Molecular-Sieve Honeycomb for Air Separation from *Picea abies*

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The cellular structure of Norway spruce (*Picea abies*) was transformed *via* a simple, single-step carbonization process into a carbon monolith with molecular-sieve properties. The monolith exhibited a genuine honeycomb structure derived from the original intrinsic H_2O channels of the wood. The micropores formed during carbonization from the walls of the channels were shown to have a high adsorption capacity. The honeycomb monolith was tested for air separation. Micropore diffusion of N_2 and O_2 was found by the frequency-response (FR) technique to be the rate-controlling process of mass transport.

Introduction. – Carbon molecular sieves (CMS) are novel types of activated carbon with almost uniform micropores having widths of several tenths of a nanometer. The narrow distribution of pore sizes leads to selective adsorption properties that depend on the close match between the size of the pores and the probe gases to be adsorbed. CMS are widely applied in gas purification and separation, gas storage and transportation, as supports in catalytic processes, and are of great importance in environmental technologies. A CMS is just like a kinetic adsorbent that separates, *e.g.*, N_2 from air *via* faster sorption of O_2, thus distinguishing the 0.2-Å size difference between O_2 and N_2 [1].

Since the pore structure of carbonized materials is highly dependent on the precursors used, selection of the proper starting material is a key factor in producing a CMS with the desired pore structure. Although the nanostructure of a CMS, *i.e.*, the graphitic microcrystallite domains several nanometers in size, is what governs the separation kinetics, transport channels of micrometer size play a critical role in influencing the effectiveness in a pressure swing adsorption (PSA) process. In this respect, honeycomb patterns are an ideal morphology. In such structures, which are prepared from ceramic materials and widely used as catalyst supports, the available channel dimensions are, however, limited [2]. Carbon honeycomb structures would be even more attractive both for adsorption and catalysis applications if the channel walls could be made of microporous carbon.

Several multi-step methods and various carbonaceous precursors have been proposed for producing CMS [2][3]. The intention is to tailor the pores created during carbonization of these materials. The basic procedure in preparing CMS is thermal treatment to increase the porosity of the raw material, followed by activation at low burn-off degrees to open closed pores. The so-called 'carbonization temperature'

has been identified as the principal parameter in preparing CMS [3]. The pore structure of CMS can, thus, be engineered for the separation of O_2 and N_2 based on differences in diffusion rates [4][5]. The molecular-sieve activity is most often improved by additional chemical vapor deposition (CVD) [6][7].

Characterization of adsorption kinetics in carbon materials is usually carried out either by gravimetric or volumetric uptake. Both techniques have their limitations for measuring dynamics. For example, concentration-step sizes of adsorbates are generally large. Corrections for effects due to heat of adsorption can be complex. Recently, the frequency response (FR) technique has been shown to be a powerful tool for characterizing mass-transfer kinetics in various sorbents including activated carbons [8]. In this perturbation method, some property of a system is varied periodically about an equilibrium state over much smaller changes than are typically used for discrete-step methods. The frequency of the oscillations introduces an additional degree of freedom that can be used to decouple individual steps occurring with different characteristic relaxation times. In principle, the method can be used to determine the mechanism of the rate-governing transport processes and the dynamic parameters of these transport processes [9][10]. The FR method may also be coupled with equilibrium gas-adsorption measurement [11].

The macro- and mesoporous texture of activated carbons of lignocellulosic origin conserves the features of the precursor, *i.e.*, the skeleton of the plants is not affected. Previously, diffuse porous hardwood, tulip poplar (*Liriodendron tulipifera*), and two tropical trees, *Tabebuia rosae* and *Hymenaea courbaril*, have been studied as starting materials for carbon monoliths [12][13]. In this paper, we report the air-separation ability of carbon monoliths prepared in a single step from Norway spruce (*Picea abies*).

