MOLECULAR SIEVES

by

P. L. Walker, Jr.

Professor of Fuel Science

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Introduction
Much has been written about diffusion of gases in and through porous solids. At least two good books are available on the subject. Diffusion of gases in solids can be conveniently divided into three main types: bulk diffusion, Knudsen or molecular diffusion, and activated diffusion. In this article we will be concerned mainly with activated diffusion as it is operative in molecular sieve materials.

When the size of the diffusing species closely approaches the size of the aperture through which it passes, the physical interaction energy between the species and aperture becomes important. This interaction energy may be considered to be essentially the sum of Lennard-Jones expressions for dispersive and repulsive interactions. When the aperture opening becomes sufficiently small relative to the size of the diffusing species, the repulsive interaction between them in the plane of the aperture becomes dominant; consequently, the diffusing species requires a certain activation energy to pass through the aperture. Thus, at some point Knudsen diffusion changes over to activated diffusion. In the activated diffusion regime small differences in the size of the diffusing species can result in large differences in activation energy for diffusion through a particular aperture. Thus, solids which have apertures of molecular size can exhibit large differences in their propensity for taking up molecules differing slightly in size. These solids exhibit a sieving effect of molecules depending upon their size and, therefore, are called molecular sieve materials.

In recent years, molecular sieve materials have become the object of major commercial interest. By far the most important commercial molecular sieve materials are the crystalline zeolitic aluminosilicates. Synthetic zeolites, which are produced commercially and commonly identified as 3A, 4A, 5A, 10X and 13X, are grown hydrothermally from an alkaline mixture of silica alumina. Single crystals of about 1-5 microns in size can be grown. On removing the water of hydration at ca.

The author, Dr. Walker, and a Research Assistant, Joseph Metcalfe, are shown examining data concerned with the exit concentrations of hydrocarbons from a packed bed of carbon molecular sieves. The data have been obtained by use of gas chromatography.
350°C, a network of empty cavities and apertures remain, which comprises ca. one-half the total volume of the crystals.

A classic example of their molecular sieve behavior is the ability of the 5A sieve to take up copious amounts of straight chain paraffins whose volumes are negligible amounts of branched chain paraffins. The use of molecular sieves to separate straight from branched chain hydrocarbons has been of value to the petroleum industry in their efforts to increase the octane rating of gasolines and to the detergent industry in their efforts to produce biodegradable detergents. Recently, molecular-sieve discriminating catalytic reactions have been demonstrated using zeolites.\textsuperscript{31,37} The normal hydrocarbons, which are accessible to the 5A zeolites, preferentially undergo cracking, dehydrogenation, and hydrogenation reactions relative to the branched chain hydrocarbons.

The fact that some naturally occurring as well as synthetic carbonaceous materials show molecular sieve properties has been known for some time. Most ranks of coal possess these properties; for example, they show a much greater uptake of normal than branched hydrocarbons.\textsuperscript{14} However, since their sorption capacity is low compared to the zeolites, coal will not be considered further in this article.

Synthetic molecular sieve carbons can be produced upon the coking of selected thermosetting polymer or co-polymer systems. As we will see later, molecular sieve carbons of high capacity and good selectivity can be produced from both polystyrene divinylbenzene and Saran.

At present carbon molecular sieve materials are not being produced commercially. However, interest is being shown in using them as high separation medium in conjunction with zeolite sieves or even as carbon zeolites.

