

CARBON MOLECULAR SIEVES AND OTHER POROUS CARBONS

Synthesis and Applications

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INTRODUCTION

Activated carbon is a predominantly amorphous solid that has an extraordinarily large internal surface area and pore volume. Its history can be traced to 350 BC when it was used by Egyptian for the reduction of copper, zinc, and tin ores. In modern day, it is still widely used and is produced as a powder, granule, or preformed shapes (pellet, extrudate, and block). An excellent description is given by Jagtoyen et al¹ in a review on activated carbon and follows:

The term “activated carbon” defines a group of materials with highly developed internal surface area and porosity and hence a large capacity for adsorbing chemicals from gases and liquids. Activated carbons are extremely versatile adsorbents of major industrial significance and are used in a wide range of applications concerned principally with the removal of species by adsorption from the liquid or gas phase, in order to effect purification or the recovery of chemicals. They also find use as catalysts or catalyst supports. The strong market position held by activated carbon adsorbents relates to their unique properties and low cost compared with that of possible competitive adsorbents.

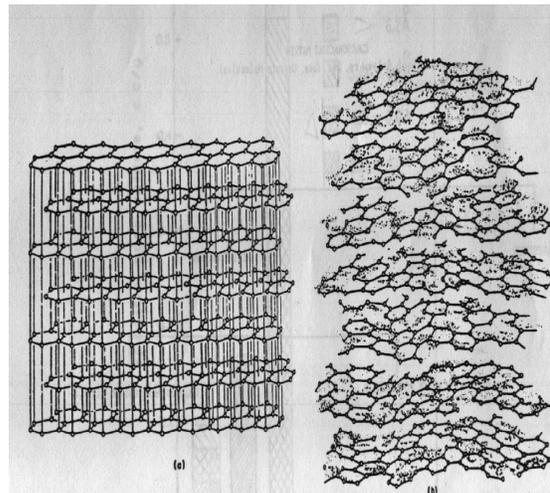
The structure of activated carbon is best described as a twisted network of defective carbon layer planes, cross-linked by aliphatic bridging groups². Activated carbon is mostly nongraphitic, remaining amorphous; a randomly cross-linked network inhibits reordering of the structure³. The surface area, dimensions, and distribution of the pores depend on the precursor and on the conditions of the carbonization and activation.

Molecular sieves can be defined as substances with discrete pore structures that can discriminate between molecules on the basis of size. Carbon molecular sieves (CMS) are a special class of activated carbons. However, pore size distribution of these materials is not always strictly discrete and furthermore, molecules are not hard spheres; they can sometimes squeeze into narrow pores. The distinction between activated or porous carbons and carbon molecular sieves is not clearly defined. Carbon molecular sieves have most of the pores in the molecular size range but some conventional activated carbons also have very small pores. The main distinction is that activated carbons separate molecules through differences in their adsorption equilibrium constants^{4,5}. In contrast, an essential feature of the carbon molecular sieves is that they provide molecular separations based on rate of adsorption rather than on the differences in adsorption capacity. This behavior is clearly evident in pressure swing adsorbents (PSA) where gas dynamics dominate. The separation of nitrogen from air by PSA is the single most important application of CMS.^{6,7}

At the same conditions, the rate of adsorption is made up of at least two important factors, the equilibrium uptake or capacity of the sieve, and the diffusivity, or rate of diffusion in the porous material. It is the relative diffusivity that determines the degree of molecular sieving. In a mixture of two gases, when one molecule is excluded from entering a pore, the diffusivity is zero for that molecule and the degree of sieving is infinite for the other molecule. In conclusion, the extent of molecular sieving can be defined as the ratio of the rate of adsorption of one molecule to another as shown in Equation 1 below:

$$\text{Extent of Molecular Sieving} = \frac{R_{A1}}{R_{A2}} \quad (1)$$

Carbon molecular sieves are non-crystalline or amorphous and quite unlike inorganic oxide molecular sieves which have a well ordered crystalline structure. Foley⁸ has described the unique features of carbon molecular sieves (CMS) and particularly their structural characteristics in an earlier publication. A hypothetical structure of a carbon molecular sieve crystallite is shown in Figure 1b. Disordered graphitic platelets of carbon are separated by interstitial spaces. The size of the gaps are determined by several factors, such as the presence of foreign atoms between the layers, hanging side groups, and cross-linking chains of carbon atoms. Also influencing the pore structure is the presence of capping groups on the edges of the layers. Also shown in Figure 1a is a well-ordered structure of graphite for comparison purposes.



