

## 표면개질 된 활성탄의 메탄흡장 특성

윤 석민<sup>1)</sup>, 김 주완<sup>2)</sup>, 조 원준<sup>3)</sup>, 김 영호<sup>4)</sup>, 이 영석<sup>5)</sup>

### Characteristics of methane sorption in surface modified activated carbon

Seokmin Yun, Juwan Kim, Wonjun Jo, Youngho Kim, Youngseak Lee

**Key words** : Activated carbon(활성탄), methane adsorption(메탄흡착), surface modification (표면개질), porosity(다공도)

**Abstract** : In this study, methane gas adsorption ability of activated carbon (AC) with surface functional group effect, adsorbed methane amount was evaluated after nitric acid and ureatreatment of AC surface. Specific surface area and pore distribution of AC were studied through nitrogen adsorption isotherm at 77 K. Micro pore volume was calculated through H-K method. Adsorbed methane amount was evaluated through volume method at room temperature by using auto adsorption apparatus. Adsorbed methane amount of AC was found to increase with to specific surface area increase. Correlation proposed between the methane adsorption amount and surface nature indicates that the surface nature plays an important role on the adsorption amount at a given temperature.

#### subscrip

AC : activated carbon  
NG : natural gas  
NGV : natural gas vehicle  
SSA : specific surface area

### 1. Introduction

The interest in NG as a possible alternative for transportation fuel has grown considerably since 1980s.

<sup>(1)</sup> Many research works have been attempted to make NGVs competitive with current ones using conventional fuels. The reason is that NG is much cheaper than conventional petroleum-based gasoline natural abundance and especially for its clean burning. <sup>(2,3)</sup> Many

researchers reported their results on adsorption storage of NG, especially its major component of methane in different porous carbonaceous materials, including activated carbon, carbon nanotubes and activated carbon fibers with different specific surface areas and pore sizes.

<sup>(4)</sup> Activated carbon has developed micropore, created by activation process. During activation, functional groups

are introduced on carbon surface. In general, gas adsorption capacity depends on not only porosity of adsorbent, but also their surface nature. Surface nature of activated carbon can be changed by various modifications, such as chemical treatment, heat treatment, fluorination and plasma treatment etc. We assume that interactions between surface of adsorbent and gas molecules are changed by surface modifications.

In this study, we used AC modified by chemical treatment using nitric acid and urea for methane storage. Experimental study was conducted in terms of adsorption isotherm of N<sub>2</sub> at 77K. The adsorption isotherms of

- 
- 1) 충남대학교 공업화학과  
E-mail : iceyun@hanmail.net  
Tel : (042)821-7689 Fax : (042)822-6637
  - 2) 충남대학교 나노기술학과  
E-mail : juwany79@hotmail.com  
Tel : (042)821-7689 Fax : (042)822-6637
  - 3) 한국가스공사 연구개발원 DME연구개발  
E-mail : wicho@kogas.re.kr  
Tel : (032)810-0321 Fax : (032)810-0330
  - 4) 충남대학교 정밀응용화학과  
E-mail : yh\_kim@cnu.ac.kr  
Tel : (042)821-7687 Fax : (042)822-6637
  - 5) 충남대학교 정밀응용화학과(교신저자)  
E-mail : youngslee@cnu.ac.kr  
Tel : (042)821-7007 Fax : (042)822-6637

methane from 263K to 298 were investigated. The relationships between the adsorption capacity with respect to temperature and the changed surface nature and SSA of the ACs are discussed.

## 2. Experimental

### 2.1 Sample preparation

Three carbon samples were investigated in this study for methane storage. The raw materials for surface modification were coconut based granular type activated carbons, purchased from Yu-rim carbon chemical Co, Korea. Before surface modification, the as such received activated carbon was washed with distilled water to remove impurities, and dried in oven at 383 K for 24 h. and named as R-AC. The R-AC was then chemically treated by nitric acid and urea. In order to introduce oxygen functional groups, activated carbons were modified in 1 M nitric acid solution at 373 K for 1 h. After acid treatment, residual nitric acid was removed by distilled water washing and dried at 383 K for 24 h. Acid treated activated carbon was marked as A-AC. Urea can endow with basic functional groups to surface of activated carbon. 1 M urea solution was prepared, and R-AC was impregnated in urea solution for 6 h by mixing in shaking machine. Heat treatment of urea-treated activated carbon was carried out in tube furnace at 723 K for 1 h. This sample was named as U-AC.

