

Properties of Carbon Black Used as Catalysts for Methane Decomposition

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Abstract : Direct decomposition of methane over three types of carbon black (N330-p, N330-f, and HI-900L) was carried out in a fluidized bed quartz reactor. Properties of carbon black before and after reaction were measured and found to be related with surface structure and weight gain. For N330-p and N330-f, some carbon deposit on the surface was considered to be the reason for the increase of BET surface area and pore volume with weight gain. Carbon deposits on the surface and the conglutination of some aggregates may explain the slight increase of particle size. Properties of HI-900L changed much more significantly with weight gain. It is supposed that the increase of aggregate size of HI-900L were due to some unknown oily components. The corresponding agglomeration might be the reason for the decrease of BET surface area with weight gain, as compared with the increase of that for the case of N330 black.

Keywords : *properties of carbon black, catalyst, methane decomposition, fluidized bed reactor, BET surface area.*

1. Introduction

Given the advantages inherent in fossil fuels such as their availability, relatively low cost, and the existing infrastructure for delivery and distribution, they are likely to play a major role in energy and hydrogen production in the near future. On the other hand, fossil fuels are the main source of air pollution, producing CO₂, NO_x, SO_x, and other pollutants that cause considerable damage to the environment of earth [1-5].

Hydrogen is increasingly considered as efficient and sustainable fuel in the future. One approach that recently attracted the attention of researchers is CO₂-free

production of hydrogen and carbon via thermal decomposition (pyrolysis or cracking) of methane[6]. Many researches on methane decomposition over transition metal catalysts (e.g. Ni, Fe, Co, Pd, etc.) have been reported. These studies point to a deactivation problem associated with the carbon lay down on the catalysts surface or gasified with steam in order to regenerate its original activity. Gasification or combustion of carbon deposits, however, results in production of large amounts of CO₂-byproduct, which is to be reduced due to the greenhouse effect. Carbon-catalyzed decomposition of methane for hydrogen production in a single step was proposed by Muradov recently [7-10]. The use of carbon-based catalysts offers certain advantages over traditional metal catalysts such as (i) high temperature resistance, (ii)

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tolerance to sulfur and other potentially harmful impurities in the feedstock, (iii) no metal carbide formed (formation of carbide may complicate the regeneration of metal catalysts), (iv) production of a marketable byproduct carbon, and (v) effect to mitigate overall CO₂ emissions from the process [4].

Many kinds of carbon materials have been used as catalysts for methane decomposition, such as activated carbon, carbon nanofiber, carbon nanotube, carbon black and so on. Carbon black was chosen as the main catalysts in this study because the application as reinforcement of rubber could potentially reduce the net cost of hydrogen production. The reinforcing action of carbon black in rubber was first discovered in the early 1900's. However, the mechanisms of reinforcement are still being studied and further developed today. Improvements of strength and abrasion resistance are two of the most obvious ways which carbon black reinforces elastomers. The key to understand the nature of carbon black is the recognition of their fundamental properties such as fineness (particle size), structure (aggregate size/shape), porosity and surface chemistry. In well-dispersed system, the particle diameter (fineness) of carbon blacks is the most important property relating to the degree of blackness and the level of elastomer reinforcement [11].

Properties of three different carbon blacks used as catalysts for methane decomposition were measured to observe the influential factors to the property changes. Proper reaction conditions are to be determined for the production of carbon blacks to apply as reinforcement of rubber in order to reduce the net cost of the whole hydrogen production process [12].

2. Experimental

2.1. Preparation of Carbon Black Samples

Three kinds of carbon black were used as catalysts in methane decomposition reaction. N330 crushed pellet black (N330-p) and N330 fluffy black (N330-f) were obtained from DC Chemical. Co., Ltd., and HI-900L black (fluffy) was obtained from Korea Carbon Black Co., Ltd.