Despite the amorphous nature of carbon molecular sieves, they do show remarkable sieving properties and as such, they have certain advantages over inorganic oxide molecular sieves. These are the following :

- Stability at high temperature. It has been reported that some carbon molecular sieves can withstand temperatures up to 1500°C.⁹
- They are stable in acid media. This is an important property in liquid phase operations. The process for purifying terephthalic acid depends on a carbon catalyst with acid stability.
- Carbon sieves have low affinity to water. The property of hydrophobicity can be controlled by the pretreatment conditions during preparation of the sieve; however, most carbon molecular sieves are hydrophobic in character.¹⁰
- Carbon sieves are easy to make, relative to zeolites.
- The pore sizes can be controlled by the method of preparation. Oxidation or activation can enlarge them, or they can be decreased by high temperature treatment in an inert atmosphere.¹¹

PREPARATION

The starting material for all carbons is carbonaceous matter, either coal, wood, polymers, etc as shown in the flow chart in Figure 2. Activated carbons are typically produced from coals by a two-step process involving carbonization and activation. When so-called caking coals (which become plastic on heating) are used as precursors for producing activated carbons, they are first converted from thermoplastic to thermosetting through the introduction of crosslinks by controlled low temperature activation. Subsequently, the activation process involves opening up of closed porosity and enlargement of existing pores.

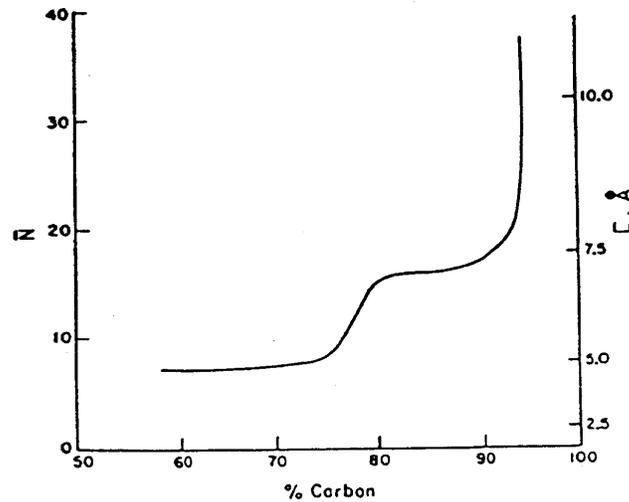
From fundamental considerations, activation should be carried out in a temperature regime in which the gasification rate is controlled by the intrinsic chemical reactivity of the carbonized material. That is, intraparticle diffusional effects should be absent. From a practical standpoint, such a situation is not really possible. Therefore a compromise in activation conditions is usually chosen which will maximize development of internal porosity while keeping surface combustion low; the main effect of combustion is to increase geometric area through particle size reduction.

Coal-Derived Carbon

For reasons of economy, the most favored starting material for making carbon molecular sieves as well as other activated carbons is coal. It should be noted that coal itself has sieving properties. For instance, it is known that well dried anthracite can separate the isomers of butane.¹² Also, it is known that methane diffuses rapidly through coal while the higher carbon number gases are held more tightly.¹³ Reasons for the sieving action of coal itself is shown in Figure 3, which shows a graph of the

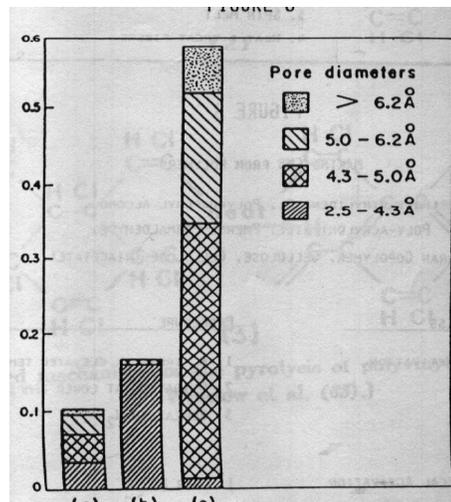
average layer diameter as a function of the carbon content in various coals.

