

## Influence of Amine Grafting on Carbon Dioxide Adsorption Behaviors of Activated Carbons

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In this work, the amine grafting treated activated carbons were studied for carbon dioxide adsorbent. The surfaces of activated carbon were functionalized by 3-chloropropyltrimethoxysilane, which was subsequently grafted with amine compounds tris-(2-aminoethyl)amine and tri-ethylenetetramine and subjected to comparison. The surface functional groups of the amine grafted activated carbons were characterized using XPS. The textural properties of the amine grafted activated carbons were analyzed by  $N_2/77$  K isotherms. Carbon dioxide adsorption behaviors of the amine grafted activated carbons were examined via the amounts of carbon dioxide adsorption at 298 K and 1.0 atm. From the results, tris-(2-aminoethyl)amine grafted activated carbons showed  $43.8 \text{ cm}^3/\text{g}$  of carbon dioxide adsorption while non-treated activated carbons and tri-ethylenetetramine grafted activated carbons showed less carbon dioxide adsorption. These results were thought to be due to the presence of isolated amine groups in the amine compounds. Tris-(2-aminoethyl)amine grafted activated carbons have basic features that result in the enhancement of adsorption capacity of the carbon dioxide molecules, which have an acidic feature.

**Key Words:** Activated carbons, Carbon dioxide, Adsorption, Tri-(2-aminoethyl)amine, Tri-ethylenetetramine

### Introduction

Global warming, as studied over the last 50 years, results from human activities and is prospected to continue throughout the present century.<sup>1</sup> Carbon dioxide generated from fossil fuel-fired power plants is a major contributor to global warming. Although a future transition to new, renewable energy is required to slow the accumulation of carbon dioxide in the atmosphere, there is a growing understanding that in the meantime fossil fuel will continue to increase the carbon dioxide levels in the atmosphere. For this reason, there are many efforts to limit the emissions of carbon dioxide today.

Usually, there are three steps in the controlling of carbon dioxide emissions. These are separation, transportation, and sequestration.<sup>2</sup> From these steps, the main point for the control of carbon dioxide emissions is the removal of carbon dioxide from flue gas by a gas separation process. The separation cost of carbon dioxide constitutes a majority of the total cost.

Available technologies for carbon dioxide separation from flue gas include absorption, adsorption, and membrane separation.<sup>3</sup> From these available technologies, the cost-effectiveness should also be considered in all its aspects. When carbon dioxide separation is applied to the flue gas in power plants, absorption using aqueous amine results in corrosion and a high regeneration energy consumption problem. Also, in the case of membrane technology, the cost of the membrane separator is very high.

Adsorption separation has advantages over other processes, including low investment, low energy cost for regeneration, and adequate selectivity of sorbent. For carbon

dioxide adsorption, many researches are in progress using such sorbents, which include both naturally occurring materials such as coal and synthetic materials such as activated carbon molecular sieves, carbon replicas and zeolites.<sup>4,5</sup> These solid sorbents can potentially offer several advantages over liquid amine systems for post-combustion carbon dioxide absorption, which advantages include such as reduced toxicity and corrosiveness.

Among various sorbents, activated carbons (ACs) are excellent adsorbents for gas adsorption and storage due to their large surface area and porosity.<sup>6,7</sup> ACs have been widely used in separation, purification, and catalytic processes. However, though activated carbons can reversibly adsorb a large quantity of carbon dioxide at room temperature, their capacity diminishes quickly at elevated temperatures and the selectivity for carbon dioxide in the presence of water and other gases is poor. To prevent these negative phenomena, there have been several studies on modified adsorbents that can enhance carbon dioxide solid interaction by amines<sup>8-12</sup> or by metal oxides.<sup>13,14</sup>

Amines have been evaluated as a potential source of basic sites for acidic carbon dioxide gas adsorption. Introduced amines offer the benefits of the typical absorption process with the added advantages of being solids that are easy to handle and that do not give rise to corrosion problems.

In our earlier work,<sup>15</sup> various amine functionalized ACs were investigated. The active ingredients impregnated on the ACs show significant influence on the adsorption for carbon dioxide and its volumes adsorbed on amine functionalized ACs are larger than that on raw ACs, which effect is due to the amine groups grafted on the AC surfaces.

For the current work, we planned to use ACs as a cheap

source for gas adsorption and storage and to graft their defective groups with 3-chloropropyltrimethoxysilane, followed by amine compounds such as tris(2-aminoethyl) amine (TREN). Carbon dioxide adsorption capacity was studied at room temperature and atmospheric pressure. Moreover, we evaluated the carbon dioxide adsorption of branched amines such as TREN.

