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Catalytic characteristics of various rubber-reinforcing carbon blacks in decomposition of methane for hydrogen production

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Abstract

Carbon black has recently been reported to act as an effective catalyst for methane decomposition and to exhibit stable catalytic behavior despite carbon deposition, and thus it can be used for CO_2-free production of hydrogen from natural gas. In this work, various carbon blacks with different primary particle size were investigated with respect to methane decomposition under atmospheric pressure from 1123 to 1223 K. Catalytic characteristics, such as activity, activation energy and reaction order, were investigated and compared. It was observed that with decreasing primary particle size (or increasing specific surface area), the specific activity increased and the activation energy decreased. The reaction orders for various pelletized, rubber-reinforcing carbon blacks were 0.6–0.7, about the same regardless of the primary particle size, while they were near 1 for fluffy carbon blacks. Fluffy carbon black showed higher activity and activation energy than the pelletized carbon black of the same primary particle size. Changes of the surface morphology during carbon deposition were observed by TEM. Variations of the number of active sites were discussed in regard of the primary particle size, carbon deposition and binder. The presence of different types of active sites was also suggested.

Keywords: Carbon black; Catalyst; Hydrogen; Methane decomposition; Rubber black; Surface morphology

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1. Introduction

Hydrogen is increasingly recognized as an efficient and sustainable fuel of the future as it is a preferred fuel for fuel cells in homes and cars. Steam reforming of hydrocarbons is currently the largest and most economical way to produce hydrogen. However, this conventional process accompanies simultaneous production of CO_2, which is to be reduced due to the greenhouse effect. Clean production of hydrogen, e.g., by water electrolysis or photocatalytic decomposition of water using renewable energy, is not competitive with current energy costs or practicable in efficiency. An attractive alternative is the decomposition of methane which produces no CO_2 [1–4].

There are several processes of methane decomposition. Noncatalytic thermal decomposition of methane requires quite a high temperature (1500–2000 K) in order to obtain a reasonable hydrogen yield. However, if the heat is supplied by burning a fossil fuel, overall CO_2 emission may not be reduced significantly. When transition metals such as Fe, Ni and Co are used as the catalyst for methane decomposition, the reaction temperature can be lowered to a great extent (around or below 1000 K). But rapid catalyst deactivation associated with carbon build-up induces other problems such as reactor blocking and bothersome catalyst regeneration [5–7]. Regeneration of those catalysts by combustion or gasification of carbon deposits results in production of a large amount of CO_2. Decomposition of methane by plasma is another approach without CO_2 emission [1,3,4].

Recently, catalytic decomposition of methane and other hydrocarbons over carbon catalysts has been proposed as a viable alternative to the conventional steam reforming [8–10]. This process produces hydrogen without CO and CO_2, which eliminates the need for water gas shift reaction, CO_2 and CO removal stages required by conventional hydrogen production processes and thus significantly simplifies the process. When carbon is used as the catalyst, regeneration of the carbon catalyst by removal of the produced carbon is not necessary and the produced carbon can be utilized as a marketable by-product

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(that could substantially reduce the net cost of hydrogen production). Other advantages of carbon-based catalysts over metal catalysts are: (i) high temperature resistance, and (ii) tolerance to sulfur and other potentially harmful impurities in the feedstock [10]. Since the decomposition of methane is a mild endothermic reaction ($\Delta H^\circ = 75.6$ kJ/mol), the required heat can be supplied by burning 10–15% of the produced hydrogen and thus CO_2 emission can be avoided.

Muradov [9,10] investigated various kinds of carbon, such as activated carbons, carbon blacks, glassy carbons, graphite, diamond, carbon fibers, carbon nanotubes and fullerenes. Among these carbons, activated carbons and carbon blacks showed reasonable activities at around 1123 K while other carbons with ordered structure showed very poor activities. Activated carbons exhibited higher initial activity but deactivated quite rapidly, while carbon blacks exhibited relatively lower initial activity but showed stable or quasi-stable activity in spite of carbon deposition. Therefore, carbon black is considered to be a better catalyst in this respect. Kinetic and deactivation studies on the decomposition of methane over activated carbons have recently been reported in more detail [10–12]. The activation energies for the activated carbons lay in a range from 160 to 201 kJ/mol and the reaction orders in a range from 0.5 to 0.6. More recently, a few carbon blacks for plastics and rubber applications have been studied for the decomposition of methane and the activation energy and reaction order have been reported [10,13]. The reported activation energies for the carbon blacks varied in a wide range from 148 to 236 kJ/mol and the reaction orders from 0.5 to 1.0. However, these differences among various carbon materials have not well been elucidated and moreover no definite conclusion has yet been made on the mechanism. Since numerous types of carbon black are present because of different raw materials, manufacturing processes, particle sizes, specific surface areas, electrical conductivities and uses, a more systematic study for various carbon blacks may be needed for better understanding of the catalytic characteristics.