It is seen that as the carbon content of coal goes up (when the coal moves into the harder classification), the average layer diameter becomes larger. The range of these layered diameters goes from 5 to 10 Å, which is within the molecular dimension range.¹⁴ However, coal has a fairly broad distribution of pore sizes, and its absorption capacity is low, thus making it a poor candidate as a carbon molecular



sieve.

A comparison between the pore size distribution of coal itself and coal thermally treated in various stages is shown in Figure 4.



The raw coal, shown in this bar chart on the far left, exhibits a fairly wide distribution

of pore diameters. However, when the coal is devolatilized, the pores shift into the small diameter range as shown in the middle bar. Following the devolatilization procedure, the coal is activated with air and the distribution of larger pores broadens again as shown on the right bar. The measurement of these pore sizes in this range can only be obtained by probe molecule adsorption. X-ray analysis cannot be made on these amorphous materials and there are no physical adsorption methods that allows a distribution below 20 \AA to be obtained.

Carbon molecular sieves are prepared from coal by several methods and these are tabulated below:

Table I
Methods to Make Carbon Molecular Sieves from Coal

Process	Procedure
1. The gas activation process is the standard method of making carbon molecular sieves from coal and also from other materials. (Fluidized)	Heat in nitrogen 800-900 C Cool to 400 C Expose to Air Reheat in nitrogen to 900 C
2. Chemical Activation	Mix with $\text{ZnCl}_2/\text{H}_3\text{PO}_4$ Heat in nitrogen 900 C
3. Gas Activation plus Hydrocarbon Cracking	Heat and treat as in process 1 Crack propylene 400-500 C Reheat 800-900 C
4. Melt Spinning	Dissolve coal in solvent Evaporate solvent Spin melt Heat and treat fibers

1. This consists of grinding the coal, drying it, and then heating in an inert atmosphere, up to a temperature of 800 to 900°C. The material is then cooled to about 400°C, a temperature just below the ignition temperature of the coal, and is then allowed to be exposed to air for a given time. This step, known as the "burn-off" creates the pore structure by partially burning into the matrix of the material. Finally, the material is reheated in an inert atmosphere up to 900°C to remove any oxide groups formed in the previous step.

2. In chemical activation ground coal is mixed with certain chemical compounds such as zinc chloride, phosphoric acid, or barium chloride and then heated in nitrogen up to temperatures of 900°C. Oxidation steps may also be included. The reasons for using these chemicals are unclear. It has been suggested that these compounds

may dehydrate the coal to help produce the porous structure.

3. This process is a variation of the first gas activation process. It consists of taking the final product of the gas activation process and then cracking a hydrocarbon, such as propene, over it at about 400-500°C then finally reheating in nitrogen up to 900°C. This produces a very narrow pore size distribution and is the main process for producing carbon molecular sieves which are used in the separation of oxygen and nitrogen, from air.¹⁵

4. The melt spinning process.¹⁶ consists of first dissolving a soft coal in a solvent such as coal oil. The solvent is then evaporated from the material and a melt is left. This melt has a melting point of around 200°C. It is heated up and can be spun out into fibers. These fibers can then be treated either to produce graphitic carbon fibers by heating at high temperatures or by activating with air to produce porous carbons or carbon molecular sieves.

