



Carbon Molecular Sieves with High Micropore Volume Derived from Bituminous Coal and Polyimide Composites†

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AJC-11332

A series of carbon molecular sieves (CMS) were obtained by carbonizing bituminous coal and polyimide composites. The process for preparing carbon molecular sieves involve three key steps: (1) preparation of the composite of bituminous coal and polyamic acid, (2) carbonization and (3) chemical activation. The process parameters including pyrolysis temperature, the content of polyamic acid and activation condition were studied. The morphology, micropore volume and pore size distribution of carbon molecular sieves were characterized by SEM and N₂ adsorption. The chemical structure of carbon molecular sieves and their precursors was confirmed by FTIR. The results showed that the carbon molecular sieves prepared at a polyimide content of 20 wt % possessed more uniform pore size distribution and higher micropore volume. Their micropore volume was 0.49 cm³/g, micropore area was 900 m²/g and average pore size was 2.31 nm.

Key Words: Carbon molecular sieves, Bituminous coal, Polyimide, Carbonization, High micropore volume.

INTRODUCTION

Carbon molecular sieves (CMS) are carbonaceous materials characterized by narrow micropore size distribution and exhibit high adsorption selectivity¹. These materials are attracting increasing attention, because they are widely used as catalysts², electrode materials³ and adsorbents and membranes for separation of gas mixtures. They exhibit interesting properties such as excellent thermal stability in non oxidizing atmosphere and high chemical stability and can have large adsorbate packing density in their slit shaped micropores. Porous carbon materials are usually prepared by controlled carbonization of various carbonaceous precursors such as wood, coal, lignite, shell, peat, *etc.*⁴⁻¹⁰. Among these carbonaceous sources, coal is a well-known precursor, including lignite, bituminous coal and anthracite, *etc.* Polyimide (PI)¹¹ is also an ideal precursor to prepare carbon molecular sieve adsorbents and membranes, which have not only good mechanical properties, but also good separation characteristics. Liu *et al.*¹² reported a method to increase micropore volume by adding α -cyclodextrin (CD) into polyimide. The micropore volume of microporous carbons increased from 0.15 cm³/g to 0.24 cm³/g when the α -cyclodextrin amount rose from 0 % to 15 % by mass. It is noted that carbon molecular sieves can be modified through several processes

such as activation of carbonaceous materials and modification of the texture of activated carbons *via* chemical vapour deposition (CVD) of an organic substance. Currently, the application of carbon deposition aims to tailor pore apertures to match the size of the desired pore size has attracted considerable attention. Consequently many research works have been carried out to control pore size and size distribution of carbon molecular sieves¹³⁻¹⁶. Several carbon sources can be used as carbon deposition agents such as acetylene, benzene, cyclohexane and some organic solvents. However, this approach inevitably produces large amounts of unreacted deposition agents as mentioned above, which are toxic substance and harmful for human and environment in the process of chemical vapour deposition.

Besides organic polymer materials, other precursors such as natural coal, petroleum coke and plant-based fiber are also used as the porous carbon precursor, because of their suitable characteristics (composition, structure, ash, *etc.*). The preparation processes have been constantly improved, but the methods of controlling aperture and pore distributions still require further improvement.

Coal is a non-renewable energy resource and it is desirable to explore the better utilization and to increase its value other than being used as the fuel. Although there are many studies in literature relating to the preparation and characterization of

†Presented to The 5th Korea-China International Conference on Multi-Functional Materials and Application.

carbon molecular sieves from various kinds of coal as mentioned before. The production of carbon molecular sieves from coal powder by polymer blending and chemical activation method has not been investigated. In this method, carbon molecular sieves could be prepared by controlling the ratio of polymer and coal powder, which doesn't require any carbon deposition agents.

In this study, we report a novel method for enhancing the micropore volume of the carbon molecular sieves for the purpose of tailoring their properties such as gas adsorption capacity and permeability. The objective of the work is to produce carbon molecular sieves mainly from bituminous coal and control carbon molecular sieve's pore structure by adding different amount of polyimide. In this paper, the main factors in controlling the pore structure of carbon molecular sieves are explored. The influence of different contents of polyimide on pore development of carbon molecular sieves is investigated.