Experimental. – Cubes of spruce (of edge 10 mm) were carbonized in a N_2 flow at 973 K for 60 min. Some of the samples were post-treated by soaking in HNO_3 at r.t. [14]. A scanning electron microscope (*Hitachi SEM-570*) provided visual information on the honeycomb structure. N_2-Adsorption/desorption isotherms were measured on the monolith samples at 77 K, with a *Quantachrome Autosorb-1* computer-controlled apparatus. The apparent surface area was derived according to the *Brunauer–Emmett–Teller* (*BET*) model. (Micro)pore analysis was performed with *Quantachrome* software, using the *Dubinin–Radushkevich* (*DR*) method. The dynamic adsorption properties of pure main components of air, N_2 or O_2 gas, were investigated in porous carbonized wood cubes by the FR method. The batch-type FR system, described by *Rees* and *Shen* [15], was used to study the transport dynamics of N_2 and O_2 at 195 K in the pressure range of 60–600 Pa in a 0.001- to 10-Hz frequency window [15]. *Ca.* 300–400 mg of sample (three pieces of the carbonized pine-wood cubes) were placed in the FR chamber in a plug of glass wool. The sample was treated *in situ* under high vacuum at 573 K for *ca.* 3 h, then cooled to the temp. of the FR measurement, and equilibrated with the probe gas at a selected pressure. The volume of the FR chamber was then modulated by a very small amount at frequencies between 0.001 and 10 Hz. A response pressure wave (P_Z) was recorded at each frequency. Reference wave functions (P_B) were obtained by FR measurements without adsorbent. From the ratio P_Z/P_B, and the phase difference (Φ_{Z-B}), the response wave functions were determined at each frequency. The FR spectrum was obtained by plotting the 'in-phase' (δ_{in}, real) and 'out-of-phase' (δ_{out}, imaginary) components of the response functions against the modulation frequency. The experimental FR spectra were compared with characteristic FR functions derived theoretically, assuming either rate-controlling sorption or rate-limiting diffusion [9][10]. The sorption or diffusion time constant was obtained as the only adjustable parameter of the best-fit characteristic function.

Results and Discussion. – Norway spruce seems to be an excellent precursor for carbon honeycombs, which form from the H_2O channels in the spruce, as shown in *Fig. 1*. The main aperture dimensions of the long straight channels are *ca.* 30 μm, offering fast gas transport with low resistance to diffusion. The 3-μm thick walls contain

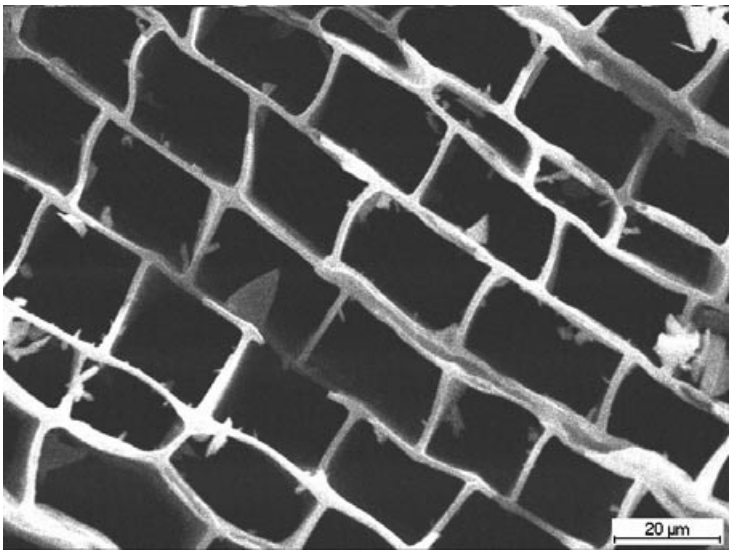

Fig. 1. *Scanning-electron-micrograph* (SEM) *image of a cross-section of carbonized Norway spruce* (*Picea abies*) *with microporous channel walls.* The probe was used as a 'honeycomb' carbon molecular sieve (CMS).

enough carbon to establish high adsorption capacity in the easily accessible graphitic crystals. The presence of this type of macroporosity makes this material suitable for applications in gas separation and/or as catalyst supports. Use of a denser species of wood will give thicker channel walls and higher adsorption capacities, but more-severe carbonization conditions would then be required. The carbonized cubes were sufficiently robust to be used in an adsorption column, even though they underwent a nonuniform size reduction of 5–35%.

