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카본블랙 활성점 연구를 위한 아세틸렌 화학흡착

이 상엽, 곽 정훈, 윤 기준*

C_2H_2 chemisorption for characterization of carbon black active sites

Sang Yup Lee, Jung Hun Kwak, Ki June Yoon*

Key words : carbon black, active site, characterization, chemisorption, acetylene

Abstract : In order to characterize the catalytically active sites on carbon black, acetylene chemisorption had been examined recently at 773 and 873 K by using a pulse technique. As the injection was repeated at 773 K, the adsorbed amount gradually decreased and eventually the adsorption did not occur any more. At 873 K a constant amount of C_2H_2 was consumed repeatedly after several injections. Good linear relationships were obtained between the methane decomposition rate at 1123 or 1173 K and the cumulative acetylene adsorption at 773 K or the constant acetylene consumption at 873 K. Reasonable models for the associative acetylene chemisorption at 773 K and the constant acetylene consumption at 873 K on the armchair face at the edges of graphene layers were proposed. The constant consumption may be explained by the "C_2H_2-addition-hydrogen- abstraction (CAHA)" mechanism.

1. 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. In this area of application, an interest is increasing in decomposition of light alkanes over carbon catalysts for CO_2-free hydrogen production. 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. 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, defects or discontinuities 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. This situation is markedly contrasted with the well-known chemisorption on metals or titration on solid acid catalysts. In this work, quantitative determination of the active sites on CB was attempted through C_2H_2 adsorption with a pulse technique; the pulse technique can control the adsorbed amount in each pulse, which is considerably smaller than saturation. Various kinds of commercial CBs were investigated under different adsorption temperatures.

2. Experimental

The CBs tested in this work are listed in Table

1) 성균관대학교 화학공학과
E-mail : sddal@hanmail.net
Tel : (031)290-7266 Fax : (031)290-7272
2) 성균관대학교 화학공학과
E-mail : sbn152@skku.edu
Tel : (031)290-7266 Fax : (031)290-7272
3) 성균관대학교 화학공학과 교수
E-mail : kijyoon@skku.edu
Tel : (031)290-7244 Fax : (031)290-7272

1. All the rubber blacks except one were in pelletized type (P); for N330, fluffy type (N330(F)) in addition to N330(P) was tested.

Table 1. Carbon blacks tested

Use	Carbon black [a]	Manufacturer	Particle diameter (nm)	Surface area [b] (m^2/g)
Rubber black	DCC N103 (P)	DC Chemical, Korea	11-19	140 (160) [c]
	DCC N220 (P)		20-25	120
	DCC N330 (P)		26-30	81 (70) [c]
	DCC N330 (F)		26-30	81 (77) [c]
	DCC N550 (P)		40- 48	42 (40) [c]
	DCC N774 (P)		61-100	29 (29) [c]
Color black	HI-900L (F)	Degussa, Germany	15	300 (256) [c]
	HI-20L (F)		28	86
	HI-170 (F)		58	23
Conductive black	EC-600JD (F)	Ketjen Black, Japan	~ 15	1270 (1369) [c]
	BP-2000 (P)	Cabot, US	~ 15	1500 [c]

a) : (F) for fluffy and (P) for pelletized type
b) : data from the suppliers
c) : measured