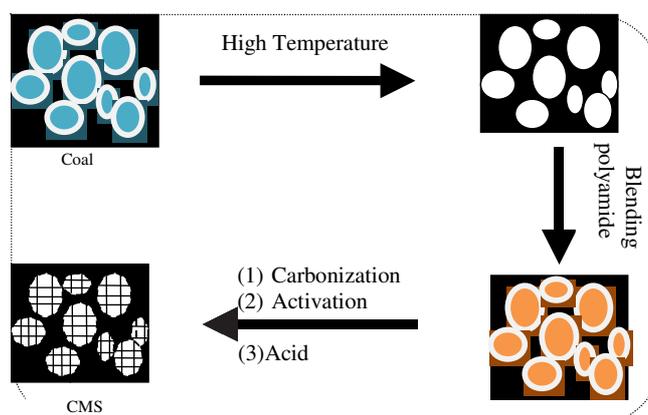
EXPERIMENTAL

Bituminous coal was obtained from Huainan coal mine Co. Anhui, P.R. China. The elemental analysis of the coal is listed in Table-1. Bituminous coal was pyrolyzed under high-purity N_2 at 600 °C for 2 h and then was milled using a planet-type grinding machine until the coal particle size was under 80 mesh. The resultant coal powder was used as the precursor for preparation of carbon molecular sieves. Because most of the non-carbon elements, hydrogen and oxygen, were removed from bituminous coal during the pyrolysis, some disordered pores were formed in the pyrolyzed coal, which was good for blending and absorbing polyamide acid.

Polyamide acid was synthesized according to the reported procedure¹⁷. Polyamide acid solution 30 wt % was prepared from an equal molar ratio of pyromellitic dianhydride (PMDA) (Aldrich) and 4,4'-oxydianiline (ODA) (Aldrich) in dimethyl formamide (DMF) (Shanghai chemical reagent factory) under nitrogen gas. The reaction was carried out in an ice-water bath at about 0 °C for 10 h. Polyimide (PI) was obtained by heating polyamide acid solution and subsequent dehydration. The chemical structure of the polyamide acid solution and polyimide was analyzed by FTIR.

Preparation of carbon molecular sieves: The overall synthetic procedures are described in **Scheme-I**. The carbon molecular sieves samples were prepared by three-step processes involving pyrolysis of bituminous coal as pretreatment, carbonization of the precursors and KOH activation of carbonized samples. The experiments were carried out according to the reported procedure^{18,19}. The first step was the pretreatment of bituminous coal by pyrolysis under high-purity N_2 at 600 °C for 2 h, followed by milling until the coal particle size was reduced to 80 mesh or below. The second step was the carbonization of precursors that were formed by blending pyrolyzed coal with the different amounts of polyamide acid solution under milling for 2 h and subsequently removing the solvent.

The carbonized precursors was heated and carbonized under flowing high-purity N_2 (at a flow rate of 0.1 L/min) in a furnace at a heating rate of 5 K/min and kept at different temperatures (*e.g.*, 650 °C) for 2 h. After the carbonization, the samples were cooled down under flowing nitrogen and then washed and dried. The resulting carbonized samples were obtained and marked as IA-CMS. The last step was activation of carbonized samples by KOH, which was carried out by mixing KOH with carbonized sample at 6:1 by weight ratio for all samples and heating under high-purity N_2 (0.1 L/min) in a furnace at a heating rate of 5 K/min at 650 °C for 2 h. The activated samples were obtained by neutralizing, washing with 0.5M HCl, hot water and cold distilled water and drying; the activated carbonized samples obtained were marked as A-CMS.