Natural zeolites (named from the Greek zea, meaning to boil, and lithos, meaning stone, because the crystals, when gently heated, give off water vapor) were first given their name several centuries ago.\textsuperscript{10} Mineralogists later distinguished four kinds of zeolites, each with its own crystal structure. The fundamental building block of any zeolite crystal is a tetrahedron of oxygen ions surrounding a smaller silicon or aluminum ion. In the case of the oxygen ions has two negative charges; each silicon ion has four positive charges; each aluminum ion, three. Each silicon satisfies one-half of the eight charges of the four oxygens which surround it. Each oxygen retains one negative charge, which enables it to combine with another silicon or aluminum ion and extend the crystal lattice in all directions. The aluminum ion, with one less positive charge than the silicon, can only satisfy three negative charges on the four oxygens which surround it. To produce a stable crystal structure another positively charged cation must be added. These cations, called exchangeable ions since they can be readily exchanged without destroying the zeolite structure,\textsuperscript{15} attach themselves loosely to the oxygens at the corners of the tetrahedron. This loose attachment plays an important part in determining the change of activity energy with the size of diffusion species in a particular zeolite.

In zeolites, the framework of silicon-oxygen and aluminum-oxygen tetrahedra forms a structure which is honeycombed with relatively large cavities. The shape and size of these cavities and the size and number of apertures leading into them depend upon the type of zeolite. When the cavities are emptied of water by heating, zeolites do not disintegrate as do most other water-bearing crystals. Chemists investigating this phenomenon in the 1920s noted that zeolites sorbed substances selectively and began to refer to zeolites as molecular sieves.\textsuperscript{16} In 1938, Barrer undertook his lengthy and continuing study of zeolite molecular sieves, showing their utility for separation of gases.\textsuperscript{17}

In 1948, researchers at the Linde Company set out to explore the commercial possibilities of zeolite sieves. Because of the relative rarity of natural zeolite crystals, they were compelled to seek ways of growing them artificially. By using a mixture of sodium and aluminum oxides and freshly prepared silica gel, they were able to grow hydrothermally many types of synthetic zeolite single crystals of over one micrometer in size, including a Type A zeolite, which to date has no natural analog. Later, a Type X zeolite was grown, which also has a high capacity, but apertures somewhat larger in size than the Type A zeolite.

Determined, quantitative x-ray diffraction studies have been made on Type A sieves in order to completely delineate their structure.\textsuperscript{11,12} The aluminum-silicate framework of the Type A zeolite is based on units which contain four AlO\textsubscript{4} and four SiO\textsubscript{4} tetrahedra in a rigid compact group.\textsuperscript{38} These units link together to form a ring of eight oxygen atoms in the center of each face of the unit cell on an irregular ring of six oxygen atoms at each corner of the 3-fold axis. In the center of the unit cell is a cavity 11.4 A. (Angstrom Unit) in diameter, which is connected to six like cavities by the 8-membered rings which form restricted openings 4.2 A. in diameter. In addition, the large cavity is connected to eight small cavities 6.5 A. in diameter by the 8-membered rings which produce openings 9.0 A. in diameter. These latter cavities are not useful in molecular sieve separation because of the very small aperture size leading into them.

Type 3A, 4A, and 5A zeolites are important commercially. The difference in their screening behavior is caused by differences in the exchangeable cation present. In the 4A sieve, the exchangeable cation is sodium. There are eight sodium ions (which take positions in or near the 4.2 A. aperture openings and partially block them) for every six apertures between 11.4 A. cavities. The free diameter of the 4.2 A. aperture is thus reduced to ca. 3.5 A., as we will see from molecular probe studies. If the sodium in the 4A sieve is exchanged for calcium, a single calcium ion replaces a pair of sodium ions. Now with only four ions available for six apertures, two apertures per cavity are unobstructed and thus have a free diameter of 4.2 A. This is called the 5A sieve. If the sodium in the 4A sieve is exchanged for the larger potassium ion, a single potassium replaces a single sodium, and there remain eight ions for six apertures. The free diameter of the 4.2 A. aperture is reduced to ca. 3.2 A., but this figure is apparently dependent on the particular diffusing species passing through the aperture. The potassium-bearing Type A zeolite is called 3A.

