

수증기 하에서 나노 알루미나실리카-수지의 탄화

이재광, 한상윤, 박승규¹, 박용기, 김희영, 이철위*
 한국화학연구원 미세기술연구소, ¹LG 생활건강
 (chylwee@kriect.re.kr*)

Carbonization of Nano Aluminosilicate-Resin Sphere under Water Vapor

J. K. Lee, S. Y. Han, S. K. Park¹, Y. K. Park, H. Y. Kim, C. W. Lee*
 Advanced Chemical Technology Division, Korea Research Institute of Chemical Technology,
¹LG Household & Healthcare Research Park
 (chylwee@kriect.re.kr*)

Introduction

The nano sized hollow carbon spheres with nano-size were represented in the recent papers [1,2]. This kind of nano particles would have some merit to apply for novel adsorbent because of having not only high surface area but also abundant mesopores shell. For being used as adsorbents, the better physical properties such as high surface area and pore volume would be useful to separate particular chemical species or environmental pollutants. Although nano-size particles itself exhibit high surface area, the properties will be improved by using new method. In this study, we carried out carbonization of the nano-particle under nitrogen and also N₂-H₂O flow of various conditions to improve the properties, and estimated one by using the BET measurement.

Experiment and Result**Preparation**

The aluminosilicate-resin (AlSiR) was prepared as follows. The aluminosilicate sphere was made from the sol-gel method [3] in EtOH solution containing ammonia water and distilled water by adding TEOS with vigorous stirring for 6 hr, and then addition of the mixture composed with C18TMS (octadecyltrimethoxysilane) and TEOS [2], followed by calcination at 550°C for 5 hr in air flow to eliminate organic materials. The dried ball was impregnated with aluminum ion and after calcination, filled by polymerization of phenol-formaldehyde in gas phase. For the polymerization, phenol and formaldehyde were used as 10 g and 5 g, respectively, to 30 g of the ball and this prepared resin was not oxidized because it is thermosetting material itself [4]. After carbonization in a tubular furnace, the AlSiR carbonized was etched by using HF solution to eliminate aluminosilicate. These balls, before and after carbonization, were analyzed through SEM images and BET-N₂ adsorption/desorption measurement at 77K.

TGA measurement

Thermal property of the AlSiR was estimated from the normal temperature to 900°C at 10°C/min in N₂ flow by TGA. As shown in Fig. 1, the pyrolysis at heating rates of 5 and 10°C/min is performed from 330 to 700°C and shows a

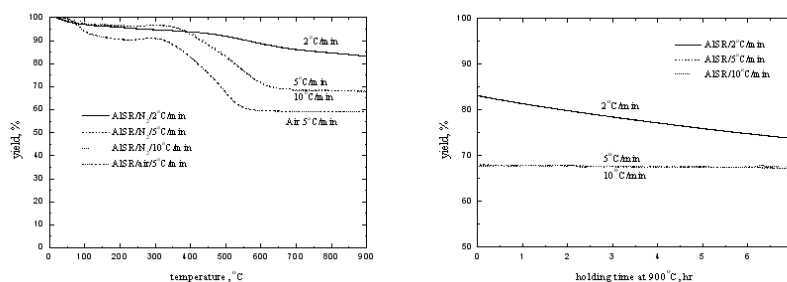


Fig. 1. TGA analysis of the AlSiR under nitrogen at the heating rates shown.

maximum near 550°C, and also decomposition of the resin is finished about 700°C. In the case of 2°C/min, a sample weight decreases slowly up to 900°C and also for the holding time. Based on this result carbonization condition of the AlSiR could be proposed by a temperature below 750°C with ramping of 10°C/min. Carbonization yield of the AlSiR is about 70 % which is similar to the TGA results.

