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Nitration and reduction route to surface groups of mesoporous carbons obtained from sucrose and phloroglucinol/formaldehyde precursors

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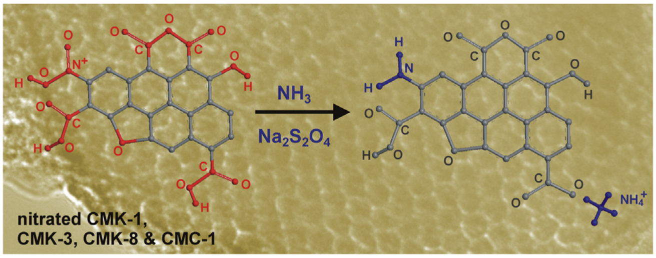
HIGHLIGHTS

- CMK-1 carbon is most easily modified by nitration as opposite to CMC-1 carbon.
- Incorporation of $-NO_2$ is accompanied by formation of oxygen-rich, acidic groups.
- After nitration number of acidic groups decreased as follows: CMK-1,-3 >> CMK-8 > CMC-1.
- Part of carboxylic groups was transformed into amino-acetate after reduction.
- During replication CMK-8 is partially transferred into I_1432 similarly to CMK-1.

GRAPHICAL ABSTRACT



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ABSTRACT

Mesoporous ordered carbons were obtained from two precursors, sucrose and phloroglucinol/formaldehyde, using a hard-template and a soft-template method, respectively. The surface of the materials was modified with the $-NH_2$ groups via nitration and subsequent reduction of the resulting $-NO_2$ groups. The modified carbon materials were investigated by elemental analysis, Boehm titration, nitrogen sorption, XRD, TEM, thermal analysis including TPD, as well as XPS and Raman spectroscopy. Apart from the $-NO_2$ groups, the nitration step resulted in formation of the oxygen-rich surface species, the concentration of which decreased after reduction. This concerned especially the carboxylic groups, a part of which transformed into the amino acetate type of species. The sucrose-based method resulted in the materials with more abounding acidic groups then in the case of the phloroglucinol-based route. The number of the acidic groups decreased after the nitration in the following order: CMK-1 > CMK-3 >> CMK-8. On the contrary, the resistance of the carbon structures to the nitration/reduction processes conformed to the order of CMC-1 > CMK-3 >> CMK-1 ~ CMK-8. The nitrogen content after the amination step exceeded slightly 2 wt.%. Such surface modifications provided attachment of the TCPP ligands, the amount of which ranged between ca. 30–60 wt.%.

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1. Introduction

Ordered mesoporous carbons have recently attracted considerable attention. Among them, carbon replicas of various structure types and arrangement of pores, such as cubic (CMK-1 [1] and CMK-8 [2]), hexagonal (CMK-3 [3] and CMK-5 [4]) or onion-like OCM structures [5] made of, e.g., sucrose, can be mentioned. In general, carbohydrates have turned out to be widely used raw materials in synthesis of the microporous carbons [6,7]. For such carbon replicas the susceptibility to chemical modifications occurring, for instance, during an oxidation process followed by monitoring of their mechanical stability can be tested. In the present work, the chemical modifications were designed to introduce functional groups on the carbon surface as a result of the nitration process, contrary to majority of reports in which the surfaces of carbons were modified with HNO_3.

As shown previously, use of nitric acid as the oxidant has led to the formation of carboxyl groups mainly [8–12]. However, a comparison of the possible changes in the structure of carbon and concentration of the introduced surface groups after nitration and HNO_3 oxidation is lacking in the available literature. Lazaro et al. [13] reported on surface properties of the CMK-3 carbon oxidized with concentrated HNO_3 at room temperature. The BET surface area of that sample decreased after such treatment from 578 to 400 m^2/g, whereas the pore volume diminished from 0.37 to 0.27 cm^3/g. It was found that the average pore size did not change after the oxidation, as well as the ordering of the porous structure, which was confirmed by the TEM results. Another interesting piece of work [14] revealed porous properties of the CMK-5 and CMK-3 sets of carbons modified with HNO_3 of various concentrations. Bazuła et al. [14] reported that neither the pore volume (from 0.87 to 0.76 cm^3/g) nor the pore diameter (3.9 nm) had changed noticeably. When treated with diluted HNO_3 of various concentrations [14], change in the surface area the CMK-5 and CMK-3 carbons was small, as it could be predicted. Similar modifications were reported for microporous/mesoporous carbons derived from polymers [15,16].

Systematic reports on nitration and reduction of mesoporous carbons are also lacking. The reaction of carbon surface with HNO_3 and H_2SO_4 mixture at 273 K results in incorporation of the nitric groups that can be next reduced to the $-NH_2$ groups. A further reaction of the amino groups and formation of the amide bonds involving these groups should enable attachment of various molecules to the surface.

