

### DIVISION 3: REVIEW OF CARBON MOLECULAR SIEVES

In this section we review the important aspects of carbon molecular sieve technology with special emphasis on their relationship to catalysis. The total literature on carbon molecular sieves, particularly that described in patents, is large and growing yearly. A STN International search of Chemical Abstracts, the Derwent International Database, and the NTIS Database for carbon molecular sieve literature from 1985 back to 1967 turned up over 168 references. Sixty-seven of these reports have appeared since 1980, consistent with the increasing growth of interest in these novel materials. It is interesting to note that a large percentage of the papers and patents are by authors and inventors from Japan.

We have compiled a comprehensive list of references on carbon molecular sieve technology from both the patent and open literature, that has been organized into one data base (see Table 1). Table 1 has been divided into three sections: (A) Fundamentals of Preparation and Properties, (B) Gas Separation Applications, (C) Catalytic Applications. In the sections that follow we briefly summarize this literature with special emphasis on the course of development of the fundamental aspects of the preparation and properties of carbon molecular sieves, and the application of these materials in catalysis.

The utilization of carbon molecular sieves for gas separation is by far their most important application. The greater portion of the reports, we have uncovered, are patents focused on the preparation and use of carbon molecular sieves for pressure swing adsorption. Recently, a number of companies both foreign and domestic, e.g. Calgon Corp., have commercialized pressure swing adsorption processes for the separation of oxygen from nitrogen in air, as an alternative to cryogenic separation. These processes have at their heart

fixed beds of carbon molecular sieves. Our compendium of literature contains a large section of references devoted to this very important technology. However, since it does not directly bear upon the catalytic applications of the materials pertinent to this program, no review of this aspect of the literature will be given. A good review of the pressure-swing adsorption technology has been published, recently, by Ray.<sup>12</sup>

**SECTION A. Background: Fundamental Aspects of Preparation and Properties.** The adsorptive properties of carbon have been recognized for a long time. Fontana and Scheele described the occlusion of gases in charcoal as early as 1777.<sup>13</sup> An excellent monograph on the adsorptive properties of porous carbon solids, including those with molecular sieving pores, has been edited by R.L. Bond and covers various aspects of the preparation and characterization of these materials.<sup>14</sup> In general porous carbons can be prepared from a variety of sources including coals, synthetic polymers and natural sources of organic residues like coconut shell and peat by pyrolysis in an inert atmosphere. There are two types of porosity that can potentially arise together or separately, depending on the nature of the precursor. The first is morphology that derives in shrunken form directly from the macrostructure of the precursor. This is exemplified in the structure of wood charcoal which has a structure reflecting the cellular structure of the wood.<sup>15</sup>

The second type of porosity is the ultramicroporosity that results from the physical processes that accompany the chemistry of pyrolysis.<sup>16</sup> During the pyrolysis of thermosetting resins to produce carbon, small gaseous products are formed, which during escape from the solidifying matrix give rise to pores with dimensions close to that of their own molecular dimensions. Examples of this kind of pore generation include the pyrolysis of polyfurfuryl alcohol to form carbon, formaldehyde, and water and that of polyvinylidene chloride to form carbon and hydrogen chloride (see Figures 2 and 3). The origin of the molecular sieving properties is not this simple, and the exact origin of ultramicroporosity is still under investigative scrutiny.

The synthetic carbons can be derived from a variety of sources which give rise to different relative amounts of carbon. Examples include:

<u>Type</u>	<u>% Carbon</u>
Coal Tar Pitch	52.5
Phenol-Formaldehyde	52.1
Liquid Polyfurfuryl Alcohol	49.1
Polyacrylonitrile (PAN)	44.3
Partially Hydrolyzed PAN	21.5
Polybutadiene Rubber	12.1
Epoxy Resin	10.1
Ethyl Cellulose	4.5
Polystyrene	1.1

Pyrolysis of natural materials like asphaltines, bituminous coal, coconut shell, and wood chips may also lead to carbon with molecular sieving properties. The properties of these materials vary widely depending upon the carbon precursor, and the method of pyrolytic decomposition. Physical and chemical properties include:

**Pore Sizes:** 3-12 Å

**Pore Volumes:** 0.2 to 0.5 cm<sup>3</sup>/gm

**Surface Areas:** 300 to > 1000 m<sup>2</sup>/gm

**Physical Properties:** Amorphous, Hard, abrasion-resistant

**Chemical Properties:** Hydrophobic (variable), inert

The first reports of molecular sieving carbons dealt primarily with the adsorptive properties of coals and charcoals.<sup>17</sup> Measurements of the sorption of helium, methanol, water, n-

hexane, and benzene on various ranks of coal by R.E. Franklin showed that the accessibility to the inner pore space was related to the porosity and adsorptive properties which varied with the rank. The width of the pores was proposed to be of the same order of magnitude as the diameters of simple molecules, and these were smallest for coals containing between 89 and 93% carbon. A subsequent study by Franklin on the structure with thermal treatment of these coals led to the observations that the porosity increased with temperature between 600 and 1000°C, specific surface areas increased between 600 and 800°C, and accessibility of the inner pores to gases and liquids decreased between 600 and 1600°C. Based on this information the pore structures of these solids were considered to function as molecular sieves, with pore sizes on the order of 2-6Å.