In this work, various grades of commercial carbon blacks for rubber reinforcement use (rubber blacks), which have different primary particle size and hence different specific surface area, were investigated to determine the catalytic characteristics in methane decomposition, in terms of the activity, reaction order, activation energy, and stability. A majority of the rubber blacks were in a pelletized form, but some fluffy (nonpelletized) carbon blacks with the same primary particle size as that of the pelletized form were also tested. The results were compared and discussed: of particular interest are the correlations between the structural and surface properties of carbon blacks and their catalytic characteristics. Based on these results, a brief discussion on the active site was presented.

2. Experimental

The rubber blacks tested in this work are listed in Table 1. All the rubber blacks are the furnace black made from coal tar (DC Chemical (DCC), Korea) or heavy petroleum oil (Korea Carbon Black with the trade name Corax). The sample designations, affixed to the company or trade name (e.g., N103), are in accordance with the ASTM designation. For a few samples, two types of rubber black for the same designation, fluffy (F) and pelletized (P), were tested. The pelletized type is normally supplied in the market because of easy handling, while the fluffy type may be supplied from the manufacturers by a special request. The pelletized rubber black is prepared from the fluffy carbon black by pelletization, i.e., by using diluted molasses as the binder. The molasses content in the carbon black on the basis of pre-dilution is ca. 1.5 wt.%.

Table 1
Rubber blacks tested

Carbon black	Surface area (m^2/g)[a]	Primary particle size (nm)[b]
DCC-N103(P or F)	140	11–19
DCC-N220(P)	120	20–25
Corax-N220(P)	119	20–25
DCC-N326(P or F)	82	26–30
DCC-N330(P or F)	81	26–30
Corax-N330(P)	83	26–30
DCC-MAF(P)	53	40–48
Corax-MAF(P)	60	40–48
DCC-N550(P)	43	40–48
DCC-N774(P)	29	61–100

[a] Data of the suppliers.
[b] In accordance with the ASTM.

The rubber black samples were dried at 373 K for 24 h in air before the reaction test and characterization. The decomposition reaction was carried out in a vertical, fixed-bed, 8 mm ID quartz-tube flow reactor heated by an electric tube furnace. The tube was narrowed somewhat in the middle and rock wool was placed there to support the carbon black particles. Methane (99.99%, Dong-a Gas, Korea) and Ar (MS Dongmin Specialty Gas, Korea) were used without further purification. The standard reaction conditions were the catalyst charge of 0.1 g, the methane flow rate of 25 cm^3(STP)/min and the volumetric hourly space velocity (VHSV) of 15,000 cm^3/h·g-cat (g-cat denotes the mass in gram of dried carbon black catalyst before-reaction). For the determination of the reaction order, the total flow rate of methane plus Ar was set to 40 cm^3(STP)/min and the flow rate of each gas was changed to adjust the partial pressure. The reaction temperature ranged from 1123 to 1223 K. Because the stainless steel sheath of the thermocouple is a good catalyst for hydrocarbon decomposition, the thermocouple was removed before the reaction experiments after the desired temperature was reached under Ar flow. The first sampling and analysis was usually done 5 min after methane was introduced, since it took time for the reaction system to reach steady state and flush the Ar gas that was initially present. The product gas was analyzed by gas chromatography, using a Carboxen column (Supelco, USA), Ar carrier and a TCD. The concentration of hydrogen or the methane conversion was determined by using calibrated data. TEM images of some samples were obtained from a HRTEM (high resolution transmission electron microscope: JEOL 300 kV).

