*Chapter 4*

# Materials

Three carbonaceous materials, MSC-30, CNS-201, and zeolite-templated carbon (ZTC) were studied repeatedly with different gases and under differing conditions in this work. These materials were obtained and characterized in varied ways described herein.

## 1. MSC-30

MSC-30 (Maxsorb) is a microporous superactivated carbon obtained from Kansai Coke & Chemicals Company Ltd. (Japan) and is an "AX21-type" superactivated carbon. MSC-30 is synthesized by activating petroleum coke with molten KOH in a process patented by Standard Oil Company (later Amoco Corporation).

Nitrogen adsorption isotherms were carried out at 77K in a Micromeritics ASAP 2420. The specific surface area was determined by applying BET theory to the data as implemented by Micromeritics ASAP 2420 version 2.02 software. The BET surface area of MSC-30 was determined to be 3244$\pm$ 28 $m^2$ $g^{-1}$. Using nonlocal density functional theory (NLDFT)[1] and a slit-pore model, the MSC-30 pore-size distribution was determined as shown in Figure 1. MSC-30 has a broad range of pore sizes (from 6 to 35 Å). Over 40% of the micropore volume is contained in pores of greater than 21 Å (width). The micropore volume was found to be 1.54 $cm^3$ $g^{-1}$ by the Dubinin-Radushkevich method[2,3]. The skeletal density was measured by helium pycnometry and the skeletal density determined to be 2.1 g $cm^{-3}$.

Cu Kα X-ray diffraction of MSC-30 on a PANalytic Pro powder diffractometer gave a broad peak at 2θ= 34 degrees, in accordance with that reported for AX21. The elemental composition (CHN) was determined by the Dumas method[4] in triplicate combustion experiments, indicating that 1.16 wt% of MSC-30 is hydrogen. X-Ray Photospectroscopy (XPS) measurements were made on a Kratos AXIS Ultra DLD spectrometer and the results are summarized in Table 1. Electron Energy Loss Spectroscopy (EELS) measurements were made on a FEI Technai F20 with a Gatan Imaging Filter system. MSC-30 has an $sp^3$ hybridized carbon content of 16%. Transmission electron microscope (TEM) images were taken with a Tecnai TF30 with a $LaB_6$ filament and 80 keV electrons (Figure 2).

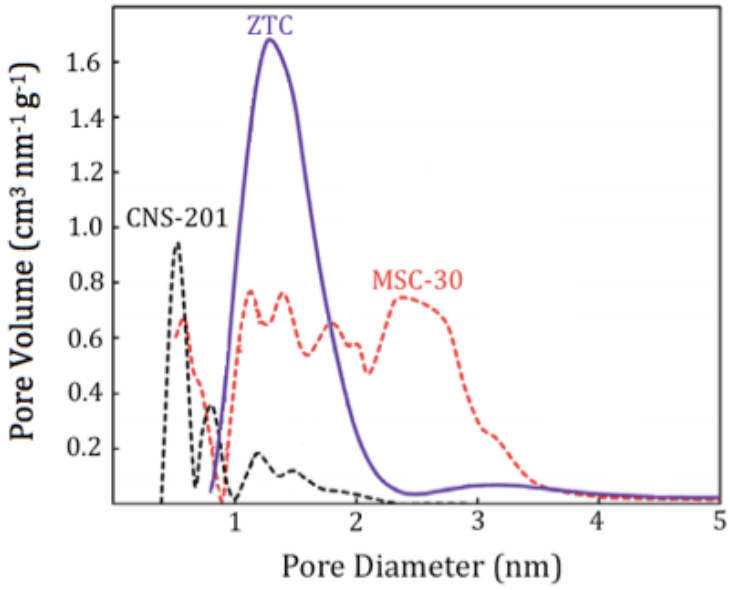


Figure 1. The pore-size distribution (left) of MSC-30 (red), CNS-201 (black), and ZTC (purple) as calculated by the NLDFT method.