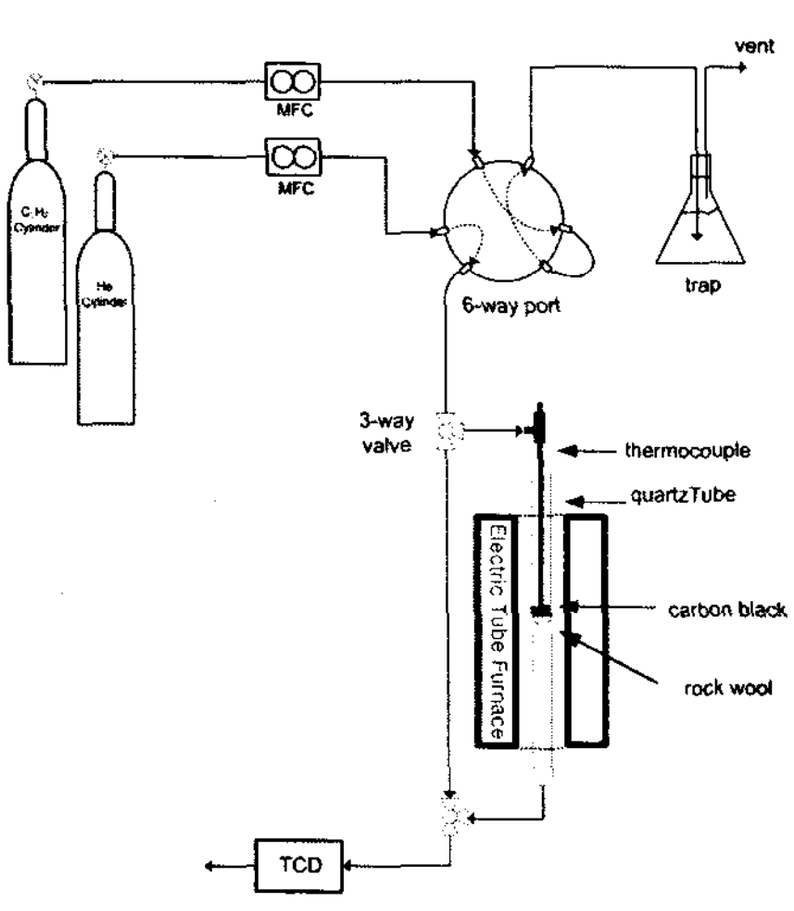

Fig. 1. Schematic diagram of adsorption apparatus for pulse injection.

The acetylene adsorption on CB was carried out in a conventional pulse experiment apparatus shown in Fig. 1 [1]. By using a 6-port sampling valve, pulses of acetylene (0.5 cm^3 at RT each) were injected to a stream of carrier gas (He, 30 sccm). The carrier gas flowed through a temperature -controlled quartz tube (8 mm I.D.) in which the CB sample was placed. Before the adsorption experiment, the sample was pre-heated at 1173 K for 0.5 h under the He flow in order to remove the impurities and CO_x complexes on the surface or to make the sample identical to that under the CH_4 decomposition temperature. After the desired adsorption temperature (673-873 K) was reached, pulses of C_2H_2 were injected and the amounts of C_2H_2 coming out of the tube were measured by using a TCD and calibrated data.

