

HOLLOW CARBON SUBMICROSPHERES WITH POROUS SHELL: CONTROLLING THE PARTICLE SIZE

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Introduction

The hard template method is widely applied for the preparation of porous carbons, with the main objective of controlling the structure of the carbon material. A particular type of carbon materials prepared by templating techniques are hollow carbon submicrospheres with porous shell¹. The peculiar morphology of these carbons, combined with their highly developed porosity, is very interesting for a variety of applications, such as catalysis, gas separation, composite coatings, among others.²⁻⁴ The main objective of this work is to study the variables affecting the synthesis of silica templates in a blade stirrer reactor with controlled feeding rates of reactants.

Materials and Methods

The synthesis of hollow carbon submicrospheres carbons was carried out by templating method.¹ The template was a silica sphere with a solid core and a mesoporous shell, whose synthesis was carried out in a reactor system with controlled temperature (303 K), with a propeller stirrer two-bladed of stainless steel with speed control and a peristaltic pump to control the feed rate of the reactants. Tetraethoxysilane (TEOS) was used as silica precursor and hexadecyltrimethoxysilane (C16TMS) as porogenic agent. The solid core was formed by mixing a reaction medium of 185 mL of ethanol and 20.3 mL of deionized water and 12.6 mL of aqueous ammonia (20%) with 15 mL of TEOS was added by a controlled speed feeding. The reaction takes place during one hour to achieve the formation of nuclei of silica spheres. The porous silica shell was the next step, where a mixture containing 12.5 mL C16TMS and 4.84 mL C16TMS was added by a pump to the colloidal solution containing the silica nuclei to form the mesoporous shell around them during one hour of reaction. This last step was repeated one time more. After completion of the time of formation, the particles were washed with ethanol, isolated by filtration and dried at 60°C during 24 hours. The sample was calcined at 823 K for 6 h under air atmosphere and the silica template were obtained. Aluminium was incorporated to silica template through an impregnation method in two steps. In each impregnation step a solution consisting in 0.54 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /g template in 6 mL of deionized water. The incorporation of aluminium into the silicate framework provides the necessary catalytic sites for the polymerization of phenol and formaldehyde inside the template. The resulting powder was dried in air at 343 K. The Al-impregnated SCMS silica was calcined at 823 K for 6 h in air to form the aluminosilicate template. A phenol-formaldehyde resin was used as carbon precursor to obtain hollow carbon submicrosphere. To introduce the carbon precursor into the mesopores of aluminosilicate template a mixture of 0.374 g of phenol per gram of template was heated at 373 K for 12 h under 200 mbar static vacuum (rotavapor equipment). Paraformaldehyde (0.238 g per g of aluminosilicate) was added to the phenol-incorporated aluminosilicate at 200 mbar, at 393 K for 24 h to form the phenol-resin. This material was heated up to 433 K at a heating rate of 1 K/min and held at that temperature for 5 h under a nitrogen flow of 100 NmL/min in an electrically heated vertical quartz tube (i.d. 26 mm, length 12 cm). Then, the temperature was raised up to 1123 K at 5 K/min and maintained for 7 h. The resulting carbon aluminosilicate was washed with HF (48%) to produce the hollow carbon submicrospheres.

Results and Discussion

The use of C16TMS during shell formation was an alternative with lower cost than C18TMS employed in other works¹⁻⁵, although it led to the formation of secondary particles with a significant influence on particle size. The stirring speed and the feeding rate of reagents were two of the main variables influencing the synthesis of the template. The stirring speed was studied for 50 and 100 rpm. The size of the spherical template increased from 525 to 890 nm when the stirring speed was increased (**Figure 1**) and the feeding rate was low (72 $\mu\text{L/s}$). The sample obtained at 50 rpm shows less homogenous particles with the presence of small spheres of 100-300 nm which resulting of a secondary nucleation that takes place during the shell formation step. Part of the TEOS feeding for the shell formation of the template react to form a new nucleus, this led to a thinner shell and a smaller particle size. At higher feeding rates of reactant (152 and 212 $\mu\text{L/s}$) the influence of the stirring speed is not observed, with the presence of secondary nucleus in all the samples. **Figure 2** shows the particle size distribution of silica templates, it can be observed in general a bimodal distribution corresponding with the silica templates (400-900 nm) and the secondary nuclei (100-300 nm), except the case of template obtained for higher stirrer speed and lower feeding rate, which mainly show the bigger size with an average value of 890 nm.