The methane decomposition reaction over carbon black was carried out in a vertical fluidized reactor (55 mm I.D. and 650 mm height quartz-tube) heated by an electric tube furnace. All experiments were conducted over 100 g of carbon black at atmospheric pressure. A feed stream of methane was preheated to 400°C and entered to the bottom of reactor contacting with fluidized bed of carbon black at the set temperature in the reaction zone where thermo-catalytic decomposition occurred. The temperature of the reactor was controlled from 800-900°C by thermocouple in the middle of the bed and the flow rate of methane was controlled from 1 Umf (minimum fluidization velocity) to 4 Umf by MFC (mass flow controller). 1 Umf is corresponding to space velocity of 4.46 cm³/g_{cat} · min for N330-f, 2.62 cm³/g_{cat} · min for N330-p, and 6.69 cm³/g_{cat} · min for HI-900L. Reaction time was varied from 2 to 20 hr.

2.2. Measurement of Properties of Carbon Black Samples

BET surface area and pore size distribution were determined by nitrogen adsorption at 77 K with a surface area analyzer (Automatic Volumetric Sorption Analyser, Autosorb-1, Quantachrome). Microstructure was observed by Scanning Electron Microscope (SEM, 3500N, Hitachi Science System Ltd, Japan). Particle size of carbon black was measured by Nano-Micro sizing Analyser (Scatter Scope I, Qudix). Structure of carbon materials was investigated by X-ray diffraction (X'pert Pro, PANalytical, Netherlands) with Cu K α radiation ($\lambda=1.5406 \text{ \AA}$). To measure pH value, carbon black sample of 1 g was put into 100

ml distilled water and stirred for 3 hr. Then pH value was measured by pH meter (pH meter 440, Corning Incorporated). In order to determine the relative resistivity of the carbon black samples, a system, which consisted of ceramic tube fitted inside of stainless steel cylinder and two removable stainless steel pistons, was used. The electrical resistance between the contact points of the two stainless steel pistons was measured with a digital multi-meter (Hioki Co., HI Tester 3540) while the carbon black samples in the chamber were kept under a constant pressure of 1,000 psi for over 15 min by using an applied power press (ISE - WP 10T, Enerpac, USA).

3. Results and Discussion

Properties of raw carbon black were used as catalysts for methane decomposition as shown in Table 1. Particle size of all N330 blacks was around 30 nm, which was as large as twice of particle size of HI-900L.

According to the pH value, N330 blacks were neutral but HI-900L blacks were alkaline. BET surface area of HI-900L was about 300 m²/g, which was more than three times of that of N330 blacks. Tap density of N330-p pellet black was much higher than those of the other two fluffy carbon blacks.

The various properties of N330-p black before and after reaction at 850°C are shown in Table 2. The resistivity of N330-p decreased but the tap density increased with the increase of weight gain. The pH value increased slightly with the increase of weight gain, though all the values were around 7. BET surface area also increased slightly with weight gain. It is supposed some protrusions of carbon deposit formed on the surface of carbon black aggregates during the reaction and led to a kind of more irregular surface morphology [13]. The decrease of resistivity can also be explained by the new-formed carbon deposit. Those protrusions of carbon deposit can contact to each other easier and led to a better electron connection so that the conductivity increased after reaction. Iron

Table 1. Properties of Raw Carbon Black Used as Catalysts for Methane Decomposition

| Sample | Particle size (nm) | Resistivity ($\Omega \cdot \text{cm}$) | pH | Iron content (ppm) | BET (m^2/g) | Tap density (g/cm^3) |
|-------------|--------------------|--|-----|--------------------|-------------------------------|--|
| Raw N330-p | ~30 | 0.062 | 7.3 | 63 | 82 | 0.411 |
| Raw N330-f | ~30 | 0.074 | 7.2 | 73 | 74 | 0.295 |
| Raw HI-900L | ~15 | 0.111 | 7.8 | 19 | 297 | 0.252 |

Table 2. Properties of N330 (Crushed Pellet) Black with Different Weight Gain before and after Reaction

| Samples | Weight gain (%) | Resistivity ($\Omega \cdot \text{cm}$) | pH | Tap Density (g/cm^3) | Iron content (ppm) | Surface area (m^2/g) |
|----------------------------|-----------------|--|-----|--|--------------------|--|
| Raw N330 (p) | 0 | 0.0616 | 7.3 | 0.411 | 63 | 82 |
| N330-p (850°C 1 Umf 8 hr) | 10 | 0.0611 | 7.5 | 0.466 | 24 | 91 |
| N330-p (900°C 2 Umf 20 hr) | 50 | 0.0396 | 7.7 | 0.635 | 14 | 111 |

content decreased with the weight gain. It can be explained as that metal particles may be blew away during fluidized operation and also there were no metal particles inside of the new-formed carbon so the total iron content decreased after reaction. XRD images of N330 (p) is shown in Fig. 1. The peak of the sample with 50% weight gain is much sharper than raw black, which indicates that a better crystallinity formed after reaction.