Polymer- Derived Carbon

Carbon molecular sieves and activated carbons can also be made from various polymers such as polyvinylidene chloride, polyacrylonitrile, phenol formaldehyde, etc. Pioneer workers in producing carbon molecular sieves from polymers^{17,18} had originally hoped to make carbons of similar structure to the original polymer framework. Unfortunately, during the process of activation and heat treatment, the polymer structure collapsed and the resulting material bore little resemblance to the starting material. The collapsed structure produced much smaller pores that were carbon molecular sieves. Chemical activation has also been reported using polymers¹⁹ and is summarized in the table below:

Table II
Methods to Make Carbon Molecular Sieves from Polymers

Process	Procedure
Gas Activation	Nitrogen treat at elevated temperatures Oxidation at lower temperature Reheat in nitrogen
Chemical Activation	Char at 800 C Granulate +15% sulfite waste Heat to 800 C in nitrogen

To understand the reorganization of the polymer to form a carbon molecular sieve, a proposed mechanism for pyrolysis of polyvinylidene chloride is shown in Figure 5. One observes fragments of the chain of the vinylidene chloride dehydrochlorinating to form conjugated, unsaturated chains. These chains condense to form condensed

ring structures similar to the graphitic layers that occur with other carbons. Finally, the layers can be cross-linked by further dehydrochlorination to form a three-dimensional graphitic structure. The dehydrochlorination occurs over a temperature range from 250 to about 600°C. The reaction takes place stoichiometrically and the final product has no chlorine present. The resulting carbon has a fairly low mesoporous structure of average diameter of 16 Å. On further heating at higher temperatures in an inert atmosphere the pores get progressively smaller.

Carbon Derived from Other Materials

Activated carbons with very high surface areas (2800 m²/g), exceptional adsorptive capacities and unique structural features can be obtained by chemical activation of petroleum coke with KOH²⁰. These carbons are frequently referred to as Amoco carbons but they are now commercially produced in Japan by Kansai Coke and Chemical and will be referred to as super activated carbon. Although various carbonaceous resources such as coal, coal coke, petroleum coke or their mixtures can be used, petroleum cokes are the preferred feedstock because of their low ash content. Since this particular active carbon is produced by controlled chemical activation, its quality is independent of the starting material and, is consistently reproducible with little variation in adsorptive and physical properties. In contrast, most the properties of most other activated carbons based on thermal activation strongly depend on the starting material.

To prepare super activated carbon, petroleum coke is mixed with KOH (KOH/coke ratio varied around 3/1). The mixture is heated at 400-500 C under an inert atmosphere to give an intermediate product, referred to as precalcinate. The precalcinate is then calcined at a higher temperature, about 850° C. The active carbon product contains occluded potassium salts, particularly carbonate with some sulfides, sulfates and unconverted KOH which are washed out with water and the final carbon product dried.

A low sulfur version of the superactivated carbon has been patented by Kansai²¹ which uses coconut shell char rather than petroleum coke to produce a superior product which eliminates the acid washing step in the process. Supporting studies by Otowa²² examined various activation parameters including KOH/coke ratio, calcination temperature and time.

In the super activated carbon, two types of structures were observed via high resolution electron microscopy (HREM). Some powders showed a homogeneous steel wool-like structure that is made of entangled single carbon layers (viewed edge-on), as seen in Figure 6 at 1,500,000 magnification. The entanglement of the carbon layers produces many enclosed voids leading to large micropore volume and high effective surface area. The steel wool-like structure is best viewed in the very edge of the powder where the overlapping of the entangled layers is minimal. In the regions away from the edge, the sample becomes too thick so that many stacks of

the entangled layers are projected to the image plane, resulting in a much denser structure. Another type of structure, that is sometimes present is segmented ribbons in association with the steel wool-like structure. It has been reported that the ribbons are composed of 2-12 parallel graphitic planes.

USES OF CARBON MOLECULAR SIEVES

The primary use of carbon molecular sieves is for the separation and purification of gases. Table 3 below lists some of these uses, starting with the most important process of separating nitrogen from oxygen, which is now in commercial operation in West Germany.²³ The Bergbau & Forshung process operates with a pressure swing adsorber and a carbon molecular sieve that is prepared by the modified gas activation plus hydrocarbon cracking method. Bergbau and Forshung, who have made extensive pilot plant studies, offer several other separation processes.^{24, 25} These include the separation of hydrogen from methane to be used in the recycling of off-gas from coke ovens. Also, the separation of hydrogen from ammonia to be used in conjunction with ammonia plants. Both of these processes uses a slightly different carbon molecular sieve called CMS H2. All of these carbon molecular sieves are produced from coal.