The recorded N_2-adsorption isotherm was of type II, with a narrow hysteresis loop (*Fig. 2*), reflecting a high ratio of micropores accompanied by limited mesoporosity. The apparent surface area, S_{BET}, was derived according to the *BET* model. Since the mechanism of adsorption in narrow pores is by volume filling rather than by surface-layer formation, the *DR* approach was used to determine the micropore volume, from which S_{DR} was extracted. This latter calculation involves the assumption that the molecules that fill the pores are in contact with the pore walls. The *BET* and *DR* specific surface areas of the carbonized sample were found to be 541 and 633 m^2/g, respectively. The divergence between S_{BET} and S_{DR} results from the difference between the models. Both methods may underestimate the specific surface area when the pores are so narrow that only a single layer can be completed. However, S_{DR} may be overestimated when the pore accommodates more than two layers, *i.e.*, when 'excess layers' are no longer in contact with the walls. It should be noted that another cause of underestimation of the surface area derived from low-temperature gas adsorption stems from the kinetic hindrance due to the low energy of the gas particles, especially in the case of narrow micropores or constrictions.

The total pore volume, calculated from the amount of N_2 vapor adsorbed at a relative pressure close to unity, and assuming that the pores are then filled with liquid

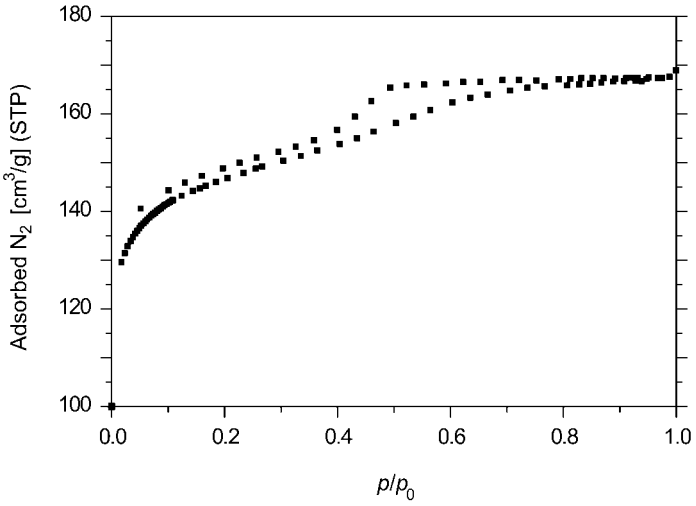

Fig. 2. *Low-temperature N_2-adsorption isotherm of a carbonized Norway-spruce monolith*

N_2, was found to be 0.26 cm^3/g; and 87% of the pores belonged to micropores. The surface area and total pore volume decreased following the post-treatment, but the shape of the isotherms also revealed the presence of micropores. The values S_{BET} and S_{DR} were found to be 67 and 85 m^2/g, respectively, and the total pore volume, which is equal to the micropore volume, was 0.03 cm^3/g.

Assuming uniform cylindrical pores, the average pore diameter (d_{ave}) was derived from the total pore volume and the *BET* surface area. Although this assumption may not be entirely appropriate for this microporous system, the result provides a useful indicator. Acid treatment reduced the average pore size from 0.96 nm to 0.44 nm.

The characteristic energy of adsorption was deduced from the slope of the *DR* plot. The effect of the acidic post-treatment (HNO_3) is reflected in a dramatic energy decrease from 12.3 to 3.3 kJ/mol.

In *Fig. 3*, N_2 and O_2 frequency-response rate spectra recorded on carbon monoliths are shown. Simple characteristic response curves fitted the data points well, and only a single rate-controlling process was observed. The 'in-phase' and 'out-of-phase' components of the FR spectrum approached each other asymptotically at higher frequencies. Theoretical analysis of the FR measurement has shown that this shape of response curve is expected when pure diffusion is the rate-determining step in the sorption process. The relative position of the spectral components suggests that the diffusion can be rate-governed either in the macro- or the micropores. The channel dimensions (see *Fig. 1*), however, suggest a very low macropore diffusion resistance. Distinct positions of O_2 and N_2 spectra appearing at different frequencies demonstrate a significant difference in the diffusion rate constants that cannot be rationalized by the minute difference between these sorptives in the main channels. However, if the sorption process was controlled by inter-microparticle effects such as macropore diffusion resistance, the FR curves should depend on the size and shape of the pellets, but not on those of the microparticulate domains, and should appear at different

