Controlling Micropore and Mesopore Structure of UAC by CVD and HTT

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Abstract：The ultra activated carbon (UAC) with a surface area of about $3000m^2/g$ was obtained from Daqing petroleum coke. Study of controlling the pore structure of UAC was undertaken and the control of both micro- and meso-porosity was specially emphasized. Heat treatment (HTT) technique was used for the control of mesopore ratio and surface area(S_{BET}) can be up to 85% and $1500m^2/g$, respectively. Such carbon molecular sieve (CMS) is more suitable for being catalyst supports. Additionally, Chemical vapor deposition (CVD) technique of Benzene had been employed to control the micropore structure. CMS with uniform micropore structure (micropore ratio can be up to 87%) was obtained, which has a good molecular sieving selectivity for CO_2 but not for CH_4.
Keywords: ultra activated carbon, carbon molecular sieve, chemical vapor deposition, heat treatment

1. Introduction

Activated carbons are characterized by their highly developed internal surface area and porosity. Due to such a valuable feature, activated carbons have been in use for thousands of years and have now become extremely versatile adsorbents of major industrial significance. [1-3] However, one of the problems of using activated carbons is the complexity of the carbon structure resulting in limited control over extent and size distribution of resultant porosities. Carbon molecular sieves(CMS) with uniform pore structure were obtained by some methods of controlling pore size distribution from activated carbon, great effort has been made toward the development of micro- and mesopores because it allows the carbons to adsorb large amounts and various types of chemicals from gases or liquids. [4-7] Carbon is resistant to acidic or basic media, the structure is stable at very high temperatures, having quilt high adsorption and reaction capacities. [8-10] All of these advantages provide new application fields, such as catalyst support, for activated carbon and CMS. In this work, the requirement of desired pore structure has been obtained by applying selective chemical vapor deposition (CVD) of carbon and heat treatment (HTT).

2.Experimental
2.1 Preparation of ultra activated carbon (UAC)

Daqing petroleum coke was used as the precursor through pre-treatment and then mixed with activated reagents. After soaking for a period time, the sample was placed into oven and dried at 110 ℃ temperature. The heating rate, activation temperature and activation time were changed under N_2 protection. The treated carbon will be referred to as UAC. UAC_1, UAC_2 and UAC_3 with different surface area were chosen as the samples for the next experiments.

2.2 Control of porous structure
2.2.1 HTT

Two sample UAC_1 and UAC_2 were heated at 800℃ and 900℃ for 1.5h in a 50ml/min inert atmosphere, named as UAC_1-800, UAC_1-900, UAC_2-800, and UAC_2-900. The surface area and pore size distribution of the each sample were measured.

2.2.2 CVD

Pyrolysis of benzene was performed by flowing a helium stream containing controlled amounts of benzene over UAC_3 (200mg) suspended in a quartz basket in microbalance (WCT-2 TGA, Peking China). The sample was heated under He flowing to the designed reaction temperature at a programmed rate of 10℃ min^{-1} and maintained at 750℃ for 1.5h. Then, a prescribed amount of benzene was supplied by a micro feeder into the He gas flow and passed over the heated sample (C-UAC_3) for a fixed period. During the heating process, the weight uptake of C-UAC_3 was recorded. Adsorption of CO_2 and CH_4 on C-UAC_3 was carried out using a volumetric adsorption apparatus. The C-UAC_3 sample was evacuated to 10^{-2} Torr at 150 ℃ for 1h. The gas volumes adsorbed by C-UAC_3 within a given time internal at 30℃ were determined from the change of pressure in the sealed system.
2.3 Method
Iodine adsorption : The number of iodine adsorption was test according to ASTM.
Benzene adsorption: The value of benzene adsorption was test according to static benzene adsorption in a sealed container with 90℃ waterbath.
BET: Nitrogen BET experiment was carried out with an American Micromeritics instrument at liquid nitrogen temperature (77K). BET surface areas and pore size distribution were estimated.
XRD: XRD patterns were obtained with a Philips PW 1840 powder diffractometer. Co Kα radiation was employed covering two angles between 2° and 90°. The mean crystallite diameters were estimated from application of the scherrer equation.