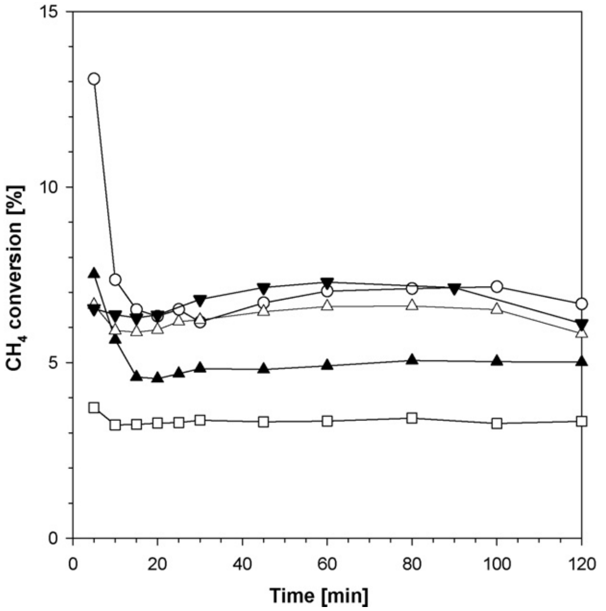

Fig. 1. CH_4 conversion vs. time over pelletized rubber blacks (temperature = 1223 K and VHSV = 15,000 $cm^3/h{\cdot}g\text{-cat}$). (○) DCC-N103(P), (▼) DCC-N220(P), (△) DCC-N330(P), (▲) DCC-N550(P), and (□) DCC-N774(P).

3. Results

3.1. Catalytic characteristics of pelletized rubber blacks

The catalytic activities of various pelletized rubber blacks at 1223 K were compared and the representative results are shown in Fig. 1. In spite of carbon deposition, all these rubber blacks exhibited stable or quasi-stable activity after initial transition periods of about 20 min. During the transition period, a decrease in the activity was observed. The stable activity, i.e., the average CH_4 decomposition rate between 20 and 45 min on-stream, is plotted in Fig. 2 with respect to the specific surface area. A tendency is observed that the activity increases with increase of the specific surface area (or decrease of the primary particle size). In addition, although DCC and Corax rubber blacks were made from different origins, both of the rubber blacks with the similar specific surface area exhibited similar activities to each other.

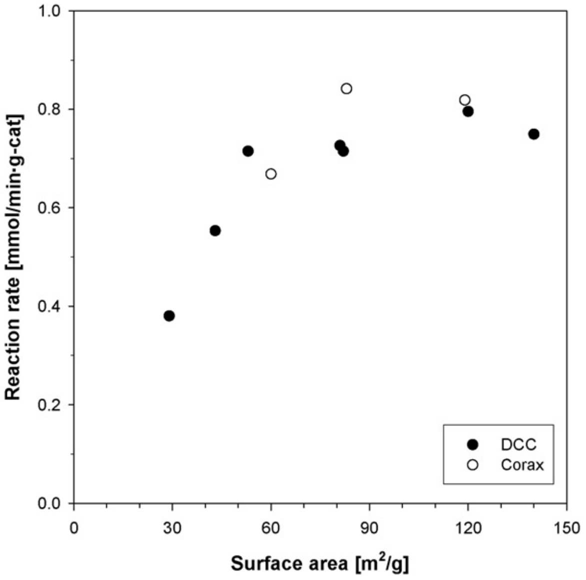

Fig. 2. Rate of CH_4 decomposition vs. specific surface area of pelletized rubber blacks (temperature = 1223 K and VHSV = 15,000 $cm^3/h{\cdot}g\text{-cat}$).

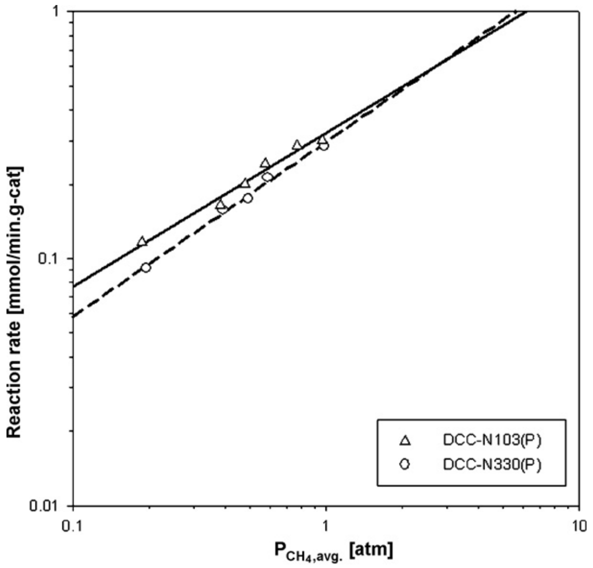

Fig. 3. Rate of CH_4 decomposition as a function of CH_4 partial pressure over DCC-N103(P) and DCC-N330(P) (temperature = 1173 K).

