

Preparation of Carbon Molecular Sieve for Pressure Swing Adsorption Concentrating Low-Concentration Methane†

JIAMING LI*, GUANGXUE LI, FENG JIANG, JIA BU, MINGZHU ZHAO, HUALU ZHAN and YANG CHU

College of Chemical Engineering, Anhui University of Science and Technology, 168 Shungeng Road, Huainan City 232001, Anhui Province, P.R. China

*Corresponding author: E-mail: gxli@aust.edu.cn

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In this paper, the samples of carbon molecular sieves were prepared by phenolic resin. The used technology of XRD, IR, SEM, BET to characterize surface properties and microstructure of carbon molecular sieves and used ZC36 high resistance meter to determine the surface and volume resistance of carbon molecular sieves. Study the influence of carbonization temperature, carbonization time, chemical vapour deposition time and chemical vapour deposition temperature on products. The results show that the carbon molecular sieves have the properties of high selective adsorption and adsorption capacity on the condition of carbonization temperature at 850 °C, carbonization time in 2.5 h, chemical vapour deposition time in 2 h and chemical vapour deposition temperature at 700 °C. XRD analysis shows: The microstructure of carbon molecular sieves is graphite layer type structure formed by amorphous carbon. The IR analysis shows that there are a small number of oxygen functional groups on the surface of carbon molecular sieves. SEM analysis shows that the surface pore basic shape of carbon molecular sieves is the narrow slit structure. BET analysis shows that the average of pore size of carbon molecular sieves is 2.3 nm. ZC36 high resistance meter determined result shows that the carbon molecular sieves we prepared belong to the static electricity conductor.

Key Words: Carbon molecular sieve, Pressure swing adsorption, Methane, Low-concentration.

INTRODUCTION

Carbon molecular sieve is a kind of nonpolar carbon adsorptive material which has nanometer level ultrafine micropores. It is composed of micropores, some mesoporous and large pores¹. Carbon molecular sieve is used in preparation of hydrogen and nitrogen in chemical industry, sewage treatment in environmental protection, military gas mask in military protection and some other areas because of its pore structure and stable chemical properties. For example, carbon molecular sieve is used in concentrating methane of coal bed gas by pressure swing adsorption, which has the globally economic and environmental meaning of energy saving and emission reduction^{2,3}. Adsorption properties of carbon molecular sieve largely depend on its microstructure. So it is significant to characterize the microscopic structure of carbon molecular sieve.

Since the 1970s, the technology of preparing the carbon molecular sieve has great progress. Raw materials and preparation methods have a great impact on the performance of carbon molecular sieve. In recent years, as carbon molecular

sieve has a very high value in utilizing coal mine gas, the requirements of antistatic and explosion-proof of carbon molecular sieve are also improved. Ngugen and Do⁴ used benzene to adjust the pore size to prepare carbon molecular sieve which has a similar pore size. Villar-Rodil *et al.*⁵ prepared carbon molecular sieve by aromatic polyamide fiber. Vansant and Hu⁶ prepared carbon molecular sieve by method of activating using walnut shell. Sunxin *et al.*⁷ used petroleum coke as the raw material and took the method of union of physical activation and chemical activation to prepare carbon molecular sieve. In this paper we used phenolic resin to prepare carbon molecular sieve and adjust the pore size by toluene⁸. Analyzed the effect of experimental conditions on the properties of carbon molecular sieve. Charactered microscopic and anti-static of products and study the relationship between microstructure and adsorption performance of carbon molecular sieve.

EXPERIMENTAL

First, grind the phenolic resin for 10 h with the ball mill, to get the raw powder whose average diameter is about 6 μm. Add the polyvinyl alcohol binder to the raw material accor-

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ding to the ratio of the raw material powder to binder 2:1. Mix them uniformly and extrude them into the cylindrical particle diameter of about 3 mm with the oil press. Then they are dried for 6 h in the drying box at 80 °C. Put the dried material particles into the tubular furnace, heat them to the carbonization temperature, which is between 600 and 1000 °C under the protection of nitrogen and keep the material particles in the carbonization temperature for 1-3 h.