### 2.2 Analysis

The nitrogen adsorption isotherms of the three activated carbons were measured on ASAP 2020 (Micromeritics Ins. Corp.) at liquid nitrogen temperature. All samples were degassed at 423 K for 3 h before analysis. The specific surface area and pore structure were obtained by Langmuir equation and Horvath-Kawazoe method. The changes of surface functional groups and total acidity of activated carbons as modification were investigated by Boehm titration. One gram activated carbon was mixed with 100 ml 0.1 N  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  solution, respectively. The flasks were covered with parafilm and shaken for 48 h at 200 rpm. The solutions were filtered by membrane filter ( $\text{Ø} = 0.45 \mu\text{m}$ ) and titrated with 0.1 N  $\text{HCl}$  solution. Total basicity of samples was obtained by  $\text{NaOH}$  titration. The method was same with Boehm titration except that 0.1 N  $\text{HCl}$  solution mixed with samples and titrated with 0.1 N  $\text{NaOH}$  solution. Further, pH change of samples was measured.

To determine the contents of C, H, O and N in activated carbons used in this study, elemental analysis was carried out with EA1110 (CE Instrument, Italia).

## 2.3 Methane adsorption

Methane adsorption isotherms were obtained by volumetric apparatus (Autosorb-1, Quantachrome, USA) at 263, 273 and 298 K.

## 3. Results and discussion

### 3.1 Characterization of ACs by adsorption isotherm of $\text{N}_2$ at 77K

Nitrogen adsorption isotherms at 77 K on the three activated carbon samples are shown in Fig. 1. Detailed information on the textural properties of the samples is presented in Table 1. All of isotherms of samples represent type I (Langmuir type) in IUPAC classification. In case of physical adsorption, Langmuir isotherm pattern is suitable for methane storage applications indicates that the pores are microporous. (See, Fig.1 and Table 1)

Table 1. Pore textural characteristics of activated carbons

Sample	<sup>a</sup> S ( $\text{m}^2/\text{g}$ )	<sup>b</sup> $V_t$ ( $\text{cm}^3/\text{g}$ )	<sup>c</sup> $V_m$ ( $\text{cm}^3/\text{g}$ )	<sup>d</sup> $W_a$ (nm)
R-AC	1249	0.46	0.44	0.74
A-AC	1245	0.47	0.44	0.74
U-AC	1310	0.48	0.46	0.73