Bouasse and Shoemaker\textsuperscript{31} as well as Barrer\textsuperscript{4} recognized that the crystal structures of the Type A and X zeolites are both based on a cube-octahedral structural unit, similar to that found in the mineral sodalite,\textsuperscript{7} which is the fundamental building block of both types of sieves. In Type A zeolites, the sodalite units, each of which contains 24 (silicon, alumin-
ium) ions interconnected with 36 oxygen ions, are arranged in a single cubic array, with each sodalite unit connected to its neighbor by four bridge oxygen ions. In Type X sieves, sodalite units are in tetrahedral coordination, with each unit connected to its neighbor by six bridge oxygen ions. The Type X structure is essentially similar to that of the naturally occurring faujasite. The apertures of importance in Type X sieves are composed of 12-membered oxygen rings. In the Type 13X sieve, where sodium is the exchangeable cation, the aperture has a free diameter of 7.5A.U., as given by x-ray diffraction studies.\textsuperscript{11} Probably the most important use of zeolite molecular sieves, at the moment, is the removal of water from gas streams. Water is readily accessible to all Types A and X zeolites and is held strongly and preferentially to most other sorbates. In order to measure the full capacity of the zeolites for other sorbates, it is absolutely essential that the zeolites be outgassed under high vacuum at 350-400°C.\textsuperscript{22}

Early sorption studies of Barrer\textsuperscript{2} and Tisei\textsuperscript{23} were concerned primarily with water uptake on natural zeolites. The properties of zeolitic water have continued to be of interest, but quantitative and thermodynamic studies have been made difficult because of the chemical reactivity of water and irreversible side reactions. Consequently, the sorption properties of ammonia, another small polar molecule but a less reactive species than water, have been studied extensively in recent years. For example, Barrer and Gibbons\textsuperscript{8} have studied the sorption of ammonia on Type X sieves.

Emmett and DeWitt\textsuperscript{16} were among the first to show the molecular sieve behavior of zeolites. Working with the natural zeolite cha-bazite (which has an aperture ca. 3.6A.U. in diameter, formed by a ring of eight oxygen atoms\textsuperscript{49}) they found little sorption of nitrogen at -190°C, but significant sorption at -78°C. They attributed these results to activated diffusion. That is, in physical sorption it is thermodynamically necessary that the amount sorbed decreases with increasing adsorption temperature at equilibrium. However, if the sorption is very slow and has not reached equilibrium under particular sorption conditions\textsuperscript{7} because of activated diffusion, increased rate uptake with increasing temperature can occur.

Because of their commercial importance we will now focus our attention primarily on sorption results of Types A and X sieves. These sieves all have large surface areas, on the order of 700-800 m²/g, potentially available.\textsuperscript{15} The amount of this area actually accessible to particular sorbates depends upon their size relative to the size of the aperture openings in the zeolite. The 3A sieve, because of its small aperture opening, effectively excludes all organic compounds. At present, it is useful primarily for the drying of gases. Encapsulation and storage of permanent gases in the 3A sieve appears to have future commercial possibilities.\textsuperscript{13} The sieve is loaded by exposure to the gas at high pressures and elevated temperatures to overcome a substantial activation energy for diffusion and then cooled to room temperature before releasing the external gas pressure.

Breck and co-workers have performed the most comprehensive sorption studies on the 4A and 5A sieves.\textsuperscript{9} As found by Emmett and DeWitt on cha-bazite, they also found that the sorption of nitrogen on the 4A sieve increases with temperature from -196°C to ca. -78°C. Similar results are found for the sorption of carbon monoxide and argon.\textsuperscript{35} In the 5A zeolite, no molecular sieve effects of these molecules are observed. That is, the volume of gas adsorbed falls off monotonically with decreasing temperature between -196°C and 0°C in each case. Both the 4A and 5A sieves have large sorption capacities for carbon dioxide at -78°C.

