HIERARCHICAL PHENOLIC RESIN-BASED CARBONS WITH HIGH SURFACE AREA AND PORE VOLUME OBTAINED BY SOFT-TEMPLATING AND ACTIVATION

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Introduction

Advanced applications often require carbons with high surface area and hierarchical porous structures. In response to this demand some efforts have been undertaken to create materials, which effectively combine the properties of both activated carbons (high surface area) and ordered mesoporous carbons (tunable and well-developed porosity). While there are activation methods, which have been successfully used to generate micropores, the preparation of pores in the mesopore range is more challenging. The first ordered mesoporous carbons were obtained by hard templating (nanocasting) method [1,2], where the pores of sacrificial hard template (usually ordered mesoporous silica or colloidal silica) were filled with a carbon precursor, which after carbonization and subsequent template dissolution resulted in the final carbon material. The main drawback of this method is the preparation of the hard template followed by its removal, which increase the time and cost of the entire fabrication route. In contrast, the recently established soft-templating method [3-5] utilizes thermally-decomposable triblock copolymers as soft templates and the thermosetting polymers as carbon precursors. During initial heating the thermally unstable copolymer is removed, while the thermosetting polymer is carbonized by high temperature treatment under neutral atmosphere. This approach was proved to be successful not only in terms of simplifying and shortening the preparation of ordered mesoporous carbons but also in terms of versatility of other carbon-based materials, which could be prepared. The most interesting aspect of the soft-templating synthesis is surprisingly high tolerance of carbon precursor/block copolymer system to accommodate foreign species without substantial deterioration of porous structure of the final carbon-based material [6-7]. This feature can be adapted in the preparation of wide range of organic-inorganic nanocomposites or carbons possessing different pore geometries.

Here we report the soft-templating synthesis of phenolic resin-based carbons possessing the hierarchical architecture of pores. Taking advantage of the possibility of introducing large amounts of inorganic species the synthesis was conducted in the presence of tetraethyl orthosilicate (TEOS) and silica colloids. Since the as-prepared carbons were mainly mesoporous the post-synthesis activation was employed to develop additional microporosity. The resulting hierarchical carbons, composed of small micropores of about 2nm, the primary mesopores of about 12nm and bigger mesopores resembling the size of the silica colloids used, exhibited high BET surface area reaching $2200m^2/g$ and the pore volume up to $\sim6.0cm^3/g$.

Experimental

Hierarchical carbons were synthesized according to a modified recipe of Wang et al. [8]. Approximately 1.25g of resorcinol and 1.25g of poly(ethylene oxide) – poly (propylene oxide) – poly(ethylene oxide) triblock copolymer (PEO-PPO-PEO; Pluronic F127) were dissolved in deionized water and ethanol. The weight ratio of water to ethanol was fixed to be 5.5:10 keeping in mind the water content in the suspension of silica colloids (50nm); the amount of the aforementioned suspension was introduced to the reaction mixture to achieve 50 wt% of silica with respect to the carbon precursors. After stirring for about 10-15min, the reaction mixture was supplied with 1.1ml of 37%HCl and kept under stirring for additional 30min. Subsequently, 1.25ml of formaldehyde and 1.87ml of TEOS were added to the synthesis mixture. The resulting solution turned milky after 2-3h and after additional 30min of stirring the aqueous and solid phases were allowed to separate. The polymer-containing bottom layer was spread on the Petri dish and left under the fume hood overnight. Then, the sample was aged at 100ºC for 24h. Carbonization was performed under nitrogen atmosphere in the tube furnace using a heating rate of 2ºC/min up to 180ºC, keeping the sample at this temperature for 5hr, resuming heating with 2ºC/min up to 400ºC and with 5ºC/min up to 850ºC, and finally keeping the sample at 850ºC for 2 hours. In order to remove silica, the resulting samples were etched with 15%wt HF, washed with deionized water and dried.

For activation, the samples were heated in the tube furnace under nitrogen atmosphere with heating rate of 5ºC/min up to 850ºC. After reaching this temperature the activating gas was connected to the tube furnace ($80cm^3/min$) and allowed to flow for 3-5hr; after activation the flowing gas was switched back to nitrogen to prevent further activation during the cooling period.

The resulting materials were labeled $C^{\#}$-*a-t*, where *a* denotes the activating agent used (cd= CO_2 or v= water vapor) and *t* denotes the activation time. To show how TEOS addition affects structural parameters of the resulting carbons, one sample was prepared just with silica colloids and without TEOS; this sample was activated with CO_2 for 4hrs (labeled as $ntC^{\#}$-cd-4h).