a: Langmuir specific surface area

b: Total pore volume at  $P/P_0 = 0.98$

c: Micropore volume by H-K method,

d: Average pore width =  $2V_t/S$

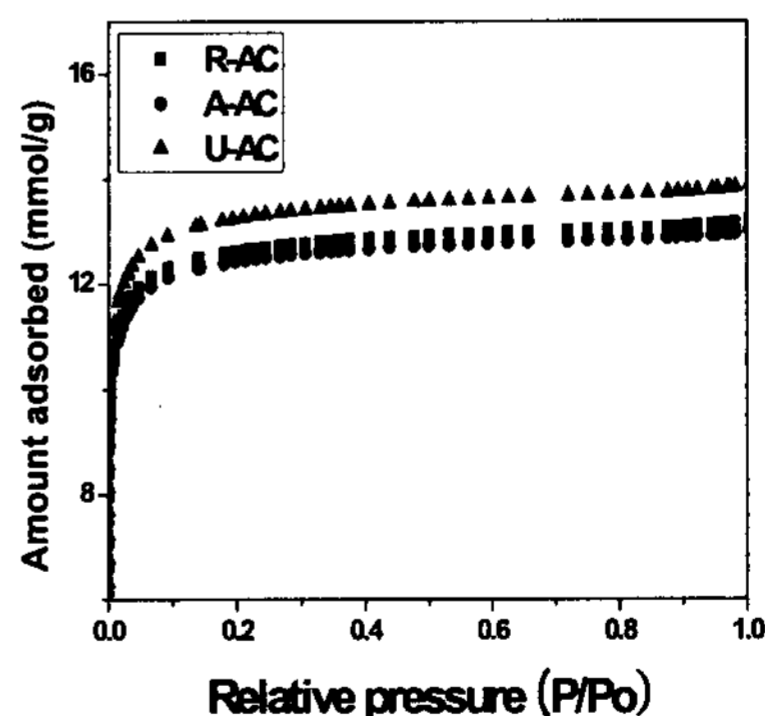


Fig. 1. Nitrogen adsorption isotherm of activated carbons.

### 3.2 Boehm Titration

Table 2 furnishes the Boehm titration results for the surface properties of the ACs used in this study. It can clearly be seen that the chemical treatments influence the pH, acid-base surface values of the ACs. This seems to

be a consequence of the changes of functional group of the chemically treated ACs. As presented in Table 2, the pH, base surface value of the A-AC sample show prominent changes compared with R-AC and U-AC. This result indicates that a strong acid–base reaction is occurred on the original base-like carbon surface. By contrast, U-AC shows an increased base value.

**Table 2. pH and acid-base values of activated carbons**

Samples	pH	Total acidity (meq/g)	Total basicity (meq/g)
R-AC	7.66	0.86	0.31
A-AC	4.34	2.04	0.11
U-AC	8.58	0.57	0.54

### 3.3 Elemental analysis

Table 3 lists the different elemental analysis results of activated carbons treated by various methods. Decrease in carbon content with corresponding increase in oxygen value of AC is noticed may be due to introduction of oxygen by HNO<sub>3</sub>.

