



# Structural features of resorcinol–formaldehyde resin chars and interfacial behavior of water co-adsorbed with low-molecular weight organics



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## ABSTRACT

Products of resorcinol–formaldehyde resin carbonization (chars) are characterized by different morphology (particle shape and sizes) and texture (specific surface area, pore volume and pore size distribution) depending on water content during resin polymerization. At a low amount of water ( $C_w = 37.8$  wt.%) during synthesis resulting in strongly cross-linked polymers, carbonization gives nonporous particles. An increase in the water content to 62.7 wt.% results in a nano/mesoporous char, but if  $C_w = 73.3$  wt.%, a char is purely nanoporous. Despite these textural differences, the Raman spectra of all the chars are similar because of the similarity in the structure of their carbon sheets with a significant contribution of  $sp^3$  C atoms. However, the difference in the spatial organization of the carbon sheet stacks in the particles results in the significant differences in the textural and morphological characteristics and in the adsorption properties of chars with respect to water, methane, benzene, hydrogen, methylene chloride, and dimethylsulfoxide.

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## 1. Introduction

Porous carbons as very effective adsorbents are widely used in industry, technology and medicine. Porous polymeric particles with phenol–formaldehyde resins, styrene divinylbenzene copolymers, etc. or different natural raw materials are main precursors of activated carbons (ACs) produced by activation of products of carbonization (chars) of these organic precursors [1–7]. Structural and textural characteristics of ACs depend on features of precursors and chars, activation conditions and a burn-off degree [8–11]. The morphological and textural characteristics, such as the porosity

(nano-, meso- and macroporosity), the pore size distribution (PSD) and particle shape of ACs can be similar to those of chars possessing, however, lower porosity and lower specific surface area than ACs [12–15]. This aspect is of importance for both structural and adsorption characteristics of the final ACs that affect the adsorbent efficiency of the materials [16–21]. Therefore, investigations of the factors governing the characteristics of both polymeric precursors and chars are of interest from both practical and theoretical points of view with respect to subsequent preparation of most effective ACs [1–7].

Resorcinol–formaldehyde resins can be used as porous polymers or precursors of chars to prepare porous carbon materials [22–30]. The properties of the final carbon materials are mainly determined by the structure of polymeric precursors which can be prepared by condensation of resorcinol with formaldehyde in

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the aqueous media. The synthesis can be carried out in a neutral medium or with addition of basic or acidic catalysts affecting the polymer structure [31–33].

Adsorption properties of carbon adsorbents in respect to low-molecular H-containing substances (water, methane, benzene, etc.) can be determined by adsorption methods, nuclear magnetic resonance (NMR), infrared (FTIR) and Raman spectroscopies, X-ray diffraction (XRD) and other methods. The NMR studies carried out on different materials showed that the amounts of bound adsorbates can be determined from intensity of proton signals of probes as a function of temperature. The  $^1\text{H}$  NMR chemical shifts of adsorbates confined in pores depend strongly on the textural and structural characteristics of adsorbents. The confined space effects can be used to compare the characteristics of adsorbents degassed, e.g. before measurements of nitrogen adsorption isotherms, and adsorbents weakly or strongly hydrated before measurements using low-temperature  $^1\text{H}$  NMR, cryoporometry, differential scanning calorimetry, DSC, thermoporometry [34,35]. These methods give quantitative information on the adsorbate location in pores of different sizes.

Polycondensation of resorcinol and formaldehyde is occurred in the aqueous media where water can play a role of a solvent and a porogen. Therefore, it is of interest to compare the characteristics of chars of resorcinol–formaldehyde resins synthesized at different content of water. Therefore, the aim of this paper was to synthesize a set of chars of resorcinol–formaldehyde resins prepared at various amounts of water and to study the surface properties of the chars with respect to nonpolar and polar adsorbates.

## 2. Materials and methods

### 2.1. Materials

Resorcinol (99.9%) and 37% aqueous solution of formaldehyde were used in synthesis of resorcinol–formaldehyde resin (RFR). The polymers were synthesized using 3 g of resorcinol, 1.67 g of formaldehyde and 2.84 g (RFR1), 7.84 g (RFR2) or 12.84 g (RFR3) of water. A mixture of resorcinol and formalin was stirred to form a transparent solution of ripe cherry color. Then 0 (RFR1), 5 (RFR2) or 10 (RFR3) ml of distilled water was added and the mixtures were heated slowly up to the boiling point. During a few minutes (0.5–5 min from the boiling start depending of the water content) the solution became turbid due to fast condensation and solidification of the reactants. This process occurs faster at a lower amount of water. The polymers were dried in air at 120 °C for 1 h. Uniform polymers formed were of different colors from dark-brown (RFR1), brown (RFR2) to reddish-brown (RFR3).

Chars (RFR1-C, RFR2-C, and RFR3-C) were prepared using the RFR powdered in a mortar and then pyrolyzed in a quartz reactor in the nitrogen atmosphere (nitrogen flow of 100 ml/min). The samples were heated to 800 °C at a heating rate of 5 °C/min and at 800 °C for 2 h.