In a similar study Anderson and coworkers investigated the sorptivity of American coals. Comparative adsorption data for polar versus non-polar adsorbates were generated. Interpretation of the data was complex and no clear cut model for the pore structure was put forth. However, the measurements showed that the coals have sizeable pore volumes, the adsorption of n-butane was considerably greater than that for isobutane, and the adsorption of nitrogen at -195°C was quite low on most coals.<sup>18</sup>

In a classic paper P.H. Emmett described the sorptive properties of charcoals and Whetlerites, especially important as the active adsorbent in gas mask cannisters. Included were materials made from: (1) zinc chloride and sawdust, (2) coal, (3) steam-activated coconut shell char, (4) steam activated wood char, and (5) Saran. Various combinations of steaming, hydrogenating, and oxidizing, with or without impregnation by oxides of iron, chromium, nickel, and copper were reported to allow for tailoring of the pore size distributions. The nature of the various coatings was found to profoundly alter the nature of the adsorptive properties.<sup>19</sup>

Pierce and coworkers investigated the capillarity and surface area of charcoal in the low relative pressure region. These authors concluded from their investigation that monolayer adsorption was not occurring, but rather capillary. This phenomenon was believed to be responsible for the very high surface areas measured by adsorption on these materials and interpreted under the assumption of monolayer adsorption.<sup>20</sup>

Porous carbon prepared by the pyrolysis (700°C) of polyvinylidene chloride was reported to show molecular sieving properties. Dacey and coworkers observed that large, bulky molecules, like 3,3- diethylpentane, were adsorbed slowly, at 1/100 the rate of linear and planar molecules, like neopentane which were adsorbed more quickly. Adsorption rates followed Fick's law for the latter molecules. Rates and activation energies were calculated from the temperature dependence of the adsorption. Based on these results, it was concluded that steric factors must play a role in the different rates of adsorption observed for different molecules.<sup>21</sup>

Walker et al., and Lamond et al., observed similar reduced efficiency for the separation of n-butane, and isobutane with saran and polyvinylidene-based carbons. <sup>8(a,b)</sup> These authors proposed that the isobutane could rotate to present to the pore entrance a critical dimension equal to that of n-butane. Then if the pore were actually slit-shaped one can envision that the isobutane would eventually position itself for adsorption into the pore. Interestingly, the carbons that Walker and coworkers made were prepared by coating a commercial porous carbon with a thermosetting resin and then carbonizing this to produce a molecular sieving screen over the underlying porous carbon. Although these materials did not have the very sharp separation efficiency of the 5A zeolite, they did have an overall high capacity for n-butane, a small capacity for isobutane, and negligible capacity for neopentane. Based on these and similar studies Walker concluded that the pore system of 1200°C PVDC was

made up of pores with widths twice the molecular diameter of neopentane or approximately 12Å.<sup>22</sup>

It is interesting to note in relation to Walker's results that Mason and Eberly reported similar adsorption ratios of n-butane to isobutane with anthracite that had been heated in hydrogen at 650°C.<sup>23</sup> However the total capacity was lower and the time necessary to reach their full adsorptive capacity was not discussed. Mason also used the decomposition of PVDC in oil as a first step to a 900°C carbon which was capable of separating toluene or n-heptane and 2-methyl pentane.<sup>24</sup> These investigators also pointed out a potential advantage of the slit-shaped pores of carbon versus the circular type pores of zeolites. The former will adsorb singly branched normal and aromatic hydrocarbons, but not the more highly branched hydrocarbons which are useful octane builders.

