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Hydrogen production by catalytic decomposition of methane over carbon catalysts in a fluidized bed

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Abstract−A fluidized bed reactor made of quartz tube with an I.D. of 0.055 m and a height of 1.0 m was employed for the thermocatalytic decomposition of methane to produce CO_2 - free hydrogen. The fluidized bed was used for continuous withdrawal of the carbon products from the reactor. Two kinds of carbon catalysts - activated carbon and carbon black - were employed in order to compare their catalytic activities for the decomposition of methane in the fluidized bed. The thermocatalytic decomposition of methane was carried out in a temperature range of 800-925 °C, using a methane gas velocity of 1.0-3.0 U_{mf} and an operating pressure of 1.0 atm. Distinctive difference was observed in the catalytic activities of two carbon catalysts. The activated carbon catalyst exhibited higher initial activity which decreased significantly with time. However, the carbon black catalyst exhibited somewhat lower initial activity compared to the activated carbon catalyst, but its activity quickly reached a quasi-steady state and was sustained over time. Surfaces of the carbon catalysts before and after the reaction were observed by SEM. The effect of various operating parameters such as the reaction temperature and the gas velocity on the reaction rate was investigated.

Key words: Hydrogen, Activated Carbon, Carbon Black, Fluidized Bed, Methane

INTRODUCTION

Hydrogen is expected to be an important energy source of the future because of its environmentally acceptable characteristics. However, hydrogen cannot be naturally produced so that it is not a primary fuel. Hydrogen must be generated from other natural resources on the earth, of which water is the most abundant one. The electrolysis of water has been widely used so far to produce hydrogen from water even though its energy efficiency is quite low [1,2]. The steam reforming of natural gas is a well-known process to produce hydrogen efficiently. Only 40.75 kJ is required for producing one mole of hydrogen in this process. However, the total CO_2 emission from the process reaches up to 0.43 moles of CO_2 per mole of H_2 produced. Therefore, the thermal decomposition of methane has been studied in order to produce H_2 without any associated CO_2 emission [3].

Natural gas can be thermally decomposed into carbon and hydrogen, and the resulting carbon can be sequestered or sold as a material commodity. Thus, hydrogen can be cleanly produced by the thermal decomposition of natural gas without production of CO_2 [4,5]. Thermocatalytic decomposition of natural gas is an alternative method for producing hydrogen with the accompanying sequestration of carbon. The thermocatalytic decomposition of methane occurs at an elevated temperature and results in the formation of hydrogen and elemental carbon.

$$CH_4=C+2H_2 \qquad \Delta H^o=75.6 \text{ kJ/mol} \tag{1}$$

Due to the absence of oxidants (e.g., H_2O and/or O_2), no carbon oxides are formed in the reaction. This approach also proposes remarkable advantages. Hydrogen can be produced in a single step without additional CO_2 removal stages commonly required in conventional technologies (e.g., steam reforming, partial oxidation). The energy required to produce one mole of hydrogen, 37.8 kJ, is somewhat less than that of other conventional processes such as the steam reforming (63.3 kJ/mol H_2). The methane decomposition is an endothermic reaction which occurs above 700 °C [5-7].

There have been many attempts to improve catalysts in order to reduce the temperature of the thermal decomposition of methane. Metal catalysts possessing Ni, Fe, Co and others have been commonly used for this purpose. However, the catalysts were deactivated by carbon buildup on the surface [8-10]. The metallic catalysts were periodically burned off in order to remove the carbon deposited on the surface. As a result, the amount of CO_2 produced during the regeneration is comparable with that of the conventional processes. The oxidative regeneration of metal catalysts causes another problem related to the unavoidable contamination of hydrogen with carbon oxides, which brings on an additional purification step. Our technical approach is based on the thermocatalytic decomposition of hydrocarbons over carbon-based catalysts in an air/water-free environment. The use of carbon catalysts offers the following advantages: (i) no need of regenerating catalysts by burning the deposited carbon off, (ii) no contamination of hydrogen with carbon oxides and, consequently, no need of additional gas purification, and (iii) the production of a valuable by-product, namely elemental carbon.