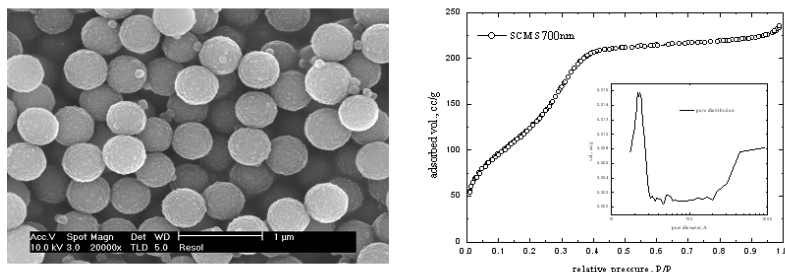


Fig. 2. SEM image and nitrogen adsorption/desorption isotherm of the SCMS.

The nano-size SCMS (solid core/ mesoporous shell) [2], which is heat treated at 550°C for 5 hr have a diameter of 700 nm and abundant mesopores with average pore size of 3.5 ~ 4 nm as shown in Fig. 2. The physical property from BET analysis shows 472 m²/g of surface area, 0.48 cc/g of total pore volume and 4.1 nm of average pore diameter. After carbonization of the AlSiR, SEM images and nitrogen adsorption/desorption isotherms of the CNB etched in HF solution are shown in Fig. 3. Both shape and size did not change from those SCMS and, especially, the CNB has an empty

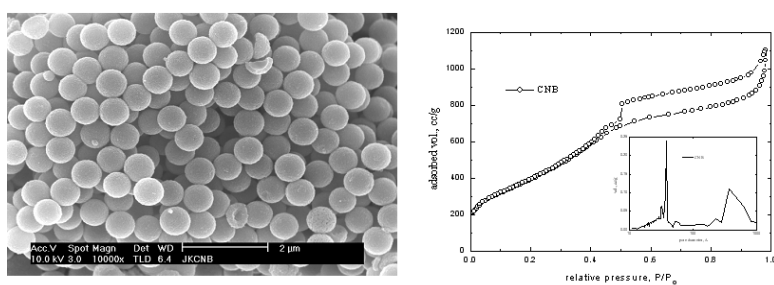


Fig. 3. SEM image and nitrogen adsorption/desorption isotherm of the CNB.

core with constant thickness shell. It is in good agreement with the result of the previous papers [1,2].

The isotherm distinctly shows hysteresis from medium to saturated pressure and increases at the saturated point. In addition, the CNB is composed of 90.5 wt.% of carbon and 1.08 wt.% of hydrogen from elemental analysis.

Effect of holding time

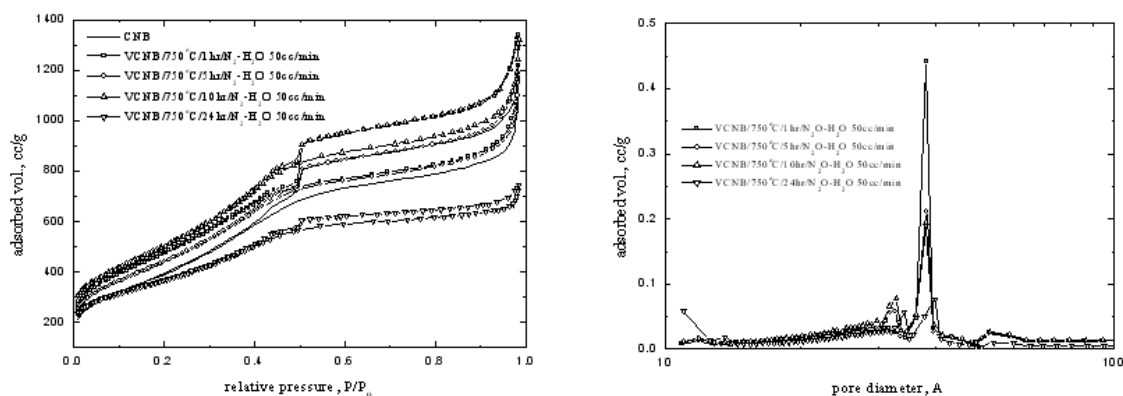


Fig. 4. Nitrogen isotherms and pore distributions of various CNB as holding time.