To determine the reaction order, the activity was measured at 1173 K under different partial pressure of methane. The average reaction rates after stabilization were used for the analysis, and representative data are shown in Fig. 3. Regardless of the primary particle size, the reaction order for all the pelletized carbon blacks was nearly the same, lying between 0.61 and 0.75, as shown in Table 2.

A typical example of the activity change with temperature is shown in Fig. 4. At temperatures below 1223 K, the activity was very stable except for the initial transition period. The results of methane decomposition carried out under the identical conditions without a catalyst showed that the methane conversion at 1223 K was quite low (less than 1%) and below this temperature the methane decomposition was negligible; the experiment above 1223 K was not carried out because it had been found that noncatalytic gas phase decomposition was

Table 2
Reaction order and activation energy for rubber blacks

Carbon black	Reaction order (*a*)	Activation energy (kJ/mol)
DCC-N103(P)	0.62	174
DCC-N220(P)	0.66	165
Corax-N220(P)	0.63	171
DCC-N326(P)	0.64	182
DCC-N330(P)	0.71	213
Corax-N330(P)	0.61	216
DCC-MAF(P)	0.67	246
DCC-N550(P)	0.75	235
DCC-N774(P)	0.69	233
DCC-N103(F)	0.99	199
DCC-N326(F)	0.86	205
DCC-N330(F)	0.92	243

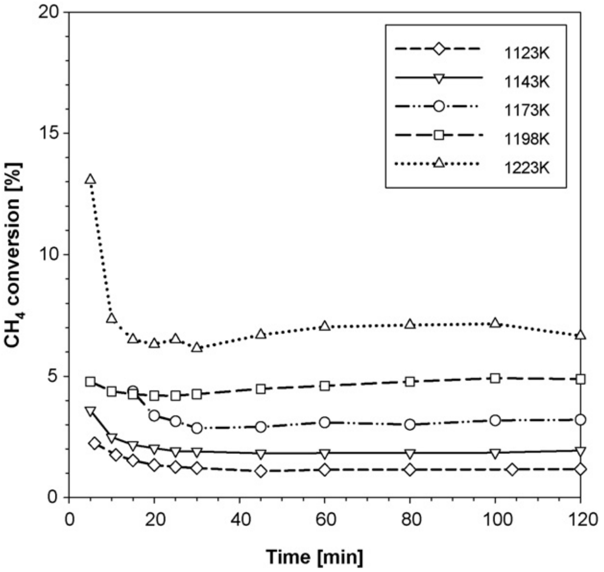

Fig. 4. CH_4 conversion vs. time over DCC-N103(P) at different temperatures (VHSV = 15,000 cm^3/h·g-cat).

significant at higher temperatures [13]. Since the reaction orders had been determined, the reaction rate constants, k_p, were calculated and then the activation energies were determined from the Arrhenius plot. Here again, the average reaction rates after stabilization were used for the analysis. Representative data are shown in Fig. 5, and the determined activation energies are presented in Table 2. It is seen that the activation energy tends to increase with increase of the primary particle size.

