

Adsorption and structural properties of mesoporous carbons obtained from mesophase pitch and phenol-formaldehyde carbon precursors using porous templates prepared from colloidal silica

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Templating synthesis of carbons by using phenol-formaldehyde (PF) precursor

The solution with molar composition of 1.0 phenol (99 wt.%) and 0.8 formaldehyde (37 wt.%) was infiltrated into the mesopores of the silica template by centrifugation at 1000 rpm for 1 h.¹ The excess of precursor and moisture were removed by evacuation. Subsequently 1 M sulfuric acid (the molar ratio of phenol to sulfuric acid was 0.1) was allowed to penetrate into the precursor composite by centrifugation for 1 h. The composite was evacuated to remove dissolved oxygen and moisture, and heated at 398 K for *ca.* 12 h to perform *in situ* polymerization. Next, the resulting polymer-silica composite was carbonized by applying the heating rate of 5 K min⁻¹ at 1073 K for 7 h in dry Ar flow to obtain a carbon-silica composite. The silica template was dissolved using 49% aqueous HF for 10 h (the dissolution of silica was checked by thermogravimetric analysis) and the resulting carbon was filtered, washed and dried at 323 K. The carbon samples are denoted C-PF-n, where n refers to the size of colloids used in the synthesis of silica templates.

Phenol-formaldehyde-based carbons

All silica templates listed in Table 1 of the paper were employed to fabricate mesoporous carbons. If the template pores are entirely filled by carbon precursor and there is no carbon disappearance during carbonization process, the resulting carbon should be a true inverse replica of the silica template used. Since the latter consists of uniform silica colloids, the carbon replica should possess spherical pores of the diameter reflecting the size of these colloids. This is not the case for the phenol-formaldehyde-based carbons (C-PF) as evidenced by analysis of nitrogen adsorption isotherms at 77 K shown in Figure S1. These isotherms exhibit extremely high volumes of adsorbed nitrogen reaching a value of about 2500 cm³ STP/g, which for C-PF-46 converts to an unprecedented pore volume of about 4 cm³/g (see Table S1). The specific surface area of these carbons was rather moderate as expected for carbons with large pores.

Nitrogen adsorption isotherms for the PF carbons exhibit very narrow hysteresis loops (H1 type according to the IUPAC classification) located at relative pressures greater than 0.9, reflecting the presence of large pores and large pore windows (see Table S1). Shown in the inset

of Figure S1 are the pore size distributions calculated from nitrogen adsorption isotherms; they exhibit a visible microporosity (range below 2 nm) and two major peaks; a narrow peak reflecting the size of colloids used in the synthesis of silica templates, and a broad peak located in the range of pore widths exceeding at least twice the size of colloids used (note the latter peak was estimated from nitrogen adsorption data at 77K, but its location is in the upper limit of the method applicability). In addition, the pores present in the carbons studied were created by removal of spherical silica colloids forming the porous template, but the pore size analysis method used was calibrated for cylindrical pores, which may lead to some underestimation of the pore widths. For mesoporous and macroporous materials the mercury porosimetry is more appropriate for the PSD evaluation but it was not used here because of the fragile nature of the PF-carbons studied.

The presence of large pores in the PF-based carbons, which exceed significantly the size of silica colloids used in their synthesis, can be caused by an incomplete filling of mesopores in the silica templates by carbon precursors and/or incomplete polymerization of phenol and formaldehyde in these pores. Consequently, carbonization of the polymer-silica composite followed by silica template dissolution led to a fragile carbon structure with several defects (large pores that do not correspond to the size of silica colloids), which were formed because of an incomplete filling of the silica template with carbon and/or a possible collapse of some thin carbon walls. This, in turn, resulted in the formation of large irregular voids giving the total pore volume that considerably surpasses the volume of primary spherical mesopores.

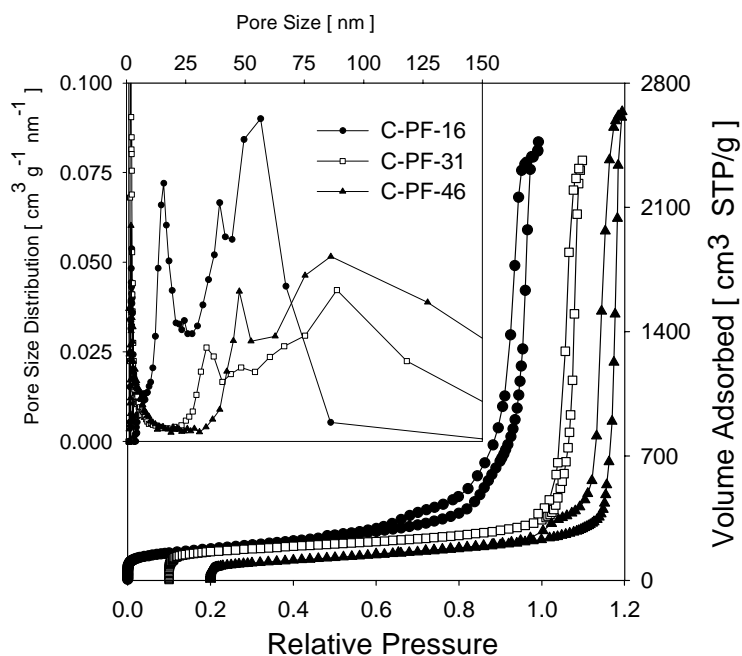


Figure S1 Nitrogen adsorption isotherms at 77K for the carbons synthesized from polymerized phenol and formaldehyde and the corresponding pore size distributions (see inset). The isotherms for C-PF-31 and C-PF-46 were horizontally offset by 0.1 and 0.2 of relative pressure, respectively.

Table S1. Structural properties of the carbons synthesized from phenol-formaldehyde evaluated by nitrogen adsorption analysis^a

| Sample | S_{BET} [m² g⁻¹] | V_t [cm³ g⁻¹] | w_{KJS,1} [nm] | w_{KJS,2} [nm] |
|----------------|---|--|-----------------------------------|-----------------------------------|
| C-PF-16 | 626 | 3.73 | 16 | 57 |
| C-PF-31 | 601 | 3.49 | 34 | 89 |
| C-PF-46 | 400 | 3.91 | 48 | 86 |

^a S_{BET} - the BET specific surface area calculated in the range of relative pressure from 0.04 to 0.25; V_t- the single-point pore volume calculated at a relative pressure of about 0.99; w_{KJS,1} and w_{KJS,2} - the pore diameters at the maxima of PSD evaluated by the KJS method.²

Refereneecs

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