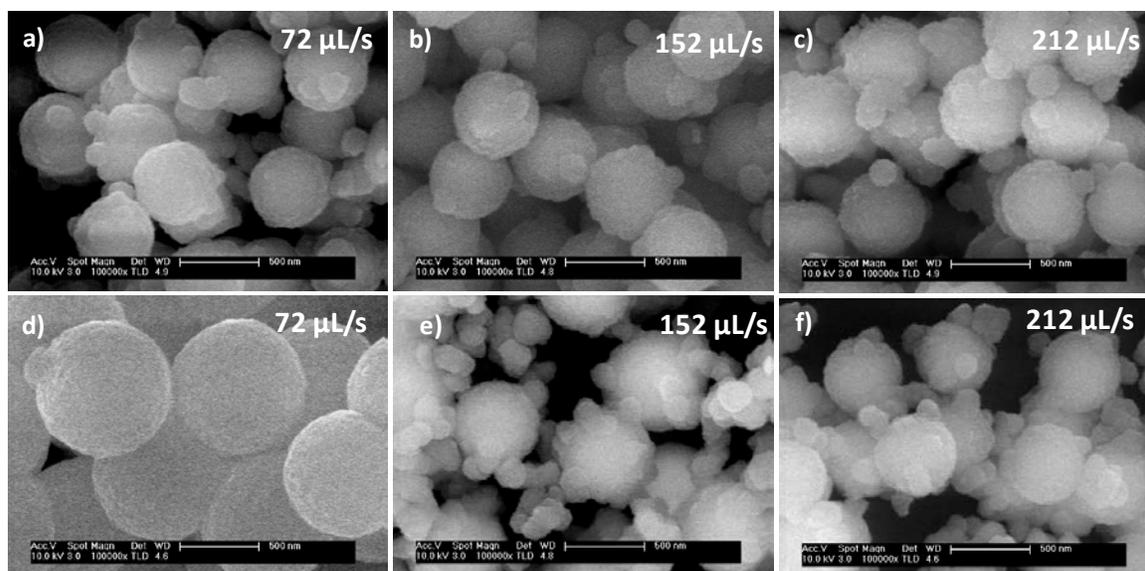


Figure 1. SEM images of silicas templates obtained at: a) b) and c) stirring speed of 50 rpm. D) e) and f) stirring speed of 100 rpm

The carbon sub-microcapsules were successfully replicated from the silica templates by infiltration of a commercial resol resin, pyrolysis at 700 °C, and removal of the template by washing with HF.

Figure 3 shows the SEM images of silica nucleus, silica template and the carbon sub-microspheres, where it can be seen that the carbon spheres maintain the spherical shape of the template, with an average particle size of 654 nm. The carbon sub-microspheres showed BET surface areas of 1000-1100 m^2/g and a pore volumes of 0.95-1.0 cm^3/g .

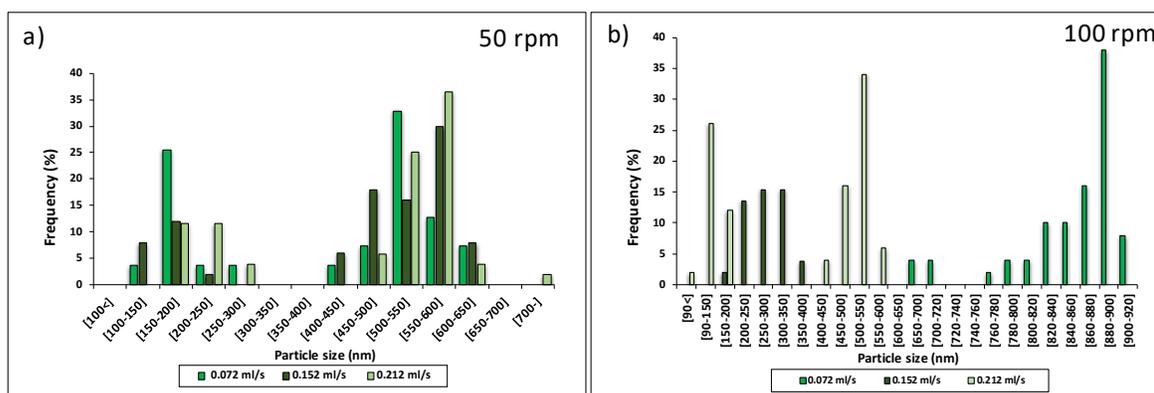


Figure 2. Particle size distribution of silica templates obtained at a) 50 rpm and b) 100 rpm.

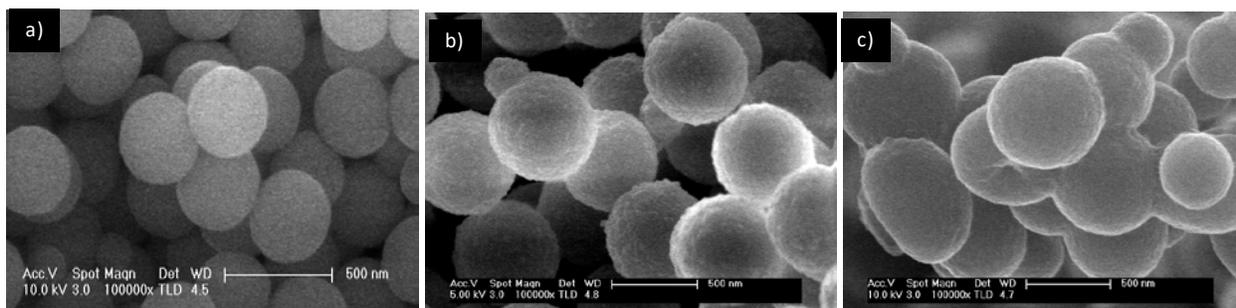


Figure 3. SEM images of a) silica nucleus b) silica template c) carbon sub-microspheres

Conclusions

Carbon submicrospheres were successfully obtained as a replica of the silica template using high stirring speed and low feed rate of reactants. The increase of stirring speed as well as the increase of the feeding rate of reactants led to a smaller particle size due to the formation of a secondary nucleus during the template shell formation. Carbon submicrospheres have an average particle size of 654 nm with a BET surface areas of 1000-1100 m²/g, which makes them suitable for a variety of applications.

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