Activation of Nano-sized Carbon Shells on Carbon Hollow Spheres under Water Vapor

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Abstract−The carbonization and activation of nano-sized aluminosilicate resin (AlSiR) spheres with a diameter of about 500 nm were performed under various conditions. The carbonization of the AlSiR under H_2O-vapor/N_2 flow resulted in greater improvement of the physical properties of the shells on the carbon hollow spheres (CHSs) than that obtained under pure nitrogen flow. The water vapor activation of the carbonized AlSiR spheres was found to constitute a useful method as compared with the water vapor activation of the CHSs etched in HF solution; however, in order to increase the pore volume for a particular pore size of 4 nm, the latter method was more effective than the former method.

Key words: Nano-sized Carbon Hollow Sphere, Activation, Water Vapor

INTRODUCTION

Recently, it was reported that novel meso-cellular carbon spheres containing uniform ultra-large mesopores were synthesized from a phenol-based resin using an aluminosilicate template [Lee et al., 2001; Yoon et al., 2002]. According to Yoon et al., who fabricated carbon capsules with hollow core mesoporous shell (HCMS) structures, the specific surface area of these HCMS carbon capsules was found to be 1,230 m^2/g and the total pore volume was 1.27 cm^3/g, as determined by nitrogen BET adsorption measurements [Yoon et al., 2002]. Certain of the physical properties of these carbon capsules have high values, and this is especially the case for the total pore volume, which is much better than that of commercial activated carbons, for which the corresponding value are about 0.4-0.6 cm^3/g. These superior physical properties of the carbon capsules are mainly attributed to the aluminosilicate templates. For the carbon capsules to be used as an adsorbent, they must first be activated, in order to improve or control their physical properties. Although various factors affect the adsorption capacity of such materials, the surface area and porosity are considered to be the major factors determining their adsorption capacity. So, it is very useful to be able to improve or control the physical properties of the nano-sized carbon shells, having a thickness of <50 nm, on the carbon capsules.

In this work, we propose appropriate methods of improving the physical properties of the nano-sized carbon shells on CHSs (carbon hollow spheres) while maintaining a completely hollow spherical shape.

EXPERIMENTAL

The CHSs used in this study were fabricated according to the method described in the literature [Lee et al., 2001; Yoon et al., 2002]. The carbon precursor was a phenol-formaldehyde resin (PF-resin), which was doped over the mesoporous aluminosilicate balls made of nano-sized aluminosilicate, otherwise known as SCMS (solid
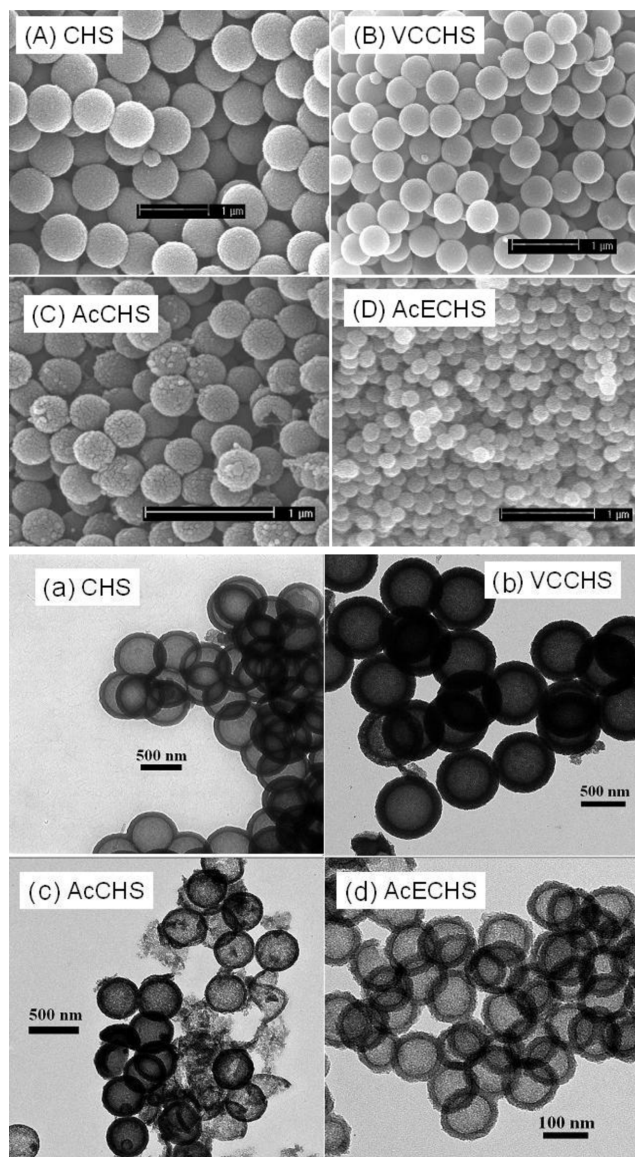
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Fig. 1. SEM (A-D) and TEM (a-d) images of the various CHSs.