### 2.2. Characterization methods

Thermogravimetric (TG) measurements were carried out in air using a Derivatograph C (MOM, Budapest) apparatus using 18–20 mg of samples placed in a ceramic crucible heated at a heating rate of 10 °C/min.

FTIR spectroscopy study was carried out in the 4000–400  $\text{cm}^{-1}$  range (attenuated total reflectance, ATR, mode) using a FTIR Nicolet 8700A (ThermoScientific, USA) spectrophotometer equipped with a Diamond Smart Orbit ATR.

SEM images were recorded using a JEOL JSM-6700F scanning electron microscope.

The textural characteristics of carbon materials were determined using low-temperature nitrogen adsorption–desorption isotherms recorded using a Micromeritics ASAP 2405N analyzer or a Quantachrome Autosorb analyzer. The specific surface area ( $S_{\text{BET}}$ ) was calculated according to the standard BET method [8]. The total pore volume was estimated from the volume of nitrogen adsorbed at relative pressure  $p/p_0 \approx 0.98$ –0.99. The pore size distributions (PSD) were calculated using nitrogen adsorption–desorption isotherms with modified Nguyen-Do (MND) [21,36] method and a slitshaped pore model, as well as nonlocal density functional theory (NLDFT) and quenched solid DFT (QSDFT) methods (Quantachrome software, an equilibrium model with slitshaped and cylindrical pores). Additionally, the nitrogen desorption data were used to compute the PSD (differential  $f_V(x) \sim dV_p/dx$  and  $f_S(x) \sim dS/dx$ ) using a self-consistent regularization (SCR) procedure under non-negativity condition ( $f_V(x) \geq 0$  at any pore half-width  $x$ ) at a fixed regularization parameter  $\alpha = 0.01$  with a complex pore model with slit-shaped and cylindrical pores and voids between spherical nanoparticles (10–100 nm in size) packed in random aggregates (SCV) for RFR2-C [37]. The differential PSDs (with respect to the pore volume  $f_V(x) \sim dV/dx$ ,  $\int f_V(x)dx \sim V_p$ ) were re-calculated to the incremental PSDs (IPSD,  $\sum \Phi_{V,i}(x) = V_p$ ). The differential  $f_S(x)$  functions were used to estimate the deviation ( $\Delta w = S_{\text{BET}}/\int f_S(x)dx - 1$ ) of the pore shape from the model [38]. The  $f_V(x)$  and  $f_S(x)$  functions were also used to calculate contributions of nanopores ( $V_{\text{nano}}$  and  $S_{\text{nano}}$  at  $0.2$ – $0.35 < x < 1$  nm), mesopores ( $V_{\text{meso}}$  and  $S_{\text{meso}}$  at  $1 < x < 25$  nm), and macropores ( $V_{\text{macro}}$  and  $S_{\text{macro}}$  at  $25 < x < 100$  nm) to the total pore volume and the specific surface area.

The  $^1\text{H}$  NMR spectra were measured using a high resolution Varian 400 Mercury spectrometer (magnetic field of 9.4T) with probing 90° pulses of 3  $\mu\text{s}$  duration. Temperature of a sensor was regulated by means of a Bruker VT-1000 device with the accuracy of  $\pm 1$  K. Relative mean errors were smaller than  $\pm 10\%$  for  $^1\text{H}$  NMR signal intensity for overlapped signals and  $\pm 5\%$  for single signals. The accuracy was improved using digital treatment of signals with compensation of phase distortion and zero line nonlinearity with the same intensity scale at different temperatures [34,35].

Before  $^1\text{H}$  NMR measurements, water was adsorbed on a char sample from air at atmospheric pressure and 60% relative humidity. To adsorb methane onto dry char pre-heated at 400 K for 20 min to remove water traces, a NMR ampoule of 5 mm in diameter containing 200 mg of a char was connected (by a flexible hose) to a methane reservoir at pressure higher by 0.1 kPa than atmospheric one. Therefore, additional portions of methane could be added to the ampoule during cooling of a sample. Hydrogen adsorption was studied in the analogous way with a char containing 1 wt.% of water and preliminarily saturated with methane at 293 K.

Quantum chemical calculations were carried out using *ab initio* method with the 6-31G(d,p) basis set using the Gaussian 03 [39] and WinGAMESS 12 [40,41] program suits or semiempirical PM7 method (MOPAC 2012 [42]) to full geometry optimization of molecules or their clusters. Solvation of different fragments of resorcinol–formaldehyde polymer was studied using the SMD method implemented in WinGAMESS [40,41]. For visualization of the fields around a RFR fragment, TorchLite 10 program [43,44] was used. The calculated structures were also visualized using the Chemcraft program [45].

## 3. Results and discussion

### 3.1. Structural and textural characteristics of RFR and RFR-C

The resorcinol–formaldehyde polymer is formed due to condensation of resorcinol and formaldehyde in the aqueous solution. The aromatic rings of resorcinol can be connected with the

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