

Preparation and Activation Mechanism of Rice Husk Based Mesoporous Carbon†

GUIHUA HOU*, GUANGZHAO XUE, LU YUE and QINFANG ZHANG

Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Yancheng 224051, P.R. China

*Corresponding author: Fax: +86 515 88298919; E-mail: houghuia@ycit.cn

AJC-17459

Mesoporous carbon was prepared by a combined method of carbonization and activation processes, in which rice husk and KOH were used as carbon source and activator, respectively. Nitrogen adsorption-desorption isotherms (ADI) were measured by specific surface area instrument, the pore size distribution and pore volume were calculated by BET equation and BJH method. The mesoporous characteristic was characterized by small angle X-ray diffraction. The gas and solid composition from husk activation process was characterized by X-ray diffraction (XRD) and simultaneous thermal analysis mass spectrometry (TG-MS), then the pore forming mechanism was speculated. The results show that the average pore size of the prepared mesoporous carbon was as high as 4.54 nm and the specific surface area and mesopore rate were 2174.09 m²/g and 78.73 %, respectively. The K₂Si₄O₉ was found in the activated rice husks, it may be from reaction SiO₂ of rice husk with the decomposer K₂O of KOH.

Keywords: Mesoporous carbon, Rice husks, Chemical activation.

INTRODUCTION

Mesoporous materials had broad application prospects in many areas such as catalysis, separation and adsorption due to unique properties. In recent years, the biomass¹, coal² and petroleum coke³ used as raw materials to prepare activated carbon with high specific surface area was widely researched, but their pore diameter was mainly in micro range and increasing the diameter to the mesoporous range will help to expand the application areas of carbonaceous porous materials. Kubota *et al.*⁴ prepared the porous materials with an average pore diameter of 2.60 nm with rice husk as raw materials, NaOH as activator. Liou⁵ prepared 3.06 nm porous materials with bagasse and sunflower seed shells as raw materials, phosphoric acid and zinc oxide as an activator average. So far, the reported highest average pore diameter of the material prepared with rice husk as raw material was 3.85 nm⁶. Based on this, in this paper, we further explored the study of mesoporous carbonaceous materials with big pore diameter prepared by rice husk and analyzed the pore formation mechanism.

EXPERIMENTAL

Rice husk was purchased from Jiangsu province Yan Cheng West City Rice Factory, KOH (AR) from Jiangsu Tong Sheng Chemical Co. and vacuum/atmosphere tube furnace was from Tianjin Central Experimental Furnace Co., Ltd.

The rice husk was washed with distilled water, dried, carbonized at 420 °C for 4 h under nitrogen in the vacuum/atmosphere tube furnace. With KOH as an activator, KOH and rice husk with the mass ratio of 3:1 were grinded in an agate mortar mix, heated from room temperature to 400 °C for heat preservation for 30 min, then 10 °C/min to the set temperature and incubated for 1 h in the atmosphere furnace, removed after cooling, washed with distilled water until neutral and finally dried at 120 °C for 2 h and the obtained sample was sealed and stored.

The phase of sample was measured by Rigaku Corporation D/Max-2400 type XRD, mesoporous carbon was measured by X'TRA XRD (Switzerland ARL company), N₂ adsorption-desorption isotherms were measured by the United States Contador instruments Autosorb-iQ-TCD-automatic physical-chemisorption analyzer at 77 K and the specific surface area, pore size distribution and pore volume were calculated by BET equation and BJH method, the gas composition was characterized by TG-MS (Germany, NERZSCH company, TG 209 F1 QMS403D).

RESULTS AND DISCUSSION

Effects of activation temperature on pore structure characteristics: Carbonized rice husk was made in tube furnace, its specific surface area was 295.68 m²/g. The effects of different activation temperature on specific surface area of

†Presented at The 8th ICMMA-2014, held on 27-29 November 2014, Hoseo University, Chungnam, Republic of Korea

carbonized rice husk are shown in Fig. 1. It can be seen that the specific surface area was $731.60 \text{ m}^2/\text{g}$ at 700°C and reached $2174.09 \text{ m}^2/\text{g}$ at 750°C , which was about three times the former. The reason should be that with the increase of activation temperature, the husk formed a large number of pores. When the temperature was higher than 750°C , the specific surface area decreased rapidly, specific surface area was $1144.8 \text{ m}^2/\text{g}$ at 800°C , which should be that the formed mesoporous structure was damaged at high temperature. Pore structure characteristics of mesoporous carbon at various temperature were calculated by BJH method and the results are shown in Fig. 2. It can be found that before 750°C , with the increase of activation temperature, the micropore, mesopore, macropore and total pore volume increased. When the temperature was higher than 750°C , micropore and mesopore volume decreased rapidly, but macropore volume increased slightly, which showed further that mesoporous structure was damaged at above 750°C .