Sorptive capacities of Types 4A and 5A zeolites for a series of adsorbates are summarized in Table 1. The uptake of molecules with minimum kinetic dimensions less than ca. 4A.U. at 20°C is essentially the same on 4A and 5A sieves and is large. For straight chain hydrocarbons having more than two carbon atoms, the uptake on the 4A sieve is small, uptake on the 5A sieve is large. Substantial sorption of normal paraffins up to at least C₄₁ has been reported on the 5A sieve. On a volume basis, between 0.3 and 0.4 cc of liquid hydrocarbon is sorbed per cc of zeolite. Negligible sorption of branched chain hydrocarbons, which have minimum kinetic dimensions of at least 5A.U., or aromatics, which have minimum kinetic dimensions of at least ca. 7A.U., occurs on the 4A and 5A sieves. These results show clearly the feasibility of using the 5A sieve to separate straight chain hydrocarbons from branched chain hydrocarbons and aromatics.

The 10X sieve has a substantial capacity for molecules with minimum kinetic dimensions of at least ca. 7.7A.U.\textsuperscript{8} (that is, (C₆F₆)₂NC₃ F₃ but not greater than ca. 8.1A.U.\textsuperscript{8} [that is, (C₅H₅)₂N]. Thus, it can sorb many of the isoparaffins, aromatics, and hydroaromatics. The 13X sieve sorbs (C₅H₅)₂N but not (C₆F₆)₂NC₃ F₃ which has a minimum kinetic diameter of ca. 10.2A.U.\textsuperscript{8} The 13X sieve has a high capacity for sorption of some aromatics with side chains, which are sorbed very slightly on the 10X sieve, such as, 1, 3, 5 triethylbenzene.\textsuperscript{35}

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Fig. 2. Proposed mechanism for the pyrolysis of polyvinylidene chloride. (Winslow, Baker, and Teger, Reference 39.)
A very important property of zeolites, not based on the molecular sieve effect, is their preferential sorption of polar, unsaturated, and aromatic compounds. The more polar or the more unsaturated the molecule, the more tightly it is held within the crystal. The sorptive forces in the zeolites are due primarily to exchangeable cations which are exposed in the crystal sorption surface. These cations act as sites of strong, localized positive charges which electrostatically attract the negative end of polar or polarizable molecules. Figure 1 shows the very high selectivity of the 4A sieve for ethylene in preference to ethane when exposed to ethylene-ethylene gas mixtures. It is recalled from Table 1 that the sorptive capacities of ethane and ethylene, when the 4A sieve is exposed to 700 torr of the pure hydrocarbons, are roughly equal. For comparison, Figure 1 also shows the relative sorptivity of ethylene-ethylene mixtures on a granular activated carbon. In this case, ethane is sorbed slightly more preferentially than ethylene. This would normally be expected, since ethane has a lower vapor pressure at 25°C than does ethylene. Polarity differences are also used to separate aromatic from saturated paraffins and hydroaromatic compounds. Type 13X sieve separates effectively benzene and toluene from paraffinic hydrocarbons and from cyclohexane and methycyclohexane.

**Carbon Molecular Sieves**

The term carbon is used in the generic sense, since carbon molecular sieves contain other elements. The synthetic polymer carbons are very low in metallic and metal oxide impurities, but usually contain some oxygen and hydrogen and sometimes contain nitrogen, sulfur, and/or chlorine.

In direct contrast to the single crystal zeolite sieves, which we have been discussing, carbon molecular sieves are composed of varying amounts of multi-crystalline and amorphous material. If carbon molecular sieves are heated to elevated temperatures (870°C and higher) where substantial crystallite growth can occur, their fine pore system disappears and their surface areas decrease to a very low value.  

To date, the approach to the production of molecular sieves from carbons has been primarily empirical. Little is understood about the relation between the original size and shape of the polymer units and the pore size and shape present in the carbon produced. Originally it was the hope of workers in this field that carbons with uniform pore size would be inherited from the regular structure of polymer predecessors and that it would be possible to predict final carbon structure on the basis of known pyrolysis reactions which polymer systems undergo. How this might be accomplished is uncertain because few valence angles and distances survive thermal decomposition unchanged. Indeed, studies have indicated that original polymer configurations have only secondary importance. Instead, the course of carbonization (charring) is determined by the overall energy requirements for formation of rigid carbon materials.