Scheme-I: Synthesis procedure for producing porous carbons with tunable pore sizes

The samples prepared by carbonization of the mixtures of coal and 50 or 20 wt % polyamide acid without activation were marked as IA-CMS-50 or IA-CMS-20, respectively. The samples obtained by carbonization of the mixtures of coal and 50 or 20 wt % polyamide acid and activation were denoted as A-CMS-50 and A-CMS-20. The samples prepared by carbonization of pure polyamide acid with or without activation were marked as A-CMS-PI or IA-CMS-PI, respectively; whereas the samples obtained by carbonization of pure coal with or without activation were marked as A-CMS or IA-CMS respectively.

Characterization of carbon molecular sieves: FTIR spectra were recorded using a WQF-300 FTIR spectrometer at 2 cm^{-1} resolution and 32 scans.

Nitrogen adsorption measurements were performed at 77.4 K using a volumetric adsorption analyzer (ASAP 2020M, Micromeritics Co., USA) at relative pressures from 10^{-7} to 1. All samples were degassed at 573 K for 10 h before analysis. Adsorption isotherms were used to analyze the surface areas and pore structures. The Brunauer-Emmett-Teller (BET) method was used to calculate specific surface area (S_{BET}). The *t*-plot method was employed to calculate the micropore surface

TABLE-1
CHARACTERISTICS OF BITUMINOUS COAL

Sample	Composition by proximate analysis (wt %)			Elemental composition (wt %)				
	Water	Ash	Volatile	C	H	Si	S	N
Coal	1.52	13.37	40.21	83.37	5.76	1.54	0.29	8.68

area and volume. Total pore volume was obtained from the single point adsorption at the relative pressure of 0.995. Pore size and size distributions (PSDs) were obtained using non-local density functional theory (DFT) for slit pore geometry. SEM analysis was carried on a Sirion 200 FEG field emission scanning electron microscope.

RESULTS AND DISCUSSION

FTIR spectra for different samples are shown in Figs. 1-4. The FTIR spectrum of polyamide acid (PAA) is shown in Fig. 1. The structure of polyamide acid is confirmed by three characteristic groups of amide group absorption bands (3281 , 1661 , 1544 and 1240 cm^{-1}), ether group of 4,4'-oxydianiline absorption bands (1108 cm^{-1}) and carbonyl group of carboxyl of pyromellitic dianhydride absorption band (1720 cm^{-1}). The characteristics imide group absorbance bands (1778 , 1725 , 1505 , 1380 and 1233 cm^{-1}) belonging to polyimide are observed, which proves that the polyimide was formed *via* dehydration of polyamide acid under heating. It is implied that the polyamide acid and polyimide are formed through polymerization and heating carbonizing process. The FTIR spectra of coal, pyrolyzed coal and activated coal are shown in Fig. 2. The FTIR spectra of coal-polyimide composites with different contents of polyimide are shown in Fig. 3. The FTIR spectra of the coal sample (IA-CMS-50) heated at different temperatures are shown in Fig. 4. From Fig. 2(A), there are some typical characteristic bands observed such as, stretching vibrations absorbance bands of free O-H at the range of 3800 - 3500 cm^{-1} , stretching vibrations bands of $-\text{CH}_2-$ at the range of 2950 - 2850 cm^{-1} , aromatic ring stretching vibrations bands of $-\text{C}=\text{C}-$ around 1600 cm^{-1} and aromatic ring out of plane deformation vibrations bands at 680 cm^{-1} . From Fig. 2(B,C), the stretching vibrations bands of Si-O in range of 1100 - 1000 cm^{-1} and stretching vibrations (Si-C) in range of 890 - 690 cm^{-1} are assigned to the carbonized residues of coal and associated minerals. By comparing the samples shown in Fig. 2, the FTIR spectrum of the pyrolyzed coal is similar to that of the activated coal and absorption intensities of organic functional groups arising from both activated and pyrolyzed coal and lower than those from the coal. It is noted that during carbonization process, some thermally unstable groups in coal such as carboxyl, carbonyl, hydroxyl, phenyl, aliphatic hydrocarbons and other small aromatic compounds evolved from coal, leading to formation of pores with various shapes and sizes. The micropore area and micropore volume of the samples could be increased by controlling the coal carbonization process. The absorption bands of silicon-oxygen bond (Si-O) in 1100 - 1000 cm^{-1} region were also observed in Figs. 3 and 4, which is the characteristic of residues of carbonized coal. After heating, some disordered pores were formed and could be easily filled up with polyamide acid. The intensity of characteristic bands in the spectra is enhanced with increasing the content of polyimide. The intensity of characteristic bands in the spectrum drops with increasing the carbonization temperature. As seen in Fig. 4, there is no obvious band (besides some absorption bands of residues) in the sample carbonized at above 650 $^{\circ}\text{C}$, indicating the decomposition of organic groups was almost completed at 650 $^{\circ}\text{C}$.