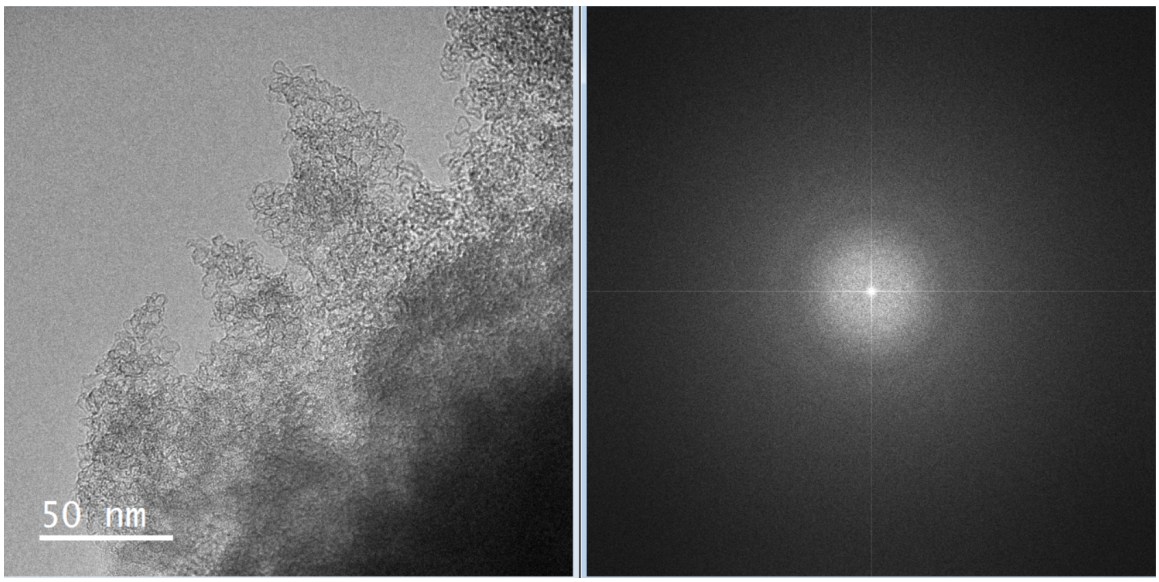


Figure 2. TEM image of MSC-30 and an accompanying fast Fourier transform of the image.

Table 1. Summary of XPS data on MSC-30 and ZTC

| peak position (eV) | 285.0 | 285.7 | 286.4 | 287.3 | 288.1 | 289.4 | 290.2 | 291.5 |
|---|---|---|---|---|---|---|---|---|
| component | C-C $sp^2$ | C-C $sp^3$ | C-OR | C-O-C | C=O | COOR | - | - |
| ZTC | 53.4 | 18.0 | 8.6 | 6.0 | 1.1 | 4.2 | 1.0 | 7.7 |
| MSC-30 | 48.0 | 18.8 | 6.8 | 4.8 | 6.1 | 4.2 | 3.6 | 7.7 |

## 2. CNS-201

CNS-201 is a microporous activated carbon obtained from A. C. Carbone Inc. (Canada). It is synthesized by pyrolysis of coconut shells. Nitrogen adsorption isotherms were carried out at 77K in a Micromeritics ASAP 2420. The specific surface area was determined by applying BET theory to the data as implemented by Micromeritics ASAP 2420 version 2.02 software. As determined by nitrogen adsorption and BET analysis, CNS-201 has a surface area of 1095 $\pm$ 8 $m^2$ $g^{-1}$. Using the nitrogen adsorption data and a slit pore model, NLDFT[1] pore-

size analysis was conducted to determine the pore size distribution (Figure 1). CNS-201 has a three dominant pore widths of 5.4, 8.0, and 11.8 Å, containing roughly 50%, 20%, and 15% of the total micropore volume respectively. The micropore volume was found to be 0.45 $cm^3$ $g^{-1}$ by the Dubinin-Radushkevich method[2,3]. The skeletal density was measured by helium pycnometry and the skeletal density determined to be 2.1 g $cm^{-3}$. Transmission electron microscope (TEM) images were taken with a Tecnai TF30 with a $LaB_6$ filament and 80 keV electrons (Figure 3).

