

탄소분자체를 이용한 온실가스 흡착 특성 연구
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performace evaluation of adsroption of green house gas
on Carbon Molecular Sieves

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1. INTRODUCTION

A sustained interest in the area of micro porous adsorbents for specific separations, has led to the development of a special class of porous materials known as Carbon Molecular Sieves. They are essentially carbonaceous substances. Total neutrality in acid and base media, high temperature stability, molecular sieving ability and overall low production cost, have made CMS a potential end product for precise separations of gas and liquid mixtures. There are two major types of CMS, namely CMS prepared from naturally occurring carbonaceous materials and CMS from polymers. Naturally occurring raw materials like coal, contains varying amounts of multi crystalline and amorphous matter [1]. These have imperfections that favor the slit likepore formation in CMS. A pretreatment of the raw material is required depending on the nature of raw material. Generally agreed sequential pattern of operations to prepare CMS is discussed elsewhere [2]. Partial oxidation of the fine coal powder is restricted to a maximum of 300 °C, whereas carbonization temperature varied over a wide range (200 to 1000°C). Extrusion of the finely powdered and partially air oxidized coal powder is done using a binder. Sulfite waste liquor, coal tar pitch, molasses, cellulose, etc. are some of the binders reported. During carbonization, most of the volatile matter is driven out, creating a pore structure normally in the plastic range. During activation, the disorganized carbon is removed and the surface area is increased due to the burn off of the boundaries of the micro pores. The extent of surface area improvement depends on the type of activating agent, time, and temperature of activation used. The commonly employed activating agents are steam and carbon dioxide, and the activation temperature range is 850 to 950 °C. Molecular sieving property is obtained through pore narrowing by the deposition of carbon. This is achieved by the pyrolysis of hydrocarbons, like benzene, diphenyl, flouro naphthalene etc. at the pore mouth of the CMS. The conditions of pyrolysis, which are mainly, the amount of the hydrocarbon used, time and temperature of pyrolysis, have to be selected to minimize pore blocking.

2. EXPERIMENTAL

2.1. Preparation of CMS

The coal and coconut char samples were ball milled for 24 hours and sieved to get ~ 150 μ m size particles. One portion of each of the samples was kept in an oven maintained at 120~150 °C for 6 hours by the pre-oxidation. After the samples were pretreated with air, it was completely mixed with 25 wt.% by coal tar pitch and extruded to get 2 to 3 mm diameter extrudes. Extrudes were dried at 80 °C for 6 hours and carbonized at 800 °C in presence of nitrogen in a rotary kiln under controlled temperature program. And then the samples were activated in the same kiln at 800 °C in CO₂ atmosphere for 30 minutes.

Pore narrowing of the activated sample was done by coke deposition on the pore mouths by using benzene entrained nitrogen gas at 600 °C for 20~60 minutes. The weight per minute of entrained benzene in nitrogen was ~0.2 g/min. Fig. 1 shows the schematic of CMS preparation process.

2.2. Carbonization and Activation

Carbonization of the pellets was done in presence of nitrogen at 800 °C for 30 min and activation with CO₂ at 800 °C for 30 min. In the case of metal impregnated samples the carbonization time was kept 60 min. A rotary kiln set with a very low temperature program was used for this purpose. Pore mouth tailoring of the activated pellets was done using coke deposition by benzene cracking at 600 °C. The CO₂, CH₄ and N₂ adsorption data on the samples were done using a volumetric adsorption setup at 14 psi. About 1g of the sample was used for the adsorption studies. The samples were degassed for 3 hours at 250 °C before any adsorption experiments.

2.3. Pore control

The Pore mouth tailoring of the activated pellets was done using coke deposition by benzene cracking at 600 °C. After activation of the samples, the temperature of the reactor was brought down to 600 °C and the sample was baked for 30 min at the same temperature. The nitrogen gas (100 ml/min.) was bubbled through a bubbler containing benzene, and then passed through the sample in the reactor kept at 600 °C for a fixed duration of time, for coke deposition at the pore mouths of the sample [5]. The benzene bubbler was then disconnected and the sample was kept at 600 °C for 30 min and then cooled to 200 °C in N₂ atmosphere.

3. RESULTS AND DISCUSSIONS

3.1. Effect of raw materials

Fig. 2. shows the amount of CO₂ adsorption through the time with CCA, IHA and GGA. CCA from coconut char adsorbed about 1.22 mmol/g but other two CMS, IHA and GGA, adsorbed 0.86 and 0.81 mmol/g, respectively.

Coal is an abundant source of carbonaceous raw material, but have a high ash content

and often have a non-uniform property [4].

The physical properties of raw material are very important for CMS. Table 1 shows volatile contents, fixed carbon, moisture, and ash in the raw materials. The materials were purchased by POSCO corporation. Comparison study of physical property and adsorption capacity of the prepared CMS samples were done.

3.2. Effect of pretreatment

The performance of CO₂ adsorption was measured in volumetric apparatus with and without pre-oxidative CMS. The pre-oxidation with (*)CMS was carried out at 150°C for 8 hours. Fig. 3 shows the adsorption capacity of CMS prepared by coconut char and coal. The pretreated CMS, in *IHA and *GGA case, adsorbed large quantity than non pretreated CMS. The equilibrium time was reached at 5 min. The reason is that pretreatment with air introduced the clear pore in CMS.

3.3. Effect of benzene cracking

CMS pore control was done by benzene cracking. The effect of benzene flow time on CMS prepared from coconut char, the pore size in turn the adsorption of CO₂ is given in Fig. 4. As the benzene flow time increases, the CO₂ adsorption quantity is slightly decreased upto 60 min but over 60 min dramatically decreased on CMS.