To produce CO_2-free hydrogen from natural gas, a fluidized bed reactor was employed. A fluidized bed reactor provides a constant flow of solids through the reaction zone, which makes it particularly suitable for the continuous addition and withdrawal of carbon particles from the reactor. In fluidization, the bed of carbon catalysts behaves like a well-mixed body of liquid, giving rise to high particle-to-gas heat and mass transfer rates [11]. The carbon catalysts are allowed to spend a certain time in the reaction zone, which

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can easily be controlled by adjusting the ratio of the feed rate and the weight of the bed. The bed can also buffer any instability that may arise during the continuous operation. In this study, the characteristics of the thermocatalytic decomposition of methane in a fluidized bed reactor were investigated.

EXPERIMENTAL

Methane (99.95 vol%) was used without further purification. Samples of carbon catalysts were obtained from carbon manufacturers in Korea in the form of fine powders. The particle size of activated carbon was 106 μm, and the effective particle size of carbon black was about 153 μm due to the agglomeration of fine particles which were of 30-40 nm in primary size. The effective particle size of carbon black was determined by measuring the minimum fluidization velocity in the fluidized bed.

A schematic diagram of the fluidized bed reactor used is shown in Fig. 1. The fluidized bed reactor was made of quartz tube with an I.D. of 0.055 m and a height of 1.0 m. The initial catalyst loadings of the activated carbon and the carbon black were 20 g and 100 g, respectively. The methane flow rate was controlled by means of a mass flow controller. A feed stream of methane which was preheated to 400 °C entered the reactor from the bottom and passed through the fluidized bed of carbon catalysts at the operating temperature where the thermocatalytic decomposition of methane occurred. The temperature of the bed was monitored by a thermocouple situated in the middle. Hydrogen-containing gas exited from the top of the reactor via a cyclone and a bag filter. The products were analyzed by gas chromatography (TCD detector) and the characterization of the carbon catalysts and the carbon products was performed by SEM. The conversion of methane was determined by GC and checked by weighing the fluidized bed materials (carbon catalysts and by-product carbons in the reactor).

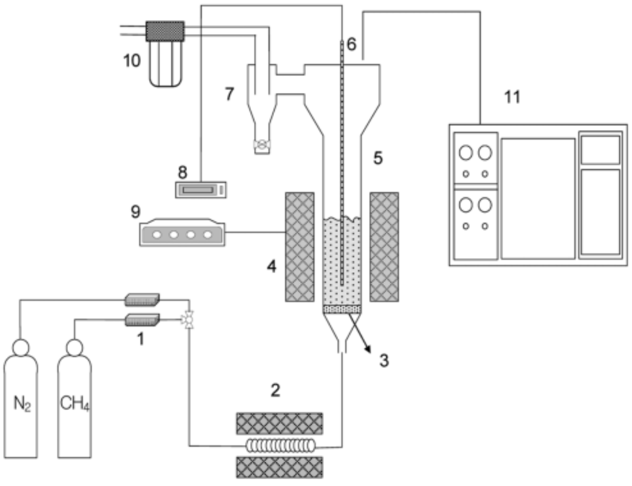

Fig. 1. A schematic diagram of the fluidized bed reactor.

1. Mass flow controller
2. Preheater
3. Distributor
4. Furnace
5. Fluidized bed reactor
6. Thermocouple
7. Cyclone
8. Data logger
9. Temperature controller
10. Bag filter
11. GC

RESULTS AND DISCUSSION

Catalytic activities of the activated carbon and the carbon black for the decomposition of methane were examined under various operating conditions in a fluidized bed.

