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Variation in Catalytic Activity of Carbon Black during Methane Decomposition: Active Site Estimations from Surface Structural Characteristics

Yuki Kameya · Katsunori Hanamura

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Abstract The variation in the catalytic activity of carbon black (CB) during methane decomposition was investigated by considering the number of active sites of CB. We demonstrated that the activity variation could be well estimated by assuming the edge length of graphitic sheets evolving from the CB surface. The results suggested that the activity variation originated from surface structural changes due to carbon deposition.

Keywords Catalytic methane decomposition · Carbon black · Active site · Surface nanostructure · Graphitic sheet · Chemical kinetics

1 Introduction

Methane decomposition ($CH_4 \rightarrow 2H_2 + C(s)$, $\Delta H = 75$ kJ/mol) has been studied as a promising technique to produce hydrogen from natural gas without the production of CO and CO_2 [1]. This CO_x-free process does not require water–gas shift and gas separation stages, which simplifies the overall process significantly [2]. Catalytic decomposition of methane over metal catalysts (e.g. Ni, Co, Pd) has been extensively reported [3]. However, metal catalysts inevitably deactivate because of carbon deposition, and the regeneration process leads to undesirable CO_2 emission via burning or steam gasification of carbon [4].

The use of carbonaceous materials as catalysts in methane decomposition has also been investigated [1, 2, 5–12]. Carbon catalysts offer several advantages over metal catalysts, such as resistance to high temperatures, tolerance to sulfur and other potentially harmful impurities in the feedstock [2], and lower cost [8]. Among carbonaceous materials, carbon black (CB) is the most promising catalyst because of reasonably high activity and long lifetime, while others exhibit low activities or rapid deactivation [1, 2, 5]. The favorable catalytic characteristics of CB are attributed to its microstructure, which has many active sites consisting of edges and defects in nanosized graphitic sheets [11, 13, 14]. CB shows long lifetime because carbon deposited on the edge site of a graphitic sheet also functions as an active site [7]. CB exhibits time variation in its catalytic activity; however, the origin of the activity variation has not yet been clarified.

Recently, we have discovered that the mass ratio of deposited carbon to CB is an important parameter for representing the variation in the catalytic activity of CB during the reaction, and that the activation energy is constant despite the varying reaction rate [12]. The constant activation energy suggests that the mechanism of catalytic decomposition, namely, the reaction at the edge sites and defects in graphitic sheets, is invariant during the reaction. On the basis of this observation, it is reasonable to consider that the variation in the number of active sites is responsible for the activity variation. Although no method has been established to determine the number of active sites of CB directly [6], the surface structural characteristics are expected to correlate with the variation in the number of

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Y. Kameya
Thermal and Fluid Technology Department, IHI Corporation,
1, Shin-nakahara-cho, Isogo-ku, Yokohama 235-8501, Japan

Y. Kameya (✉) · K. Hanamura
Department of Mechanical and Control Engineering,
Tokyo Institute of Technology, 2-12-1, Ookayama,
Meguro-ku, Tokyo 152-8552, Japan
e-mail: yuki.kameya.jp@gmail.com

active sites because the active sites consist of edge sites and defects in nanosized graphitic sheets. In the present study, therefore, we present an approach to consider the variation in the number of active sites during the reaction from a surface structural viewpoint. We also discuss the origin of the catalytic activity variation of CB. This study presents for the first time, to the best of our knowledge, estimations of the variation in the number of active sites on a carbon catalyst.

2 Experimental

A commercial color CB, SB905 (Asahi Carbon, Japan), was employed in this study because it exhibits a relatively broad range of the initial deactivation stage in terms of the reaction time [12], which would make it easy to investigate the initial variation in catalytic activity. The primary particle diameter was 15 nm.

A catalytic activity test was conducted using a fixed-bed reactor consisting of a vertical quartz-glass tube heated by an electric furnace. The methane decomposition rate was determined by measuring the gas composition at the reactor outlet. In addition, several CB samples at different carbon deposition states were prepared to investigate the change of surface properties during the reaction. A detailed description of the experimental setup and procedure can be found in Ref. [12].

Adsorption and desorption isotherms of nitrogen gas were measured for CB samples at 77 K by an automatic adsorption apparatus, Autosorb 1-MP (Quantachrome Instruments, USA), and the specific surface area and the pore size distribution were determined. Raman spectra were measured using a RMP-330 laser Raman spectroscopy system (JASCO, Japan). The wavelength of the excitation beam was 532 nm (frequency-doubled Nd:YVO_4 laser). To directly observe the surface structure evolving on CB, transmission electron microscope (TEM) observation was conducted using a JEM-2010F (JEOL, Japan).