The toluene vapour is used as the adjustable hole agent to fill the holes of the carbide with the method of gas-phase carbon deposition⁹. The gas-phase carbon deposition process is completed by using nitrogen gas carrying adjustable hole agent vapour into the tube type furnace. The temperature of carbon deposition is 600 to 800 °C and the time of deposition is 40 to 200 min. Make it cool after the carbon deposition, to get the carbon molecular sieve product.

To characterize the phenolic resin material by use thermogravimetric analyzer in the program of temperature control. Take 25 mg samples, then heat them from room temperature to 1000 °C with the nitrogen flow rate of 150 mL/min and the heating rate of the 4 °C/min. To characterize the catalyst by using the XD-3 diffractometer, which is produced by the Beijing Beijing Purkinjie general limited at the room temperature. The apparatus takes Cu as the target, K α as the diffraction source and $\lambda = 0.15406$ nm. The pipe pressure is 36kV, the current is 36 mA, the scan rate is 4°/min and the diffraction angle (2θ) is 10° to 60°. Test the catalysts by using the VECTOR33 type infrared spectrometer, which is produced by the Germany Brook, with the wavenumber range of 4000-400 cm^{-1} . Grind the catalysts fully, mix them and press them into tablets, after completing the steps above, you can start the test under the setting conditions. The static volumetric method and other mixed adsorption principles are used by the GEMINV230 automated surface area and pore analyzer, which is produced by the America Mike company of the United States, to determine the specific surface area, pore volume, pore size and so on. The principle is also used in the isothermal adsorption and desorption analysis. To characterize the carbon molecular sieve product and observe the surface morphology of the product by using the S-3000 N scanning electron microscope of Japanese Hitachi. We made a single column pressure swing adsorption apparatus ourselves for carbon molecular sieve performance test¹⁰ and used gas chromatograph to detected product gas. In room temperature, quantity of carbon molecular sieve filling is 250 g. Adsorption pressure is 1.5 MPa. The raw gas is mixture of methane and nitrogen and concentration of methane is 20 %. Diagram of experimental setup is given in Fig. 1.

RESULTS AND DISCUSSION

Thermal gravimetric analysis of phenolic resin materials: Fig. 2 is the TG curve of raw material, which shows that the free water remove under 100 °C. There are thermal decomposition and polycondensation reactions below 700 °C and the volatile components remove, micropores are formation. The weightlessness is balanced above 700 °C and the microporous starts to shrink. We replace O₂ when the weightlessness is balanced. It is observed that the phenolic resin has the characteristic of low ash content. It is excellent raw material of preparation of carbon molecular sieve¹¹.