In a separate and earlier investigation of polyvinylidene chloride-based carbons, Culver et al., had shown that average pore radii, of 7-8Å calculated from the expression  $2V/A$ , were consistent with observed sieving effects in the adsorption of various sized molecules. Also progressive activation increased the surface area, pore volume, and pore dimensions.<sup>25</sup>

More recently, Sofer and Koresh have investigated the properties and characteristics of carbon molecular sieving membranes, produced by pyrolysis of hollow polymer (polyacrylonitrile) fibers. By the use of air or nitric acid activations these workers have been able to generate a series of adsorbents of extremely high adsorptive selectivity.<sup>26(a-c)</sup> These investigations have shown that the carbon pore dimensions can be fitted to separate any two adsorbates having critical dimensions in the range of 3 to 5.2Å with selectivity greater than 100 to 1 if the molecules differ by merely 0.2Å. The dimensions of small molecules have been assessed in this way.<sup>26(d)</sup> Also the kinetics and mechanisms of adsorption on these materials have been evaluated.<sup>15,26(e)</sup>

**SECTION B. Gas Separation Applications.** Based on our survey of the literature devoted to carbon molecular sieves, the application of these materials is a high technology approach to solving a wide range of problems in difficult gas separations. We intend only to briefly review this here, and refer the interested reader to the second section of the compendium of literature that forms Table 1.

A large number of gas separations involving small molecules have been effected with carbon molecular sieves. This is not too surprising since the pores that do the separation, probably originate by the escape of small gaseous molecules from the insipient carbon matrix during pyrolysis. Because of this formation process, the slit-shaped pores are of molecular dimensions.

Gas separations that have been claimed include the following:

Oxygen/ Nitrogen

Hydrogen/ Coke Gases

Methane/ Carbon Dioxide, Methane/ Xenon

Ethanol/ Air

Ethylene/ Ethane, Propylene/ Propane

The most notable advance has been the oxygen/ nitrogen separation from air. A number of companies have pursued this as a non-cryogenic method of producing oxygen from air, including Calgon, Air Products, and Bergwerksverband G.m.b.H. Calgon has recently demonstrated and offered for sale a commercialized system for oxygen production based on their carbon sieve technology and the dual bed pressure swing adsorption method.

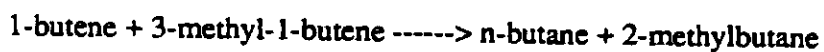
**SECTION C. Catalytic Applications.** Relatively few reports of catalytic applications for the carbon molecular sieves were found in both the open and patent literature. This is somewhat surprising considering that the carbon molecular sieve materials have been known for nearly as long as the synthetic zeolitic molecular sieves and also because catalytic inquiries were among the earliest reports in the area.

The catalytic reports that we have identified include:

- olefin isomerization and hydrogenation
- cis-trans isomerization of 1,2 dimethylcyclopentane
- aromatization of cyclohexane
- dehydrocyclization of isooctane
- dehydration of alcohols
- CO hydrogenation
- Diels-Alder cyclodimerization of conjugated dienes

The research groups of Walker and Trimm appear to have investigated the reactant shape-selectivity of carbon molecular sieves modified with platinum metals for olefin isomerization and hydrogenation.

In a series of papers and patents Trimm and Cooper, both separately and in collaboration, investigated the preparation of a variety of metal-containing carbon molecular sieves and their adsorptive as well as catalytic properties. Their first paper appeared in 1970 and detailed the results of an investigation into the selectivity of platinum-containing carbon molecular sieves for the hydrogenation of olefins. <sup>27</sup>





<u>Catalyst</u>	<u>Selectivity*</u>
Pt/CMS	0.61
Pt/Carbon	1.00

$$*Selectivity = (C_{\text{linear alkane}} / (C_{\text{linear alkane}} + C_{\text{branched alkane}}))$$

Subsequent reports included a study of thiol poisoning of the CMS hydrogenation catalysts, isomerization of olefins over these catalysts, and the kinetics of hydrogenation.<sup>28</sup>

Walker et al. described the preparation of a platinum-containing carbon molecular sieve from polyfurfuryl alcohol. In order to test the shape-selectivity of the resultant Pt-CMS material they also studied the products when a mixture of a linear and branched olefin was passed over the catalyst with hydrogen. As in the work of Trimm, these results indicated that the linear olefin was reduced but the branched was largely unreacted. In contrast, when the same experiment was conducted with platinum supported on a standard porous activated carbon, both reactants were observed to be hydrogenated.<sup>29</sup> It is interesting to note that the shape-selective effect reported here was considerably stronger than that reported by Trimm for the same reaction and nominally the same catalysts.