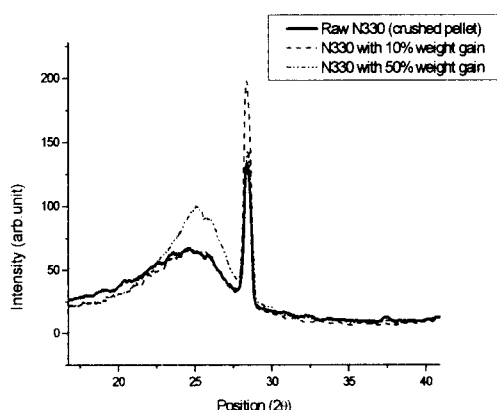


Fig. 1. XRD image of N330-p blacks.

Pore analyses are shown in Fig. 2 and Table 3. Both micropore volume and mesopore volume increased significantly after decomposition reaction, and total pore volume increased almost twice. It's also can be explained as that there were some new pores formed on the surface of the carbon deposited during the reaction.

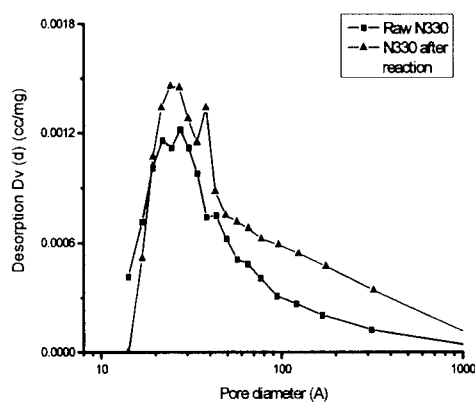


Fig. 2. Pore distribution of N330-p before and after reaction at 850°C, 1 Umf.

Table 3. Pore Analyses of Carbon Black Samples before and after Reaction

| Samples | Pore volume (cm ³ /g) | | |
|----------------------------|----------------------------------|------------------|-------------------|
| | Micro pore volume | Meso pore volume | Total pore volume |
| Raw N330-p | 0.0361 | 0.1390 | 0.1751 |
| N330-p (850°C 1 Umf 8 hr) | 0.0472 | 0.2868 | 0.3340 |
| Raw N330-f | 0.0333 | 0.0817 | 0.1150 |
| N330-f (850°C 4 Umf 8 hr) | 0.0392 | 0.1505 | 0.1897 |
| Raw HI-900L | 0.1301 | 0.5713 | 0.7014 |
| HI-900L (850°C 2 Umf 8 hr) | 0.1160 | 0.5048 | 0.6028 |

Table 4. Properties of N330-f Black before and after Reaction for 8 hr with Different Weight Gain

| Samples | Weight gain (%) | Resitivity (Ω · cm) | pH | Tap Density (g/ cm ³) | Iron content (ppm) | Surface area (m ² /g) |
|---------------------------|-----------------|---------------------|-----|-----------------------------------|--------------------|----------------------------------|
| Raw N330-f | 0 | 0.0744 | 7.2 | 0.2948 | 63 | 74 |
| N330-f (900°C at 1 Umf) | 13 | 0.0689 | 7.2 | 0.2412 | ~ | 83 |
| N330-f (850°C at 4 Umf) | 15 | 0.0757 | ~ | 0.2691 | 14 | 81 |