3. Result and discussion

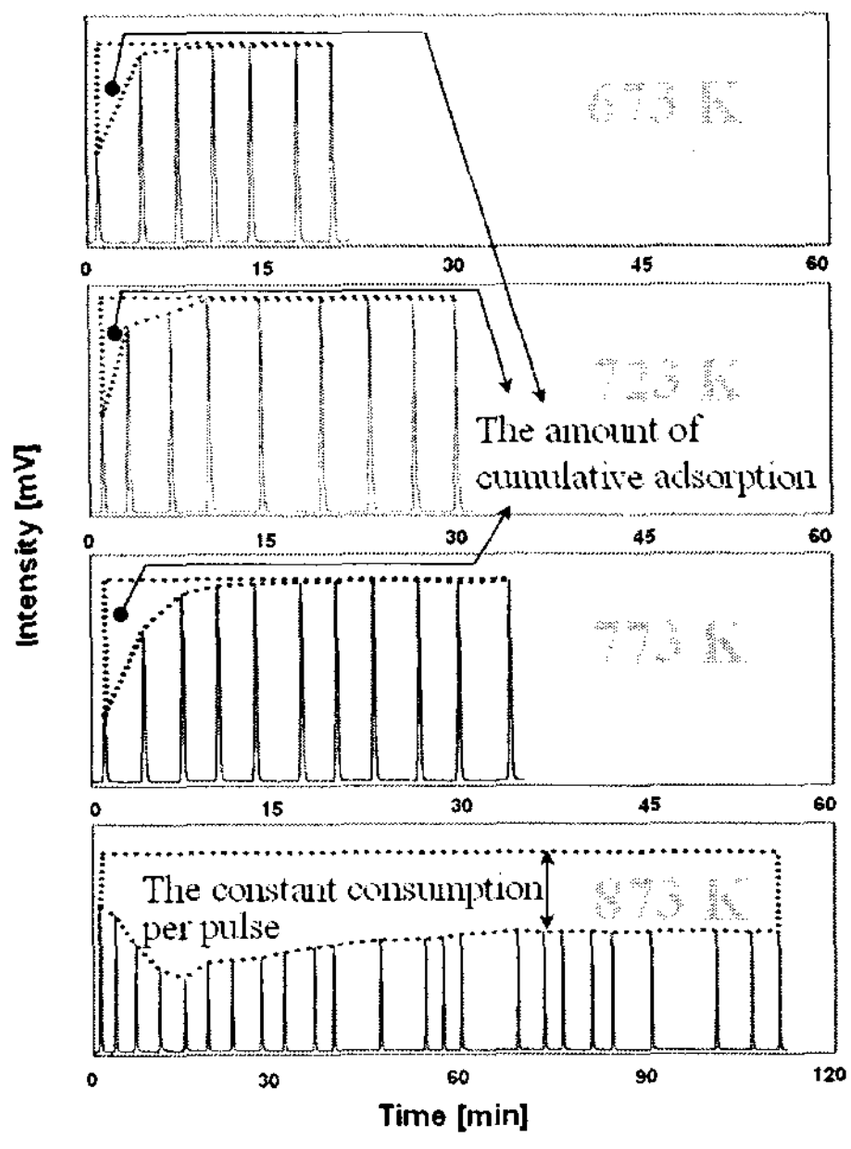

Fig. 2. TCD responses from acetylene pulse injections for N330(P) at different adsorption temperatures.

The responses from C_2H_2 pulse injections for N330(P) is shown in Fig. 2 as the representative raw data. At 673 K a part of the injected C_2H_2 was observed to adsorb at the first pulse; through the next pulses the adsorbed amount decreased rapidly and eventually the adsorption did not take place any more, which suggests that the surface was saturated. Therefore, we regarded the cumulative amount up to this point as "the amount of adsorption saturation"at the specified temperature. At 773 K the trend was similar, but the amount of adsorption saturation

increased considerably compared with that at 673 or 723 K. This is a well-known phenomenon, so-called "activated chemisorption", which means that the rate of adsorption by forming chemical bonds increases with temperature according to the activation energy of adsorption, resulting in increase of the amount adsorbed with temperature in a usual, reasonable period of time [2]. At 773 K and below, the hydrogen atoms in the adsorbed C_2H_2 do not seem to be abstracted due to the low temperature, and hence further adsorption of C_2H_2 on the adsorbed species may not be possible. At 873 K, a quite different behavior from that at the lower temperatures was observed. The amount of C_2H_2 disappeared for each pulse gradually increased for a few pulses and then decreased, and finally, after around 10-30 injections depending on the sample, reached a nearly constant value. This value is ca. 45% on the average when compared with the amount of adsorption saturation at 773 K. It is considered that the hydrogen atoms in the adsorbed C_2H_2 can be more easily abstracted due to the high temperature and generate new active sites. The process at 873 K may be called "the C_2H_2-addition-hydrogen-abstraction(HACA) mechanism" [3].

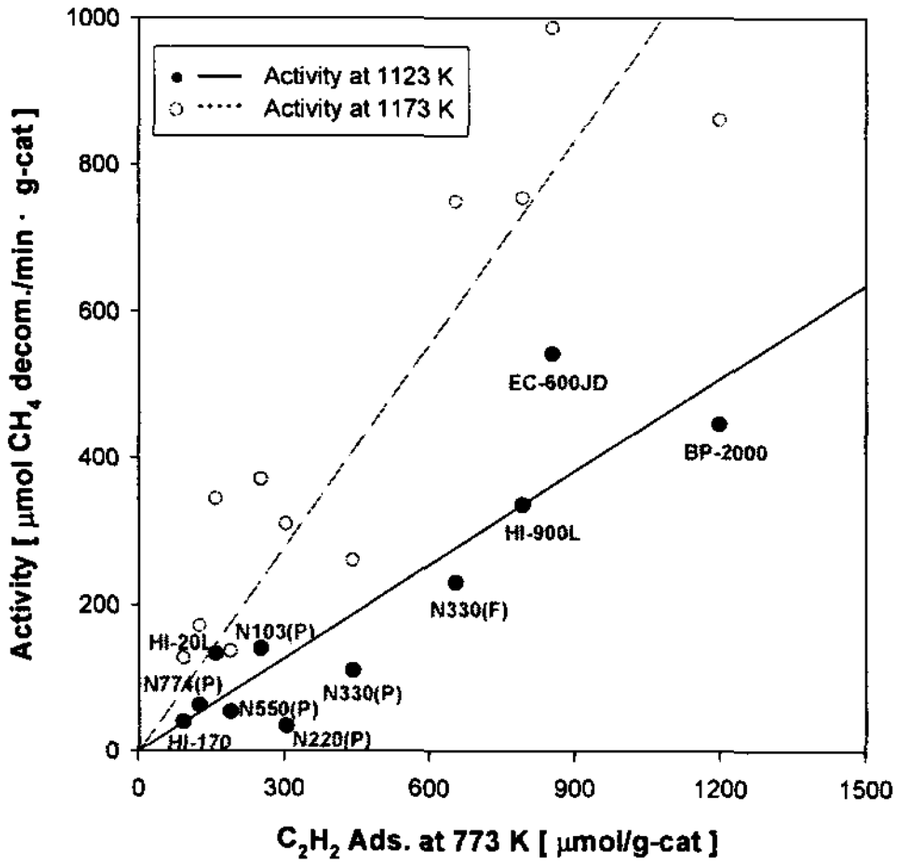

Fig. 3. CH_4 decomposition rate vs. cumulative C_2H_2 adsorption at 773 K on various carbon blacks (correlation coefficient r^2 and slope [mol CH_4/mol C_2H_2·min] = 0.806 and 0.424 for 1123 K data 0.792 and 0.924 for 1173 K data).