core mesoporous shell) aluminosilicate, having a surface area of 472 m^2/g, a total pore volume of 0.48 cm^3/g and an average pore diameter of 4.1 nm. This phenol resin is known to be a useful material for carbonization, because of its being a thermally stable resin, and it has been used by many research workers in various fields [Lee et al., 2000; Nakorn et al., 2003]. The carbonization of the AlSiR (aluminosilicate resin) was carried out at a temperature of 950 °C with no holding time, after being heated with a heating rate of 2 °C/min. At that time, the carbonization was carried out within two different atmospheric conditions, the first being pure nitrogen gas flow and the second being H$_2$O-vapor/N$_2$ flow at a rate of 80 cm^3/min. The water vapor flow (H$_2$O-vapor/N$_2$ flow) was generated in a bubbling chamber containing 50 ml of deionized water at a fixed temperature of 30 °C, maintained using a thermostat, and pure nitrogen gas flow. The relative humidity in the water vapor flow was 87% on average. After carbonization, both of the carbonized AlSiRs were etched in 50%-HF solution. The resulting carbon hollow spheres are referred to as CHSs in the case of the AlSiR spheres carbonized within pure nitrogen flow and VCCHS in the case of the AlSiR spheres carbonized under water vapor flow. The activations were performed at a temperature of 950 °C for 5 hr under water vapor flow at a rate of 80 cm^3/min, for both the CHSs and non-etched carbonized AlSiR spheres. AcECHS (activated etched CHS) refers to the CHS activated after etching in HF solution, while AcCHS (activated CHS) refers to the CHS activated before etching and then etched in HF solution. The physical properties of the nano-sized carbon shells on various types of CHSs and activated CHSs obtained from the carbonized nano-sized AlSiRs (aluminosilicate resin)

spheres, which are used as the precursor material to fabricate the CHSs, were estimated under various conditions from the nitrogen adsorption and desorption isotherms measured at 77 K using a Micromeritics ASAP 2000. The SEM images were obtained on a JEOL JSM 840-A microscope, while the TEM studies were performed on a JEOL JEM 2000 EX-2 microscope.

RESULTS AND DISCUSSION

Fig. 1 shows the SEM and TEM images of the various CHSs. In this figure, (A) show the CHSs which are spherical with a hollow cores having an average diameter of 350-400 nm and a shell thickness of about 40-50 nm. Both the VCCHSs and AcCHSs, shown in Figs. 1(B) and (C), respectively, are similar in shape and size to the CHSs. In the case of Fig. 1(D), which shows the AcECHSs, both the average hollow diameter and shell thickness are markedly decreased by an average of 80-90 nm and 10 nm, respectively, in comparison to the CHSs. This shrinkage of the CHSs suggests that vapor activation can be used to control the size of the CHSs.

