카본블랙 촉매의 다른 활성점상에서 아세틸렌 화학흡착 모형

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Models for acetylene chemisorption on different active sites on carbon black

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Introduction

Carbon black (CB) is widely used as reinforcing fillers in tires and mechanical rubber products, pigments, and conductive materials. In addition to these, application of carbon blacks (CBs) as a catalytic material has long been studied [1]. Among the carbon catalysts, CBs are interesting because many of them show stable and reasonably high activity in decomposition of methane despite carbon deposition ($CH_4 \rightarrow C(s) + 2H_2$), which may provide a promising catalytic process for CO_2-free hydrogen production [2,3]. Although numerous studies have been reported on the catalytic property of carbon materials and it is generally accepted that the active sites are located at the edges of graphene layers of graphite crystallites, the nature of its active sites has not yet been well elucidated. Moreover, quantitative determination of the active sites has not been well established.

Many studies of adsorption and desorption on carbon surfaces have been reported in the literature [4-6]. Recent works [5,6] have reported that the initial activity of various activated carbons and carbon blacks for CH_4 decomposition could be related to the concentration of COx complexes on the surface, but not to the surface area, which infers that the active sites are unsaturated sites formed by elimination of the surface complexes. However, the method in Refs. 5 and 6 is short of generality in that this method is only applicable to fresh carbon samples stored at room temperature.

Because C_2H_2 adsorbed on CB is considered as a plausible intermediate during the process of CH_4 decomposition [7], quantitative determination of the active sites on CB had recently been attempted by C_2H_2 adsorption with a pulse technique [8]. Various kinds of commercial CBs had been investigated under different adsorption temperatures, and fairly good linear relationships had been obtained between the activity and the amounts of C_2H_2 chemisorbed or consumed. A model for C_2H_2 adsorption on the armchair face had been proposed in the previous work [8]. As a continuing study of the previous work, schemes of C_2H_2 adsorption processes on the zigzag face and corners at the edges of graphene layers of CB were suggested in this work.

Main Results of the Previous Work [8]

Various CBs had been tested in the previous work [8]. They included rubber blacks(N103~N774, DC Chemical), color blacks(Hiblack series, Degussa) and conductive blacks(BP-2000, Cabot; and EC-600JD, Ketjen Black) with wide-ranging specific surface area.
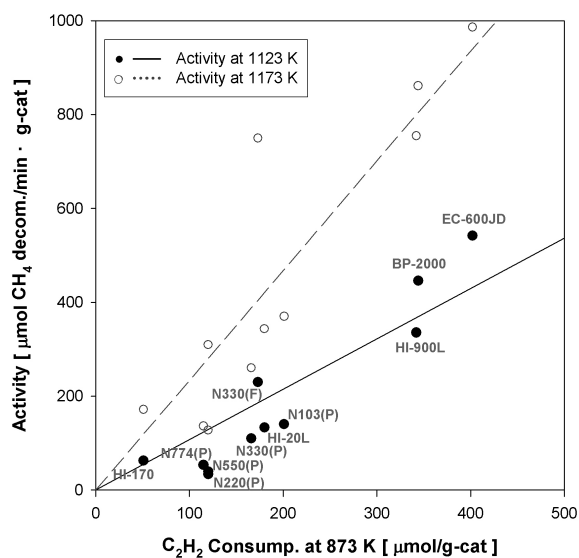

Fig 1. CH$_4$ decomposition rate vs. C$_2$H$_2$ consumption at 873 K per each pulse on various carbon blacks [8].

Since the C$_2$H$_2$ consumption per pulse became constant after several injections, the CH$_4$ decomposition activity was plotted against the constant C$_2$H$_2$ consumption at 873 K. As shown in Fig. 1, fairly good relationships were obtained. The constant C$_2$H$_2$ consumption at 873 K has been explained as follows on the armchair face. The hydrogen atoms on the chemisorbed C$_2$H$_2$ can be readily abstracted due to the high temperature [4] and generate new active sites. Only a part of the original active sites is occupied from a pulse, and then the unoccupied original sites as well as newly formed sites can be occupied from the next pulse (Fig. 2). Hence, number of active sites occupied from one pulse and the next pulse may be nearly the same. Thus, this scheme can explain the constant consumption of C$_2$H$_2$ from repeated pulses at 873 K. This process at 873 K may be called "the acetylene-chemisorption-hydrogen abstraction (ACHA) mechanism". In addition, this mechanism can equally be applicable to elucidation of the stable activity of CB for CH$_4$ decomposition since the number of active site is kept constant despite carbon deposition.