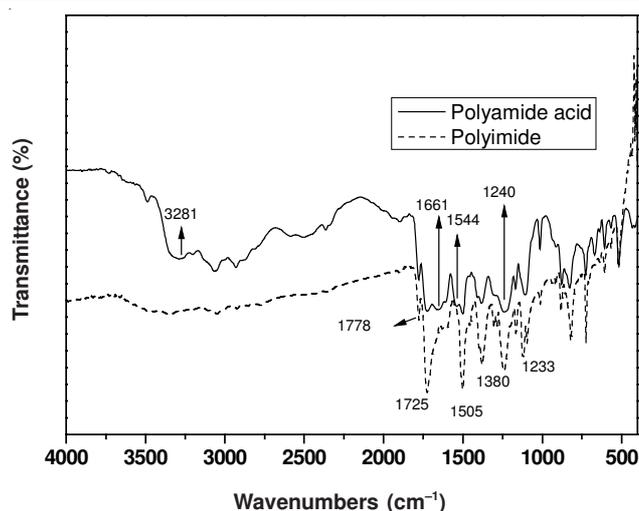


Fig. 1. FTIR spectra for polyamide acid and polyimide (PI)

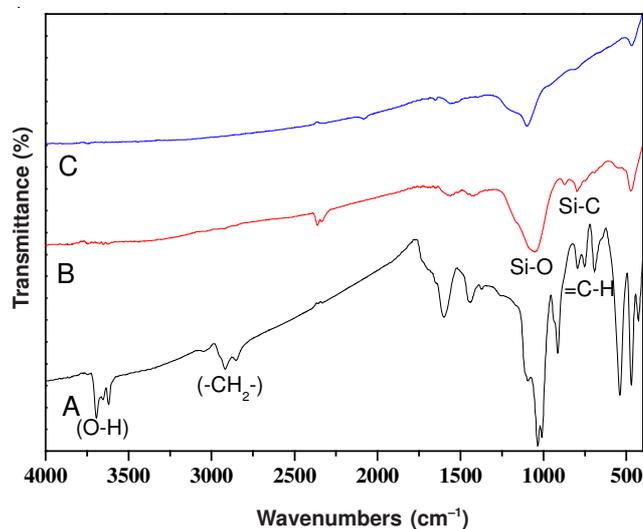


Fig. 2. FTIR spectra for coal, pyrolyzed coal and activated coal: A: bituminous coal; B: pyrolyzed coal; C: activated coal

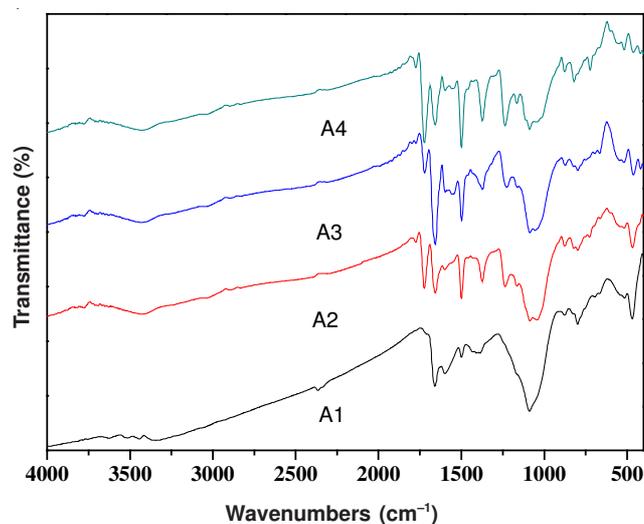


Fig. 3. FTIR spectra for coal with different contents of polyamide acid: A1-10 %, A2-20 %, A3-30 %, A4-50 %

