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 CO2 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 CO2 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 quenching process, and CO2 is produced. CO2 emission can be decreased by using methane instead of steam in the quenching process, and the total carbon 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 LD (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>
<thead>
<tr>
<th>Manufacturer/supplier</th>
<th>Trade name</th>
<th>Particle diameter [nm]</th>
<th>Surface area [m²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber black OCI Ltd.</td>
<td>DCC-N330</td>
<td>30</td>
<td>85</td>
</tr>
</tbody>
</table>
Methane decomposition over carbon black at high temperatures

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 chromatography (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