Catalyst

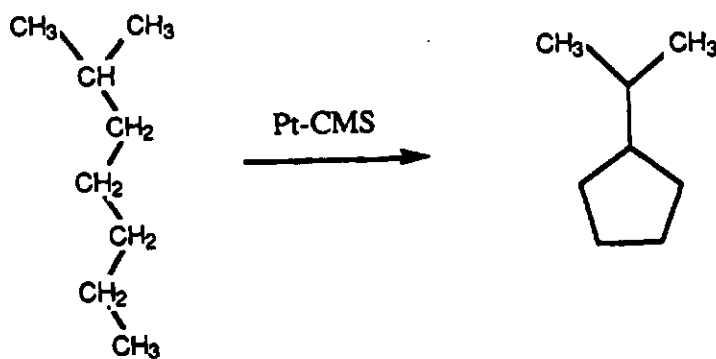
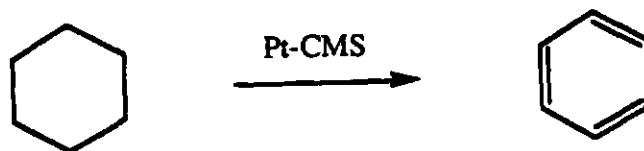
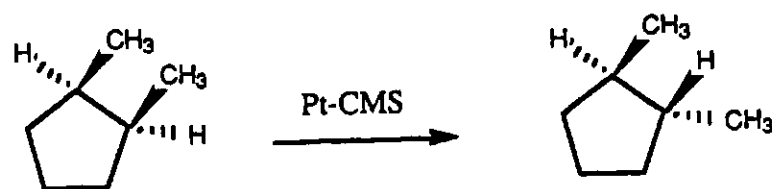
<u>Substrate</u>	<u>% of Substrate Hydrogenated</u>	
	<u>1% Pt/Carbon</u>	<u>1%Pt/CMS</u>
1-butene	90	70
3-methyl-1-butene	50	0

This demonstration, although not surprising, suggested that the branched molecule could not enter the molecular sieving pores of the carbon molecular sieve material because of its steric bulk. Hence the branched olefin was not able to gain access to the platinum sites within the pores, and passed through the catalyst bed unreacted. This was an example of reactant shape-selectivity, basically the catalyst did a chromatographic separation of the reactants and then hydrogenated the sterically unhindered molecule. This did not demonstrate the more significant transition state selectivity that has been observed with the zeolitic molecular sieves.

More recently Walker and Vannice have published a detailed investigation of the use of iron carbon molecular sieves, Fe-CMS, for the hydrogenation of carbon monoxide. This report was particularly thorough and rich in detail regarding the preparation of the Fe-CMS materials. The study included the chemisorption of CO and H<sub>2</sub>, as well as the kinetics of CO hydrogenation and methanation.<sup>30</sup> Another investigation by Walker and coworkers examines the effect of heat treatments on the pore structure of carbon molecular sieve catalysts used for hydrodesulfurization and coal liquification.<sup>31</sup>

A particularly interesting investigation has more recently been published by Bragin et al. Three reactions were studied: cis-trans isomerization of 1,2-dimethylcyclopentane, aromatization of cyclohexane, and the dehydrocyclization of isooctane. The catalysts contained Pt on various carbon molecular sieve supports with varying pore radii. The

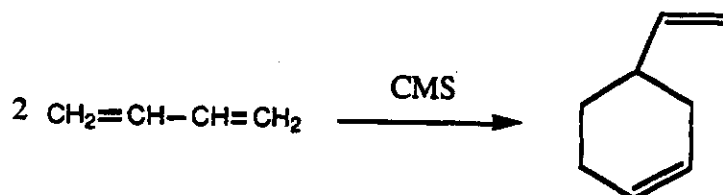
highest specific activity for the first two reactions was determined with the catalysts with the smallest pore size. In contrast, the the catalysts with the smallest pore radii had immeasurably low activity for the last reaction.<sup>32</sup>



Connor has recently demonstrated the utility of carbon molecular sieves as supports for molten indium metal catalysts used to produce aldehyde and ketones by dehydration of primary and secondary alcohols. The molten indium is held in the pores of the carbon molecular sieve and at loadings as high as 7.5 wt%. This approach provides a means of containing the molten indium and provides a higher metal surface area for commensurately higher activity.<sup>33</sup>



Finally, Dessau has shown that "large-pore" carbon molecular sieves will cyclodimerize alkydienes in an Diels-Alder fashion. An example is the conversion of 1,3 butadiene into 4-vinylcyclohexene (30%), over a fixed bed of carbon molecular sieve.<sup>34</sup>



These are the references that we have uncovered with carbon molecular sieve catalysts. It is evident that relatively little research has been devoted to the topic, in view of the amount of recent interest there has been in novel catalytic materials, and especially in zeolitic molecular sieves. Of all of these reports the latter two dealing with alcohol dehydration over In-CMS and Diels-Alder dimerizations with CMS materials seem the most interesting and appear to be the appropriate types of reactions to study with the carbon molecular sieves.