/mol. The activation of non-catalytic decomposition is considerably lower than the C-H bond energy of CH₄, and it is also evident that the carbon steel reactor acted as a catalyst for methane decomposition.

2. Catalytic Decomposition of Methane at High Temperature

The catalytic activities at various reaction temperatures (1,293-1,443 K) were compared and the results are shown in Fig. 2. Almost all the reaction temperatures exhibited stable activity after an initial transition period of about 30 min. The active site of carbon black was covered with the deposited carbon from methane decomposition and thus activity decreased. However, the deposited carbon formed a new structure and the newly formed structure was believed to provide a new active site, as suggested by previous works [2, 7,8,11]. On the carbon atoms at the edge, probably unsaturated or in radical form under sufficiently high temperature of the pretreatment, methane molecules can chemisorb and form hexagonal rings [11-16]. The hydrogen atoms on the chemisorbed methane can be readily abstracted due to the high temperature [12] and generate new active sites [11]. The comparison of TEM images of new and used carbon catalyst showed it.

Muradov [2] examined activated carbon, carbon black, graphite, glassy carbon and acetylene black for methane decomposition and described that the rate of crystallites growth and nuclei formation became comparable in methane decomposition over carbon black

with low surface area. Thus, the deposited carbon had disordered structure and stable activity. Since the number of active sites decreased or the structure of active sites changed by deposited carbon, the activity of carbon black usually decreased during the initial transition period. Another reason for the decrease of conversion in the initial period may be due to a structural change of the fine particles formed by the methane decomposition, such as growth and agglomeration of the fine particles or sticking of these fine particles to the original particles [8]. However, the methane conversion at 1,343 K increased in the initial period, then reached a steady state after slight decrease in the methane conversion. Fig. 2 shows a comparison of the non-catalytic and catalytic activity on methane decomposition. At temperature of 1,293-1,393 K, the effect of temperature on methane conversion was considerable. However, at 1,443 K, the difference was very small. Thus, non-catalytic decomposition was a dominant at 1,443 K.

As shown in Fig. 2, methane conversion decreased at 1,343 K; however, at 1,393 and 1,443 K, methane conversion was almost constant. Since the reactor was made of carbon steel, the reactor wall acted as catalyst. However, carbon produced from the decomposition of methane deposited on the reactor wall, and catalytic activity of reactor wall decreased. Finally, carbon steel reactor was not acting as catalyst because the reactor wall was covered with produced carbon. Since a new reactor was used at 1,343 K, the reactor wall acted as catalyst at initial reaction time. However, since the reactor was used at 1,393 K and 1,443 K, the effect of reactor wall as the catalyst was insignificant. Thus, methane conversion showed constant.

The activation energy for catalytic decomposition of methane was determined as mentioned in the previous section and presented in Fig. 3. The activation energy for catalytic decomposition was 198 kJ/mol. In the previous work, the activation energy over carbon black was 183 kJ/mol [8].

The effect of gas velocity on the methane conversion is shown in Fig. 4. The experiments were performed with different gas velocities by changing the methane flow rate. Since higher gas velocity means shorter contact time, the methane conversion became lower as the gas velocity decreased. Another reason for this is that as the gas velocity was lowered the methane partial pressure also decreased, which resulted from the higher conversion methane together with dilution by the produced hydrogen [17].
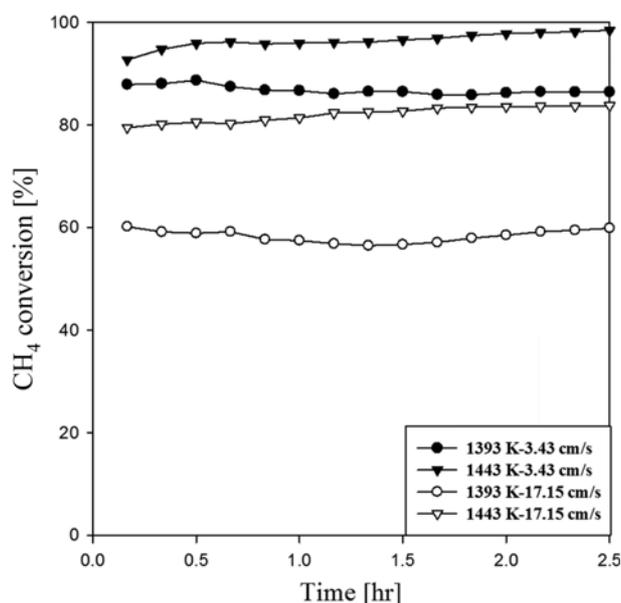
3. Analysis of Surface and Physical Property of Carbon Black

Since carbon black particles are very small and have very large cohesive force, they are observed as aggregates instead of elementary particles. The aggregates have a tendency to agglomerate in dispersion into large units, which may be redispersed by shear but reagglomerate on standing [1].