Fig. 4 shows nitrogen isotherms and pore distributions of the CNB and various CNB carbonized under various conditions and here in after the VCNB is the CNB carbonized under water vapor generated by bubbling of distilled water through N_2 flow. All isotherms of the VCNB behave as similar to the CNB. Among them the difference between adsorption and desorption lines is very broad for the VCNB-750-1-50 (numbers indicate temperature, $^{\circ}C$ - holding time, hr - vapor flow rate, cc/min) which indicates that the pores in the range of 3.5 ~ 4 nm could major contribute to the hysteresis of the CNB. So 1 hr of holding time under N_2 - H_2O flow rate of 50 cc/min seems to be effective to increase the size of mesopore.

Effect of flow rate

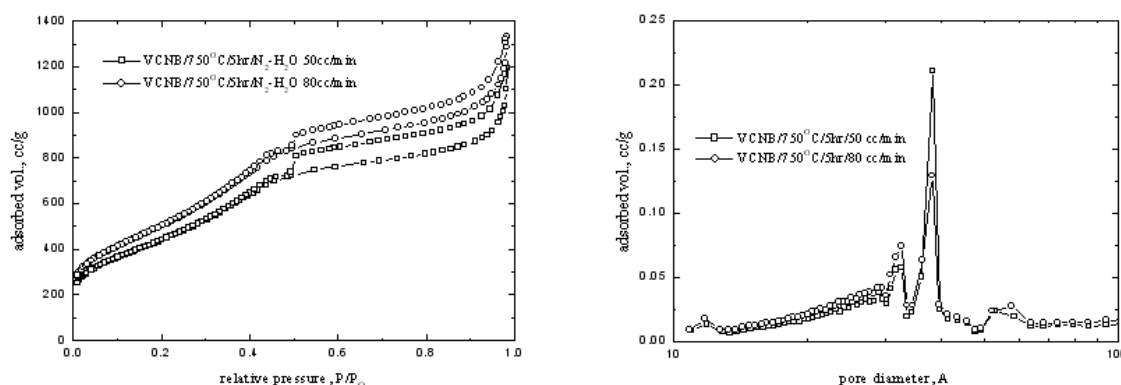


Fig. 5. Nitrogen adsorption/desorption isotherms and pore distributions as water vapor flow rates.

Fig. 5 shows the effect of flow rate during carbonization under water vapor atmosphere. The higher flow rate reduces the difference between the lines due to the fact that while the pores between 3.5 and 4 nm decrease, the other size pores increase, just increasing of total pore volume except the volume of 3.5 ~ 4 nm pores. Hence, the higher flow rate of water vapor should contribute to development of pores on the CNB by reaction between the water vapor and carbonized plane with expanding and creating pores.