3.2. Catalytic characteristics of fluffy rubber blacks

Catalytic characteristics of fluffy rubber blacks were investigated in the same way as for the pelletized rubber blacks, and the results are presented in Table 2. Since the activity change with time was very similar to that for the pelletized rubber blacks, the activity data for the fluffy rubber blacks are not shown here in graphs for brevity, but typical results for DCC-N330(F) have been reported in a previous work [13]. It has recently been confirmed that DCC-N330(F), which was run in a fluidized bed at 1173 K, maintained its activity for 8 h, that is, the methane conversion at 8 h on-stream was the same as that at 2 h on-stream [14]. The catalytic stability of fluffy rubber black was also good, similar to that of the pelletized carbon black. However, when compared with the pelletized rubber black having the same primary particle size, the fluffy rubber black exhibited higher activity, higher reaction order (closer to 1) and higher activation energy (by 25–30 kJ/mol). For example, the stable methane conversions at 1223 K with the same VHSV were as follows: 9.2% for DCC-N103(F) and 6.4% for DCC-N103(P); 7.2% for DCC-N326(F) and 6.2% for DCC-N326(P); 17.1% for DCC-N330(F) and 6.2% for DCC-N330(P). For the fluffy rubber blacks, the activation energy appeared to increase with the primary particle size, but there seemed to be no trend between the activity and the primary particle size. However, since the number of tested materials was small due to the limited supply, a definite conclusion may not be made at this moment. Nonetheless, the differences in the activity, reaction order and activation energy from the pelletized rubber black are significant. The reason for this is apparently due to the effects of the binder in the pelletized carbon black, and more discussion will be made later in Section 4.2.

3.3. TEM images

Representative TEM images of some DCC-N330(F) samples are presented in Figs. 6–9. The particles of fresh DCC-N330(F) are largely round and the surfaces look smooth

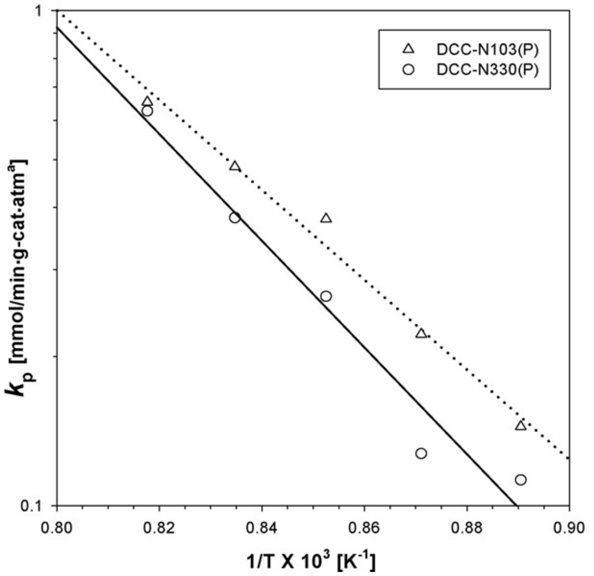

Fig. 5. Arrhenius plot for CH_4 decomposition over DCC-N103(P) and DCC-N330(P) (VHSV = 15,000 cm^3/h·g-cat; a is the reaction order).

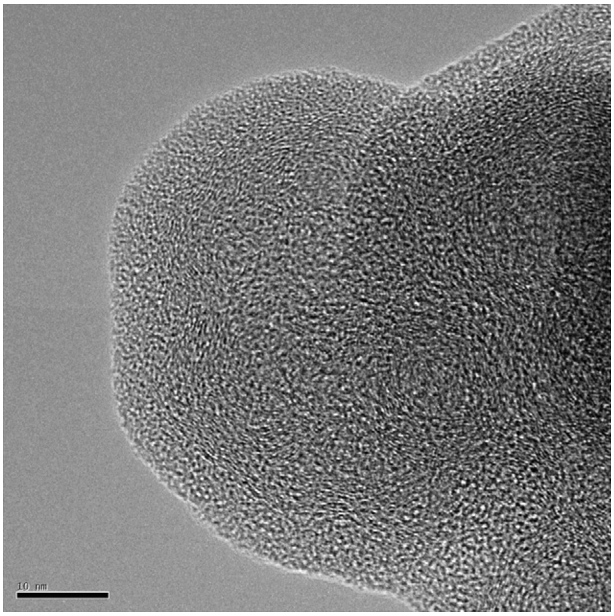

Fig. 6. TEM image of fresh DCC-N330(F) (scale bar = 10 nm).