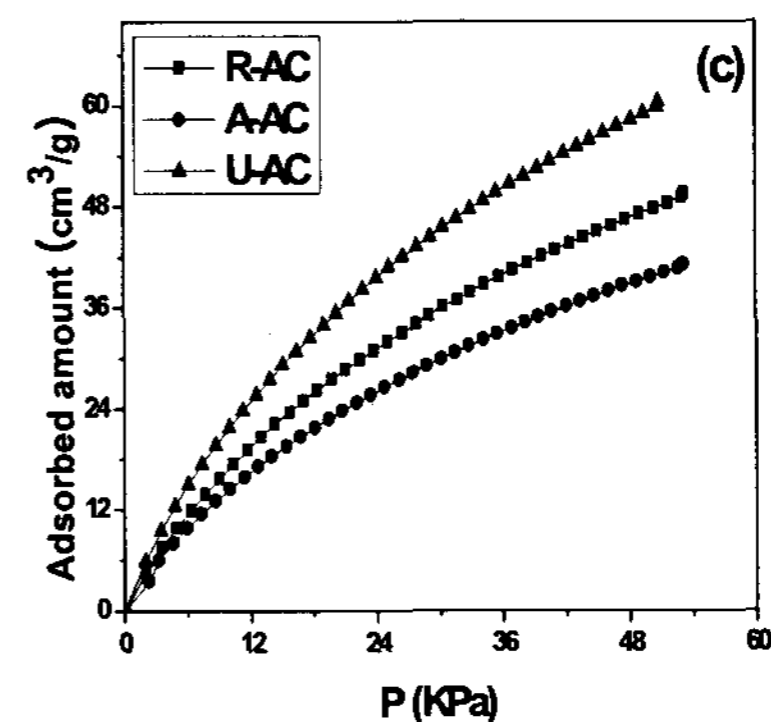
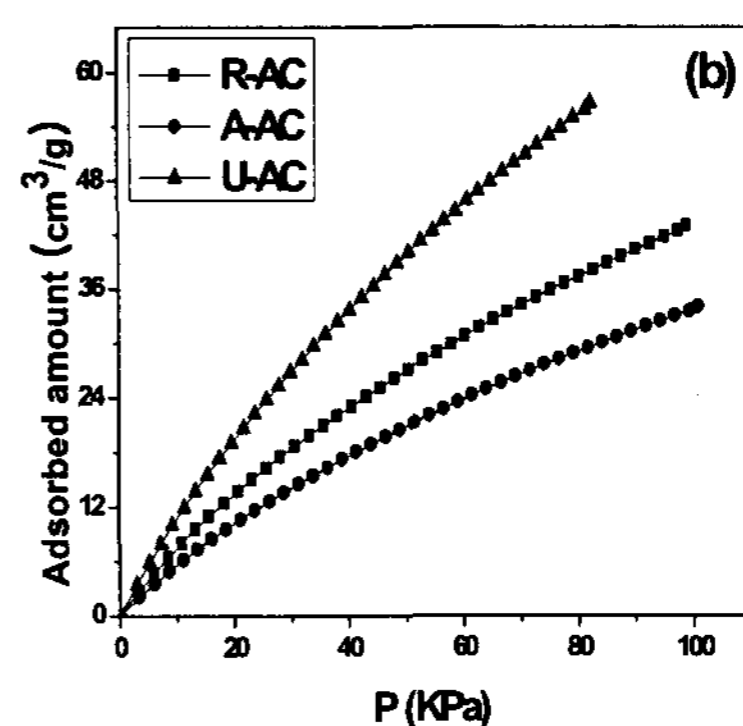
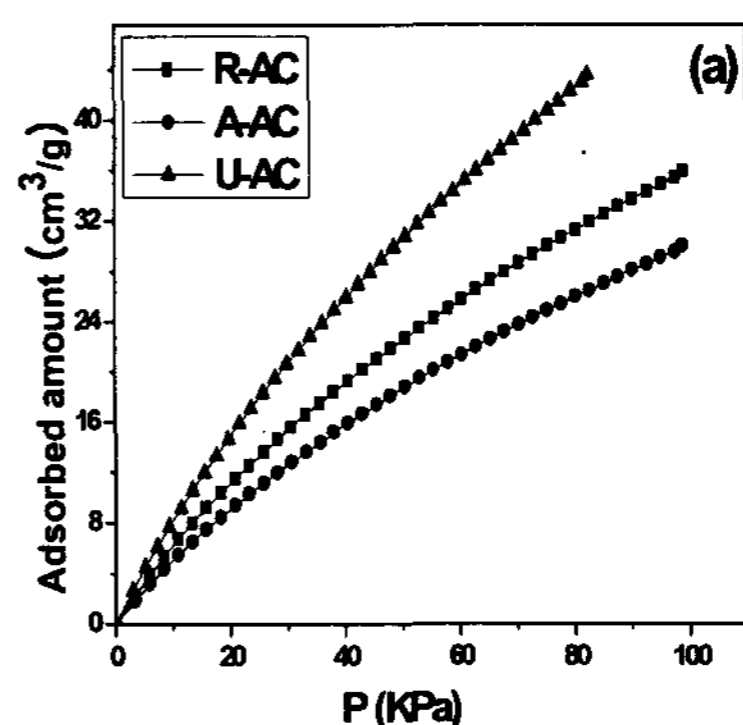
**Table 3. Elemental analysis of activated carbons**

Sample	C (wt%)	H (wt%)	N (wt%)	O <sup>a</sup> (wt%)
R-AC	93.6	0.5	0.01	5.89
A-AC	88.2	0.6	0.43	10.77
U-AC	94.3	0.2	0.27	5.23

a: The oxygen is assessed by difference

### 3.4 Methane adsorption isotherms on ACs

Fig. 2 illustrates methane adsorption isotherms of samples at various temperatures. From the experimental results, it is found that the methane adsorption amount increases monotonically with pressure at the three temps studied, which is quite similar to the Langmuir isotherms given by activated carbon. <sup>(3)</sup> Methane adsorption amounts of U-ACs were the largest at all temperatures whereas A-ACs was the least of samples on all of the adsorption temperature. This result suggests that the methane adsorption amount depend strongly on surface nature. U-ACs has small acid and large basicity. To investigate the relations of surface nature and methane adsorption amount, we calculated the adsorbed amount of methane versus total acidity and basicity, and depicted in Fig. 3, respectively. As the correlation coefficient in Fig. 3, the amount of methane adsorption is more dependent on basicity than acidity onto ACs. The increase in oxygen of AC leads to less storage for methane.