3. Results and discussion
3.1 Controlling mesopore of UAC

The surface areas of heat treated (UAC$_1$-800, UAC$_1$-900, UAC$_2$-800, UAC$_2$-900) activated carbon are shown in Table 1. 800℃ HTT made the surface areas of UAC$_1$ decrease from 3012m^2/g to 2268 m^2/g , the mesopore ratio of UAC$_1$ increases from 19% to more than 85%. The similar pore size distribution appears in Fig.4. It indicates that the basic structure of activated carbon was not disturbed at 800℃. When the temperature went to 900℃, the surface areas shrinked to 229 m^2/g dramatically. The similar phenomenon was detected on UAC$_2$, which surface areas decreased from 2987 m^2/g to 423 m^2/g. At the same time, the pore size distribution has a large change and large lost of pore volume are observed by N$_2$ adsorption method.

Table1 Specific surface area of unmodified and modified carbon

Sample	S_{BET}(m^2/g)	Mesopore volume(ml/g)	Mesopore ratio(%)[*]
UAC$_1$	3012	0.203	19
UAC$_1$-800	2268	0.860	87
UAC$_1$-900	229	0.230	74
UAC$_2$	2987	0.245	21
UAC$_2$-800	1833	0.791	86
UAC$_2$-900	423	0.302	65

[*] =the ratio of the mesopore surface areas to the total surface areas

The sample UAC$_1$-900 has meso and macropores only, the pore size of which is concentrated on 2.5nm. The micropores (pore size below 2nm) were dispeared almost.(Fig.1)
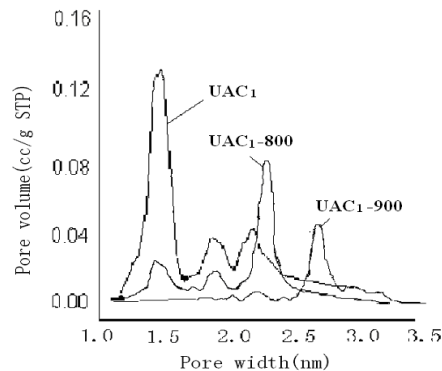

Fig.1 Pore size distribution of UAC$_1$, UAC$_1$-800 and UAC$_1$-900

Fig.2 shows the XRD patterns of UAC$_2$ and UAC$_2$-900. It is seen that the intensities of the XRD peaks (002) were weak before HTT however it has scattering obviously at low angles. After 900℃ HTT, the intensities of the XRD peaks(002) grow weaker, the peak position was shifted to smaller

angles and the intensities of scattering are also decreasing. These results indicate that the distance between layers get shorter and it possesses a highly ordered graphite-crystallographic structure.
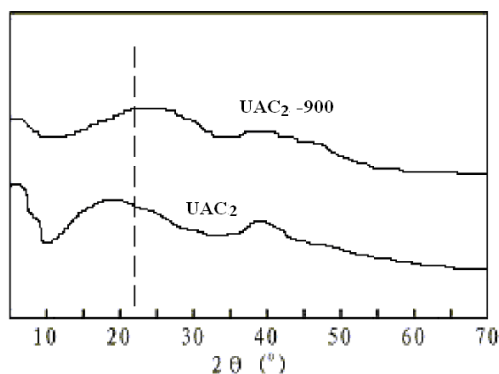

Fig.2 X-Ray diffraction patterns of UAC_2 and UAC_2-900

HTT has deeply effect on UAC, the changes on pore structure can be explained from the two theories[11-12] as followed. (1)Collapse theory. HTT makes basic lattices exhibiting a strong degree of anisotropy generate thermal expanding to different extent, which causes some pore wall too thinner to collapse. (2) micro-crystallographic theory. The amount of odd atoms(–H,–O et al.) is poorer through HTT. Larger aromatic lamellars are formed after breaking the bonds between aromatic lamellar and oxygen atom. The interlamellar distance grows smaller however the length of lamellars becomes larger. That mean graphitization degree is improved by HTT. Therefore, adjusting HTT temperature can be help for achieving CMS with rich mesopores and uniform pore size. It is more suitable for such CMS to being catalyst supports. [13]