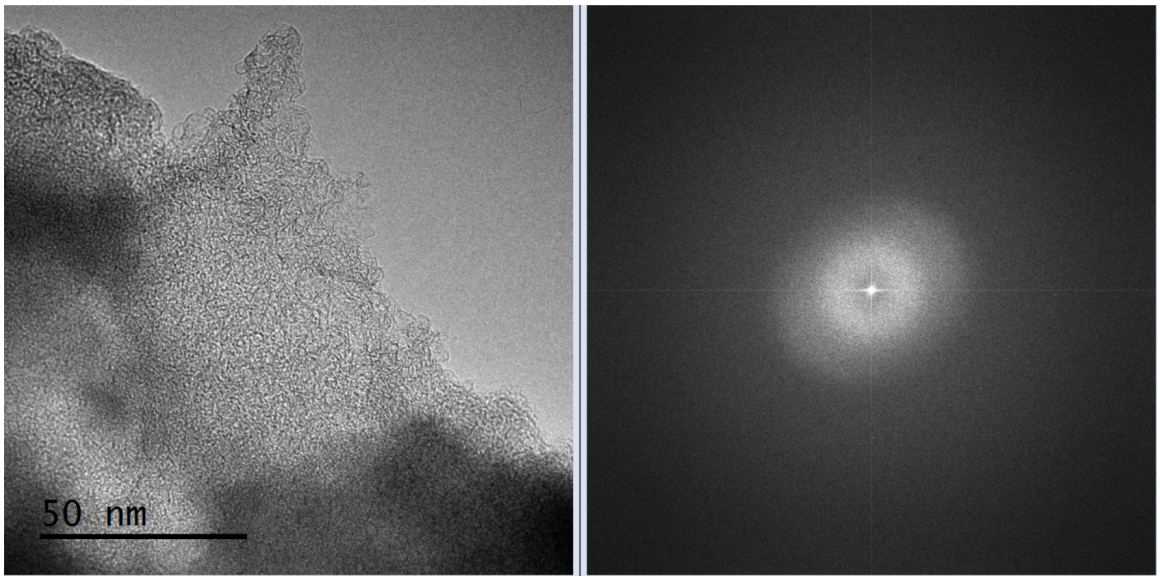


Figure 3. TEM image of CNS-201 and an accompanying fast Fourier transform of the image.

# 3. Zeolite-Templated Carbon

Zeolite-Templated Carbon (ZTC) is a microporous templated carbon synthesized in multi-gram quantities with the following procedure at HRL Laboratories.

## 3.1 ZTC Synthesis

Faujasite-type Zeolum® zeolite Nay, HSZ-320NAA (faujasite structure, Na cation, $SiO_2/Al_2O_3$ = 5.5 mol/mol) (NaY) was obtained from Tosoh Corporation. 6.0 grams of zeolite NaY were dried under vacuum at 450 °C for 8 hours. This powder was cooled and mixed with 12 mL of furfuryl alcohol (98% Sigma Aldrich) and stirred under Argon for 24 hours. The resulting zeolite-furfuryl alcohol mixture was separated by vacuum filtration and rinsed four times in 100 mL aliquots of xylenes.

Next the powder was loaded in a quartz boat and placed in quartz tube-furnace/CVD reactor. The tube furnace was purged with argon and held under argon at 80 °C for 24 hours. The reactor was heated to 150 °C (under argon) for 8 hours to induce polymerization. Next the temperature was ramped up at a rate of 5 degrees °C per minute to a final temperature of 700 °C whereupon the gas flow was switched to a 7% propylene/ 93% nitrogen mixture for 4 hours. After 4 hours, the reactor was purged with argon at 700 °C for 10 minutes. Next the temperature was increased to 900 °C and held for 3 hours under argon.

This product was then cooled and transferred to a PTFE beaker. 200 milliliters of aqueous hydrofluoric acid (48% Sigma Aldrich) were added. The solution was left for 16 hours before collecting the ZTC by vacuum filtration and rinsing 10 times with 50 mL aliquots of water. Finally the ZTC product was dried at 150 °C under vacuum. Careful control of the

inert atmosphere and thorough drying were found to be critical to obtaining high surface area product.

3.2 ZTC Characterization

Nitrogen adsorption isotherms at 77K were measured on a BELSORP-max volumetric instrument (BEL-Japan Inc.). This data was analyzed with BET theory to determine a specific surface area of 3591 $\pm$ 60 $m^2$ $g^{-1}$ (among the highest to date for carbonaceous materials)[5]. Using nitrogen adsorption data and a slit-pore model, NLDFT[1] pore-size analysis was conducted to determine the pore-size distribution (Figure 1). Other geometrical models including a cylindrical pore model were also tried, but none fit the data better than the slit-pore model. ZTC has a narrow pore-size distribution centered at 12 Å. Over 90% of the micropore volume is contained in pores of widths between 8.5 and 20 Å. The micropore volume was found to be 1.66 $cm^3$ $g^{-1}$ by the Dubinin-Radushkevich method[2,3]. The skeletal density was measured by helium pycnometry and determined to be 1.8 g $cm^{-3}$. This is lower than most carbonaceous adsorbents (2.1 g $cm^{-3}$), likely owing to a higher percent of hydrogen terminations. The elemental composition (CHN) was determined via the Dumas method[4] in triplicate combustion experiments, indicating that 2.44 wt% of ZTC is hydrogen. This higher percentage of hydrogen terminations may result from the hydrofluoric acid treatment during synthesis.