### Experimental Section

**Materials and Sample Preparation.** ACs that were purchased from Tokyo Chemical Industry Co. were used as the neat material for this work. Before grafting the amine onto the surfaces of the ACs, the ACs were purified with an acid treatment of 5 M of nitric acid solution. 3-chloropropyltrimethoxysilane (CPTMS), tris-2-aminoethylamine (TREN), and tri-ethylenetetramine (TETA) were purchased from Aldrich and were used without purification.

Under stirring, 50 mmol of CPTMS was added dropwise to 50 mL of dry toluene containing 1 g of vacuum dried ACs. Then the mixture was refluxed at 353 K for 24 h and the final product was filtered, washed with toluene and alcohol, and dried under vacuum at 343 K for 8 h. The products were represented as ACs-CPTMS.

The branched amine compounds of TREN were then grafted onto chloro-functionalized ACs by dropwise addition of 1 mmol of amines to 1 g of chloro-functionalized ACs dispersed in 50 mL of dry toluene. After refluxing the mixture at 353 K under stirring for 24 h, the final product was filtered, washed with toluene and ethanol, and dried at 343 K for 8 h. The products were represented as TREN-ACs. Also, as comparison group, TETA, which are the straight chain amine grafted ACs, were represented as TETA-ACs. Amine grafting of CPTMS-ACs is illustrated in

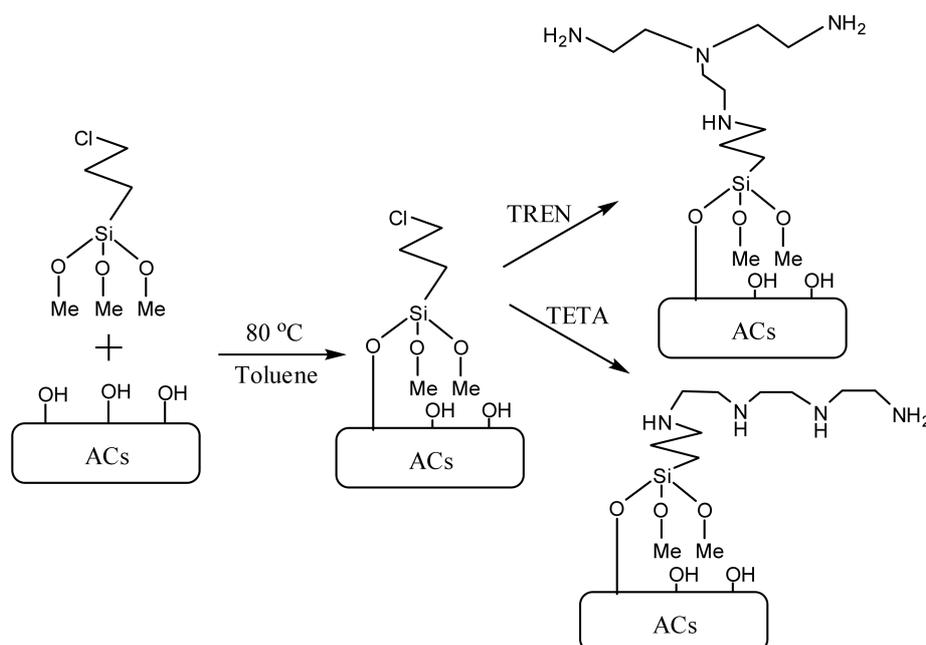
Figure 1.

**Characterizations.** To quantify the degree on nitrogen content on activated carbons, the prepared sorbents were analyzed with X-ray photoelectron spectroscopy (XPS) using an ESCA LAB MK-II (VG Scientific Co., UK) with monochromatic Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV), operated in the constant analyzer mode. The XPS spectra peaks were collected to show the binding energy (BE) from C<sub>1s</sub> spectra (BE = 284.6 eV) and N<sub>1s</sub> spectra (BE = 396.6 eV) as reference.

The amine grafting onto ACs was also confirmed by a thermogravimetric analyzer (TGA). TGA was performed using a Netzsch Simultaneous Thermal Analyzer STA 409 PC, under a nitrogen flow of 200 mL/min. Samples were heated at a heating rate of 10 °C/min from room temperature to 900°C.

