

# PICEA ABIES – A PRECURSOR FOR MOLECULAR SIEVE HONEYCOMB MONOLITH

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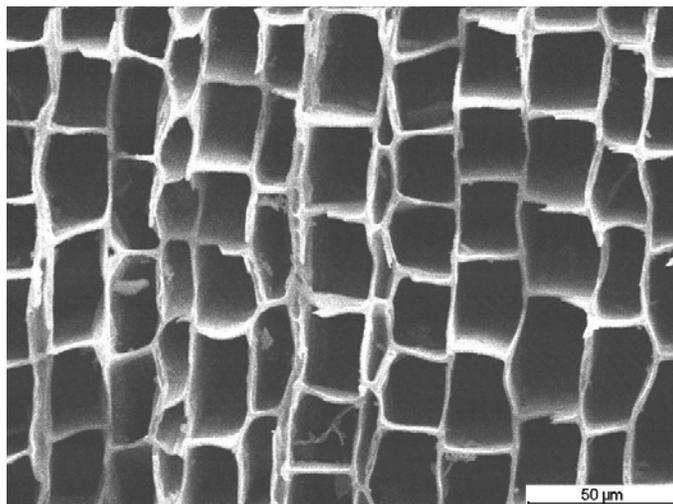
Carbon molecular sieves (CMS) are new, novel types of activated carbon with almost uniform micropores of several tenths of a nanometre in width. The narrow distribution of pore sizes leads to a selective adsorption property that depends on the close fit between the pores and the probe gases to be adsorbed. CMSs 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, for example, nitrogen from air through the faster sorption of oxygen, thus distinguishing the 0.02 nm size difference between O<sub>2</sub> and N<sub>2</sub> [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 CMS, i.e., the graphitic microcrystallite domains of several nanometers size, is the region that 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, the honeycomb pattern is an ideal morphology. In such structures prepared from ceramic materials, which are widely used as catalyst supports, the available channel dimensions are, however, limited. Carbon honeycomb structures would be even more attractive both for adsorption and catalytic applications if the channel walls could be made of a microporous carbon.

Several methods and various carbonaceous precursors have been proposed for producing CMS. The intention is to tailor the pores created during carbonization of these materials. The basic procedure in preparing CMSs is a heat treatment to increase the porosity of the raw material, followed by activation at low burn-off degrees to open closed pores. Carbonization temperature has been identified as the principal parameter in preparing CMSs. The pore structure of CMSs can thus be engineered for oxygen and nitrogen separation based on differences in diffusion rates [2].

The macro- and mesoporous texture of activated carbons of lignocellulosic origin conserves the features of the precursor, i.e. the skeleton of the plants used. Wood from several trees common in Europe lime, poplar, silver fir, Scotch fir, black fir, thuya, apple, plum, Normandy and Norway spruce were examined. Cubes of these woods, of edge 10 mm, were carbonized in nitrogen flow at 700 °C for 60 minutes. The yield was found to vary between 12 – 20 % with non-isotropic shrinkage in the range of 30-40 %. Of all the samples studied the last, Norway spruce (*Picea abies*), seems to yield an excellent regularity for use as carbon honeycomb precursors. The carbonized cubes were sufficiently robust to be used in an adsorption column. The effect of the temperature and the duration of the heat treatment were studied systematically. The carbon honeycomb structure forms from the water channels in the spruce, as shown in Fig. 1. The main aperture dimensions of the long straight channels are around 30 µm, offering fast gas transport with low resistance to

diffusion. The 3  $\mu\text{m}$  thick walls contain enough carbon to establish high adsorption capacity in the easily accessible graphitic crystals. The presence of this type of



**Fig. 1** SEM images showing cross-section of carbonized Norway spruce (*Picea abies*) as a honeycomb with microporous channel walls.