Cu K$\alpha$ X-ray diffraction of ZTC was measured with a PANalytic X'Pert Pro powder diffractometer and produced a single sharp peak at $2\theta = 6$ degrees, indicative of the template periodicity (14 Å). No signal from the original zeolite material was registered in the final product. The absence of other peaks suggests that the product is (as expected) amorphous

carbon without any remnant zeolite. Applying the Scherrer equation[6] to the peak (with a Scherrer constant K=0.83 for spherical particles) suggests an ordering length scale of 24 nm.

X-Ray Photospectroscopy (XPS) measurements were made on a Kratos AXIS Ultra DLD spectrometer and the results are summarized in Table 1. No significant differences were noted as compared to MSC-30. Electron Energy Loss Spectroscopy (EELS) measurements were made on a FEI Technai F20 with a Gatan Imaging Filter system. Similar to MSC-30, ZTC has an $sp^3$-hybridized carbon content of 18%. Transmission electron microscope (TEM) images were taken with a Tecnai TF30 with a $LaB_6$ filament and 80 keV electrons (Figure 4). The samples were prepared by placing the powder on an aluminum foil square and putting a lacey carbon copper TEM grid on top to pick up some particles. Unlike MSC-30 and CNS-201, ZTC shows nongraphitic crystalline order in the Fourier transform of the TEM images. In the fast Fourier transform of the images (Figure 4), ZTC shows spots indicative of a spacing of 1.2 to 1.3 nanometers, in agreement with other measurements of the periodicity of the pores. The spots also suggest hexagonal symmetry in the pore arrangement.

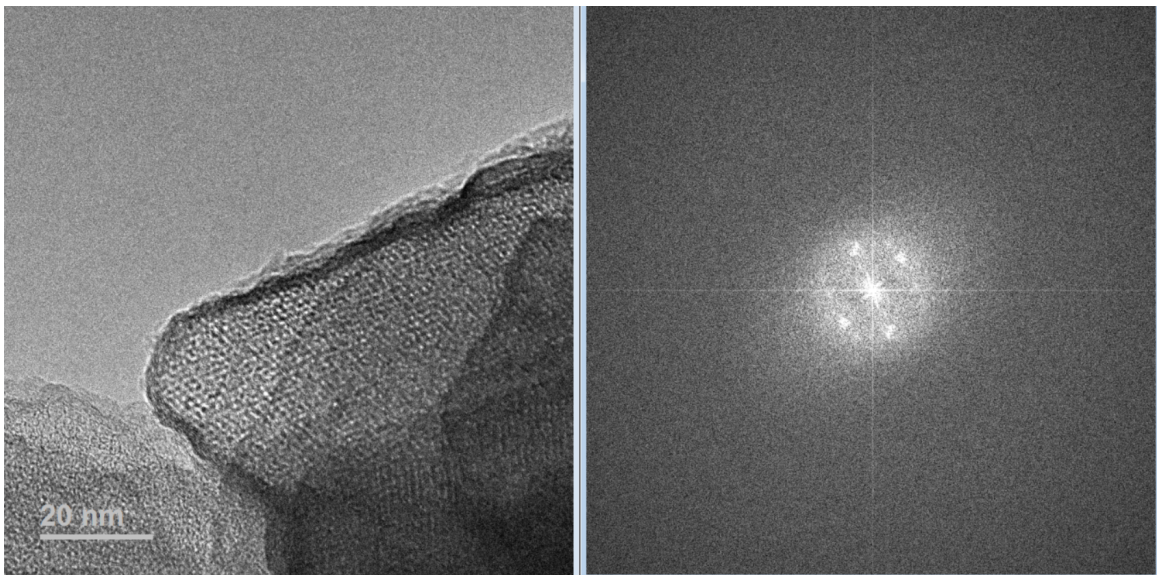


Figure 4. TEM image of ZTC and an accompanying fast Fourier transform of the image.

## References:

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