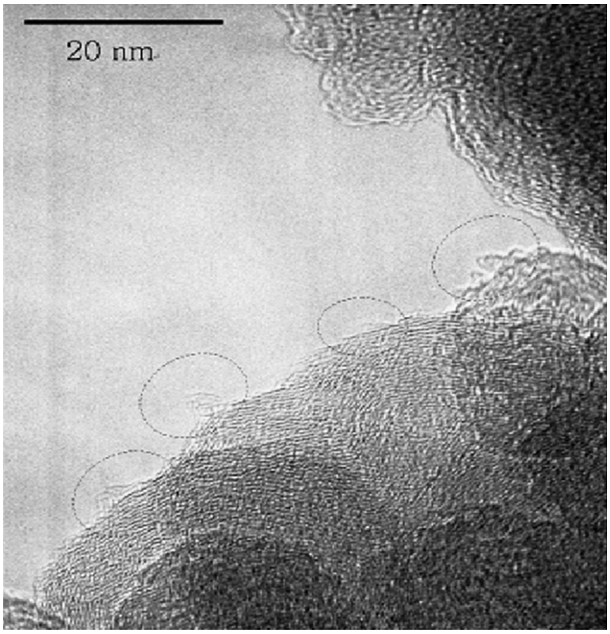

Fig. 7. TEM image of DCC-N330(F) after reaction at 1173 K for 30 min (0.19 g deposited C/g-cat).

(Fig. 6), which is almost identical to those shown in the literature [15]. A fresh particle is composed of stacked graphene layers; however, most of the layer planes are not well-oriented in parallel. Instead they are rather disordered with many curved planes, distortions and discontinuities seen in various places. After methane decomposition had commenced for about 30 min at 1173 K, it was observed that the produced carbon did not deposit evenly on the surface but instead formed protrusions in several places on the surface. When the amount of deposited carbon was small, i.e., less than ca. 0.2 g/g-cat, the protrusions were formed on the scattered places and were mostly conical, as pointed out by dotted circles in Fig. 7. As the deposition continued, the protrusions became bigger and some of them developed into steeples or pillars (Figs. 8 and 9). It was also observed that new protrusions started to grow on the side of the old protrusions and hence knotty, branched and bent protrusions were formed. The protrusions appeared to grow in a direction perpendicular to the surface where the starting points are present. The protrusions were also composed of stacked graphene layers and the layer planes were largely oriented parallel to the periphery of the protrusions. Around the foot of a big protrusion, graphene layers that were largely parallel to the original round particle surface and connected to one or more adjacent big protrusions were formed. Hence, as the carbon deposition continued, it seems that protrusions located in the neighbourhood of each other merged and formed a much bigger protrusion. In fact, from the SEM images shown in a previous work [13], protruding ridges, which were formed by the merging, were observed on the samples with high amounts of deposited carbon.

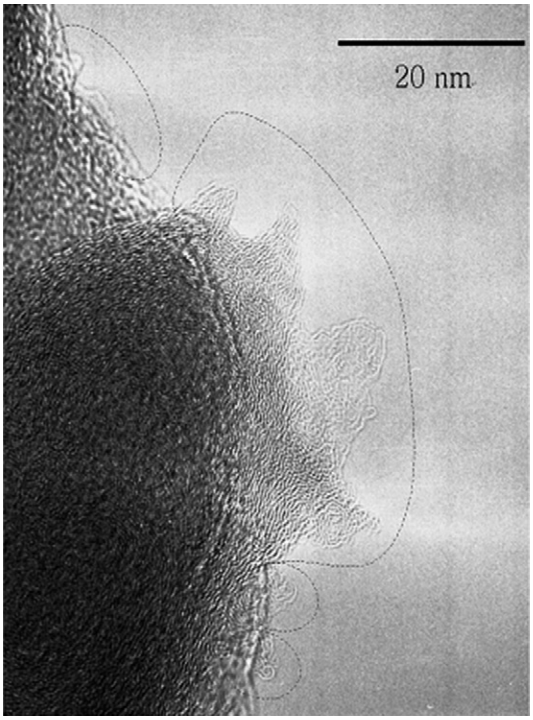

Fig. 8. TEM image of DCC-N330(F) after reaction at 1173 K for 60 min (0.41 g deposited C/g-cat).

Fig. 9. TEM image of DCC-N330(F) after reaction at 1173 K for 180 min (1.50 g deposited C/g-cat).

4. Discussion

It is generally accepted that the active sites on the carbon materials are where the regular array of carbon bonds is disrupted, forming free valences, discontinuities (i.e. the edges and corners of graphite crystallites) and other energetic abnormalities such as surface defects and dislocations [10]. Hence, disordered (or amorphous, microcrystalline) carbons such as carbon black and activated carbon can have a large number of active sites. However, a more detailed description of the structure of active sites, specifically for methane decomposition, has not yet been resolved. Anyhow, those active sites exist scattered on the surface, and Fig. 7 may provide an evidence for that.

