Structural and adsorption studies of activated carbons derived from porous phenolic resins

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Abstract

Several carbon adsorbents characterised by different matrix-confined microporosity and textural meso- and macroporosity were prepared by heat-treatment of porous phenolic resins. These were investigated using adsorption, one-pass temperature-programmed desorption (OPTPD) with mass-spectrometry (MS) control (300–850 K), ^{1}H NMR spectroscopy (190–280 K) and thermally stimulated depolarisation current (TSDC, 90–260 K) methods. Variations in resin composition and carbon preparation conditions allow us to control microporosity and/or textural porosity as well as adsorptive properties (energy of adsorption, adsorption potential and Gibbs free energy of adsorption) of the carbon adsorbents. According to the NMR and TSDC data, a portion of water (small clusters) in aqueous suspensions of the carbon adsorbents has the same structure as in bulk water. However, extended water structures undergo significant changes in the presence of carbon or carbon/nanosilica. TSDC-cryoporometry gives pore size distributions for carbons similar to those obtained using standard adsorption methods.
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1. Introduction

Depending on the chemical structure and the morphology of the precursor, as well as on carbonisation, burn-off, and additional activation conditions, carbon adsorbents can be characterised by different contributions of micropores, supermicropores, narrow and broad mesopores, and macropores [1–8]. Carbon adsorbents with significant meso- and macroporosity caused by voids between nanoparticles aggregated in microsized clusters [9] can be more effective adsorbents for both low-molecular organics (under static [10–16] and dynamic [17–19] adsorption conditions [1–8]) or high-molecular compounds (under static conditions [20–22]). This is due to the textural transport pores providing high connectivity of the narrow pores and allowing deep penetration of adsorbate molecules into the pore network in a thick surface layer of adsorbent parti-

cles for shorter time on dynamic adsorption. Carbon activation to various burn-off levels can strongly affect both textural and framework-confined porosities [1–8]. The activation burn-off can also change the amounts of oxygen-containing surface functionalities affecting the adsorption properties of the materials and the behaviour of interfacial water (as well as other polar adsorbates), which can have a negative role on the competitive adsorption of toxic organics from air [17–19]. Simultaneous analysis of these effects and the structural characteristics of carbon adsorbents is of interest from both practical and theoretical points of view.

NMR spectroscopy is widely used to study carbon materials and the most interesting results can be obtained by measurements of chemical shifts of the corresponding resonances (e.g. protons, δ_H) for adsorbed molecules because these values give information on structures of adsorption sites and adsorption complexes [23–26]. For instance, the ^{1}H and ^{19}F NMR spectra of toluene and benzene derivatives adsorbed on graphitized carbon black [25] showed two signals for both adsorbates displaced toward strong magnetic field in comparison with the

signals of liquids alone because of the effects of local magnetic anisotropy at graphene surfaces, the pore structure and a variety of adsorption sites [27–30]. The maximum shielding effect ($\delta_H \approx -18$ ppm) was observed for partially graphitized carbons with a high density of π-electrons at the basal planes [29]. The ^{1}H NMR spectra obtained on layer-by-layer freezing-out of adsorbed liquids (e.g. water, benzene, chloroform, etc.) can be also used in the NMR-cryoporometry method to analyse the effects of adsorbates and temperature on the structural and other characteristics of carbon adsorbents and the adsorption phase.

The aim of the present paper was to study changes in the structural and adsorption characteristics of carbon adsorbents prepared with different levels of the burn-off and characterised by broad pore size distributions (PSD) with significant contributions from micropores, narrow and broad mesopores and macropores; i.e., including framework-confined and textural porosities.