**Fig. 2. Methane adsorption isotherm of activated carbons: (a) 298 K, (b) 273 K, and (c) 263 K.**

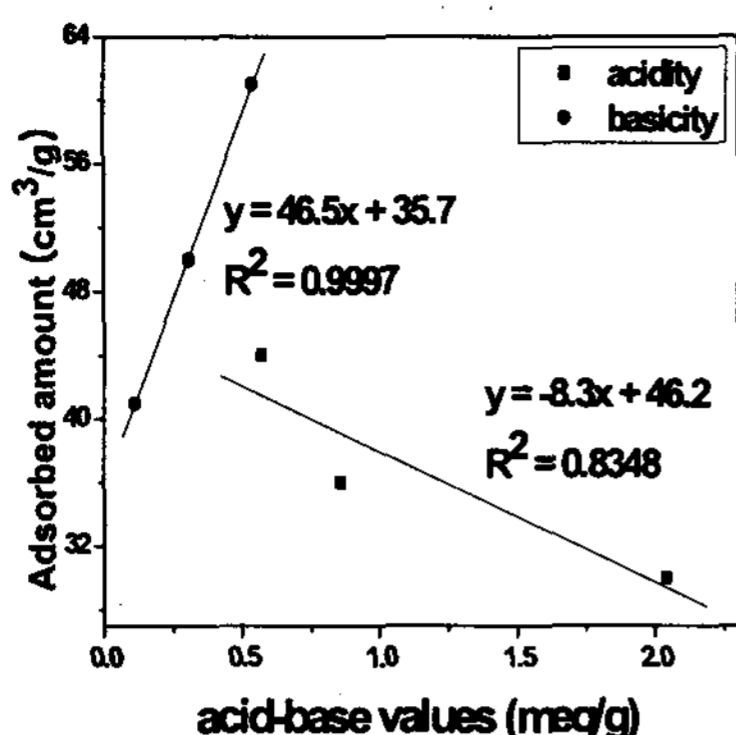


Fig. 3. Amount of methane adsorbed according to acid-base values.

#### 4. Conclusions

Adsorbed methane amount was evaluated through volume method at room temperature by using auto adsorption apparatus. Adsorbed methane amount of AC was increased according to specific surface area. Correlation proposed between the methane adsorption amount and surface nature indicates that the surface nature plays an important role on the adsorption amount at a given temperature. The amount of methane adsorption is more dependence total basicity than acidity.

#### Acknowledgment

This work was supported by the Korea Research Foundation Grant funded by the Korean government (MOEHRD, Basic Research Promotion Fund) (KRF-2005-005-J00403).

#### References

- [1] D. Lozano-Castello, J. Alcaniz-Monge, M.A. de la Casa-Lillo, D. Cazorla-Amoros and A. Linares-Solano, 2002, "Advances in the study of methane storage in porous carbonaceous materials," J. of Fuel, Vol. 81, pp. 1777-1803.
- [2] J. Alcaniz-Monge, M.A. Dela Casa-Lillo, D. Cazorla-Amoros and A. Linares-Solano, 1997, "Methane storage in activated carbon fibres," J. of Carbon, Vol. 35, pp. 291-297.
- [3] X. Shao, W. Wang, X. Zhang, 2007, "Experimental measurements and computer simulation of methane adsorption on activated carbon fibers," J of Carbon, Vol. 45, pp. 188-195.

- [4] X. R. Zhang and W.C. Wang, 2002, "Methane adsorption in single-walled carbon nanotubes arrays by molecular simulation and density functional theory," J of Fluid Phase Equil, Vol. 194, pp. 289-295.