3 Results and Discussion

The variation in the catalytic activity of SB905 was determined in a kinetic study. The following rate equation is used here:

$$r_{\mathrm{CH_4}} = k_p p_{\mathrm{CH_4}}^n \tag{1}$$

where $r_{\mathrm{CH_4}}$ is the methane decomposition rate per unit mass of CB, k_p is the rate constant, $p_{\mathrm{CH_4}}$ is the partial pressure of methane, and n is the reaction order. The degree of change in the surface property of the catalyst is represented by the mass ratio of deposited carbon to CB, $m_{\mathrm{dep}}/m_{\mathrm{CB}}$, where m_{dep} is the mass of deposited carbon and m_{CB} is the mass of the initial CB. The mass of deposited carbon m_{dep} is determined by using the amount of methane decomposed during the reaction. To include the influence of carbon deposition in the rate equation, the modification coefficient f, a function of the mass ratio $m_{\mathrm{dep}}/m_{\mathrm{CB}}$, is introduced in the expression of the rate constant as follows:

$$k_p = f(m_{\mathrm{dep}}/m_{\mathrm{CB}}) \cdot k_0 \cdot \exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \tag{2}$$

where k_0 is the pre-exponential factor, E_{a} is the activation energy, R is the universal gas constant, and T is the absolute temperature. In the catalytic activity test, the time variation of the methane decomposition rate was measured at 1173, 1233, and 1273 K. The amount of CB supplied in each test was 50 mg. The methane flow rate was 50 mL (STP)/min, and thus the volumetric hourly space velocity (VHSV) was 60 L/(h g_{CB}). Time-varying behavior was observed at all temperatures, and the time-varying features in the methane decomposition rate were characterized by the following three stages: (1) initial decrease, (2) transitory increase, and (3) secondary decrease. The mass ratios $m_{\mathrm{dep}}/m_{\mathrm{CB}}$ that determined the boundaries between stages (1) and (2) and between (2) and (3) were 0.23 and 0.79, respectively. In our previous study [12], we determined that the reaction order was 0.62, and the activation energy of 199–204 kJ/mol was nearly constant throughout the stages (1)–(3). The relative value of the modification coefficient was evaluated from the rate constant: $f/f_{(2–3)}$ equals $k_p/k_{p,(2–3)}$ at constant temperatures, where the subscript (2–3) denotes the value at the boundary between stages (2) and (3). A function can be determined by curve fitting with the relative modification coefficients evaluated at three temperatures, and therefore, this uniquely determined function is used in the following discussion to represent the variation in the catalytic activity.

The specific surface area was measured for nine CB samples at different carbon deposition states: their mass ratios $m_{\mathrm{dep}}/m_{\mathrm{CB}}$ were 0 (fresh), 0.06, 0.10, 0.21, 0.43, 0.70, 0.92, 1.16, and 1.93. The obtained specific surface area s was, by definition, based on the total mass of CB and deposited carbon. Therefore, the surface area exposed in the reaction field a was calculated as $a = s\,(m_{\mathrm{CB}} + m_{\mathrm{dep}})$. The relative value $a/a_{(2–3)}$ was compared to the relative modification coefficient, as shown in Fig. 1. There was no quantitative agreement between $f/f_{(2–3)}$ and $a/a_{(2–3)}$, although the increasing and decreasing tendencies in stages (2) and (3), respectively, were observed for both. This issue appears to originate from the fact that the number of active sites on CB is not simply proportional to the surface area, which suggests that the relationship between the number of active sites and surface area should be explored.

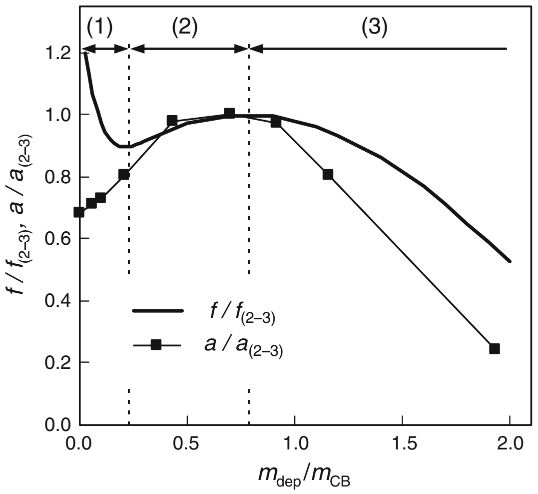

Fig. 1 Relative modification coefficient $f/f_{(2-3)}$ and relative specific surface area $a/a_{(2-3)}$ as a function of the mass ratio of deposited carbon to CB, $m_{\mathrm{dep}}/m_{\mathrm{CB}}$. The ranges of the three stages in the variation of the catalytic activity, (1)–(3), are indicated by *vertical dashed lines*