The nitrogen adsorption isotherms were measured at 77 K using a gas adsorption analyzer (BEL-SORP, Bel Co.). The samples were out-gassed at 383 K for 24 h to obtain a residual pressure of less than 10<sup>-3</sup> torr. Specific surface areas and micropore volumes of the samples were determined from the BET equation and the t-plot method, respectively. Mesoporous volumes of the samples were determined by the BJH method. The amount of N<sub>2</sub> adsorbed at relative pressures ( $P/P_0=0.98$ ) has been employed to determine the total pore volume, which corresponds to the sum of the micropore and mesopore volumes. The peak pore diameter of the sorbents can be investigated from the pore size distribution, determined from the BJH method.

**Carbon Dioxide Adsorption Measurements.** The carbon dioxide adsorption performance of the sorbents was evaluated at 298 K using a gas adsorption analyzer (BEL-SORP, Bel Co.). The samples were out-gassed at 393 K for 24 h to obtain a residual pressure of less than 10<sup>-3</sup> torr. After degassing, under a vacuum, the carbon dioxide adsorption of



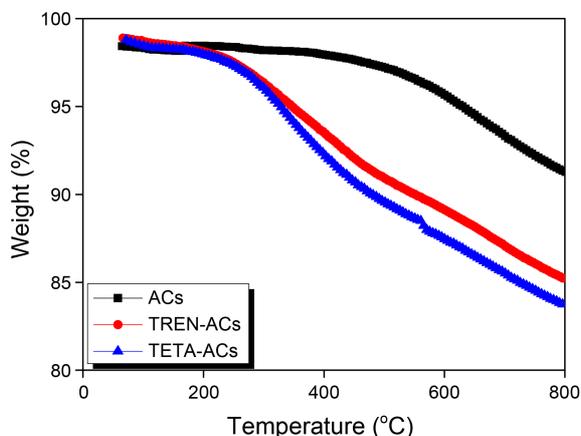
**Figure 1.** Schematic of TREN and TETA grafting on chloro-functionalized ACs.

the sorbents at relative pressure ( $P/P_0$ ) was evaluated at 298 K.

## Results and Discussion

**Characterization.** To study the interaction between the amine compound and the AC surfaces, the sorbents were pyrolysed and their thermal stability was studied. The amines under evaluation were subjected to pyrolysis in 200 mL/min of  $N_2$  at a heating rate of  $10^\circ\text{C}/\text{min}$  to study their thermal stability. The loss of mass took place at similar temperatures. TREN-ACs and TETA-ACs start to decompose at  $200^\circ\text{C}$ , as shown in Figure 2. Mass loss is related to the desorption and decomposition of the amine on the AC surfaces. This mass loss may cause a detachment of the amine coating from the AC surfaces, and this detachment was responsible for the carbon dioxide adsorption decrease at high temperature. From these results, amine grafted ACs seem to adsorb carbon dioxide effectively until  $200^\circ\text{C}$ .

The amounts of loading of amine on the AC surfaces are evaluated by XPS. Table 1 shows the atomic concentration percentages of the samples. Nitrogen content of the prepared samples was higher than that of raw ACs. The carbon dioxide molecules have a soft acidic nature.<sup>16,17</sup> This shows that the presence of base functional groups can enhance the carbon dioxide adsorption capacity. Thus, the increase of



**Figure 2.** Thermal stability of the ACs, TREN-ACs, and TETA-ACs.

**Table 1.** Surface properties of the samples

Specimens	Atomic conc. (%)			$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ ) <sup>a</sup>	$V_{\text{Total}}$ ( $\text{cm}^3/\text{g}$ ) <sup>b</sup>	$V_{\text{Micro}}$ ( $\text{cm}^3/\text{g}$ ) <sup>c</sup>	$V_{\text{Meso}}$ ( $\text{cm}^3/\text{g}$ ) <sup>d</sup>
	C	N	O				
ACs	93.5	0	5.7	1608	1.57	0.20	1.37
TREN-ACs	73.6	4.8	21.6	1185	1.22	0.11	1.11
TETA-ACs	72.0	5.0	22.9	1145	1.18	0.10	1.08