4.1. Initial transition activity and stable activity

During the initial transition period, the activity of carbon blacks usually decreased. This may be due to the decrease of the number of active sites or to changes of the structure of active sites. As the carbon deposits, some active sites may be transformed into a stable structure and become inactive, which brings a decrease in activity. The TEM results render an evidence for the change of the surface structure. The original active sites on the fresh carbon black particles may have higher activity, but as the carbon deposits and the protrusions are formed, the surface structure is changed and the activity of the newly formed active sites, probably located at the discontinuities of graphene layers on the protrusions, may have a slightly lower activity compared with the original active sites.

After stabilization of the activity, the number of active sites seems to change little. The growing protrusions support this argument. Some new active sites may be produced at the surface of the growing protrusions, but on the other hand, some active sites may disappear due to merging of protrusions (or growing graphitic layers) or transformation of active sites into a stable structure owing to the carbon deposition. Despite the carbon deposition, which changes the surface structure, carbon surface area, particle size and agglomeration of particles, a plausible explanation of the stable activity of carbon blacks is that the overall number of active sites remains almost constant during the reaction [13].

4.2. Activity and activation energy versus specific surface area or primary particle size

Since the various forms of amorphous carbon differ in the size of crystallites and in their mutual orientation, a good correlation may not exist between the specific activity and the specific surface area (per unit mass of fresh carbon) even though similar classes of carbon materials were compared. In fact, it has been reported that the rate of methane decomposition per unit mass of various activated carbons or carbon blacks does not correlate well with the specific surface area regardless of starting material or treatment employed [10,12,13]. If the specific surface area differs greatly by one or two orders of magnitude, the specific activity of a high surface area carbon would be significantly (though not proportionally) higher than that of a low surface area carbon. Such is the case for activated carbon, carbon black and graphite; as reported earlier, the catalytic activity of various carbons, ranging from graphite (a few m^2/g) to activated carbon (near 1000 to over 3000 m^2/g), increases with the specific surface area [10]. Nevertheless, for the rubber blacks investigated in this work, it was observed that the activity increased as the primary particle size decreased or the specific surface area increased. Since the rubber blacks tested in this work are the same types and hence may be considered to have similar morphology, a likely reason for this is the increase in the number of active sites with the specific surface area. Therefore, a good correlation can exist between the specific activity and the specific surface area in this case. If the number of active sites on the carbon materials could be determined, the activity difference can be elucidated more clearly; however, an appropriate method to determine the number of active sites, specifically for methane activation, has not yet been established.

Another reason may be that several kinds of active sites exist on the surface, which is discussed below together with the activation energy. The activation energy for the pelletized rubber black increased with the primary particle size. This reflects that the active sites are not energetically uniform. At the periphery of a graphite crystallite, at least three types of active sites may exist: edge of zigzag face, edge of armchair face, and corners. The armchair face or a corner would be more active than the zigzag face since the former has a lower coordination number than the latter. As the primary particle size decreases, it is more probable that the number of corners or armchair face increases. Hence, a smaller primary particle size results in a lower activation energy and at the same time a higher activity.

The activation energies for different forms of carbon have been reported in the literature. For activated carbons, they were in a range of 160–201 kJ/mol [10,12]. For carbon blacks whose main uses are for pigment and plastics, they were in a range of 205–236 kJ/mol [10]. The activation energies in this work are largely in good agreement with those reported earlier. However, the activation energies for the rubber blacks in this work span a wider range depending on the primary particle size.

The fluffy rubber black exhibited higher activity and activation energy than the pelletized one. These differences are probably due to the molasses binder which was added for pelletization. Molasses contains carbohydrates and it has surely been decomposed under the high reaction temperature. The resulting carbon residue, as well as some impurities in the molasses, will block a significant portion of the active sites on the fluffy rubber black particles, and in addition, the carbon residue seems to form new active sites of different carbon structure with higher activity, but the number of new active sites may be significantly smaller than that of blocked active sites. This may explain the lower activity and activation energy for the pelletized rubber black compared with the fluffy rubber black.