In general, the CB surface consists of nanosized graphitic sheets [13, 14]. Because the edge site of a graphitic sheet is considered to function as an active site for methane decomposition, its growth due to carbon deposition is expected during the reaction. To support this point, the TEM image of a catalyst sample at the mass ratio of 0.73, the latter part in stage (2), is shown in Fig. 2. Several graphitic sheets expanding outward from the CB surface can be observed. Therefore, a sheet-shaped structure is characteristic to the evolving surface structure on CB due to carbon deposition. Although some curved and folding graphitic sheets were observed, we can assume that the development of planar sheets is the dominant feature in surface structure evolution. With regard to sheet structure, the edge length L, where active sites are located, is proportional to the square root of the surface area A, i.e., $L \propto \sqrt{A}$. On the basis of this observation, we present two ways to approach the estimation of the variation in edge length. The first is to use the square root of the surface area $\sqrt{a/a_{(2-3)}}$ to represent the relative edge length. Although this calculation is simple and easy to handle, it does not contain detailed textural characteristics; the evolving surface structure is not uniform and the expanding graphitic sheets differ in size, as shown in Fig. 2. The second approach is, therefore, to use the surface area distribution obtained from the Barrett–Joyner–Halenda (BJH) pore size analysis of N_2 adsorption–desorption isotherms. We determined the surface area distribution $D_a(\tau)$ as a function of the pore diameter τ, estimated the edge length at each pore diameter using the relation $L \propto \sqrt{A}$, and calculated the total edge length as follows:

$$l = \int_{\tau_1}^{\tau_2} \sqrt{D_a(\tau)}\,d\tau \tag{3}$$

where τ_1 and τ_2 are approximately 2 nm and 160 nm, respectively. The exact integration range depends on each isotherm. The relative modification coefficient during stages (2) and (3) is in good agreement with the estimated relative edge length $\sqrt{a/a_{(2-3)}}$ and $l/l_{(2-3)}$, as shown in Fig. 3. This result supports the validity of considering that

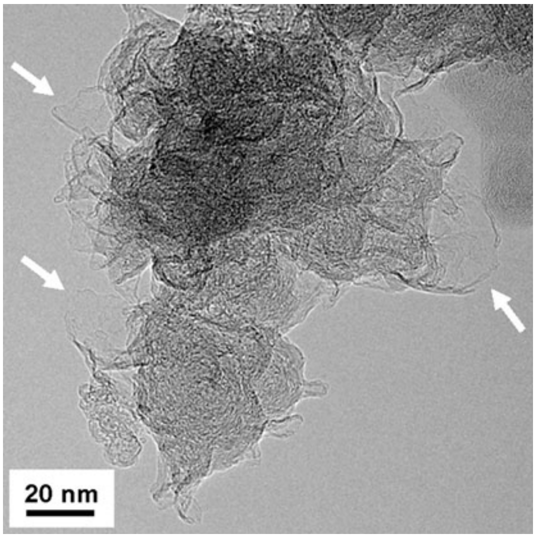

Fig. 2 TEM image ($m_{\mathrm{dep}}/m_{\mathrm{CB}} = 0.73$). The graphitic sheets exhibiting prominent expansion from the CB surface are indicated by *arrows*

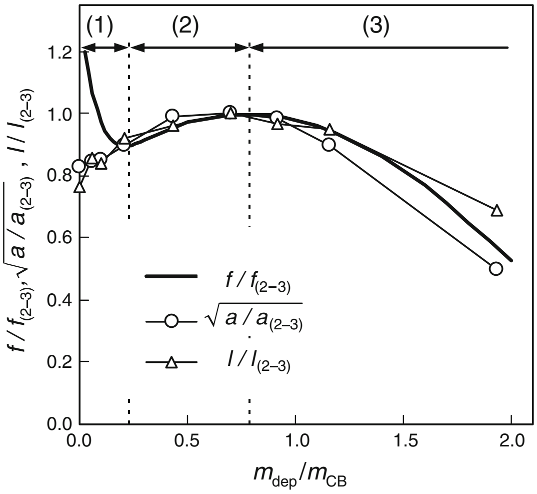

Fig. 3 Relative modification coefficient $f/f_{(2-3)}$ and estimated variations in the length of edge site $\sqrt{a/a_{(2-3)}}$ and $l/l_{(2-3)}$. The ranges of the three stages in the variation of the catalytic activity, (1)–(3), are indicated by *vertical dashed lines*

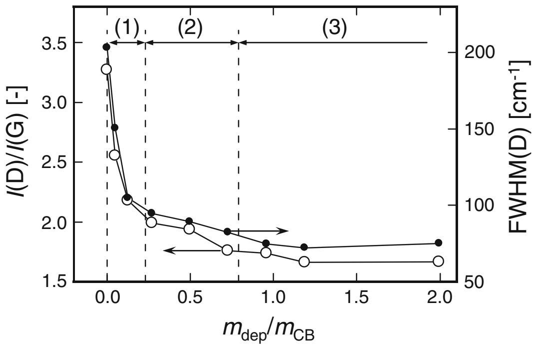

Fig. 4 Spectral parameters of the Raman spectra. The ranges of the three stages in the variation of the catalytic activity, (1)–(3), are indicated by *vertical dashed lines*

the variation in the catalytic activity originates from the evolving surface structure that is characterized by growing graphitic sheets due to carbon deposition in stages (2) and (3).