In the present work mesoporous carbons of the CMK-1, CMK-3, and CMK-8 types, being replicas of MCM-48 [17], SBA-15 [18] and KIT-6(40) [19], respectively, as well as the CMC-1 carbon [20] were exposed to a nitrating mixture. The CMK-1, CMK-3, and CMK-8 structures were obtained from sucrose while the CMC-1 carbon was obtained using the phloroglucin-formaldehyde thermopolymer as a carbon source and the Pluronic® F 127 triblock copolymer as a soft template to be destroyed during carbonization. The aim of this study was to determine the impact of harsh experimental conditions on structural stability, possibility of additional development of the porous structure, and preservation of a characteristic pore size distribution. The nitration process enables formation of the nitrogen-containing surface groups. Alternatively, the post-synthesis treatment with nitrogen-containing reactants can be applied but it results in lower nitrogen incorporation [21] as compared to the carbons obtained by pyrolysis of the nitrogen-containing polymers, such as pyrrole [22–24]. The extent to which the above-mentioned parameters are modified controls the appropriate porosity of the carbonaceous structure and concentration of the resulting surface acidic groups. They can participate in the adsorption or attachment of spacious molecules active in selected catalytic processes, such as porphyrines in oxidation. Anchoring of active compounds to the backbone formed by carbons modified with definite surface groups has been widely reported [25,26]. In this work yet another rout of carbon materials modification with the $-NH_2$ groups is explored. The modified carbons are tested in adsorption of the TCPP (5,10,15,20-tetracarboxyphenylporphine) ligand from the DMF solution and covalent attachment of the TCPP molecule by its carboxyl groups to the $-NH_2$ surface groups. The studied materials were thoroughly characterized at various stages of the modification by X-ray diffraction, transmission electron microscopy (TEM), nitrogen sorption, elemental analysis, thermal analysis, temperature-programmed desorption (TPD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS).

2. Experimental section

2.1. Synthesis

The processes of nitration and reduction were studied on CMK-1 (*I4₁/a*) [1], CMK-3 (*P6mm*) [27], and CMK-8 (*Ia3d*) [2] ordered carbon replicas. The materials were prepared from sucrose and synthesized in the pores of respective ordered silica matrices: MCM-48 (*Ia3d*) [17], SBA-15 (*P6mm*) [18], and KIT-6 (*Ia3d*) [19]. The siliceous matrices and carbons were synthesized according to the referenced procedures with slight modifications. The KIT-6 silica was aged for 24 h at 313 K in a polypropylene bottle that was rotated. The P-123 (Aldrich) template was removed by Soxlet extraction in ca. 0.02 M HCl ethanolic-aqueous solution. The concentrated hydrochloric acid (35–38%), and ethanol (96%), were used for preparation of this solution (POCh, Poland). The sample was calcined at 783 K for 5 h. The heating rate was 1 K/min. The sulfuric acid (min. 99.5%), (POCh, Poland), hydrofluoric acid (40%), (POCh, Poland), sucrose (POCh, Poland), acetone (99.5%) (POCh, Poland), and the deionized water (Millipore system) were used for the syntheses of carbons of CMK-type. The calcined KIT-6(40) was impregnated with an aqueous solution of sucrose, containing sulfuric acid. The procedure was similar to the synthesis of the CMK-1 and CMK-3 carbons, except for different amounts of sucrose and acid. 1 g of KIT-6 was added to the solution obtained by dissolving 1.06 g of sucrose and 0.12 g of H_2SO_4 in 4.25 g of H_2O. The mixture was heated for 6 h at 373 K and, subsequently, for 6 h at 423 K. The obtained composite, after addition of 0.64 g of sucrose, 0.08 g of H_2SO_4 and 4.25 g of H_2O, was kept for 6 h at 423 K. The CMK-1, CMK-3, and CMK-8 carbons were carbonized at 1173 K for 4 h under argon flow. The heating rate was 0.5 K/min. The silica matrix was removed from the composite with a ca. 15% HF acetonic/aqueous solution. The samples were washed with deionized water up to pH = 5 and then dried at 363 K. Before nitration, the CMK carbon replicas were kept in a vacuum oven at 293 K overnight and under flow of H_2 at 363 K for 2 h.

The CMC-1 carbons were synthesized using a slightly modified Liang and Dai recipe [28]. In an exemplary procedure, 6.25 g of F 127 (BASF, USA) and 6.25 g of phloroglucinol (Fluka) were dissolved in 36.5 g of the 10:9 weight ratio solution of ethanol and water under magnetic stirring at 303–338 K. After the copolymer was completely dissolved, 0.4 ml of 37% HCl was added. The solution was stirred for additional 2 h until it turned orange. Next, 6.5 g of 37% formaldehyde (Fischer Scientific, UK) was added. Immediately after that, the solution turned cloudy and, one hour later, it fell into two layers. The polymer-rich bottom layer was separated and thermopolymerized at 373 K for 12 h. The carbonization was performed under argon atmosphere using heating rates as reported by Liang and Dai [28].