4.3. Reaction order

The reaction order for coal-derived and coconut shell-derived activated carbons has been reported to be 0.5 [12] and that for lignite-derived activated carbon to be 0.6 [10]. The reaction order for a carbon black with a very high surface area, Black Pearls 2000 (Cabot Corp.), has been reported to be 0.5 in a study [10] and near 1.0 in another study [13]. The reaction orders for the pelletized rubber blacks in this work were around 0.67, i.e., 2/3, nearly the same regardless of the primary particle size. This indicates that the reaction mechanism is the same on all the pelletized rubber blacks in this work. In contrast, the reaction order for the fluffy rubber blacks was closer to 1. The different reaction orders suggest that different mechanisms may be working on different forms of carbon or different structure of active sites. Since no definite conclusions have yet been made on the detailed structure of active sites and the mechanism for carbon-catalyzed methane decomposition, further work may be needed.

5. Conclusions

In order to determine the catalytic characteristics, various commercial rubber blacks with different primary particle size were investigated with respect to methane decomposition in a temperature range from 1123 to 1223 K. All the rubber blacks showed stable catalytic activity in spite of carbon deposition, which suggests that the number of active sites remains almost constant during the reaction. TEM showed that the active sites existed scattered on the surface and that protrusions were formed and grew at the active sites as the carbon deposited. A tendency was observed that with decreasing primary particle size, the specific activity increased and the activation energy decreased. One reason for this is that the number of active sites increases since the specific surface area increases as the primary particle size decreases. Another reason is suggested that the number of active sites with higher activity such as the corners of crystallites increases as the primary particle size decreases. Since the active sites with higher activity require lower activation energy, it can also explain the reason for the decrease of activation energy with decrease of the primary particle size. The pelletized carbon black showed lower activity and lower activation energy than the fluffy carbon black of the same primary particle size. This is due to the molasses binder which was added for the pelletization. The carbon residue produced by decomposition of molasses blocks a significant portion of the original active sites and seems to form new active sites that require lower activation energy, but the number of new active sites may be significantly smaller than the original ones. The reaction orders for the pelletized carbon blacks were around 0.67 and were nearly the same regardless of the primary particle size, while they were near 1 for fluffy carbon blacks.

Acknowledgements

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References

[1] M. Steinberg, H. Cheng, Int. J. Hydrogen Energy 14 (1989) 797.
[2] N. Muradov, Int. J. Hydrogen Energy 18 (1993) 211.
[3] L. Fulcheri, Y. Schwob, Int. J. Hydrogen Energy 20 (1995) 197.
[4] B. Gaudernack, S. Lynum, Int. J. Hydrogen Energy 23 (1998) 1087.
[5] M.G. Poirier, C. Sapundzhiev, Int. J. Hydrogen Energy 22 (1997) 429.
[6] A. Steinfeld, V. Kirillov, G. Kuvshinov, Y. Mogilnykh, A. Reller, Chem. Eng. Sci. 52 (1997) 3599.
[7] R. Aiello, J.E. Fiscus, H.-C. zur Loye, M.D. Amiridis, Appl. Catal. A 192 (2000) 227.
[8] N. Muradov, Int. J. Hydrogen Energy 26 (2001) 1165.
[9] N. Muradov, Catal. Commun. 2 (2001) 89.
[10] N. Muradov, F. Smith, A. T-Raissi, Catal. Today 102 (2005) 225.
[11] M.H. Kim, E.K. Lee, J.H. Jun, G.Y. Han, S.J. Kong, B.K. Lee, T.-J. Lee, K.J. Yoon, Korean J. Chem. Eng. 20 (2003) 835.
[12] M.H. Kim, E.K. Lee, J.H. Jun, S.J. Kong, G.Y. Han, B.K. Lee, T.-J. Lee, K.J. Yoon, Int. J. Hydrogen Energy 29 (2004) 187.
[13] E.K. Lee, S.Y. Lee, G.Y. Han, B.K. Lee, T.-J. Lee, J.H. Jun, K.J. Yoon, Carbon 42 (2004) 2641.
[14] J.U. Jung, W. Nam, K.J. Yoon, D.H. Lee, G.Y. Han, Abstracts of Fifth TOCAT, Tokyo, Japan, July 23–28, (2006), p. 448.
[15] J.-B. Donnet, A. Voet, Carbon Black, Marcel Dekker, New York, 1976, p. 104.