Table III
Separation Applications of Carbon Molecular Sieves

Separation	Possible Application	Type of Molecular Sieve
Nitrogen from Oxygen	Nitrogen production	Bergbau-Forshung CMS
Hydrogen from Methane	Off gas coke ovens	CMS H2
Hydrogen from Ammonia	Ammonia Plants	CMS H2
Hydrogen from CO	Ethylene production	Russian Carbon
Hydrogen from Product Gas	Refineries	RSM (Calgon)
Methane from carbon dioxide	Gases/Oil Wells/CO2 flooding	RSM (Calgon)
Alcohol from water	Gasohol	Calgon
Methane from ethane ethane from propane propane from butane	Academic Studies(Japan)	MSC-5A(Takeda)
Butane from neopentane		(PVS + pitch) char
Olefins from Isoprene	Synthetic rubber	UOP Carbon
C4 olefins from Isoprene	Synthetic rubber	UOP Carbon
Butane isomers	PET Chemical	(PVA-Phenol) Kanebo KK
Polynuclear aromatics from hydrocrackate	Refinery	UOP Carbon

Pentane from carbon disulfide	Foamed Plastics	El Paso CMS
Hydrogen from stack gas	Power Station	Calgon CMS & FeCl ₃
SO ₂ from Off gas	Sulfuric Acid	CMS (B-F)

The separation of hydrogen from product gases used for refinery applications^{26,27} has been studied by Calgon Company with supporting pilot plant studies. Also they have investigated the separation of methane from CO₂ in conjunction with the off-gases from oil wells when CO₂ flooding is employed to stimulate oil flow. The removal of water from alcohol for use in gasohol (10% blend of ethanol-gasoline) has also been explored. The sieves used in these processes are manufactured from coal.

Takeda Company in Japan, produces two molecular sieves, MSC-5A and MSC-7A.^{28, 29} While no application has been reported for MSC-7A, several studies have appeared in the literature for the use of 5A in the separation of light hydrocarbon gases.

UOP has applied carbon molecular sieves for certain applications in the synthetic rubber industry to separate olefins from isoprene and butadiene.^{30,31} Also from UOP, a patent has been issued for the separation of polynuclear aromatics from hydrocracking product.³² This is used in the recycle gas stream from hydrocrackers, presumably to preserve the catalyst from excess coking. Several other patents have been issued for the separation of other hydrocarbon gases.³³

Numerous patents have also been obtained for the purification of gas streams when certain pollutants are present in small quantities. These include the separation of carbon disulfide from pentane, the removal of mercury from stack gases, and finally, the removal of SOX from off gases in sulfuric acid plants.³⁴ All of these claim carbon molecular sieve as the adsorbent. Removal of many other sulfur pollutants have also been claimed to be removed by carbon molecular sieves.

The standard process used in gas separation is Pressure Swing Adsorption.³⁵ Figure 7 shows a schematic of a Pressure Swing Adsorber for the separation of nitrogen from oxygen. In this typical example a reactor-adsorber A is compressed with air to about four atmospheres and then releasing the pressure after 60 seconds. The product obtained is 99.9% pure nitrogen. The valve is then closed and the adsorber is then evacuated to less than 100 torr to remove oxygen, CO₂, and water. While Reactor A is being evacuated, Reactor B is being compressed with a fresh charge of air. In this way, continual operation is maintained during the cycling operation, of the two parallel units.

CATALYSIS

Carbon as a support for catalyst has several unique characteristics and carbon molecular sieves are no different. First, carbon is chemically neutral; It needs the presence of other active ingredients for catalysis to occur. Secondly, carbon catalysts cannot be regenerated to remove deposited coke. However, despite these drawbacks, carbon molecular sieves as catalysts have been reported in both the academic and patent literature.^{36, 37}

The list in Figure 8, first shows a Japanese report on the isomerization of meta-xylene to para-xylene over a carbon molecular sieve impregnated with aluminum bromide.³³ These conditions are fairly mild and the product is mostly para-xylene with some ortho-xylene by-product. An interesting patent from Mobil shows the use of carbon molecular sieve for the dealkylation of durene.³⁴ Durene (tetramethyl benzene) is an unwanted by-product made when using the Mobil M process to convert methanol to gasoline. A carbon molecular sieve is used in conjunction with a methyl transfer agent such as pyrene.