To date, far more studies have been conducted on the conversion of polyvinylidene chloride, (C₂H₃Cl₂)n and Saran® to molecular sieve carbons than on any other polymer systems. By process of elimination, their popularity appears reasonable. First, all thermoplastic polymers can be eliminated, since upon carbonization they yield coalescence of medium to very good crystallite alignment possessing small internal surface areas. Second, many thermosetting polymers, upon being coked, yield chars characteristic of the 4A zeolite; whereas polyvinylidene chloride and Saran yield chars which have large specific areas and show molecular sieve properties useful for the separation of hydrocarbons. Third, the coking of polyvinylidene chloride and Saran results in a reasonably good yield of carbon, ca. 25%.

When polyvinylidene chloride undergoes pyrolysis, it loses HCl stoichiometrically, leaving essentially pure carbon. That is:

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(C₂H₃Cl₂)ₙ → 2nHCl + 2nC. 
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Workers have studied the kinetics of HCl release during carbonization. They found that about half the HCl is released below 200°C by a first order reaction with an activation energy of ca. 30 kcal/mole. Further liberation of HCl requires progressively higher temperatures until the process finally approaches completion at 600°C, producing a yield of carbon equal to 25% of the starting polymer weight. A mechanism has been proposed for this conversion, as shown in Figure 2. The first step is the loss of one HCl molecule per pair of carbon atoms, leading to the formation of a polymer chain.

It is concluded that the loss of HCl from a single chain is both chemically and sterically unlikely and that crosslinking of the chain by a Diels-Alder type of reaction, as shown in reaction 2, must occur before further HCl elimination takes place. Each cyclic adduct produced in reaction 2 has additional hydrogen and chlorine in highly reactive tertiary positions. It is concluded that these immediately split out, by reaction 3, leaving thermally stable aromatic rings combined by polyene chains. Further crosslinking can occur either with other parts of the same chain or with another adjacent chain. Examination of space models shows that the crosslinking reaction has a complicated stereochemistry, but it is tentatively concluded that it is probably third order in the concentration of C₂HCl units.  

Upon pyrolysis, polyvinyl chloride loses essentially all of its HCl at 255°C, leaving a residue still relatively rich in hydrogen. As a result, further heating yields large quantities of tar, with the residue remaining viscous up to about 400°C. Loss of hydrogen and hydrocarbons continues up to at least 800°C, yielding a carbon equal to ca. 15% of the starting polymer weight.
ide and polyvinyl chloride upon carbonization to 1000°C and higher temperatures. As a result of quantitative measurements of the total x-ray scattering, it was shown that in the polyvinylidene chloride carbon prepared at 1000°C, 65% of the carbon is in the form of graphite-like layers (condensed aromatic rings) 10A.U., in diameter and the remaining 35% is in a form so disordered as to give only a gas-like distribution to the total x-ray scattering (amorphous material). Of the small graphite-like layers, ca. 45% show no parallelism (single layers) and ca. 55% are grouped in parallel pairs with an interlayer spacing of 3.7A.U. It was concluded, on the basis of the poor graphitizability of the carbon, that neighboring layers or layer packets are poorly aligned and strongly crosslinked by amorphous material. The low apparent density of the material, 1.59 g/cc is also consistent with its poor layer alignment.

It was concluded that the polyvinyl chloride carbon heated to 1000°C that 85% of the carbon is in the form of graphite-like layers 18A.U. in diameter and the remaining 15% is in an amorphous form. The graphite-like layers which show parallelism are grouped, on the average, in packets of between four and five. On the basis of the good graphitizability of this carbon and its relatively high density of 1.99 g/cc, it was concluded that its neighboring packets are well aligned. Because of the relatively small amount of amorphous material, the crystallites in this material are much less crosslinked than in the polyvinylidene carbon.