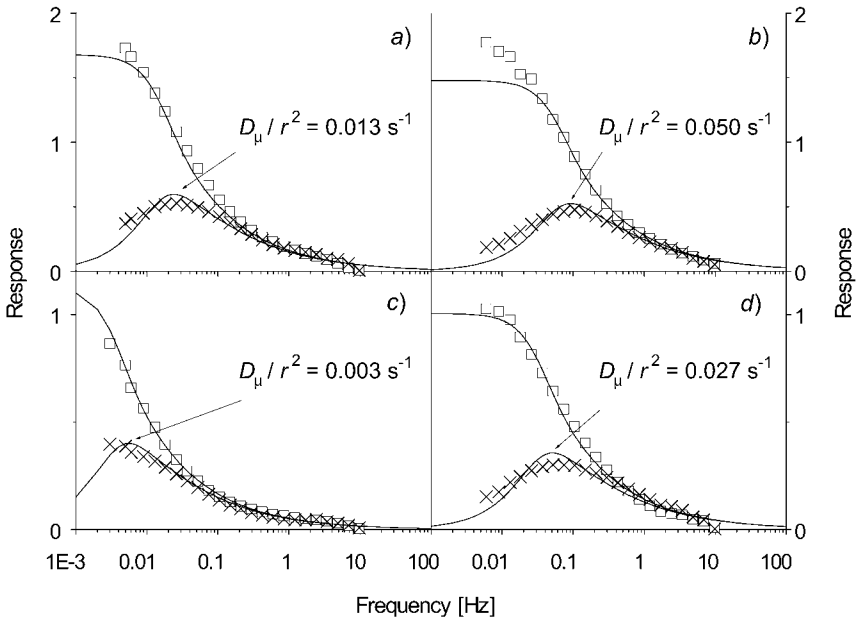

Fig. 3. *Frequency-response spectra of the sorption of N_2* (*a* and *c*) *and O_2* (*b* and *d*) *by carbonized* (*a* and *b*) *and HNO_3-post-treated* (*c* and *d*) *spruce cubes.* The spectra were recorded at 195 K and 133 Pa. Each measurement was made on three cubes. Symbols correspond to 'in-phase' (□) and 'out-of-phase' (×) components of the experimentally determined response functions. Full lines are the best-fit characteristic curves. Logarithmic frequency axis.

frequencies for differently sized macroparticles. FR Spectra measured on crushed monoliths of the size fraction 0.25 – 0.50 mm displayed no such effect. Therefore, the rate-determining role of the macropores can be excluded. Consequently, FR spectra obtained with both probes can be assigned to intra-crystalline diffusion. The kinetic selectivity, expressed in the nearly four times larger relaxation rate for O_2, also shows that micropore diffusion is controlled only by sorption. Selectivity data varying between 1.2 and 24 were recently determined by the same technique for five different commercially available CMS probes [16].

A remarkable finding of this work is that oxidative treatment induces a significant change in the dynamic adsorption properties of the sample. It could be the consequence of the dramatic reduction of the pore size. FR Spectra shift toward lower frequencies, although not by the same amount. The ratio of the relaxation rates increased to 9 : 1 – the diffusion rate of the larger N_2 molecules becomes much slower than for O_2, resulting in improved kinetic selectivity. The striking change following the HNO_3 treatment is that the FR-signal intensities decrease significantly, *i.e.*, less surface area and fewer micropores are accessible, while the diffusional resistance of the remaining slit-shaped pores increases. Besides the morphological changes, the surface functional groups generated by oxidative treatment may have a combined influence on both the equilibrium and dynamic properties of the carbon monolith [17].

The FR technique is a unique tool for studying the molecular mobility of air components, especially in the case of carbon monoliths. The latter can easily be prepared from various woods. As the method is very sensitive to changes of diffusivity caused by various carbonization and post-treatment methods, and for identifying mass-transfer mechanisms, it can be used to optimize the preparation conditions of CMS samples.

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