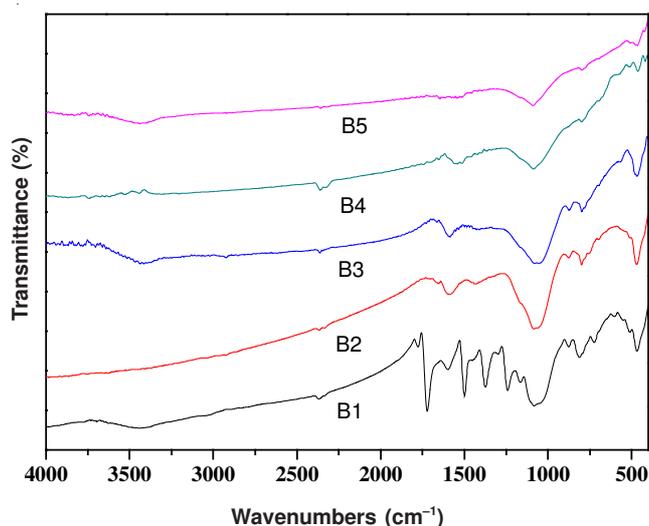


Fig. 4. FTIR spectra for the coal containing 50 wt % polyamide acids heated at different temperatures: B1-450 °C, B2-550 °C, B3-650 °C, B4-750 °C, B5-850 °C

Nitrogen sorption: The effect of different amounts of polyimide and KOH on the pore structure of porous carbon materials was studied using N₂ sorption measurements. The adsorption-desorption isotherm curves are shown in Fig. 5. All samples exhibit typical type I isotherms and are typical porous solid features²¹. The flatter of isotherm curve is, the more dominant the micropores in porous solid are and *vice versa*. For all isotherms, the low-pressure adsorption steps are the result of the micropore filling with N₂. After completion of micropore filling, the isotherms become level-off over the relative pressure (P/P_0) range of about 0.1-0.9. The BET surface area, micropore surface area, micropore volume and median pore diameter of all samples are listed in Table-2. It can be seen that the adsorbed quantity of samples after activated process rises significantly as shown in Fig. 5. The porosity of bituminous coal prepared by pyrolyzed only is very low. The BET surface area, micropore area, micropore volume of samples prepared from the mixture of coal loaded with 20 wt % polyimide *via* carbonization (650 °C for 2 h) and activation temperature (650 °C for 2 h) are obviously higher than those reported in the literature²².

Influence of the polyimide content on micropore area, volume and pore size: It can be seen from Table-2 that the carbon molecular sieves' micropore area, micropore volume are 391.6 m²/g and 0.23 cm³/g for carbonized coal and 900 m²/g and 0.49 cm³/g for the coal loaded with 20 wt % polyimide. As the content of polyimide increases, the micropore area and micropore volume decrease. And the activated

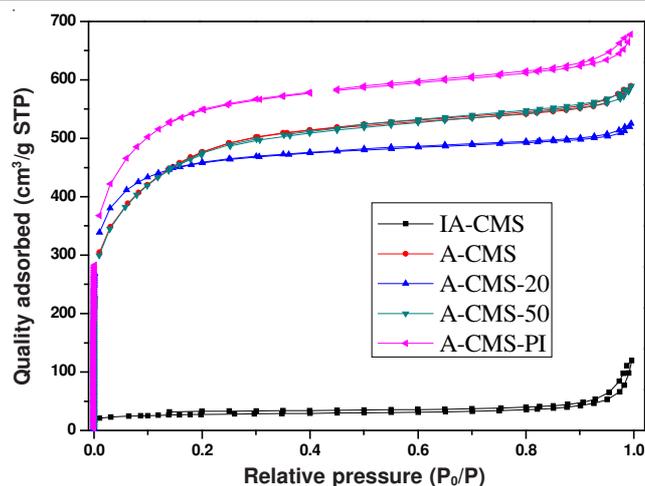


Fig. 5. N₂ adsorption-desorption isotherms of carbon molecular sieves prepared at different contents of polyimide