The properties of N330-f blacks with different weight gain after reaction for 8 hr are shown in Table 4. Different from N330-p, no significant trends were found for all the properties measured except for particle size distribution and pore analyses. BET surface area also increased with the increased weight gain, which was the same as the pellet one. As shown in Fig. 3, the peak of particle size distribution increased twice, from 277 nm to 546 nm after reaction at 850°C, 2 Umf for 8 hr with the weight gain of 15%. Same as N330-p, the pore volume of N330-f also increased after reaction. The mesopore volume increased almost as much as twice of the raw sample as shown in Fig. 4 and Table 3. Fig. 5 shows the SEM image of N330-f before and after reaction at 850°C, 4 Umf for 8 hr. Protrusions of carbon deposit can be clearly seen in forms of cone-shape or pillars scattered on the surface of the catalyst [13]. Also, some of the aggregates are supposed to conglutinate to each other by the new formed carbon deposits. Those carbon deposits on the surface and the conglutination of some of the aggregates may explain the increase of particle size and pore volume.

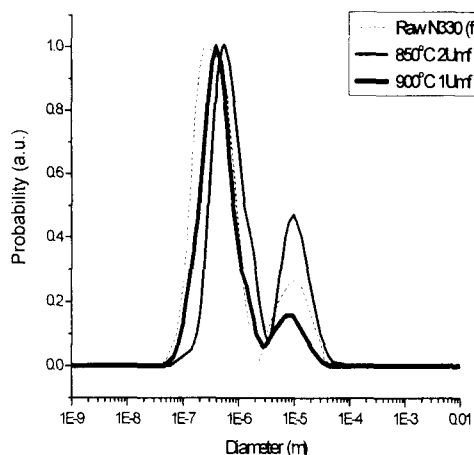


Fig. 3. Particle size distribution of N330-f before

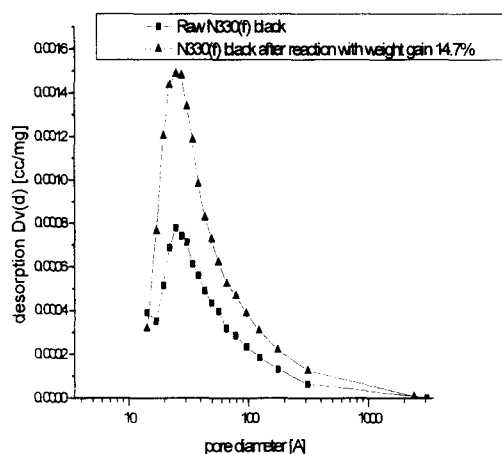


Fig. 4. Pore distribution of N330-f before and after and after reaction for 8 hr reaction at 850°C, 4 Umf for 8 hr.

Table 5 shows the properties of HI-900L blacks with different weight gains after methane decomposition reaction at 850°C. Same as N330-p blacks, resistivity of HI-900L decreased with the weight gain. The pH values seldom changed, still remaining around 8. The tap density of HI-900L increased a little with the increase of weight gain, but the BET surface area decreased, which is opposite to that of N330 blacks. Same as N330-p blacks, the iron content of HI-900L blacks decreased with the increase of weight gain. The particle size distributions of HI-900L blacks before and after methane decomposition reaction at 850°C at different flow rate are shown in Fig. 6. The peak of particle size distribution (aggregate size distribution) of HI-900L increased by over 50 times, from 129 nm before reaction to 7.7 μm after reaction. While in the case of N330 blacks, whose original particle size is bigger, aggregate size increased only twice as much as the raw sample. But for HI-900L, large quantities of relative small aggregates were supposed to adhere to each other nearby to form bigger agglomerates so that the particle size increased obviously after reaction. The