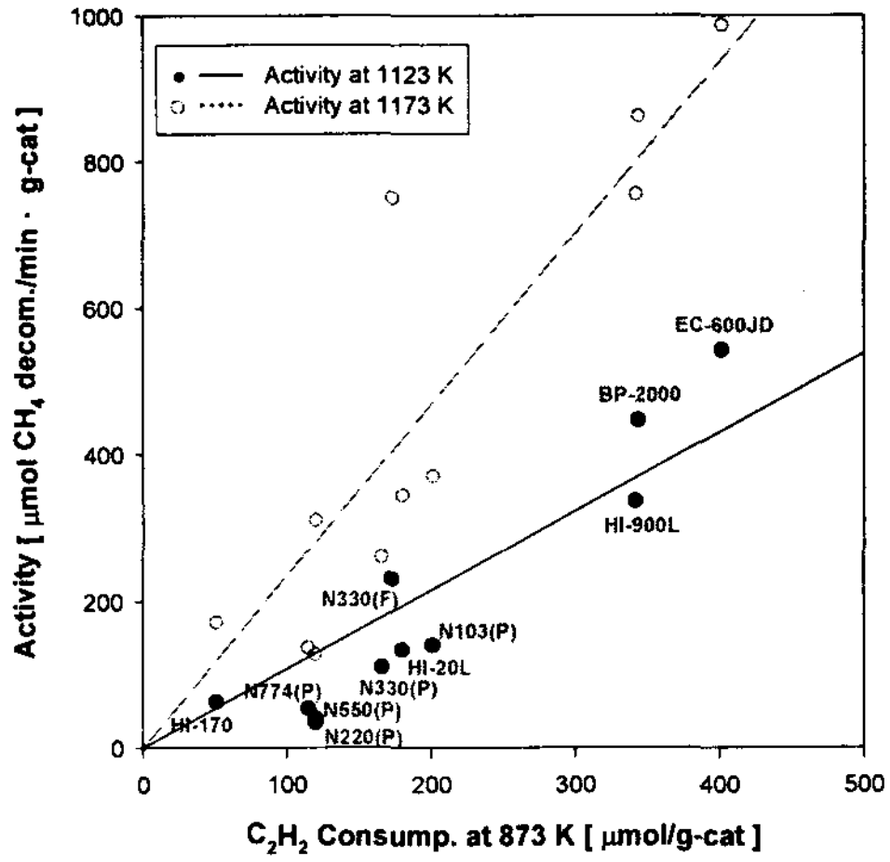

Fig. 4. CH_4 decomposition rate vs. constant C_2H_2 consumption at 873 K per pulse on various carbon blacks (correlation coefficient r^2 and slope [mol CH_4/mol C_2H_2·min] = 0.814 and 1.074 for 1123 K data; 0.795 and 2.338 for 1173 K data).

All the CBs in this work showed stable activity for CH_4 decomposition at a temperature range from 1073 to 1223 K as reported in the previous articles [4]. The stable activity at 1123 K or 1173 K for each CB is plotted against the amount of adsorption saturation at 773 K and the constant amount of C_2H_2 consumed at 873 K. As shown in Figs. 3 and 4, good linear correlations were obtained between the activity and either the data at 773 K or those at 873 K; all these plots show almost equal goodness-of-fit. Hence, these results may be used for the determination or as a measure of the number of active sites.

4. Conclusion

In this study, the active site, the most important factor determining the catalytic effect of CB, was investigated through acetylene adsorption. C_2H_2 molecules adsorbed at 773 K form hexagonal rings and retain their hydrogen atoms and thus prevent additional adsorption onto them, while those at 873 K also form hexagonal rings but their hydrogen atoms are abstracted to form new active sites, which thus allow further adsorption of C_2H_2. The amount

of adsorption saturation at 773 K and the amount of constant consumption at 873 K were well correlated with activity of CH_4 decomposition, which can be used for the determination of active sites on CB.

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