polyimide has high micropore area and volume (762 m²/g, 0.42 cm³/g), which indicates that polyimide is an ideal precursor for preparing carbon molecular sieves. But the results show that the micropore area and volume of samples are not simply the sums of both derived from pure polyimide and pure coal at their weight ratio. The polyimide blending does not improve the total adsorbed quantity for the samples, but it is effective for increasing micropore area and volume. The results suggest that the carbon molecular sieves with optimal value of micropore area and volume can be prepared from the composite with 20 % polyamide acid. The results show that at this amount, polyamide acid effectively fills up some disordered pores of the coal, forming the optimal precursor for carbonization.

The pore size distributions of samples prepared with different contents of polyimide are plotted in Fig. 6. Apparently, the pore sizes mainly lie in the range of 0.5-4.0 nm. In contrast, A-CMS-20 shows a narrow pore size distribution, the majority of the pores lie in the range of 0.5-2.0 nm. Meanwhile, the micropore area and micropore volume of A-CMS-20 increase significantly after carbonization and activation (Table-2). The results may be explained by the fact that coal is compatible with polyamide acid to a certain degree. Because the coal is composed of various aromatic compounds, the pore surface of coal was modified by blending the polyamide acid. The carbonization process of the samples likely follows the similar mechanism to chemical vapour deposition as proposed by Kawabuchi *et al.*¹⁴. The BET surface area, micropore area, total pore volume and micropore volume of the IA-CMS-50 are smaller than those of IA-CMS. The suitable amounts of polyimide would deposit on pore walls during the carbonization,

TABLE-2
NITROGEN SORPTION RESULTS OF CARBON SAMPLES PREPARED WITH
DIFFERENT AMOUNTS OF POLYIMIDE (PI), ACTIVATED AND UNACTIVATED SAMPLES

Sample	Activated by KOH	S _{BET} ^a (m ² /g)	S _{mi} ^b (m ² /g)	V _t ^c (cm ³ /g)	V _{mi} ^d (cm ³ /g)	Median pore width (Å)
IA-CMS	Unactivated state	86.04	48.96	0.18	0.026	5.54
IA-CMS-50	Unactivated state	70.56	41.96	0.099	0.022	5.13
A-CMS	KOH:C (w/w) = 6:1	1547.00	391.60	0.91	0.23	5.81
A-CMS-20	KOH:C (w/w) = 6:1	1406.31	900.01	0.81	0.49	5.66
A-CMS-50	KOH:C (w/w) = 6:1	1522.45	430.10	0.91	0.25	5.87
A-CMS-PI	KOH:C (w/w) = 6:1	1721.20	762.51	1.05	0.42	5.82

^aS_{BET}: BET surface area; ^bS_{mi}: *t*-Plot micropore area; ^cV_t: total pore volume; ^dV_{mi}: *t*-Plot micropore volume.

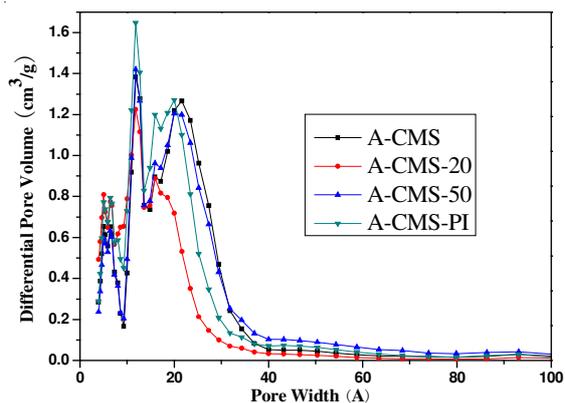


Fig. 6. Pore size distributions calculated by the DFT method from N_2 adsorption isotherms at 77 K of carbon molecular sieves samples at different content of polyimide

resulting in the decreased pore size and narrowed distribution. The same process of polyimide yields higher BET surface area and micropore volume. In the carbonization process, the polyimide could block the pore of pyrolyzed coal completely. After activation, carbon deposition sites in the pore of carbonized coal were corroded by KOH. Thus activation was to enlarge the diameters of the pores which were created by carbonization and to create some new pores, thus resulting in the formation of a well-developed and readily accessible pore structure with large internal surface area.