Next, we present an interpretation of the variation in catalytic activity during stage (1). From a surface structural viewpoint, the initial state of the CB surface is largely different from the states during stages (2) and (3). The initial surface is assumed to have many defects in the nanosized graphitic sheets [11]. These defects are active sites for methane decomposition, but they lose catalytic activity when a vacancy in a graphitic sheet is filled by produced carbon [15]. To the contrary, edge sites continue to function as active sites during the reaction. The decrease in the number of defects can be supported by the variation of Raman spectra. Raman spectra of carbonaceous materials are highly sensitive to the existence of disorder in a graphitic structure [16]. Figure 4 shows the spectral parameters in the Raman spectra. The intensity ratio of the D band to the G band and the full width at half maximum (FWHM) of the D band are both parameters representing the structural disorder [17, 18]. A remarkable decrease in those two parameters during stage (1) suggests that the number of defects in the graphitic sheets decreases and graphitic sheets grow in an ordered structure. On the basis of this observation, it is clear that the variation in catalytic activity during stage (1) is not directly correlated with the surface area itself. To express the variation in the number of defects, we need to use another variable; for instance, the surface density of an active site. Although a quantitative estimation of catalytic activity during stage (1) was not achieved here, the results strongly suggested that the activity decrease was caused by the loss of active sites due to carbon deposition.

We have demonstrated an approach to describe the variation in the catalytic activity of CB by considering the development of surface structure. The present results would be beneficial also from the viewpoint of synthesis of carbon spheres [19, 20].

4 Conclusions

The variation in the catalytic activity of CB during methane decomposition was investigated from the viewpoint of the number of active sites. The catalytic activity of color CB (SB905) was characterized by the three stages: (1) initial decrease, (2) transitory increase, and (3) secondary decrease. We demonstrated that the activity variation during stages (2) and (3) was in good agreement with the estimated variation in the edge length of graphitic sheets evolving from the CB surface. In addition, we proposed an interpretation regarding the decrease in catalytic activity during stage (1); i.e., the number of defects in graphitic sheets decreases and the graphitic sheets grow in an ordered structure. The discussion was supported by Raman spectra showing a remarkable decrease in structural disorder during stage (1). The present results provide evidence that the variation in catalytic activity originates from surface structural changes due to carbon deposition.

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References

1. Muradov N (2001) Catal Commun 2:89
2. Muradov N, Smith F, T-Raissi A (2005) Catal Today 102–103:225
3. Li Y, Li D, Wang G (2011) Catal Today 162:1
4. Hermes NA, Lansarin MA, Perez-Lopez OW (2011) Catal Lett 141:1018
5. Lee EK, Lee SY, Han GY, Lee BK, Lee TJ, Jun JH, Yoon KJ (2004) Carbon 42:2641
6. Lee SY, Kwak JH, Han GY, Lee TJ, Yoon KJ (2008) Carbon 46:342
7. Lee SY, Ryu BH, Han GY, Lee TJ, Yoon KJ (2008) Carbon 46:1978
8. Pinilla JL, Suelves I, Lázaro MJ, Moliner R (2008) Chem Eng J 138:301
9. Lázaro MJ, Pinilla JL, Suelves I, Moliner R (2008) Int J Hydrogen Energy 33:4104
10. Serrano DP, Botas JA, Guil-Lopez R (2009) Int J Hydrogen Energy 34:4488
11. Serrano DP, Botas JA, Fierro JLG, Guil-Lopez R, Pizarro P, Gomez G (2010) Fuel 89:1241
12. Kameya Y, Hanamura K (2011) Chem Eng J 173:627
13. Donnet JB, Bansal RC, Wang MJ (1993) Carbon black, 2nd edn. Marcel Dekker, New York
14. Ban S, Malek K, Huang C, Liu Z (2011) Carbon 49:3362
15. Huang L, Santiso EE, Nardelli MB, Gubbins KE (2008) J Chem Phys 128:214702
16. Jawhari T, Roid A, Casado J (1995) Carbon 33:1561
17. Ivleva NP, Messerer A, Yang X, Niessner R, Pöschl U (2007) Environ Sci Technol 41:3702
18. Al-Qurashi K, Boehman AL (2008) Combust Flame 155:675
19. Deshmukh AA, Mhlanga SD, Coville NJ (2010) Mater Sci Eng R 70:1
20. Nieto-Márquez A, Romero R, Romero A, Valverde JL (2011) J Mater Chem 21:1664