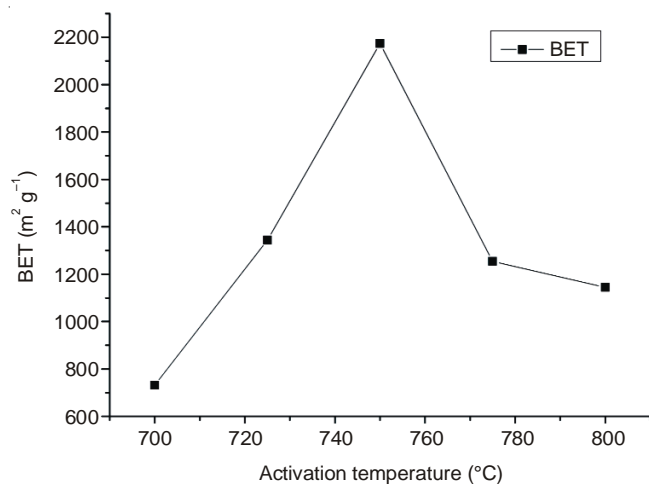


Fig. 1. Effect of the temperature on specific surface area

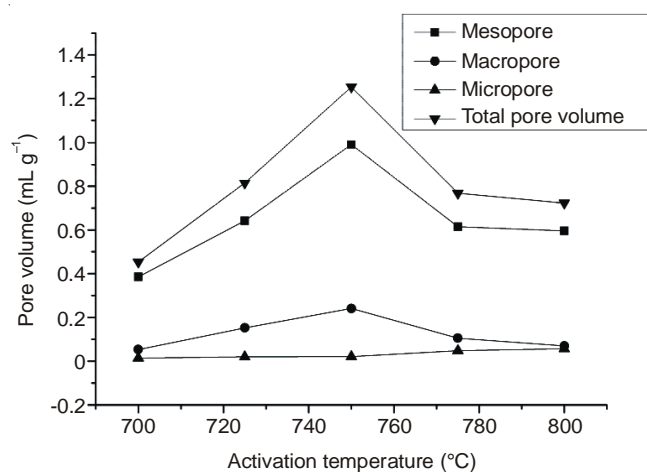


Fig. 2. Pore volume at various temperature

Mesoporous structure characteristics of the carbon:

Fig. 3 shows the absorption-desorption isotherm of mesoporous carbon at 750°C . It belonged to Type-IV adsorption isotherm, indicating the presence of a large number of mesopores carbon.

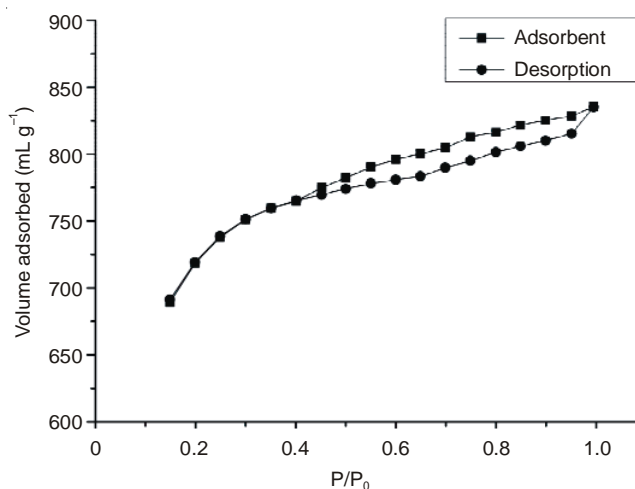


Fig. 3. Adsorption-desorption isotherms

The pore distribution of mesoporous carbon activated at 700°C , 750°C and 800°C for 1 h is shown in Fig. 4. It can be seen that the average pore sizes of samples at 700°C , 750°C and 800°C were 3.02 nm , 4.54 nm and 3.25 nm , respectively. Fig. 5 is the small angle XRD pattern of mesoporous activated carbon at 750°C . There was a strong diffraction peak at 0.53° , indicating further the presence of mesopores. Its mesopore volume was $0.99 \text{ cm}^3/\text{g}$, with the rate up to 78.73% by BJH method.