In this study, the size of carbon black (dispersed using alcohol and surfactant) was measured by a particle size analyzer and named aggregates size. Aggregates sizes of fresh and used carbon black with different reaction conditions are plotted in Fig. 5 with W_c, which was obtained by calculating the ratio of the deposited carbon and original carbon black.

$$W_c = \text{g of deposited carbon/g of original carbon black.} \qquad (2)$$

The W_c of fresh carbon black is equal to 0. The aggregates size of fresh carbon black was 250 nm, which was much bigger than elementary particle size (in the previous work, the elementary particle size of fresh carbon black was 30 nm from TEM analysis.) [7]. The increase of W_c resulted in higher aggregates size of carbon black in Fig. 5 and the aggregates size of carbon black increased as an exponential curve of W_c. As protrusions were formed by the deposited carbon from methane decomposition, the cohesive force of carbon black increased. Thus, the aggregates size of carbon black increased because more carbon black particles united with the increase of cohesive force. Since small amounts of protrusions have a weak cohesion with small amounts of deposited carbon ($W_c<1$), the increase in aggregates size is not significant. However, with a large amount of deposited carbon ($W_c>2$) from methane decomposition


Fig. 4. CH₄ conversion vs. time over carbon black with different gas velocities.
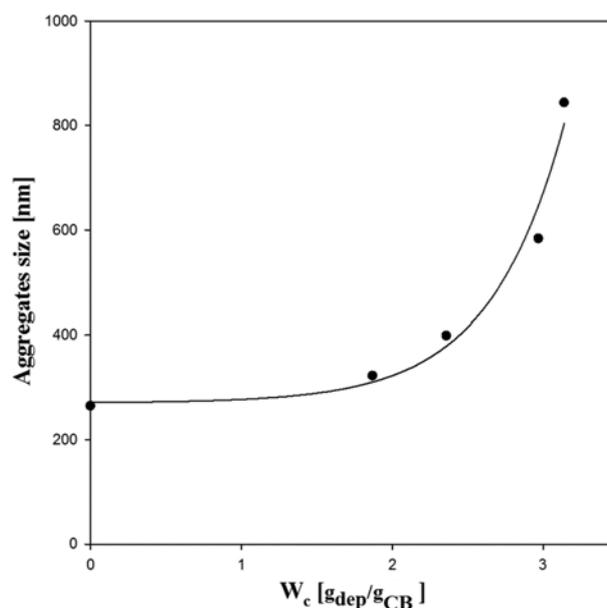
Fig. 5. Aggregates size of used carbon black vs. W_c.
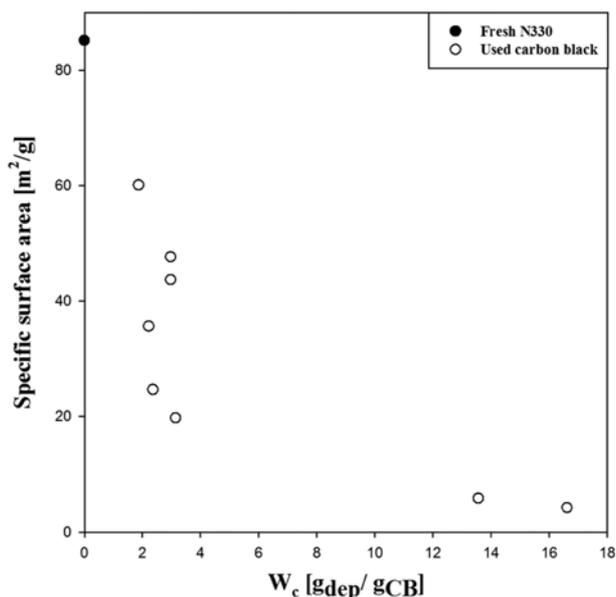
Fig. 6. Specific surface area vs. W_c with different reaction conditions.

(a)

(b)

Fig. 7. TEM images of fresh and used carbon black (N330) (a) Fresh carbon black, (b) used carbon black (Experiment condition : temperature 1,343 K, gas velocity 3.43, W_c 2.36).

existing on the carbon black, the cohesive force increased dramatically and the difference in aggregates size was significant with the increase of W_c.