An interesting use of carbon molecular sieve is in the cyclic dimerization of 1,3-butadiene to produce vinyl cyclohexene in a Diels-Alder type reaction.³⁸ This compound presumably is an intermediate in the formation of styrene. The other major use of carbon molecular sieve catalyst is in Fisher-Tropsch reactions.³⁹ The catalyst is a carbon molecular sieve with iron used to convert syngas into Fisher-Tropsch products. In comparison with an iron catalyst, this carbon based catalyst shows higher activity and a higher olefin-to-paraffin ratio. There has also been recent reports of a carbon-based ammonia synthesis catalyst using supported ruthenium and it has the potential to replace the iron catalyst that has been used for the last several years.⁴⁰ One commercial ammonia plant using this new carbon based catalyst is in operation.

POSSIBLE SIEVING MECHANISM

Koresh and Soffer have provided insight into how the sieving mechanism possibly works in carbon molecular sieve through a series of papers.^{41, 42, 43} Starting with a Carbone-Lorraine carbon molecular sieve, they proceeded to heat treat it in different stages until the largest molecule that would be adsorbed into the carbon was established. The molecular size ranged from carbon dioxide, the smallest, to sulfur hexafluoride, the largest.

There were two main discrepancies observed in these results. First, is the pore enlargement disagreement. The opening of the pores are enlarged by the removal of an atom from the ring of the pore and one should expect a large integral step increase in the pore size to occur (several angstroms in size.) However each successively larger molecule has only a small difference in the diameter (small fraction of an angstrom unit). This is difficult to understand.

The second discrepancy is in the amount of material that is actually lost on heat treatment. The gas evolved on heat treatment was carbon dioxide; knowing the density of liquid carbon dioxide, it is possible to calculate approximately the pore expansion as a result of each treatment. Going from pore sizes which adsorb carbon dioxide to larger pores which adsorb oxygen, the diameter expansion is only about 1.7%. Yet looking at the differences in the molecular diameter, diameter expansion would have to be almost 6% for the pore opening to be large enough to allow the larger molecule to enter. This difference between the experimental and the calculated expansion of the pores gets progressively larger. Evidently some factor other than pore size will better explain these results.

The authors proposed a semi-permeable outer layer model to explain this concept and it is shown in Figure 9. This model assumes that there is a shell of higher density than the bulk of the material around each carbon particle. This shell provides a rate determining barrier to the diffusion of molecules. Once the molecules have penetrated through the outer barrier, they can freely condense in the broad distribution of pores within. The outer barrier consists of several channels with an average number of constrictions.

OTHER NOVEL APPLICATIONS FOR POROUS CARBONS

High surface area carbons are also finding application in other fields such as electrical storage and specifically, the electrical capacitor field. The discharge-charge mechanism is shown in Figure 10 with a liquid electrolyte used to transfer charges between the electrical double layers. Referring to Figure 11, discharge capacitance has been plotted versus discharge current and various batteries and capacitors compared⁴⁴. The standard lead rechargeable battery is shown in the upper right corner of the diagram. Interestingly, we see that high performance carbon capacitors begin to approach this performance area being just below it, with a smaller discharge capacitance.

A relatively new consumer product, called an electric bicycle is finding wide application in Japan and is based on storing electrical energy when the bike is on a level or down hill slope so that this energy can be used to drive an electric motor in up hill situations.⁴⁵ Kansai Coke and Chemical has recently increased production of their super activated carbon(Maxsorb) expressly for this application.

Bonded carbon is a new development that is finding applications in replacing granular carbon. For example, bonded carbon can be used for gasoline vapor canisters in automobiles and offers the advantage of higher density, with a corresponding increase in the butane working capacity, less abrasion, and eliminates bed settling if the canister is oriented in a horizontal, rather than a vertical configuration. Mega-Carbon has two patents⁴⁶ for a medium and high temperature

binding system and they describe bonding technology to make shaped carbon blocks. Other applications include natural gas storage and storage of refrigerants, such as ammonia.

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