3.2 Controlling micropore of UAC
Fig.3 shows the adsorption and sieving ability of CO_2 and CH_4 on UAC_3. The amount of CO_2 and CH_4 adsorption on UAC_3 is found to be 55 mg/g and 25 mg/g, respectively. After benzene CVD, the amount of CO_2 adsorption has little decrease and still maintained 50mg/g. On the contrary, the UAC_3 adsorbed a little amount of CH_4 3mg/g only. (Fig.4)

It can be seen from Fig.3 and Fig.4, the sieving ability of CO_2 and CH_4 was 30mg/g before CVD. After benzene CVD, it has enhanced to 47mg/g. The figure clearly indicates that the carbon deposition on UAC significantly improved its CO_2 selectivity without serious reduction in CO_2 adsorption capacity.
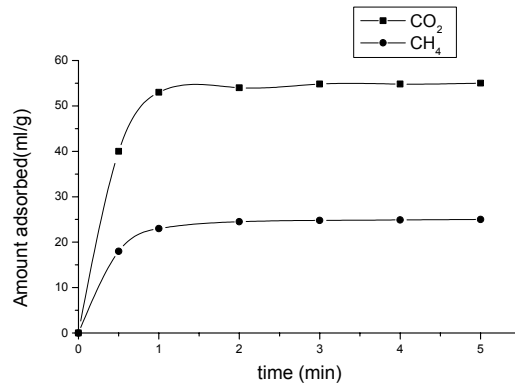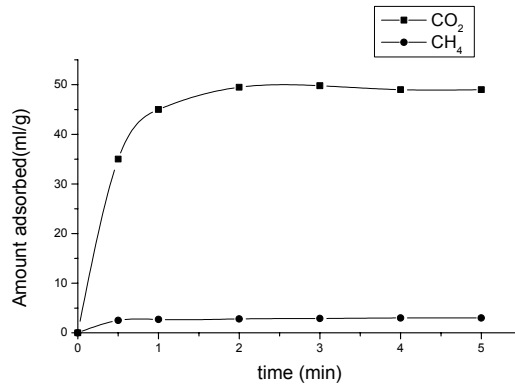
Fig.3　Adsorption profiles of CO_2 and CH_4 for UAC_3 (30℃)

Fig.4　Adsorption profiles of CO_2 and CH_4 for C-UAC_3 (30℃)

Some of the physical and chemical properties of the UAC_3 and C-UAC_3 are list in Table 2.

Table 2 The physical and chemical properties of the UAC_3 and C-UAC_3

Sample	$S_{BET}(m^2/g)$	Micropore volume(ml/g)	Micropore ratio(%)
UAC_3	2278	0.506	51
C- UAC_3	1923	0.460	87

[*] =the ratio of the micropore surface areas to the total surface areas

The BET surface areas and pore volume are reduced but micropore ratio goes up to 87% through CVD treatment. This may be explained by the theory [14-15] that at 750℃, benzene moleculars adsorb only on the pore wall and then they were carbonized on the wall, resulting in reduction of pore size. The pore diameter and pore volume keeps decreasing with deposition period and then the deposition is spontaneously stopped when the pore diameter is reduced to 0.37nm that corresponds to the molecular thickness of benzene.

The pore size of 0.37nm, which is between the sizes of CO_2 (0.33nm) and CH_4 (0.38nm) can separate these two molecules.

4. Conclusion

(1) Carbon molecular sieve with the mesopore ratio＞85% and S_{BET}＞ 1500m²/g was obtained from the UAC through heat-treatment. If acid oxidation can be carried out to give the CMS surface appropriate acidities distribution, then it will have a great potential as principal material to be used in the field of catalyst support. [16-18]

(2) The carbonization of the benzene CVD over UAC gave CMS with uniform micro porosity (Micropore ratio is above 87%), which has a good molecular sieving selectivity for CO_2 but not for CH_4.

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