2. Experimental

2.1. Materials

Porous phenol formaldehyde resin beads [31] were carbonised in a CO_2 flow to 1073 K at a ramp rate of 3 K/min (sample 1 labelled as C-0). Additional activation by CO_2 at 1183 K and different residence times results in 30% (sample 2, C-30) and 47% (sample 3, C-47) burn-off. The carbon particle size was 0.15–0.50 mm. A carbon adsorbent MAST-48 (48% burn-off) [20] prepared using a similar technique was used for comparison with C-47. These two carbons are characterised by similar levels of burn-off and microporosity but different textural meso- and macroporosity. Fumed nanosilica A-300 ($S_{BET} = 292$ m^2/g) [19] was used as a dielectric material in a mixture with carbon adsorbent to reduce the electrical conductivity of the system on the TSDC measurements. Nanosilica A-500 ($S_{BET} = 492$ m^2/g) was used for comparison with sample C-0 with respect to the shape of the nitrogen adsorp-
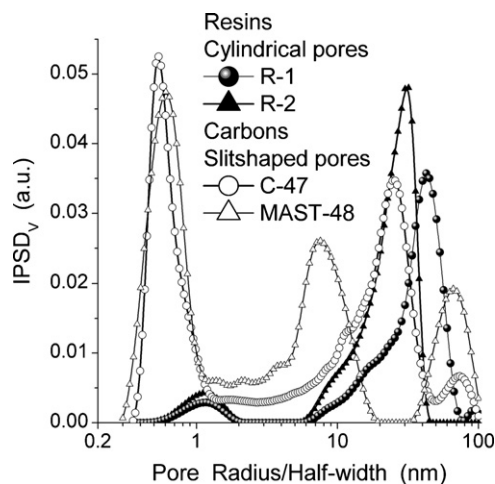

Fig. 1. IPSD functions (DFT) of resins (R-1 and R-2) (model of cylindrical pores) and corresponding carbon samples C-47 and MAST-48 (model of slit-shaped pores) with close burn-off but different textural porosity (MAST-48 [20] at $S_{BET} = 1340$ m^2/g and $V_p = 1.32$ cm^3/g).

tion isotherms and absence/existence of micropores in primary nanoparticles.

2.2. Methods

2.2.1. Adsorption

Resins used as precursors for C-0 and MAST-48 (R-1 and R-2, respectively) are characterised by different PSD functions (Fig. 1) derived from low temperature (77.4 K) nitrogen adsorption isotherms recorded using a Gemini II instrument (Micromeritics, USA). Nitrogen adsorption/desorption isotherms for carbon adsorbents (Fig. 2a) were recorded using a Micromeritics ASAP 2010 adsorption analyser. The specific surface area (Table 1, S_{BET}) was calculated according to the standard BET method [4]. For the studied carbons, despite a significant contribution of micropores to the total porosity, the c_{BET} value criterion (to use the BET method) is satisfied; i.e., $c_{BET} < 450$. The total pore volume V_p was evaluated by convert-
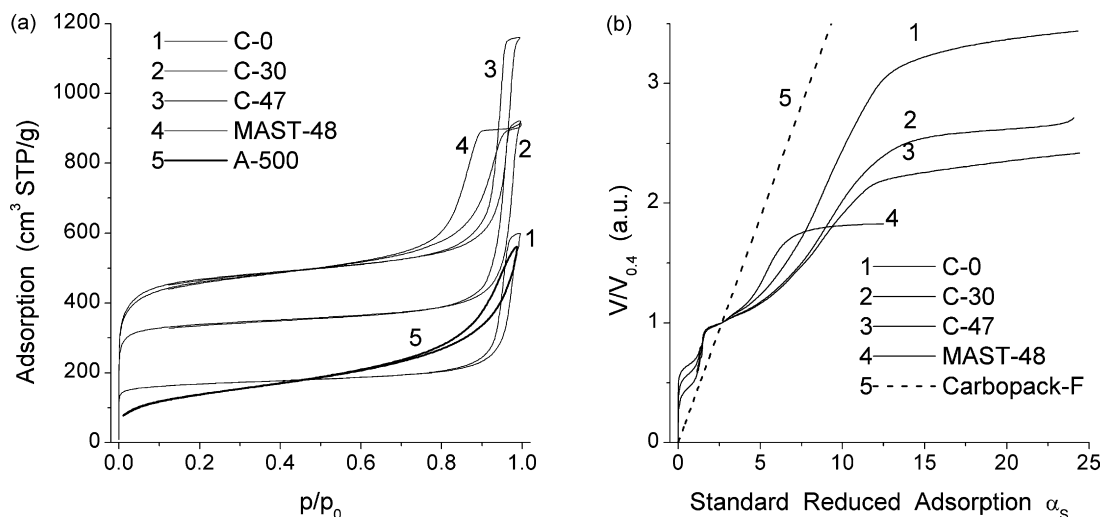

Fig. 2. (a) Nitrogen adsorption isotherms for carbons and fumed silica A-500 ($S_{BET} = 492$ m^2/g) and (b) α_S plots.