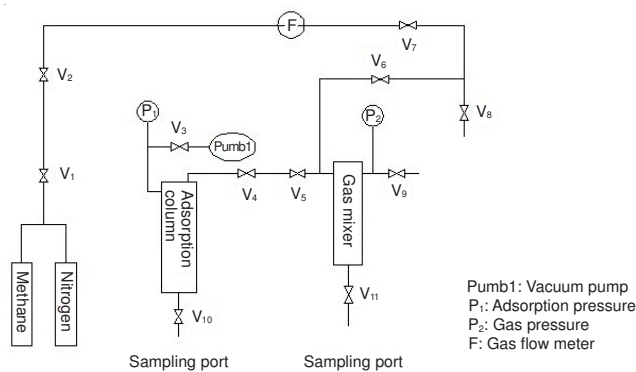


Fig. 1. Diagram of single column pressure swing adsorption apparatus

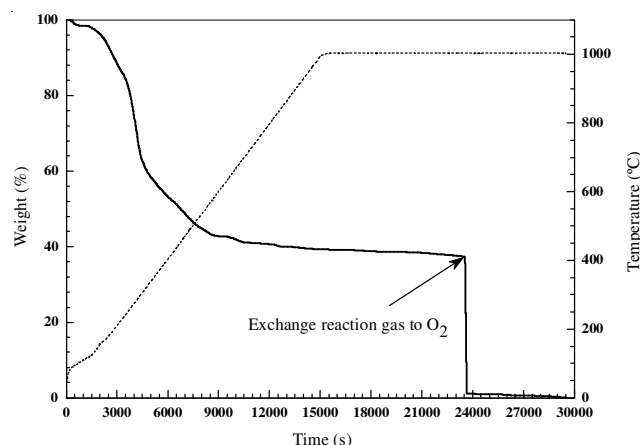


Fig. 2. TG curve of phenolic resin

XRD analysis of carbon molecular sieve: Fig. 3 shows that the XRD diagram has no characteristic diffraction peaks. The product is composed of amorphous carbon. Diffraction peaks appears when 2θ is 25° and 45°. There are (002) and (100) diffraction peaks of the graphite layer type structure^{12,13}. This shows the structure of production is the graphite layer type structure. It has the tendency of regent, so the microstructure of carbon molecular sieve is graphite layer type structure formed by amorphous carbon.

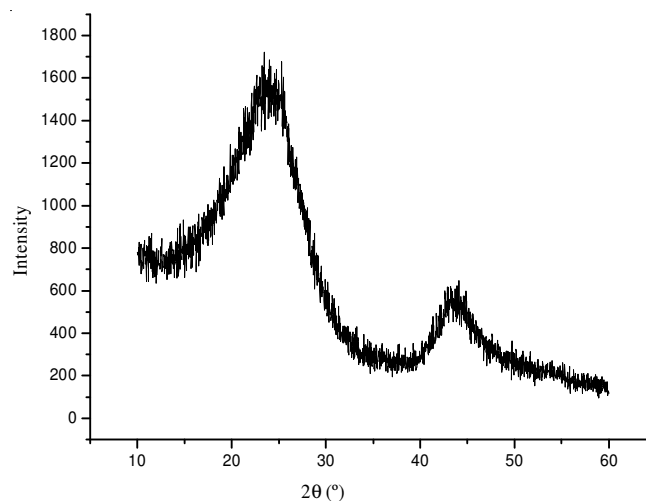


Fig. 3. XRD diagram of carbon molecular sieve

Anti-static of carbon molecular sieve: We used ZC36 high resistance meter to determine the surface and volume

resistance of carbon molecular sieve. Table-1 shows that the surface and volume resistance of carbon molecular sieve are less than 10^6 , so carbon molecular sieve is electrostatic conductor. When concentrating low-concentration gas, carbon molecular sieve can emit the static electricity in time and prevent the explosion of methane. This performance of carbon molecular sieve we made has great significance in the low concentration gas utilization field.

TABLE-1
SURFACE AND VOLUME RESISTANCE OF CMS

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Surface resistance (Ω)	2.12×10^4	1.87×10^4	1.43×10^4	2.24×10^4	1.55×10^4
Volume resistance ($\Omega \cdot \text{cm}$)	4.89×10^4	4.65×10^4	4.11×10^4	5.37×10^4	4.33×10^4

BET analysis of carbon molecular sieve: We used full automatic surface area and pore analyzer to characterize the pores of carbon molecular sieve. Fig. 4 shows the pore size distribution of carbon molecular sieve. The ideal holes of carbon molecular sieve should be all micropores. The result of BET and pore size distribution figure that most of the pores of carbon molecular sieve are micropores, the average size of pores is 2.3 nm. Pore structure of carbon molecular sieve is improved significantly by chemical vapour deposition. Micropore volume is enlarged and the average of pores size is reduced.