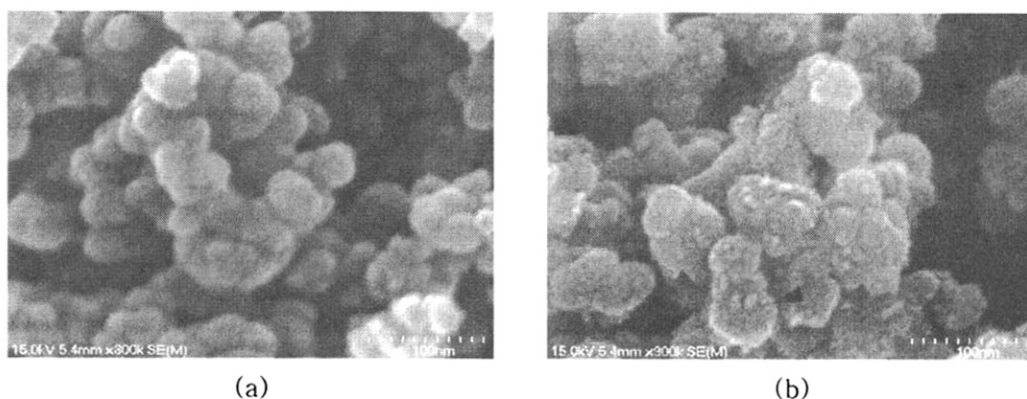


Fig. 5. SEM images of N330-f before (a), and after reaction (b) at 850°C, 4 Umf for 8 hr.

Table 5. Properties of HI-900L black before and after reaction at 850°C for 8 hr with different weight gain

| Sample | Weight gain /% | Resitivity ($\Omega \cdot \text{cm}$) | pH | Tap Density ($\text{g} \cdot \text{cm}^3$) | Iron content (ppm) | Surface area (m^2/g) |
|-----------------|----------------|---|-----|--|--------------------|--|
| Raw HI-900L | 0 | 0.111 | 7.8 | 0.252 | 19 | 297 |
| HI-900L (1 Umf) | 20 | 0.0801 | 8.1 | 0.328 | 12 | 252 |
| HI-900L (3 Umf) | 30 | 0.0717 | 8.0 | 0.331 | 7.4 | 239 |

large extent increase of aggregate size caused by agglomeration also can be the reason for the decrease of BET surface area. It's suspected that there are some oily components existing in HI-900L blacks so that aggregates are easily to agglomerate when fluidized.

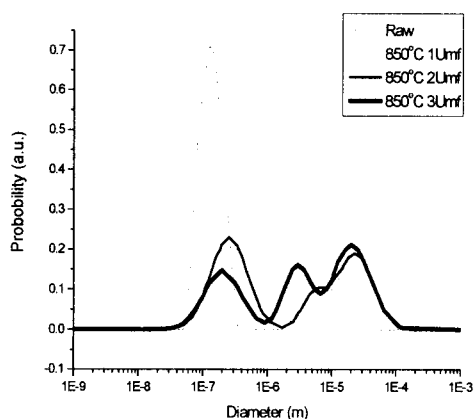


Fig. 6. Particle size distribution of HI-900L black.

In order to confirm the existence of oily components in HI-900L black, 1.5 g of HI-900L was treated in a nitrogen flow at 500°C for 20 hr and weighed. The weight decreased to 1.38 g and the lost weight was supposed to be the anticipated oil component, which was about 8 wt% of the sample. Fig. 7 and Table 3 show the pore analyses of HI-900L black. Both the micropore volume and mesopore volume decreased with the weight gain, which is also the opposite to that of N330 blacks. Initial pore volume of raw HI-900L was much larger than that of raw N330 black. So in case of HI-900L blacks, there are more chances for pores to be plugged up than for pores to form in and on the carbon deposits during the reaction. Relative rich initial pore volume was supposed to be the reason that pore volume decreased after reaction.

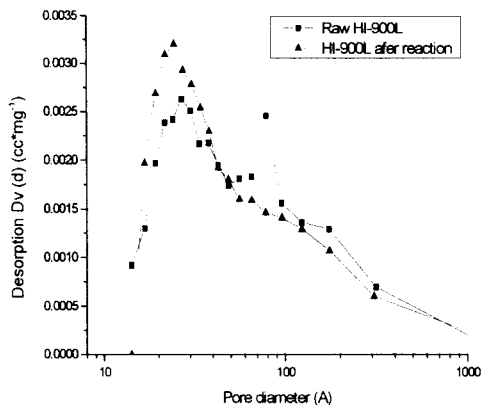


Fig. 7. Pore distribution of HI-900L before and after reaction at 850 °C, 1 U_{mf} for 8 hr

Summary of different properties of N330-f and HI-900L black are shown in Fig. 8. Compared with HI-900L black, the properties of N330-f changed very little as fluffy blacks. It may be caused because of their different particle size and surface properties. For HI-900L all the properties shown in Fig. 9 decreased remarkably with weight gain. The remarkable changes of properties might cause a serious dispersion problem in rubber composites and N330 black would be better choice for used catalysts as reinforcement of rubber in future work.