The sorptive properties of Saran carbons appear to have been first investigated in some detail by Pierce and co-workers. The char produced upon carbonization to 600°C had a surface area, as calculated from ethyl chloride sorption at 0°C, of 720m²/g. Of prime interest was the observation that the hydrophobicity of the char could be altered markedly. The material as first prepared exhibited high water sorption at low relative pressures, which the authors attribute to the presence of a chloride complex in the surface. Following treatment with hydrogen at 600°C, low-pressure water sorption became quite small. Significant water sorption only commenced at a relative pressure of ca. 0.45. It was concluded that this is consistent with the removal of the chloride complex as hydrogen chloride upon hydrogen treatment.

Further sorption studies on Saran molecular sieve carbons have been numerous. Sorption of neopentane was slower, but could be made significant by using a finely ground powder. On the basis of benzene being sorbed more rapidly than neopentane, the authors concluded that the pores were slit-shaped, perhaps arising from the presence of condensed aromatic-like layers in the char. Kipling and Wilson found that polyvinyl chloride carbon carbon prepared at 700°C has close to the same capacity for neopentane and water at 20°C. They further found that the sorption of α-pinene (molecular diameter of ca. 8A.U.) is negligible.

Recently, Walker and co-workers have examined the possibility of modifying the molecular sieve properties of Saran carbons by carbonizing Saran at temperatures up to 1000°C. The extent of uptake of carbon dioxide (-78°C), butane, isobutane, and neopentane (all at 0°C) at a relative pressure of 0.5 was measured, using an equilibrium time of one hour. Surface areas were reported as "monolayer area equivalent," following the suggestion of Barrer. Surface area results are summarized in Figure 3. The very high surface area of the carbon prepared above 500°C and the significant separation between isobutane and neopentane are noteworthy. Sorption of benzene and cyclohexane on the Saran carbons was found to be considerably greater than sorption of neopentane, supporting the conclusion of slit-like pores in these carbons.

Walker and co-workers have examined briefly the possibility of producing composite carbon molecular sieves. Activated carbons having no molecular sieve properties for molecular diameters less than 2A in size, but having large surface areas, were coated with a thermosetting polymer, which upon carbonization yielded a molecular sieve carbon. The object was to use the more expensive polymer carbon coating as a "gate." Molecules passing through the "gate" would be taken up on the high capacity and relatively cheap activated carbon. The carbon coating was produced from phosphoric acid polymerized furfuryl alcohol. Static adsorption results showed that sieves could be produced having a large capacity for normal or small capacity for isobutane, and a negligible capacity for neopentane.

Very recently, Metallic has examined another approach to producing composite carbon molecular sieves. Results have been most encouraging. Saran, carbonized at 900°C, was used as the filler material in the fabrication of composite sieves. Binders used were a medium to light asphaltenic coal tar pitch, a light pitch, and methyl cellulose. The filler and binders, both ground to 100 mesh, were mixed at room temperature and then pressed into pellets, also at room temperature. The pellets were heated at 900°C in nitrogen in order to carbonize the binder phase. Static adsorption results showed that coating of the carbonized Saran filler particles with the above binders, in most cases, decreased the adsorption capacity of the particles for hydrocarbons and altered their molecular sieve behavior as shown previously in Figure 3. Consequently, where necessary the pellets were subsequently slightly activated in carbon dioxide in order to open up closed pores in the binder carbon and permit ready access to the filler particles.

The pellets were evaluated as to their ability to separate hydrocarbons in a fixed bed dynamic adsorption apparatus. The hydrocarbons to be separated were entrained in the desired concentration in a helium carrier stream. Following passage of the stream through the fixed bed, the concentrations of hydrocarbons remaining in the exit helium were measured using a gas chromatograph. Figures 4 and 5 summarize some of the interesting dynamic adsorption results. The exit concentrations of the hydrocarbons are plotted against the cumulative time which the gas stream has been passed through the fixed bed. The final exit concentrations for the hydrocarbons closely approached their inlet values.