Proposed Models and Discussion

The chemisorption scheme on the active sites on the zigzag face combined with a corner is
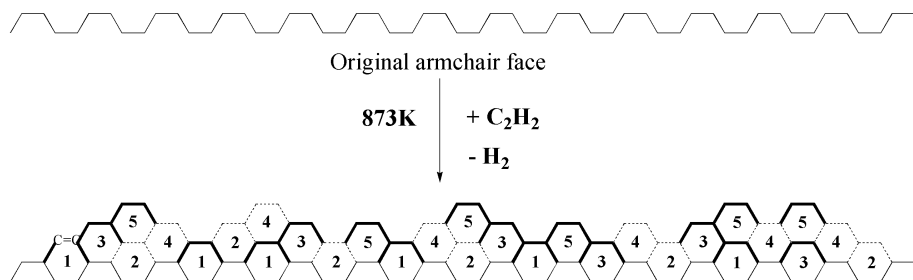

Fig 2. Proposed scheme for adsorption processes at 873 K on armchair face [8].

proposed in Fig. 3. A C_2H_2 molecule is first adsorbed on the zigzag structure and forms a 5-member ring. Another C_2H_2 molecule is adsorbed on the corner site and this molecule interacts with the 5-member ring, resulting in transformation into a 6-member ring which is located on the original corner atoms. This process is similar to that proposed in Ref. 7. As the H atoms on the 6-member ring are abstracted, two armchair structures are formed at both the right and left sides of the 6-member ring, which are newly formed active sites owing to the H abstraction. Similarly to the processes shown in Fig. 2, two C_2H_2 molecules can adsorb on the two armchair structures and form two 6-member rings with new armchair structures and active sites. These steps can continue repeatedly and thus the graphene layer grows. It is notable that the edge of the grown layer looks similar to that of the original layer.

   On the zigzag-only face, two C_2H_2 molecules are first adsorbed and form a 7-member ring. As the third C_2H_2 molecule is adsorbed on the adjacent site and interacts with the 7-member ring, with the subsequent rearrangements shown in Fig. 4 a 6-member ring and an adsorbed -CH=CH-CH$_2$· intermediate are formed. This intermediate rotates to the other side and forms another 6-member ring. When H atoms on the two 6-member rings are abstracted, two armchair structures are formed at the right side of one 6-member ring and at the left side of the other 6-member ring, respectively. Once the armchair structures are formed, the next steps can proceed in the same way as described above and the graphene layer grows.

   Likewise to the scheme in Fig. 2 [8], the above two schemes also show that the number of the active sites can be maintained nearly constant during the growth of the graphene layer by the carbon deposition. Therefore, these schemes are consistent with the observed stable activity of CBs in CH_4 decomposition. However, the scheme in Fig. 2 would occur the most easily owing to the fewest steps while the scheme in Fig. 4 would be the most difficult to occur.
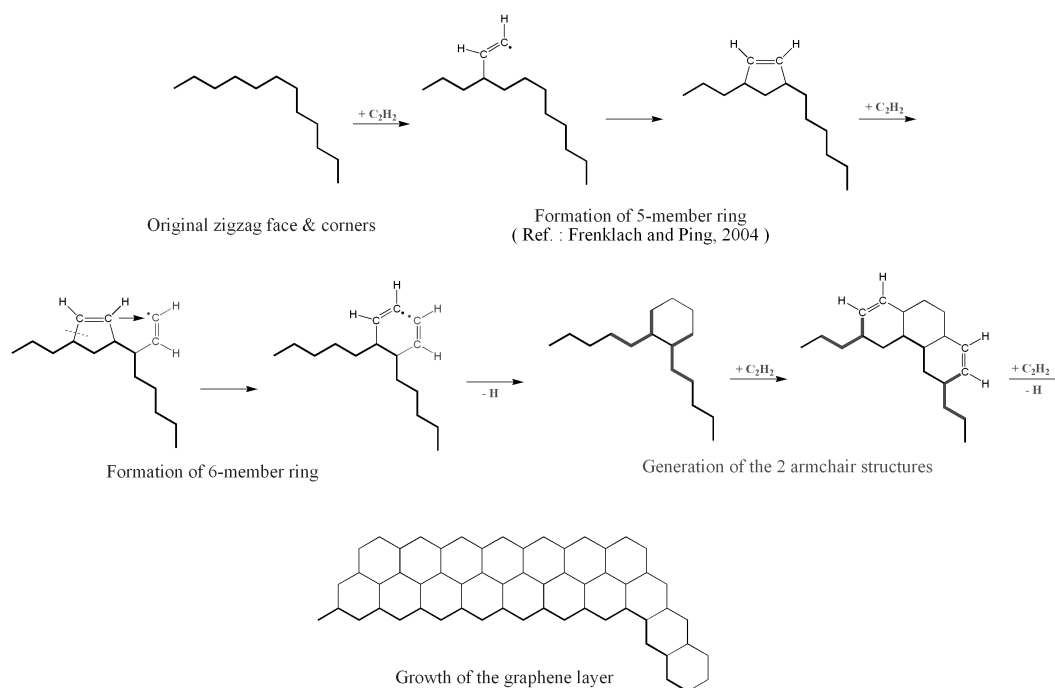