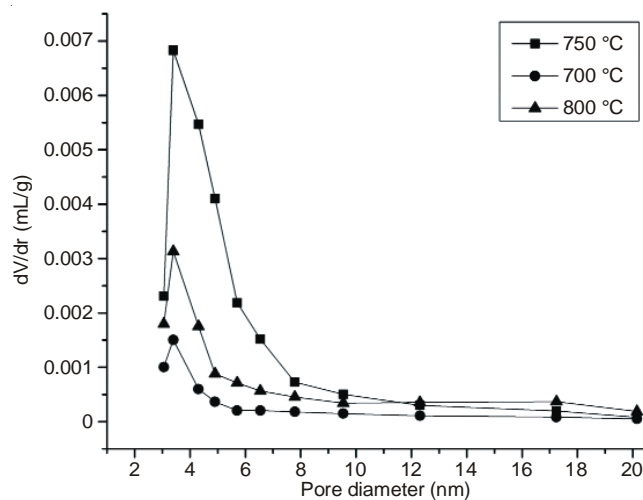


Fig. 4. Pore distribution of mesoporous carbon at 700°C , 750°C and 800°C

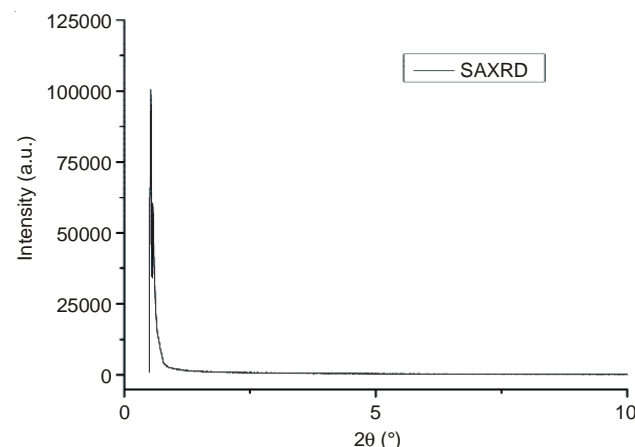


Fig. 5. Small angle X-ray diffraction pattern

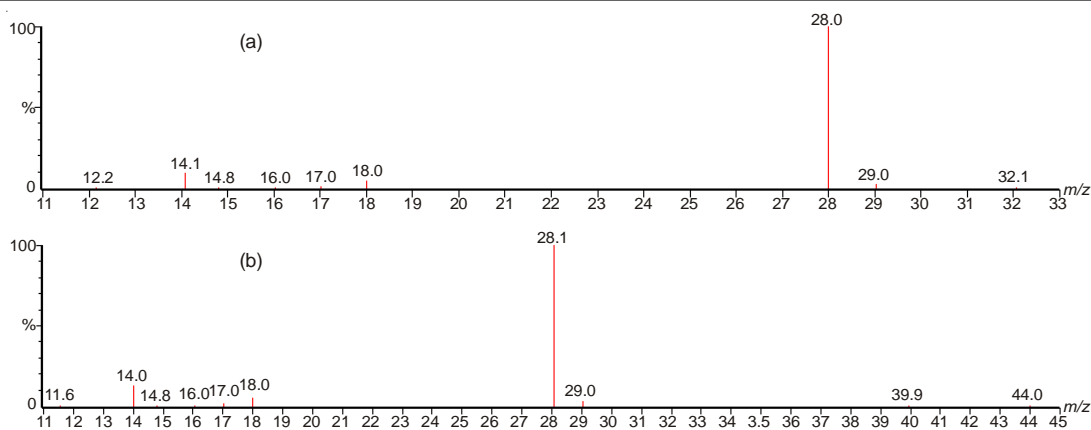


Fig. 7. Gas mass spectra of activation process

Pore formation mechanism of mesoporous activated carbon: The white solid was found on the bottom of mesoporous carbon sample after activated (referred to as sample A) and the mesoporous carbon was washed with distilled water, the filtrate was dried at 120 °C to obtain the white solid (referred to as sample B), which were analyzed by XRD. It can be seen from Fig. 6 that the rich husk was activated with KOH to generate K_2CO_3 and $K_2Si_4O_9$. It is also found that there was a small amount of light yellow substance in the surface of unwashed activated product and a strong reaction occurred when water was added, which may be due to the generation of K or K_2O in the activation process of KOH⁷.