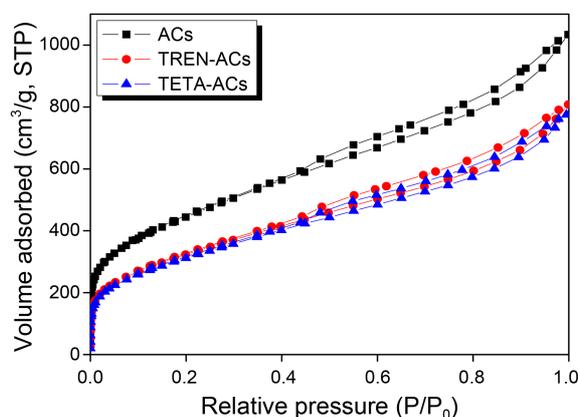
<sup>a</sup> $S_{\text{BET}}$ : Specific surface area calculated using BET equation at a relative pressure range of 0.2-0.35. <sup>b</sup> $V_{\text{Total}}$ : Total pore volume is estimated at a relative pressure  $P/P_0 = 0.98$ . <sup>c</sup> $V_{\text{Micro}}$ : Micropore volume determined from the Dubinin-Radushkevich equation. <sup>d</sup> $V_{\text{Meso}}$ : Mesopore volume determined from the subtraction of micropore volume from total pore volume.

mean nitrogen content enhanced base properties on AC surfaces. Also, the base functional groups on the AC surfaces can enhance selective adsorption of carbon dioxide in the complex exhaust gas. Table 1 shows that the nitrogen contents of TREN-ACs and TETA-ACs were similar due to the isomeric character of TREN and TETA. From these results, TETA-ACs may act as better a adsorber than TREN-ACs.

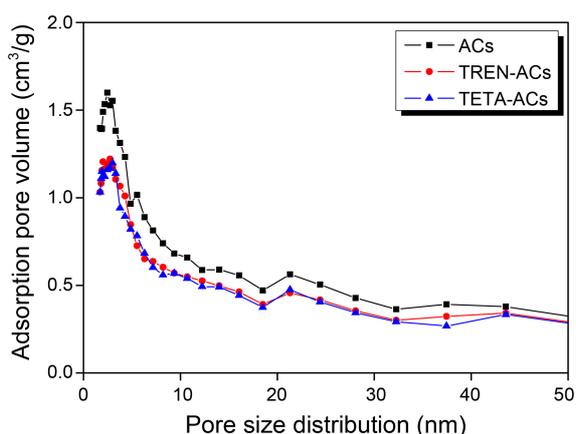
The influence of the TETA/TREN on the textural characteristics of the prepared samples is measured by the analysis of the  $N_2$  adsorption isotherms. The surface area of all the materials was evaluated using the BET method; the pore size was evaluated by the BJH method.<sup>18,19</sup> Table 1 summarizes the textural properties of the prepared samples and the neat ACs. From the Figure 3, the nitrogen adsorption-desorption of the neat ACs shows type IV isotherms<sup>18</sup> with most of the adsorbed volume contained in the mesopores. Similar to that of neat ACs, the  $N_2$  adsorption-desorption of TREN-ACs and TETA-ACs shows type IV Langmuir isotherms, which shows that there is a hysteresis loop between partial pressure,  $P/P_0=0.4-1.0$ , indicating capillary condensation of nitrogen in the mesopores. However, successive functionalization of TREN/TETA of ACs results in decreased specific surface area, pore volume and pore diameter. Such significant decreases of textural properties of ACs are summarized in Table 1. It can be seen that the treatment of TREN/TETA causes a decrease in the surface area because of the pore filling or the blocking behaviors of the amine functional groups of the pores.<sup>20,21</sup> Moreover, in the samples of branched amines (TREN) and straight chain amines (TETA) grafting treated activated carbons, branched amine treated activated carbons decreased the adsorption capacity and the specific surface area less than did linear chain amine treatment. This shows that shape of the linear amine was more of a block than the branched amine on the AC surfaces.

Figure 4 illustrates the pore size distribution of the samples. The average pore diameters ( $D_p$ ) were estimated by pore size distribution of the samples using the followed equation:<sup>22,23</sup>

$$D_p = \frac{4V_t}{S_{\text{BET}}} \quad (1)$$



**Figure 3.**  $N_2$  adsorption-desorption isotherms at 77 K of the ACs, TREN-ACs, and TETA-ACs.

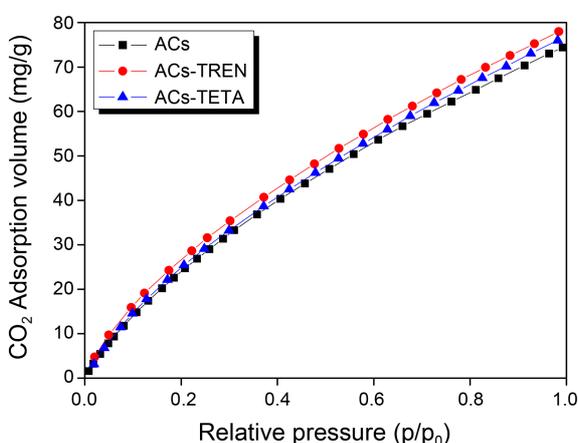


**Figure 4.** Pore size distribution of the ACs, TREN-ACs, and TETA-ACs.

where  $V_t$  is the total pore volume and  $S_{BET}$  the specific surface area.