1. Activated Carbon

Catalytic activity of the activated carbon was measured at various temperatures. The activity changes along time on stream are plotted in Figs. 2 and 3. The activated carbon showed high activity

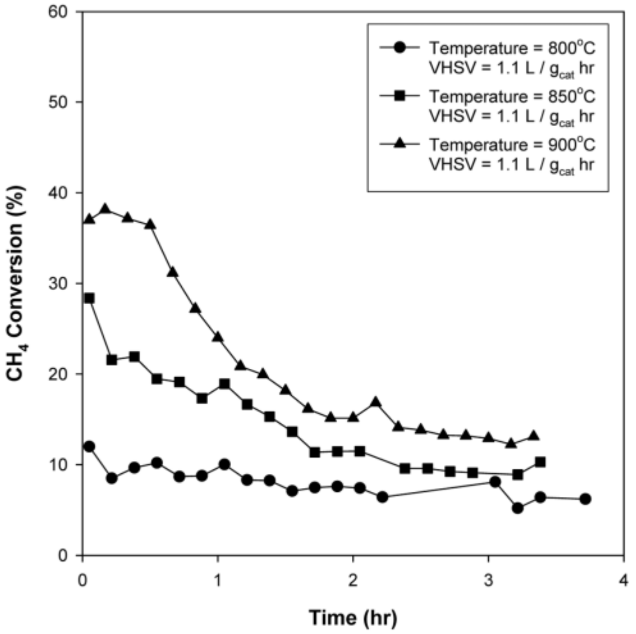

Fig. 2. The effect of reaction temperature on the CH_4 conversion over activated carbon at a gas velocity of 1.0 U_{mf}.

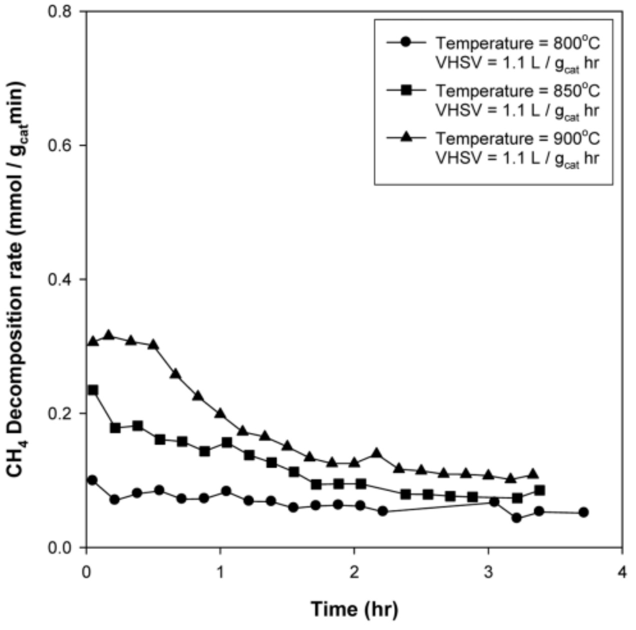

Fig. 3. The effect of reaction temperature on the CH_4 decomposition rate over activated carbon at a gas velocity of 1.0 U_{mf}.

at the beginning of the reaction and became rapidly deactivated regardless of the reaction temperature. This indicated that the deactivation of the active carbon resulted from the blocking of the mouths of the pores by the deposited carbon. As the temperature increased, the initial activity increased, but the deactivation occurred more rapidly. The activation energy determined from the Arrhenius plot was about 140 kJ/mol CH_4 and was much lower than the methane C-H bond energy of 440 kJ/mol. The effect of the methane gas velocity on the methane conversion is given in Figs. 4 and 5. In the case of a fluidized bed, it is convenient to express the gas velocity in terms of the minimum fluidization velocity, U_{mf}, so that the flow regime of the fluidized bed can be easily understood. A gas velocity of 1.0 U_{mf} in the fluidized bed of activated carbon is equivalent to a space velocity of 1.10 L/g_{cat} hr. As can be seen in Figs. 4 and 5, the effect of the gas velocity on the CH_4 conversion was significant in the fluidized bed reactor. Unlikely in a fixed bed reactor, all gases exceeding the amount required for the minimum fluidization seemed to pass through the bed as bubbles. In addition, the increase of the gas velocity reduced its residence time in the reactor as well as lowered the contact efficiency between the gas and the carbon catalysts due to the formation of large bubbles. SEM images of the surfaces of activated carbon before and after the reaction are given in Figs. 6 and 7, respectively. They showed the carbon was deposited on the surface of activated carbon catalyst and it was believed that this carbon deposition blocked the mouths of the pores of activated carbon, thus causing rapid deactivation of the catalyst.