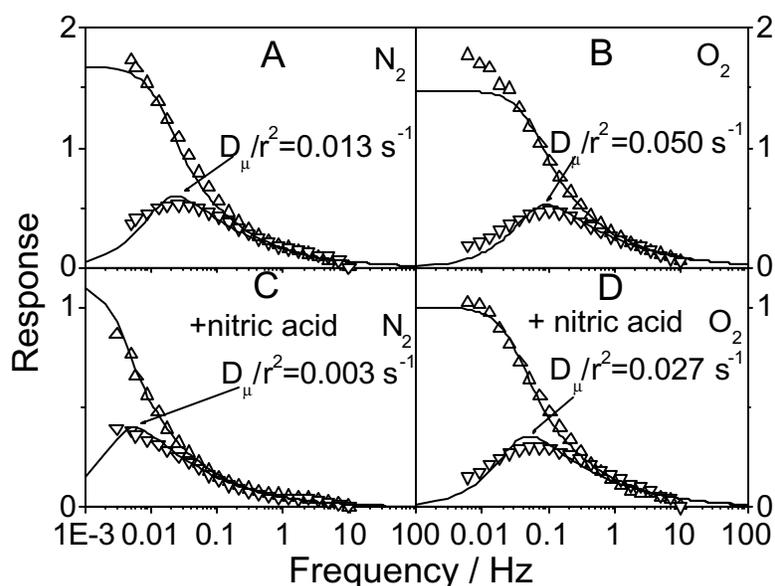
macroporosity makes this material suitable for application in gas separation and/or as catalyst supports. Use of a denser species of wood will give thicker channel walls and higher adsorption capacities, but more severe carbonization conditions would then be required. These samples were also post-treated by soaking in  $\text{HNO}_3$  at room temperature.

Nitrogen adsorption isotherms were determined at 77 K using a computer controlled Quantachrome Autosorb -1. The BET specific surface area of the carbonized sample was found to be  $428 \text{ m}^2/\text{g}$ . This value decreased following the post-treatment, but the shape of the isotherms reveals the presence of microporosity in both cases.

Characterization of adsorption kinetics in carbons is usually carried out either by gravimetric or volumetric uptake. Both of these techniques have their limitations for measuring dynamics, e.g. concentration step sizes of adsorbates are generally large. Corrections for heat of adsorption effects 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 [3]. 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 process [4,5]. The batch type FR system, described by Rees and Shen, was used to study nitrogen and oxygen transport dynamics at 195 K in the pressure range 60-600 Pa [6]. About 300-400 mg of sample was placed in the FR chamber in a plug of glass wool. The sample was treated *in situ* under high vacuum at 300  $^\circ\text{C}$  for about 3 hours, then cooled to the temperature of the FR measurement and equilibrated with the probe gas. 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 was recorded at each modulation frequency. When the characteristic modulation time is close to that of the rate-determining mass transport time constant in the sorbent particles, resonance occurs. The experimental FR spectra were compared with characteristic FR functions, derived theoretically assuming either rate-controlling sorption or rate-limiting diffusion. The sorption or diffusion time constant is obtained as the only adjustable parameter of the best-fit characteristic function.

Nitrogen and oxygen FR rate spectra recorded on carbon monoliths are shown in Fig. 2. Simple characteristic response curves fit the data points well. Only a single rate-controlling process is observed. The in-phase and the out-of-phase components of the FR spectrum approach 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 micro-pores. The channel dimensions shown in Fig. 1, however, suggest a very low macropore diffusion resistance. Distinct positions of oxygen and nitrogen spectra appearing at different frequencies demonstrate a significant difference in the diffusion rate constants that cannot be explained by the minute difference between these sorptives in the main channels. On the other hand, if the sorption process were 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 frequencies for differently sized macroparticles. FR spectra measured on crushed monoliths of size fraction 0.25-0.50 mm display no such effect. Therefore the rate-determining role of the macropores can be excluded.



**Fig. 2** FR spectra of nitrogen and oxygen sorption by carbonized (A, B) and HNO<sub>3</sub> post-treated (C, D) spruce cubes at 195 K and 133 Pa. Each measurement was made on three cubes. Symbols correspond to in-phase (Δ) and out-of-phase (∇) components of the experimentally determined response functions. Full lines are the best-fit characteristic curves.

Consequently FR spectra obtained with both probes can be assigned to intracrystalline diffusion. The kinetic selectivity expressed in the three times larger relaxation rate for oxygen, also shows that micropore diffusion is controlled only by sorption. A remarkable finding of this work is that the oxidative treatment induces a significant change in the dynamic adsorption properties of the sample. FR spectra shift toward lower frequencies, although not by the same extent. The diffusion rate of the larger nitrogen molecules becomes much slower than for oxygen, resulting in improved kinetic selectivity. The striking change following the nitric acid 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. The results confirm that the morphological changes and the surface functional groups generated by the oxidative treatment have a combined influence on both the equilibrium and dynamic properties of the carbon monolith [7]. The FR technique is a unique tool for studying the molecular mobility of air components, especially in the case of carbon monoliths, which can easily be prepared from various woods. As the method is very sensitive to changes of diffusivity caused by various carbonization and post-treatment conditions and for identifying mass transfer mechanisms it can be used to optimize the preparation conditions of CMSs.

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