Post heat treatment

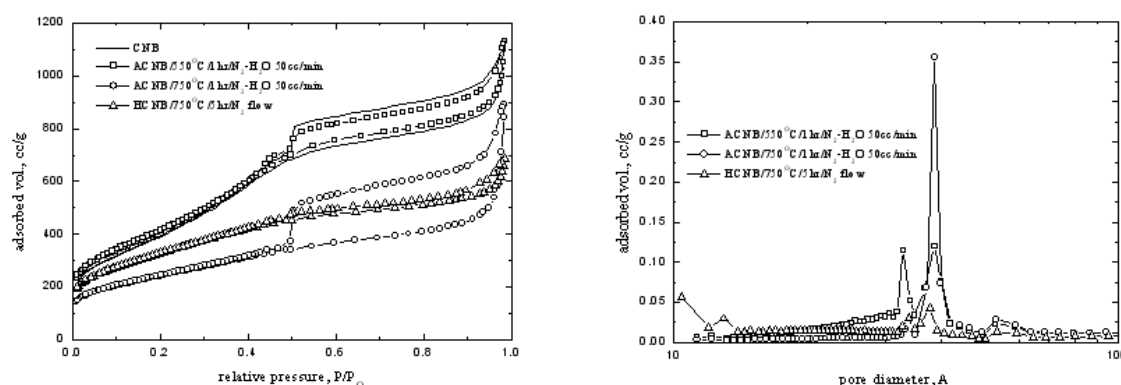


Fig. 6. Nitrogen adsorption/desorption isotherms and pore distributions of various post-heat treated CNB.

The CNB etched in HF-solution was heated in several conditions to estimate effect of post-heat treatment. The simple heat treatment of fresh CNB in N_2 flow abruptly decreases hysteresis and pore

volume except micropore, Fig. 6. It is suggested that post heat treatment shrinks the shell of CNB having empty core with about 600 nm in diameter. Almost pore volume of the HCNB (post heat treated CNB in the same condition for the carbonization) is diminished as shown in Fig. 6, pore distribution. Considering this result, the heat treatments at 750°C in the water vapor flow contribute to the shrinkage of the pore below 3.4 nm but remarkably development of the pores with 3.5 ~ 4 nm, comparing with the pore distribution of CNB in Fig. 3. These post heat treatments of the CNB would be not useful to extend surface area because of pore shrinkage.

The physical properties of various CNB evaluated from BET measurement are summarized in Table 1, Considering the VCNB series from the Table 1, BET surface area decreases with increasing holding time except 10 hr and both total volume and average diameter of pore shows similar trend. Therefore, it could be estimated that pore in shell of the CNB had been breaking with increasing of contact time to the vapor and also developing, but the amount of former would be more than the latter, except the case of 10 hr at 50 cc/min.

Table 1. Physical properties of the CNB and various VCNB from BET measurement.

Temp.	Holding Time	N ₂ -H ₂ O	Surface Area	Total Volume	Average Pore Diameter
[°C]	[hr]	[cc/min]	[m ² /g]	[cc/g]	[nm]
750	5	0	1430	1.70	4.7
750	1	50	1658	2.07	5.0
750	5	50	1471	1.84	5.0
750	10	50	1692	2.04	4.8
750	24	50	1270	1.15	3.6
750	5	80	1819	2.05	4.5
850	5	50	1857	2.34	5.0
950	5	50	1527	1.04	2.7
Heat Treatment of CNB etched in HF-solution					
750	5	0	1186	1.05	3.5
550	1	50	1484	1.74	4.7
750	1	50	871	1.37	6.3

Conclusion

Conclusively, it could be suggested that the treatment by using water vapor bubbled through N₂ flow during carbonization of the AlSiR is possibly control the physical properties on the CNB and useful method for the preparation of various CNB for adsorbents having different properties.

Reference

1. Lee, J. W., Sohn, K. N. and Hyeon, T. W., "Fabrication of Novel Mesocellular Carbon Foams with Uniform Ultralarge Mesopores", *J. Am. Chem. Soc.*, 123, 5146-5147 (2001).
2. Yoon, S. B., Hohn, K. N. and Kim, J. Y., "Fabrication of Carbon Capsules with Hollow Macroporous Core/Mesoporous Shell Structures", *Adv. Mater.*, 14, No. 1 (2002).
3. Vacassy, R., Flatt, R. J., Hofmann, H., Choi, K. S. and Singh R. K., "Synthesis of Microporous Silica Spheres", *Journal of Colloid and Interface Science*, 227, 302-315 (2000).
4. Worasuwanarak, N., Hatori, S., Nakagawa, H. and Miura, K., "Effect of oxidation pre-treatment at 220 to 270°C on the carbonization and activation behavior of phenolic resin fiber". *Carbon*, 41, 933-944 (2003).