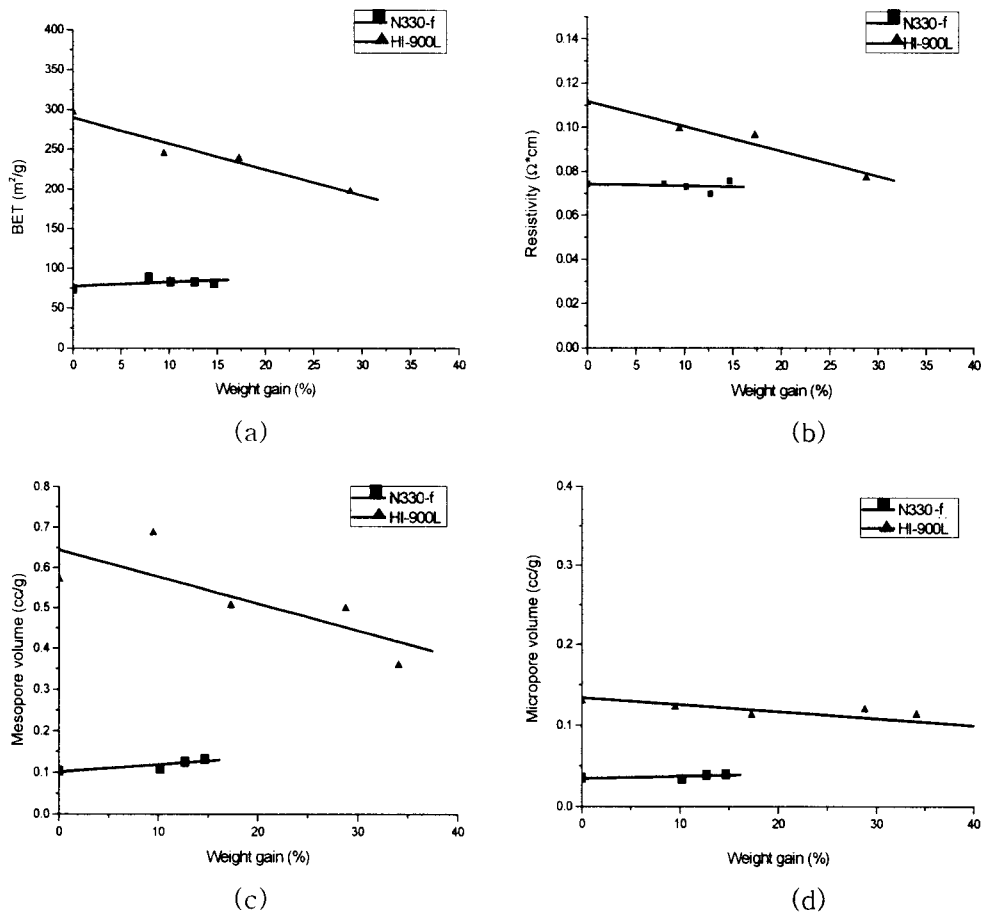


Fig. 8. Summary of various properties of N330-f and HI-900L black with methane decomposition.

4. Conclusions

The changes of properties of carbon blacks after methane decomposition were found to be related with surface structure and weight gain. For N330-pand N330-f, some carbon deposit in and on the surface was considered to be the reason for the increase of BET surface area and pore volumes with weight gain. Because of their relative bigger particle size, obvious agglomeration was not found. Aggregate size increased slightly because some of the aggregates were conglomerated to each other by the new formed carbon deposits. It is supposed that aggregates of HI-900L black much more easily adhere to each other due to the existence of some oily components so that after reaction the particle size distribution changed remarkably and surface area decreased with weight gain. Rich initial pores of HI-900L black led to a decrease of pore volume after reaction.

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