The specific N_2 BET surface areas (the area per unit mass of total carbon) for the carbon products after the reaction are presented in Fig. 6 as a function of the amount deposited carbon, W_c. Carbon black interacts with methane through its surface. The surface is open and relatively easily accessible to methane molecules. Since the produced carbon was deposited on the carbon black surface or in the voids, the specific surface area changed after methane decomposition. Since it is believed that the produced carbon first filled in the voids and then formed protrusions on the surface, the specific surface area data were scattered with the small amounts of produced carbon [18]. However, when there was a significant amount of the produced carbon, the specific surface area of the used carbon black carbon showed a tendency to decrease with W_c. The specific surface area decreased to about 30% that of the fresh carbon black when W_c was small, and it decreased as W_c increased to about 90% of the initial surface area when W_c was 17 g_{dep}/g_{CB}. The drastic decrease of the specific surface area can be explained by the blocking of micropore [8]. Carbon black has micropores and mesopores, and their volume was changed since carbon was deposited over the surface and in pores. Micropore and mesopore volume increased after methane decomposition with small amounts of deposited carbon. It is can be explained as that there were some new pores formed on the surface of the carbon black [19]. However, mesopore and micropore volume decreased with large amounts of deposited carbon. Despite this large decrease of specific surface area, it is noteworthy that methane conversion was almost stable as shown Fig. 2. TEM images of a carbon black sample are presented in Fig. 7. The particles of fresh carbon black are largely rounded and the surfaces look smooth in Fig. 7(a). As mentioned in the previous section, the elementary particle size of the fresh carbon black is approximately 30 nm. As observed in Fig. 7(b), the deposited carbon formed many protrusions
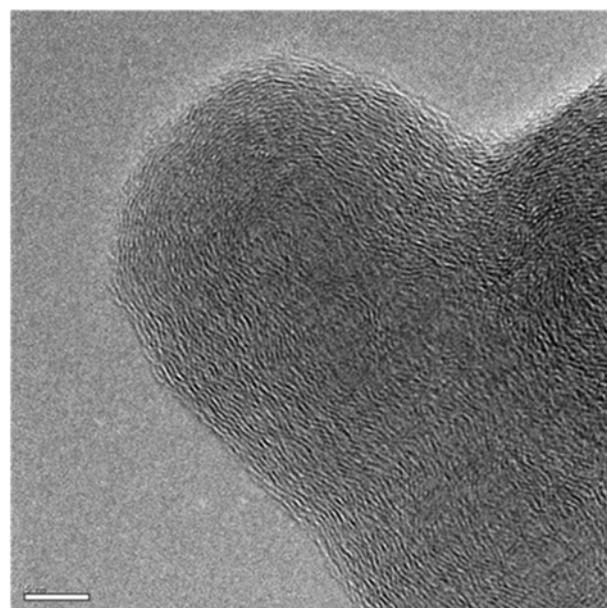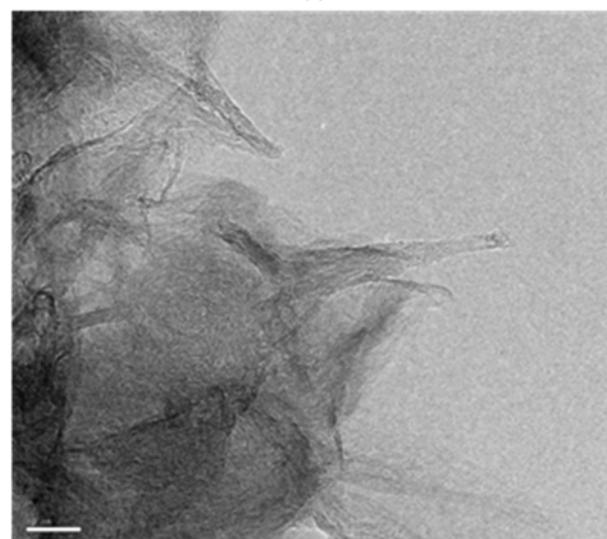
on the surface and it did not deposit evenly on the surface. It was also observed that the protrusions became longer and more protrusions became bigger, and some of them developed into steeples as the carbon deposition went on. The produced carbon overlaid the primary particles and also formed many conical or pillar-shaped protrusions. However, when a relatively small amount of the produced carbon was deposited on the carbon black, it first filled in the voids and then formed round, flat protrusions or grapheme layers over the outer surface [7].

CONCLUSIONS

Methane decomposition was carried out over carbon black catalyst at 1,293-1,443 K in a fixed bed made of carbon steel. Non-cata-

lytic decomposition occurred significantly at high temperatures, and methane conversion was considerably higher due to the catalytic action of the carbon steel reactor. Moreover, since the carbon black produced by the decomposition of methane acted as a catalyst, the methane conversion increased during the reaction. Carbon blacks exhibited stable catalytic activity for decomposition of methane after a short transition period. Almost 100% methane conversion was observed at 1,443 K, and the activation energy of catalytic reaction over carbon black was 198 kJ/mol. Since the methane partial pressure got lower as the decrease of gas velocity, methane conversion increased. The specific surface area increased as the W_c increased due to deposited carbon form methane decomposition. Since a large amount of produced carbon was deposited on the surface, the increase of aggregates size and protrusions size of the deposited carbon was larger than in the results of previous work.

NOMENCLATURE AND UNITS

F_A : molar feed rate of methane [mmol/min]
g_{dep} : mass of deposited carbon [g]
g_{CB} : mass of fresh carbon black [g]
k_p : rate constant [mmmol/min g_{CB} atm]
$P_{A,O}$: feed partial pressure of methane [atm]
x_{Af} : methane conversion at reactor outlet
W_c : deposited carbon/initial catalyst loading [-]

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