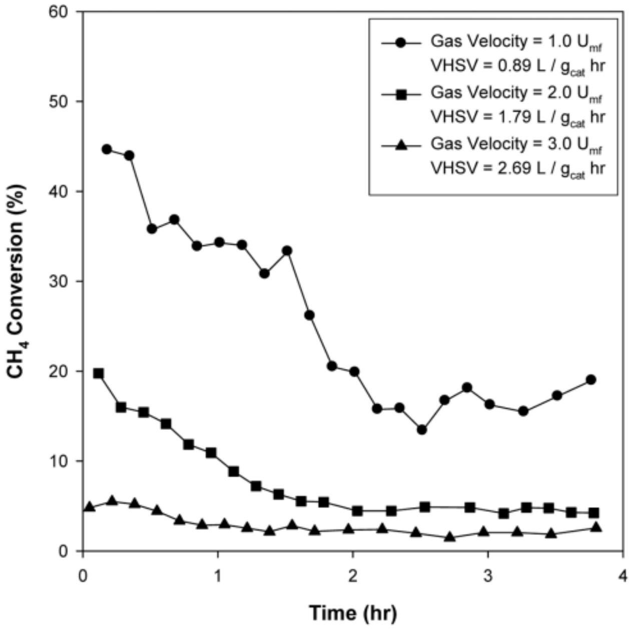

Fig. 4. The effect of gas velocity on the CH_4 conversion over activated carbon at a temperature of 850 °C.

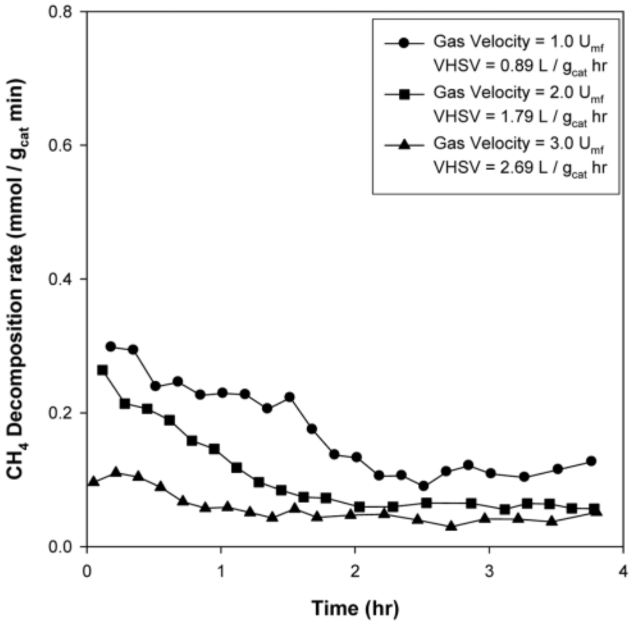

Fig. 5. The effect of gas velocity on the CH_4 decomposition rate over activated carbon at a temperature of 850 °C.

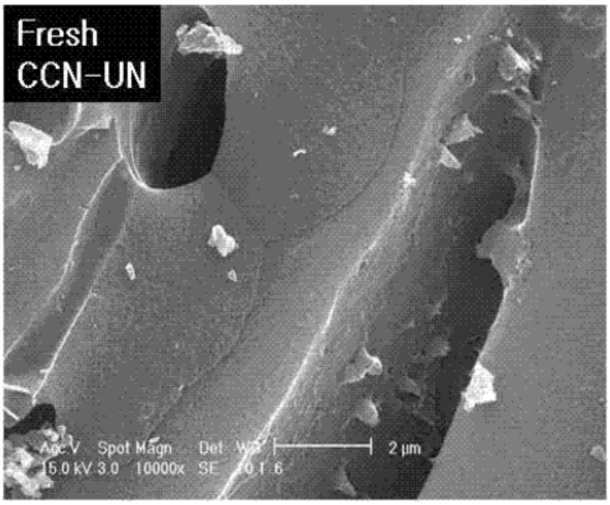

Fig. 6. SEM images of the surfaces of the activated carbon before the reaction.