The nitrogen adsorption/desorption isotherms were used to estimate the physical properties of the shells on the various CHSs and are shown in Figs. 2 and 3. In Fig. 2, the isotherm of the CHSs shown in Fig. 1(A) was designated as type H4, as recommended in the IUPAC manual, indicating that it is nearly horizontal and parallel over a wide range of relative pressure. A type H4 isotherm has previously been obtained with adsorbents having slit-shaped pores [Gregg and Sing, 1982], so it can be assumed that the shells of the CHSs consist of mostly slit-shaped pores, and the formation of these pores is at-
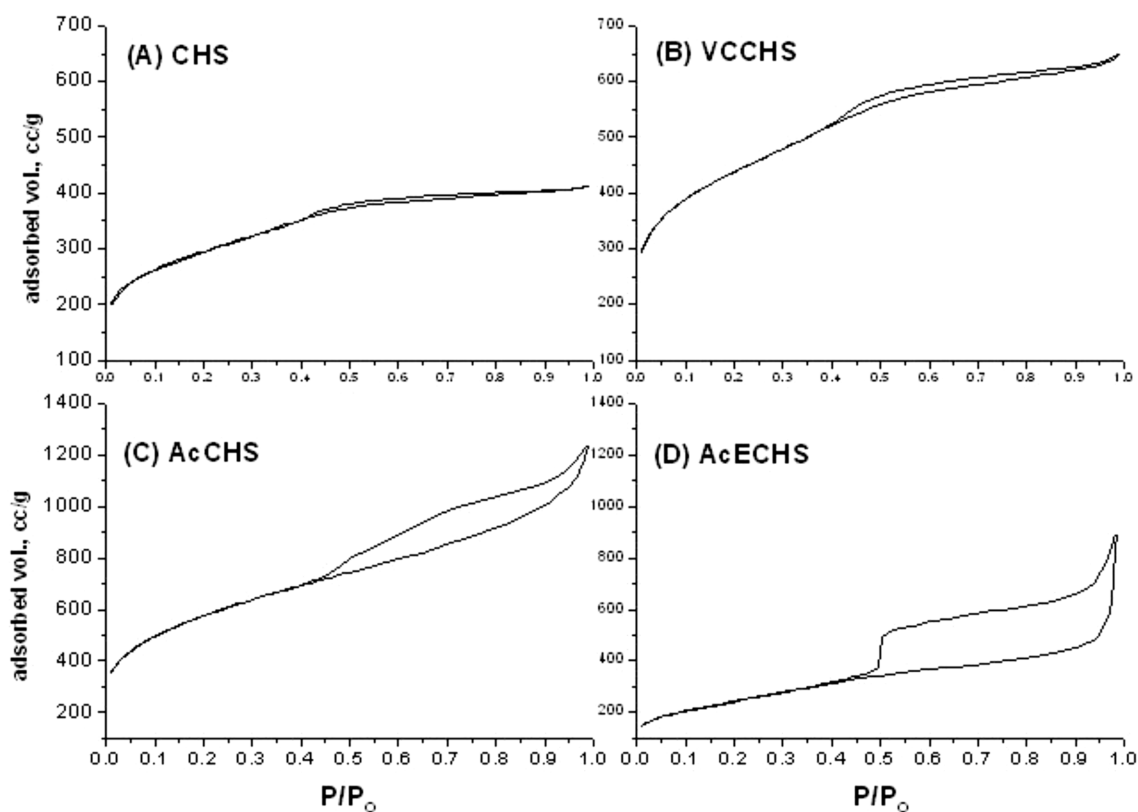

Fig. 2. Nitrogen adsorption/desorption isotherms of the various CHSs [(A) CHS, (B) VCCHS, (C) AcCHS, (D) AcECHS].
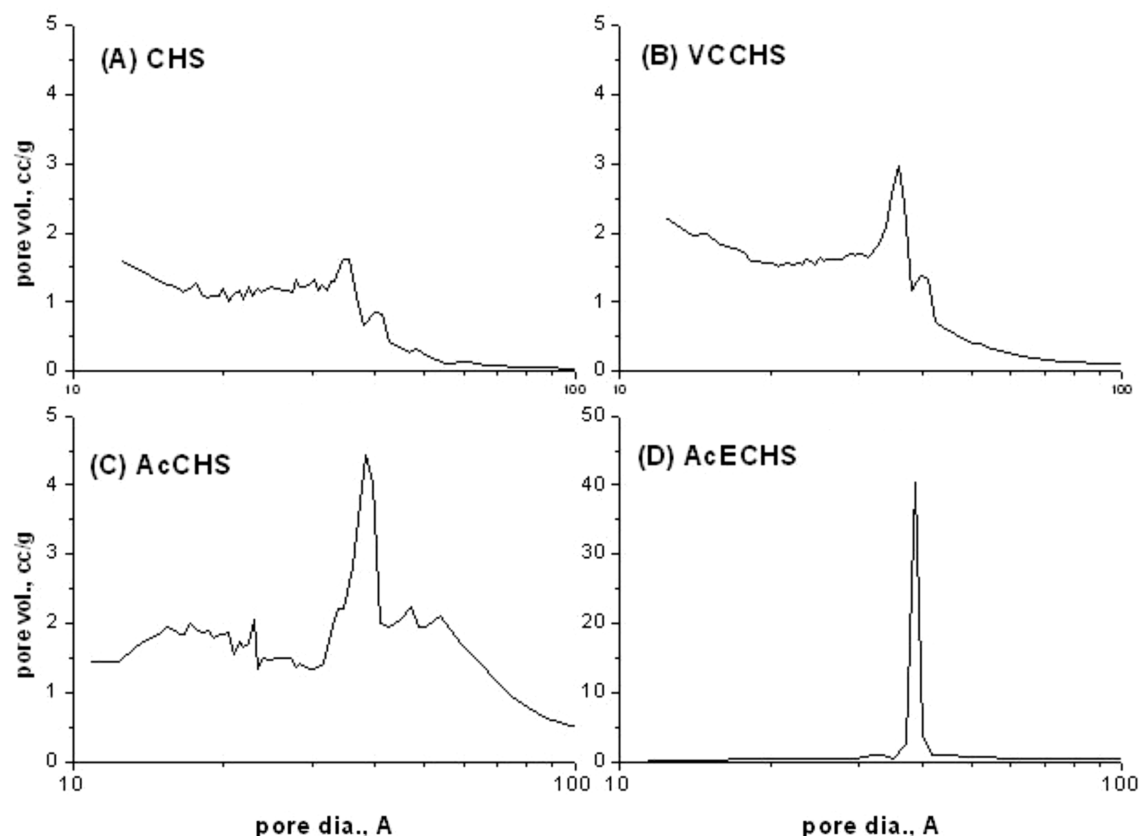
Fig. 3. BJH pore distributions of the various CHSs [(A) CHS, (B) VCCHS, (C) AcCHS, (D) AcECHS].