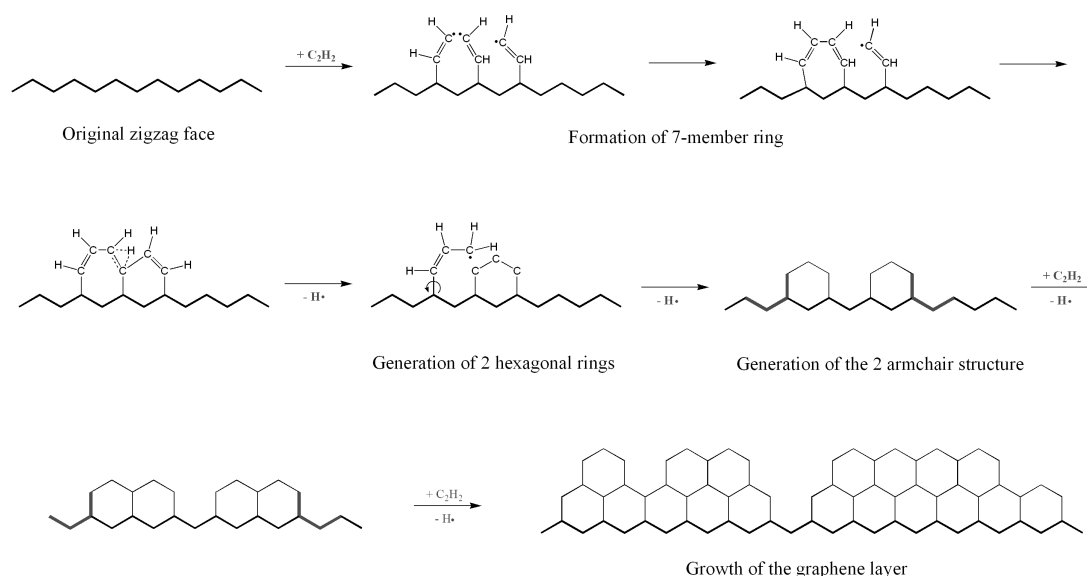Fig 3. Proposed scheme for adsorption processes at 873 K involving zigzag face & corners.

Fig. 4. Proposed scheme for adsorption processes on zigzag face

Conclusions

Based on the C_2H_2 adsorption study through a pulse study, which showed constant C_2H_2 consumption on CBs at 873 K, the nature of the active sites on the edges of graphene layers was discussed. In addition to the scheme on the armchair face, schemes were proposed for C_2H_2 chemisorption on the zigzag face combined with corners and on the zigzag-only face. The adsorbed C_2H_2 molecules first form 5- or 7-member rings and these rings are eventually transformed into 6-member rings with the armchair structures at their sides. Then, one C_2H_2 molecule adsorbs on one armchair structure and forms a hexagonal ring. These steps continue repeatedly and the graphene layer grows. The proposed schemes show that the number of active sites can be maintained constant during the carbon deposition, which is consistent with the observed stable activity of CBs in CH_4 decomposition.

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