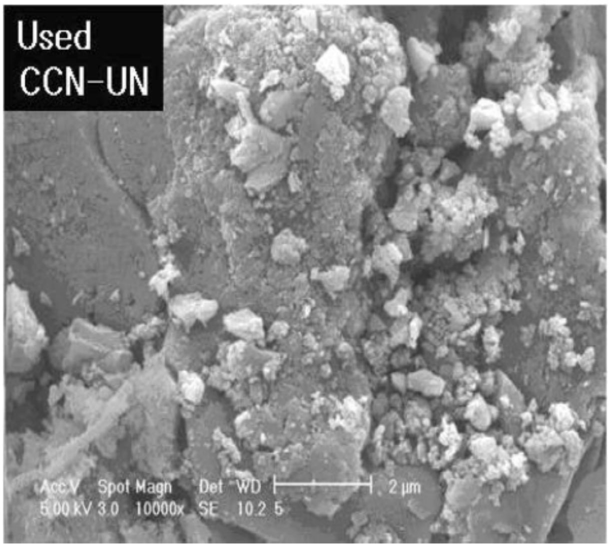

Fig. 7. SEM images of the surfaces of the activated carbon after the reaction.

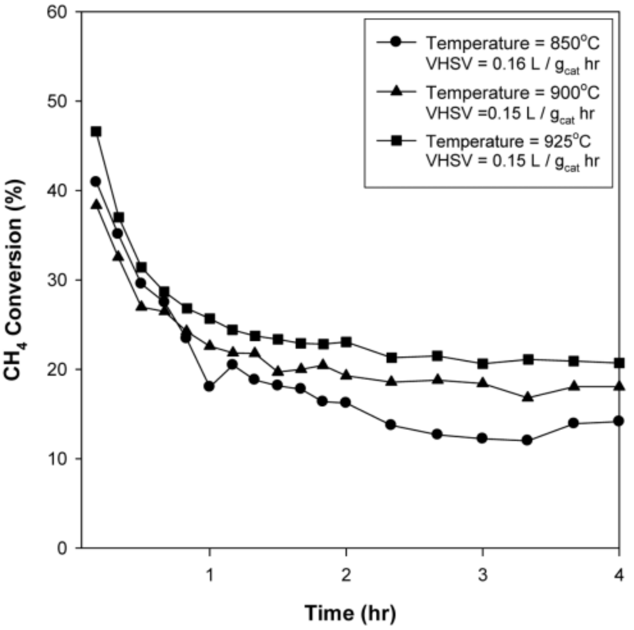

Fig. 8. The effect of reaction temperature on the CH_4 conversion over carbon black at a gas velocity of 1.0 U_{mf}.

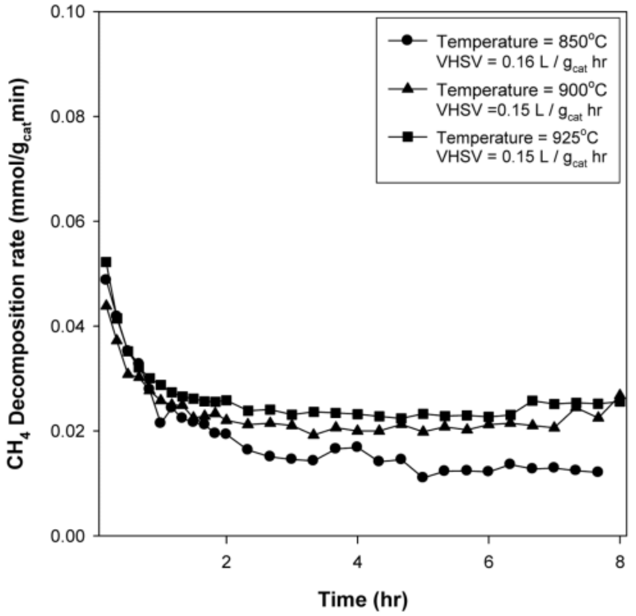

Fig. 9. The effect of reaction temperature on the CH_4 decomposition rate over carbon black at a gas velocity of 1.0 U_{mf}.