The result indicates that the optimal mass ratio for adjusting pore size is 1:5 by weight ratio of polyimide to coal, which may be due to effective control of the pore aperture. In addition, at this ratio, polyamide acid stays inside the macropores of coal, in favour of forming the uniform pore structure of samples during carbonization. But when the amount of polyamide acid is less than the optimal value, the macropores of coal are not fully filled up and the role of the polyimide becomes less pronounced. Therefore, the polyimide content is an important factor in producing samples with high micropore volume.

Influence of the activation on micropore size: The micropore size distributions of the activated samples prepared with different content of polyimide and different process are shown in Figs. 7 and 8, respectively. It is clear that the polyimide content has a significant effect on the micropore size of pyrolyzed coal as shown in Fig. 7. Comparing the Figs. 7 and 8, the micropore volume is obviously increased after activation. The positions of the jump-point were shifted with the different content of polyimide (A-CMS at 4.49 Å, A-CMS-20 at 4.47 Å, A-CMS-50 at 4.50 Å) as shown in Fig. 8. Comparing the curve of A-CMS-20 and A-CMS-PI, though the two curves have the same jump-point, the volume of the two samples is different. According to the kinetic theory, this pore size and volume change would significantly affect their gas separation properties²³. The experimental work is under way to determine the gas separation performances of the micropore carbons prepared in this work.

SEM: SEM images of the samples shown in Fig. 9 reveal a typical morphology of porous carbon materials. Some larger and disordered pores are viewed in Fig. 9(A) and (B). Compared with Fig. 9(A) and (B), there are some uniform pores in