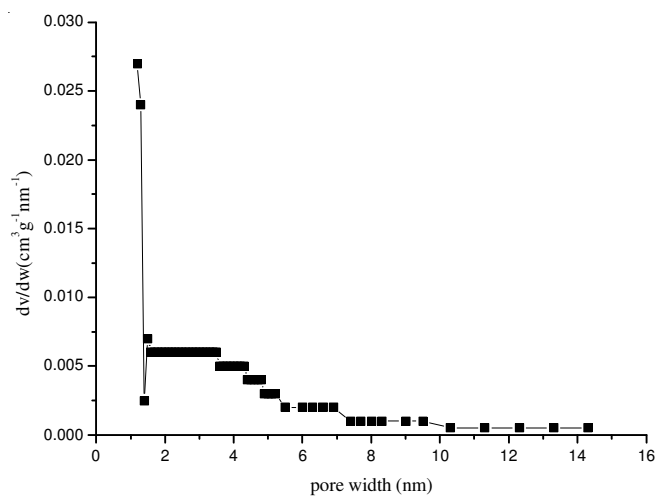


Fig. 4. Pore size distribution diagram of carbon molecular sieve

FT-IR analysis of carbon molecular sieve: There is a strong absorption peak appearing in 1126 cm^{-1} . This shows the main oxygen containing functional groups on the surface of carbon molecular sieve are C-O. Those oxygen containing functional groups in the form of polar carbon-oxygen complexes exist on the surface of carbon molecular sieve. There is a absorption peak appearing in 1400 cm^{-1} . This shows that there are a small number of inorganic oxygen containing functional groups or compounds in carbon molecular sieve. These materials are mainly derived from the ash content in raw material. The absorption peak in 1600 cm^{-1} is attributed to the telescopic and vibration of the C=C bond in aromatic

ring. The absorption peak in 3500 cm^{-1} is attributed to the telescopic and vibration of the O-H bond among molecules.

SEM analysis of carbon molecular sieve: The surface pore basic shapes of carbon molecular sieve are observed by SEM. The result shows that the surface pore basic shapes of carbon molecular sieve is the narrow slit structure. This is because aromatic carbon sheet of microcrystalline is removed when pyrolysis happens.

Influence of reaction conditions on the product performance: The factors that influence the carbon molecular sieve performance are complex. So we use the single factor method. Study on the influence of carbonization temperature, the time of carbonization temperature, the time of chemical vapour deposition of carbon and chemical vapour deposition temperature on products.

Influence of carbonization temperature: The Fig. 5 shows different carbonization temperatures influence on carbon molecular sieve performance. Below $850 \text{ }^\circ\text{C}$, the concentration of methane increases as the carbonization temperature rises. Phenolic resin removes volatilization and forms pores. As the carbonization temperature rises, the pyrolysis process is completed and more number of the pores are formed. At the same time the thermal shrinking process happens and the big pores shrink to micropores, which improves the performance of carbon molecular sieve to concentrate methane. The concentration of methane reduces as the carbonization temperature rises above $850 \text{ }^\circ\text{C}$. The thermal shrinking process happens dramatically because of the high carbonization temperature. Micropores are jammed. The performance of carbon molecular sieve to concentrate methane drops¹⁴. We can see from the Fig. 3 that $850 \text{ }^\circ\text{C}$ is the most suitable carbonization temperature to prepare carbon molecular sieve.