2. Carbon Black

Catalytic activity of the carbon black was measured at various temperatures, and it is plotted as a function of time on stream in Figs. 8 and 9. The carbon black catalyst showed a relatively lower activity compared to the activated carbon catalyst at the beginning of the reaction. However, the activity of the carbon black quickly reached a quasi-steady state and remained constant for more than 8 hrs regardless of the reaction temperatures. It is believed that since the carbon morphology changes continuously due to the deposition of carbon (as shown in Fig. 13), some active sites may disappear due to the merging of protrusions or the agglomeration of particles, while others may be generated at the edges or defects of the growing graphite layer in the carbon black. One plausible explanation for the catalytic activity sustained at the quasi-steady state may therefore be that the overall number of active sites remains almost constant during the reaction. The effects of the methane gas velocity on the methane conversion and the decomposition rate are given in Figs. 10 and 11. A minimum fluidization velocity of 1.0 U_{mf} is equivalent to a space velocity of 0.16 L/g_{cat} hr in this case. As can be seen in Fig. 10, the effect of the gas velocity on the CH_4 conver-

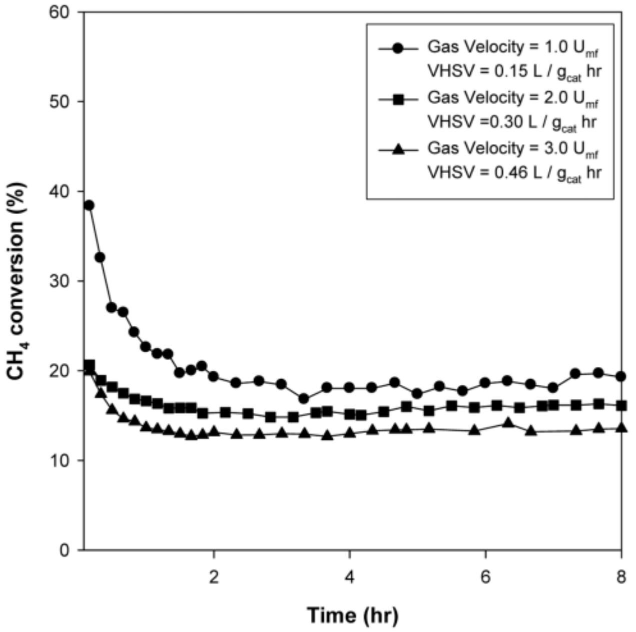

Fig. 10. The effect of gas velocity on the CH_4 conversion over carbon black at a temperature of 900 °C.

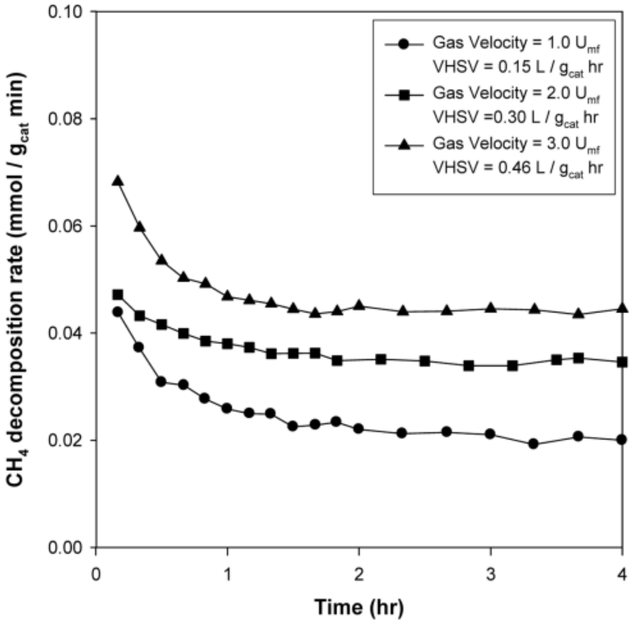

Fig. 11. The effect of gas velocity on the CH_4 decomposition rate over carbon black at a temperature of 900 °C.