Results and Discussion

The goal of the project was to show the effect of post-synthesis CO_2/water vapor activation on the phenolic resin-based mesoporous carbons. Nitrogen adsorption isotherms and the corresponding pore size distributions (PSD) for the samples studied are presented in Figure1 and their structural parameters are listed in Table 1. All samples exhibit type IV adsorption isotherms characteristic for mesoporous structures. Additionally, all of them show two capillary condensation

steps, which reflect the presence of two distinct systems of mesopores. From PSD curves one can see two peaks in the mesopore range, the first one at about 13nm, which can be assigned to cylindrical mesopores created by thermal removal of the soft template, and the second one at about 50nm resembling the size of the silica colloids used. The third peak at about 2nm is attributed to micropores; as can be seen from low pressure range of nitrogen isotherms the lowest adsorption in micropores is visible for the carbon synthesized without TEOS and activated in CO_2 for 4hrs.

Table 1. STRUCTURAL PROPERTIES of CARBONS[a]

Sample	S_{BET}	V_t	V_{mi}	V_{me}	V_{me}*	w_{KJS}	SiO_2
	m^2/g	cc/g	cc/g	cc/g	cc/g	nm	%
C#	1577	3.84	0.17	2.75	3.60	14.3	4
ntC#-cd-4h	1327	2.54	0.14	1.16	2.21	13.2	7
C#-cd-4h	1873	4.59	0.19	2.81	4.34	14.5	6
C#-v-4h	2213	5.72	0.22	3.36	5.46	14.3	7

[a]S_{BET}-specific surface area, V_t- total pore volume calculated at $0.98p/p_o$, V_{mi}-pore volume of fine pores up to 3.5 nm, V_{me}- mesopore volume calculated in the range of 3.5-20nm, V_{me}*- mesopore volume calculated for the whole range of mesopores, w_{KJS}- width of mesopores created by soft-template (note that in addition to these mesopores there are larger mesopores of about 50 nm obtained after removal of colloidal silica), SiO_2- percentage of residual silica obtained by using TG analysis in air.
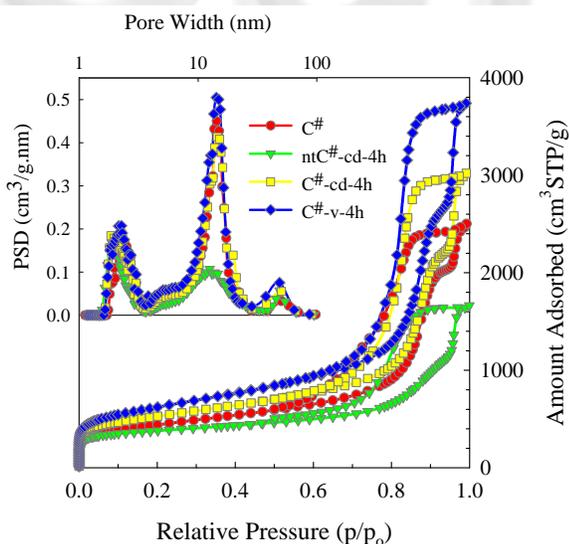

Fig. 1 Nitrogen adsorption isotherms and the corresponding pore size distribution curves for the representative carbon samples.

It is interesting that all carbons prepared with both the silica colloids and TEOS, even those without activation (C#), showed higher N_2 uptake than the ntC#-cd-4h material. The structural parameters clearly reflect the changes in the carbons due to CO_2 and water vapor activation. The specific surface area of all carbons studied were found to be in the range from $1300 m^2/g$ for ntC#-cd-4h to $2200 m^2/g$ for C#-v-4h. The latter sample also exhibited the highest micro-, meso- and total pore volumes. The pore widths in all cases almost did not change (~14nm).

Conclusions

Hierarchical carbons with two distinct pore geometries and sizes were successfully synthesized via combined soft- and hard-templating strategy. The overall structural properties were additionally enhanced by post-synthesis activation. All carbons studied exhibited high surface area and large pore volume. Regardless the activating medium used there is no indication of structure deterioration for activations carried out below 4hrs proving an exceptional thermal stability under these activation conditions. A comparison of CO_2 and water vapor activation, it seems that the latter is more effective for the enhancement of micro- and mesoporosity. Interestingly, it was found that the addition of TEOS to the reaction mixture provides additional microporosity in the original carbon, which result in enhancing the effect of post-synthesis activation.

References
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