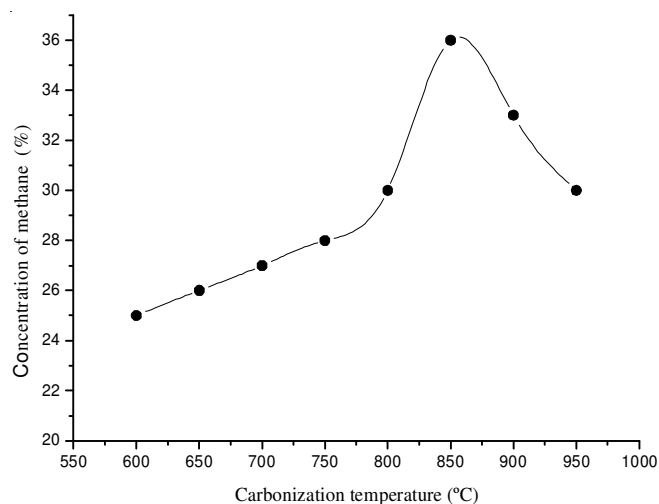


Fig. 5. Effect of carbonization temperature on methane concentration

Influence of carbonization time: Fig. 6 shows influence of carbonization time on carbon molecular sieve performance. Carbon molecular sieve performance of concentrating methane improves as carbonization time goes. The concentration of methane drops when arriving to the maximum. When the carbonization time is short, thermal decomposition of raw materials is incomplete. Volatile matters can not be fully removed and this is not conducive to form and expand pores.

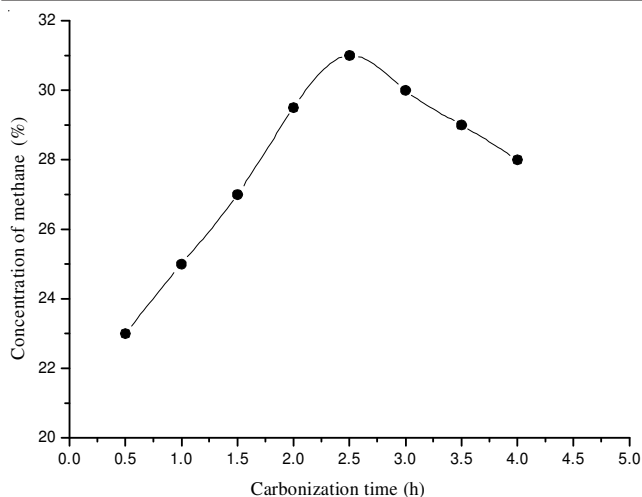


Fig. 6. Effect of carbonization time on methane concentration

The number of pores is less and the volume of pores is small. Carbon molecular sieve performance of concentrating methane is not good. When the carbonization time is too long, the pores are easy to collapse and deformate. So the carbonization time in 2.5 h is the best time to prepare carbon molecular sieve.

Influence of chemical vapour deposition time: Fig. 7 shows influence of carbonization time on carbon molecular sieve performance. We can see that when chemical vapour deposition time is less than 120 min the concentration of methane increases as the carbonization time goes. At the beginning of chemical vapour deposition, the big pores become micropores because toluene are carbonization on pores wall. The volume of pores increases. Carbon molecular sieve performance of selective adsorption can be improved. After 120 min, the concentration of methane drops. After 120 min, micropores are jamed because deposition is excessive. So 120 min is the best time of chemical vapour deposition.

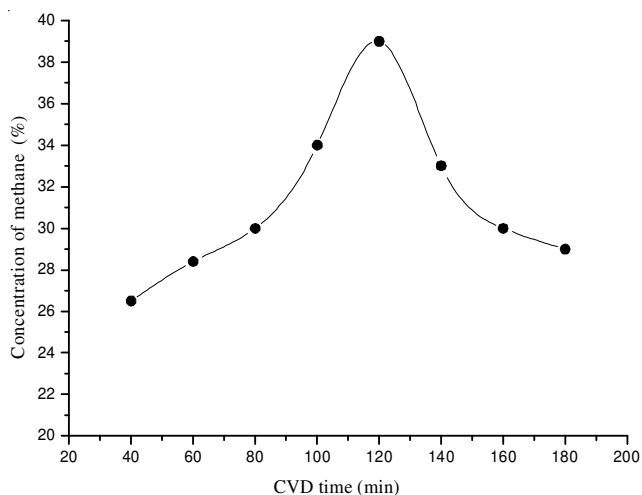


Fig. 7. Effect of chemical vapour deposition (CVD) time on methane concentration

Influence of chemical vapour deposition temperatures: Fig. 8 shows influence of chemical vapour deposition temperatures on carbon molecular sieve performance. Below 700 °C, the concentration of methane increases as the chemical vapour deposition temperature rises. This is because as the chemical