According to the equation, the average pore diameters ( $D_p$ ) in the neat ACs, TREN-ACs, and TETA-ACs were approximately 3.98 nm, 4.11 nm, and 4.12 nm, respectively. Therefore, both amine treated ACs and neat ACs are thought to be mesoporous materials. Also, amine treatment is thought to cause a decrease in the average pore diameter of the samples.

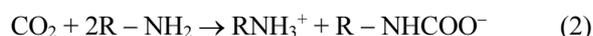
**Carbon Dioxide Adsorption.** To verify the effect of amine type on the carbon dioxide adsorption capabilities, 298 K isothermal curves at 1.0 atm for the carbon dioxide gas were obtained. Figure 5 shows the carbon dioxide adsorption of the prepared samples. It was found that the neat ACs showed an adsorption capacity of 41 cm<sup>3</sup>/g. At the same time, for both TREN-ACs and TETA-ACs, carbon dioxide adsorption capacity was increasing compared to that of neat ACs. Amines are determined to be a potential source of basic sites for acidic carbon dioxide gas adsorption. Therefore, the base properties of amines on the AC surfaces enhanced the adsorption capacity and selectivity of carbon dioxides due to their acid-base properties. However, from the Figure 3, physisorption capacities of neat ACs is limited



**Figure 5.** Carbon dioxide adsorption behaviors of the ACs, TREN-ACs, and TETA-ACs.

after the amine treatment due to pore filling or blocking behaviors of the amine coating. Although physisorption was limited by treated amine on the AC surface, total adsorption capacity was enhanced by chemisorption of amine on the ACs.<sup>24,25</sup> From the results shown in Figure 5, The branched amine TREN grafted ACs show a CO<sub>2</sub> adsorption of 43.8 cm<sup>3</sup>/g while the straight chain amine TETA grafted ACs show an adsorption value of 42.4 cm<sup>3</sup>/g at 298 K. Typically, active Lewis basic amine functional groups have a lone pair of electrons on a nitrogen atom, which initiates a nucleophilic attack on the acidic carbon dioxide due to the carbamate formation through the carboxyl group. The active hydrogen atom in the carboxyl group forms ion pairs through hydrogen bonding with the neighboring amine functional group for the stabilizing of the adsorption of carbon dioxide.<sup>25,26</sup>

The adsorption between amine active sites and carbon dioxide is the driving force for sorption of carbon dioxide by amine-modified carbon materials.



Since the reaction involves two nitrogen atoms of amine groups two nitrogen atoms in close proximity are required on the surface. From Hiyoshi *et al.*,<sup>27</sup> the isolated amine groups are found to be ineffective in carbon dioxide capture. Therefore, stabilization of 1 mol of carbon dioxide takes two moles of amine groups. In this respect, TREN-ACs show high carbon dioxide adsorption because they have two free primary amine functional groups while TETA-ACs have one free primary amine functional group. In addition, TREN have the property of three-dimensional stabilization. This was found to stabilize the adsorbed carbon dioxide and enhance the carbon dioxide adsorption capacities. On the other hand, TETA is impossible to use for three dimensional stabilization. From these phenomena, TREN on the AC surfaces enhances carbon dioxide adsorption capacities compared with TETA on the AC surfaces.

## Conclusions

In this work, the activated carbons were functionalized by 3-chloropropyltrimethoxysilane, and the sample was subsequently grafted with branched amine compound tris-(2-aminoethyl)amine; sample was then subjected to carbon dioxide adsorption. From the XPS, nitrogen content of the amine compound grafted ACs was found to be higher than that of raw ACs. The incorporation of a mean nitrogen group provided base properties on the AC surfaces. This shows that the presence of base functional groups can enhance the carbon dioxide adsorption capacity. From the results of BET, successive functionalization of ACs resulted in decreased specific surface area, pore volume and pore diameter, resulting from pore filling or blocking by amine functional groups. Nevertheless, the branched amine TREN grafted ACs show higher CO<sub>2</sub> adsorption than that of neat ACs. This higher adsorption was attributed to the incorporation of TREN, which has two free amine functional group on ACs.

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