Table 2 shows the comparison study on the uptake ratio of CO₂ to CH₄ with coal based CMS before and after pore control. It is found that CMS (*PDB20) with 50 CO₂/CH₄ uptake ratio was better compared to other samples.

4. CONCLUSION

The CMS samples for carbon dioxide adsorption, from four different types of coal were prepared. The GG and PD coal was found to be good carbon precursor for the CMS preparation, whereas the IH and CH coal showed a loss of mechanical strength due to the slight swelling occurring during carbonization and activation. It is also noticed that the pre-oxidation of coal powder is very important to develop a CMS sample with good micro porosity and good selectivity. The CMS samples showed a decreasing trend in CO₂ adsorption with the increase in benzene flowtime. The CMS prepared from PD coal showed a meager adsorption of CH₄ (< 0.03% by weight), but a good adsorption of CO₂ (~ 6%). This indicates that this sample has micropores of molecular dimension and can be used for the separation of molecules having close molecular dimensions.

5. REFERENCE

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Table. 1. Proximate and analysis of raw coal

| Sample code | Place of Origin | Volatiles | Fixed Carbon | Moisture | Ash content | |
|-------------|-----------------|------------|--------------|----------|-------------|-----|
| Coal | GG | Australia | 30.9 | 61.2 | 5.7 | 2.2 |
| | PD | Australia | 19.6 | 71.0 | 8.3 | 1.0 |
| | IH | USA | 29.0 | 62.9 | 6.4 | 1.6 |
| | CH | China | 31.4 | 50.1 | 9.9 | 8.5 |
| Coconut | CC | Philippine | 22.0 | 69.7 | 1.4 | 7.8 |

Table. 2. Uptake ratio of binary gas mixtures along with the adsorption capacity on the CMS samples prepared before and after pore control (*: after pretreatment)

| Sample name | Adsorption weight at After 5min | | Uptake ratio at after 5min |
|-------------|---------------------------------|-----------------|-----------------------------------|
| | CO ₂ | CH ₄ | CO ₂ / CH ₄ |
| *GGA | 38.6 | 3 | 12.8 |
| *GGB20 | 72 | 2.4 | 30 |
| *PDA | 54 | 1.9 | 28.4 |
| *PDB20 | 50 | 1.0 | 50 |
| *IHA | 39.6 | 1.8 | 22 |
| *IHB20 | 45 | 1.7 | 26.5 |
| *CHA | 70.6 | 12.9 | 5.4 |
| *CHB20 | 60 | 9.8 | 6.1 |

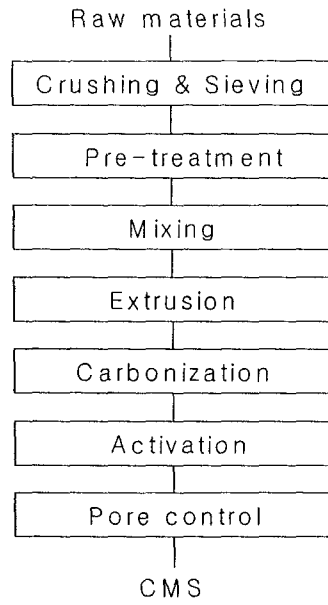


Fig. 1. Experimental procedure for preparing CMS

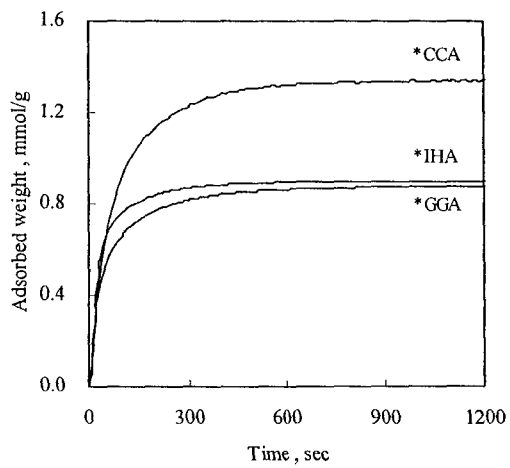


Fig. 2. Effect of raw material on adsorption of CO₂

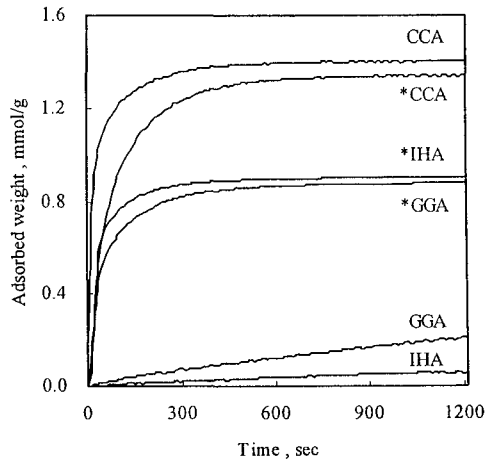


Fig. 3. Effect of pretreatment on adsorption of CO₂

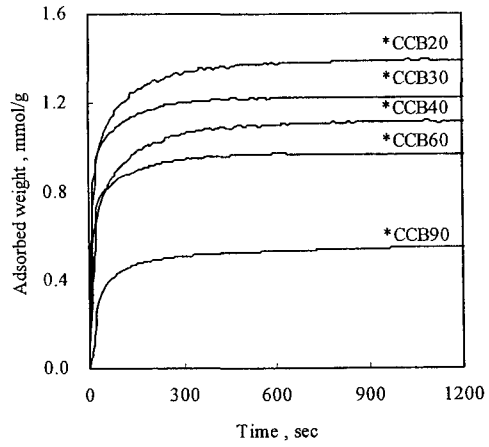


Fig. 4. Effect of benzene cracking Time