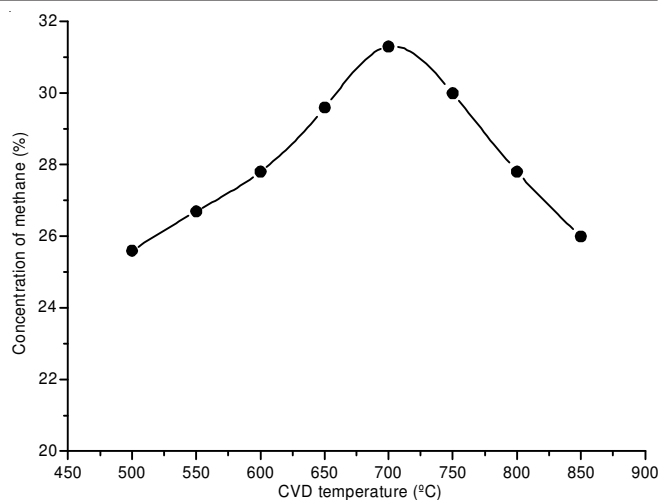


Fig. 10. Effect of CVD temperature on methane concentration

vapour deposition temperature rises, the pyrolysis process of toluene is complete. Carbon deposition happens fully and effect of adjusting the aperture is good. The concentration of methane reduces as the chemical vapour deposition rises above 700 °C. Carbon deposition will happen on the surface of the carbon molecular sieve for high chemical vapour deposition temperature and pores will be jamed. So the performance of carbon molecular sieve to concentrate methane drops¹⁴. We can get that carbon deposition has the best effect in 700 °C of the chemical vapour deposition temperature.

Conclusion

The samples of carbon molecular sieve were prepared by phenolic resin. The results show: carbon molecular sieve have the properties of high selective adsorption and adsorption capacity on the condition of carbonization temperature at 850 °C, carbonization time in 2.5 h, chemical vapour deposition time in 2 h and chemical vapour deposition temperature at 700 °C. The microstructure of carbon molecular sieve is graphite layer type structure formed by amorphous carbon.

REFERENCES

1. Y. Zhang, L.B. You and H.Q. Hu, *New Carbon Mater.*, **15**, 55 (2000).
2. K.W. Liu, M. Gu and X.F. Xian, *Mod. Chem. Ind. Monthly*, **12**, 15 (2007).
3. Y. Huang and D.R. Paul, *Ind. Eng. Chem. Res.*, **46**, 2342 (2007).
4. C. Nguyen and D.D. Do, *Carbon*, **33**, 1717 (1995).
5. S. Villar-Rodil, A. Martnez-Alonso and J.M.D. Tascon, *J. Colloid. Interf. Sci.*, **254**, 414 (2002).
6. E.F. Vansant and Z.H. Hu, *Carbon*, **33**, 561 (1995).
7. X. Sun, Q.F. Zha and M.B. Wu, *Carbon Techniq.*, **23**, 14 (2004).
8. G.X. Li, J. He and H.L. Zhang, A Method of Preparing Carbon Molecular Sieves, China Patent ZL10062526 (2009).
9. T. Horikawa, J. Hayashi and K. Muroyama, *Carbon*, **40**, 709 (2002).
10. G.X. Li and J.B. Wang, A Method of Concentrating Low Concentration Gas by Pressure Swing Adsorption, China Patent CN101596391A (2009).
11. L. Zeng and K.W. Liu, *Carbon Techniq.*, **3**, 26 (2007).
12. Y.K. Qu and Y. Li, *Appl. Chem. Indust.*, **37**, 1338 (2008).
13. S.P. Xu and S.C. Guo, *Coal Con.*, **18**, 43 (1995).
14. H.Y. Zhou, Synthesis, Characterization and Application of the Mesoporous Carbon, DaLian, Dalian University of Technology, China (2009).