Table 1. Physical properties of various CHSs and AC from BET measurements

Properties	Unit	CHS	VCCHS	AcCHS	AcECHS	AC
Surface area	[m²/g]	1054	1567	2064	871	1453
Total pore volume	[cm³/g]	0.63	1.00	1.91	1.37	0.63
Average pore diameter	[nm]	2.42	2.55	3.70	6.32	1.75
Micropore surface area	[m²/g]	352	530	384	25	1157
Micropore volume	[cm³/g]	0.14	0.22	0.14	0.0036	0.45

tributed to the cracking of the shells, which have nano-sized thickness, during carbonization, and not to the SCMS aluminosilicate template. The isotherms of the VCCHSs and AcCHSs, shown in Figs. 1(B) and (C), respectively, are slightly different, being of type H3, and their hysteresis loops are somewhat larger than that of the CHSs. These variations can be attributed to an increase in the number of mesopores, as shown in Figs. 3(A), (B) and (C). In the case of the AcECHSs, the isotherm is entirely changed to type H3, and the difference between the adsorption and desorption lines is markedly increased as compared with the VCCHS and AcCHSs. This variation can be attributed to the increased number of mesopores with a diameter of about 4 nm, as shown in Fig. 3(D). The pore distribution of the shells on the AcECHSs is very narrow, consisting of mesopore ranging in diameter from 3.7 to 4 nm, with the other sized pores almost disappearing from the CHSs. The disappearance of these pores can be interpreted as resulting from the shrinkage of the CHS during the process of activation, as shown in Figs. 1(A) and (D), and which was mentioned above.

The physical properties inferred from the nitrogen adsorption/desorption isotherms are listed in Table 1. The values obtained for the CHSs are lower than those of activated carbon (AC, as determined in the case of commercial activated carbon, supplied by Korea Carbon Ltd.), except for the average pore diameter. In the case of the VCCHSs, the values are higher than that of AC, except for the micro-properties, and show an improvement in comparison to the CHSs. It can be assumed that the water vapor effectively supported the pyrolysis of the PF-resin during the carbonization of the AlSiRs, starting from a temperature near to 400 °C because, according to a previous report [Nakorn et al., 2003], the PF-resin is decomposed to produce phenol and formaldehyde species which then activate the carbonized PF-resin following the completion of the carbonization process.

In the case of the activated CHSs, the surface area and microproperties of the AcECHSs were lower than those of the CHSs, but the total pore volume and average pore diameter were higher, as was to be expected. These results indicate that the water vapor acti-

vation of the CHS etched in HF solution provides an effective method of improving the pore volume for a particular pore size, as shown in Fig. 3(D), but not of the other properties, because of shrinkage, as shown in Fig. 1(D). However, another activation of the non-etched CHS be identical to the carbonized AlSiR is very effective to improve the mesopore properties, because the micro-properties are similar to those of the CHS. The occurrence of this phenomenon within the water vapor activations can be attributed to the presence of the SCMS aluminosilicate template, because template material can support appropriate porosities for carbon materials [Lee et al., 2002; Inagaki et al., 2004]. Moreover, it can also be assumed that the water vapor opens up the clogged pores and simultaneously increases the porosity, thus contributing to the activation process [Ryu et al., 2003; Lee and Lee, 2001; Hong et al., 2000; Ramesh et al., 2004].

CONCLUSION

We suggest that the carbonization of the AlSiR spheres under H_2O-vapor/N_2 flow provides an effective method for improving the physical properties of the shells on carbon hollow spheres, in the absence of another activation procedure. In addition, the water vapor activation of the carbonized AlSiR spheres constitutes a useful method compared with the water vapor activation of the CHSs etched in HF solution; however, in order to increase the pore volume for a particular pore size of 4 nm, the latter method is more effective than the former method.

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