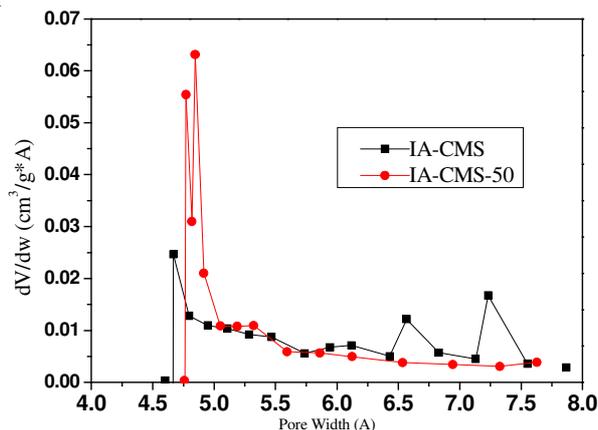


Fig. 7. Micropore size distributions of inactivated samples

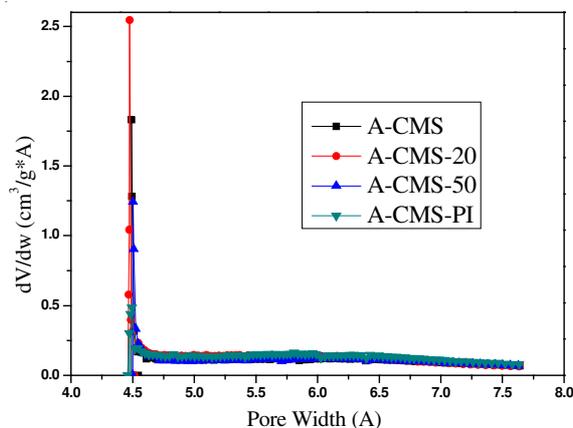
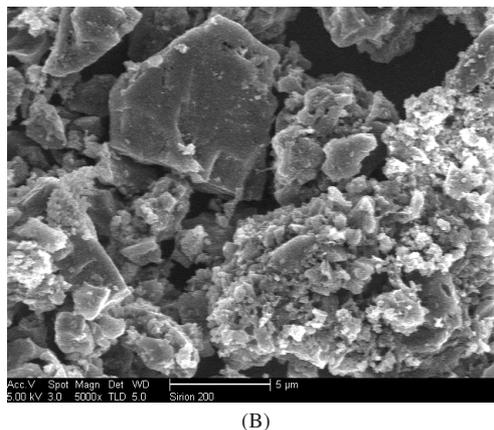
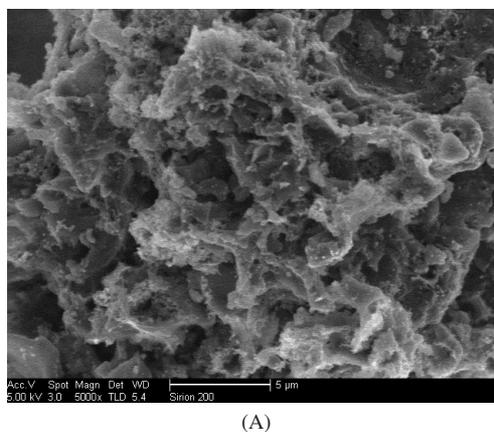
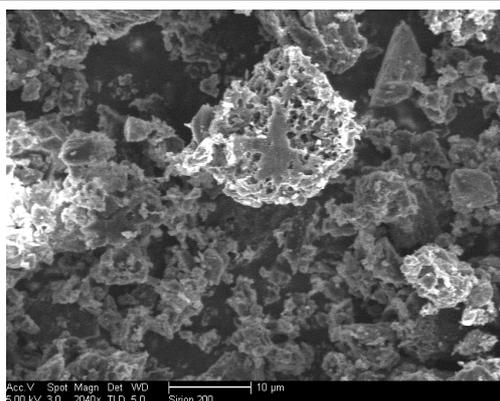
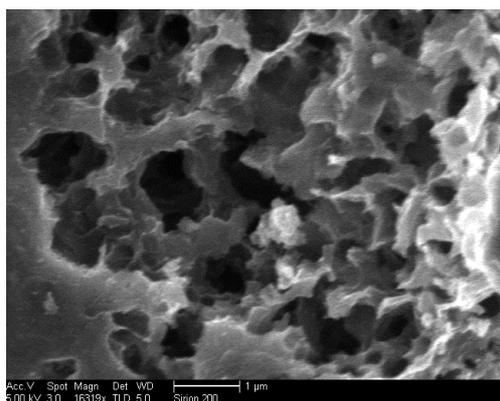


Fig. 8. Micropore size distributions of activated samples





(C)



(D)

Fig. 9. SEM images of the samples prepared from coal with different contents of polyimide: (A) A-CMS, (B) A-CMS-50 and (C,D) A-CMS-20

Fig. 9(C) and (D). This is consistent with the increase in t -plot micropore area and volume in N_2 sorption experiments. Again, that polyimide contributed to adjusting pore size and its distribution.

Conclusion

In this paper, the composites of bituminous coal with polyimide have been successfully used as the precursors to prepare carbon molecular sieves through three successive stages, which are formation of bituminous coal and polyimide composites, carbonization and activation. Our results show the pore aperture of carbon molecular sieves can be controlled by blending bituminous coal with different amounts of polyimide under different conditions. The micropore area,

micropore volume of carbon molecular sieves increased from $391.6 \text{ m}^2/\text{g}$ and $0.23 \text{ cm}^3/\text{g}$ to $900 \text{ m}^2/\text{g}$ and $0.49 \text{ cm}^3/\text{g}$ after loaded with 20 wt % polyimide. The content of polyimide has been shown to strongly affect the micropore area and micropore volume of carbon molecular sieves.

ACKNOWLEDGEMENTS

This work was supported in part by the National Natural Science Foundation of China (21171004) and the Natural Science Foundation of Anhui Province Education Department (KJ2011A064).

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