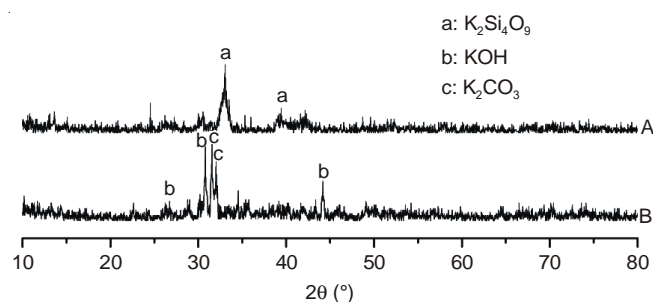
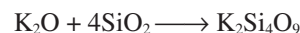
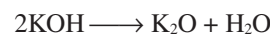
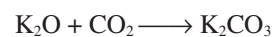
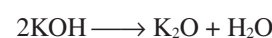


Fig. 6. XRD patterns of the activated residue

Fig. 7 shows the gas mass spectra of activation process. Fragment ion peak pairs of m/z 12, m/z 16 in the reaction of the carbonized rice husk (sample A) and KOH-activated rice husk (sample B) appeared and the presence of m/z 28 indicated the generation of CO and this ion peak pairs also appeared for sample B, while the presence of m/z 44 indicated the generation of CO_2 . The m/z 18 always existed in Fig. 7, indicating the presence of H_2O .

Rice husk was used as raw material and rice husk contained SiO_2 , therefore, the formation process of rice husk based mesoporous carbon was the pyrolysis of KOH to generate K_2O and H_2O in the activation reaction. They respectively combined with amorphous reducing carbon were activated and generated mesopores. Synchronous thermal analysis mass spectrometry (TG-MS) measured that the gas composition in the KOH activation process of rice husk contained CO, CO_2 , H_2O . Ehrburger *et al.*⁸ confirmed the presence of H_2 and the mesoporous carbon filtrate contained K_2CO_3 ⁹. Meanwhile, SiO_2 of the carbonized rice husk reacted with high-temperature decomposer K_2O of

KOH to form $K_2Si_4O_9$, thereby the chemical reaction was deduced as follows:



Conclusion

Mesoporous carbon was prepared by a combined method of carbonization and activation processes. Its average pore size, specific surface area and mesoporous rate were 2174.09 m^2/g , 78.73% and 4.54 nm, respectively. Before the activation temperature of 750 °C, with the increase of the temperature up to 750 °C, the mesopores and micropores increased and after 750 °C, micropore and mesopore volume decreased sharply, macropore volume slightly increased. Meanwhile, K_2CO_3 , $K_2Si_4O_9$, H_2O , CO, CO_2 and H_2 were formed in the formation of mesopores.

ACKNOWLEDGEMENTS

Financial support of the work by the Natural Science Foundation of Jiangsu Province (No. BK2012676, BK20130428, BK20140463) and National Key Technology R&D Program (2013BAC13B01-03) is greatly acknowledged.

REFERENCES

1. K.F. Cen, X. Gao, M.J. Ni, R.B. Wu, G. Xiao and H.L. Zhou, *J. Combustion Sci. Technol.*, 14 (2014).
2. W.-G. Li, X.-J. Gong, K. Wang, X.-R. Zhang and W.-B. Fan, *Bioresour. Technol.*, **165**, 166 (2014).
3. Y. Shi, J.W. Chen, J. Chen, R.A. Macleod and M. Malac, *Appl. Catal. A*, **441**, 99 (2000).
4. M. Kubota, T. Ito, F. Watanabe and H. Matsuda, *Appl. Therm. Eng.*, **31**, 1495 (2011).
5. T.H. Liou, *Chem. Eng. J.*, **158**, 129 (2010).
6. L. Lin, S.R. Zhai, Z.Y. Xiao, Y. Song, Q.-D. An and X.-W. Song, *Bioresour. Technol.*, **136**, 437 (2013).
7. W.M. Qiao, Q.F. Zha and L. Liu, *Carbon Techniques*, **4**, 8 (1994).
8. P. Ehrburger, A. Addoun, F. Addoun and J.B. Donnet, *Fuel*, **65**, 1447 (1986).
9. W.M. Qiao and L. Liu, *New Carbon Mater.*, 25 (1996).