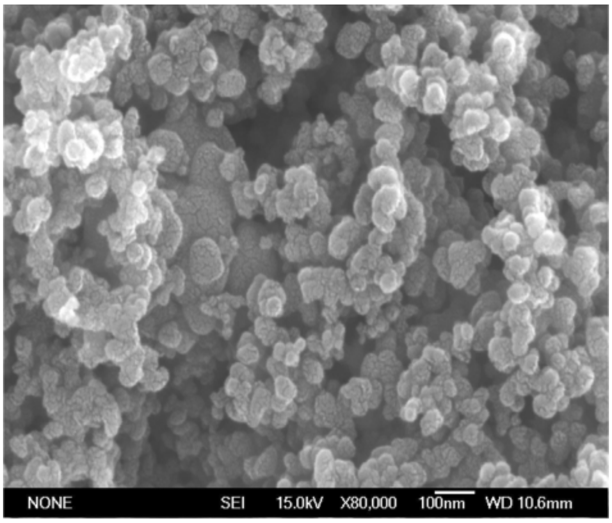

Fig. 12. SEM images of the surfaces of the carbon black before the reaction.

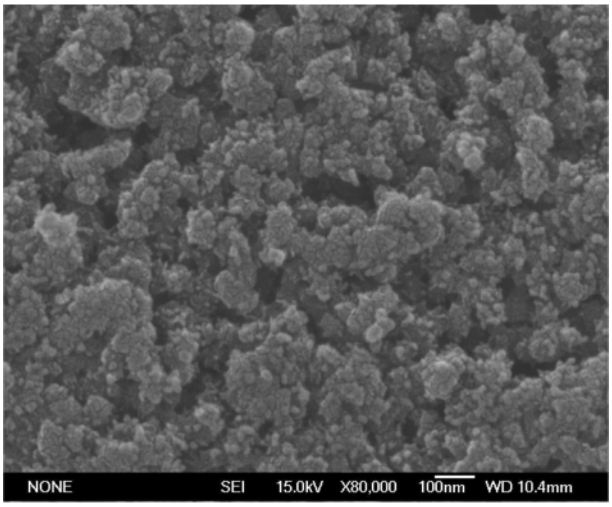

Fig. 13. SEM images of the surfaces of the carbon black after the reaction.

sion was also significant in the fluidized bed reactor with the carbon black catalysts. Higher methane flow rate resulted in a lower methane conversion due to the lower residence time and the reduced contact between the gas and the carbon catalysts because of bubble formation. However, as can be seen in Fig. 11, higher methane flow rate resulted in a higher methane decomposition rate (hydrogen production rate) due to the larger throughput per unit volume of the reactor. Therefore, the optimal methane flow rate should be chosen in terms of the hydrogen production rate and the methane conversion. It may be proposed that extensive investigation of the characteristics of the reaction rate in conjunction with hydrodynamics in the fluidized bed is required for the optimal operation of the fluidized bed reactor. SEM images of the surfaces of carbon black before and after the reaction are given in Figs. 12 and 13. The fresh carbon black particles shown in Fig. 12 are mostly round and their surfaces look smooth. As observed in Fig. 13, the deposited carbon formed many cone- or pillar-shaped protrusions on the surfaces, and the particles looked like sea squirts. As the carbon deposition proceeded, the particles tended to become larger and more particles became stuck together.

CONCLUSIONS

The characteristics of the thermocatalytic decomposition of methane in a fluidized bed reactor with activated carbon and carbon black catalysts were investigated experimentally. Distinctive difference was observed in the catalytic activities of the two carbon catalysts. The activated carbon catalyst exhibited high initial activity which decreased significantly with time. It seemed mainly attributed to the deposition of carbon on the surfaces of the activated carbon catalyst, thereby decreasing the number of active sites inside the pores. However, the carbon black catalyst exhibited somewhat lower initial activity compared to the activated carbon catalyst, but its activity was sustained for more than 8 hrs. The difference in the reaction activity was examined by studying SEM images of the used carbon catalysts. The effect of the operating parameters such as the reaction temperature and the gas velocity on the reaction rates was investigated.

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