# Review:
# The Use of Molecular Probes for the Characterization of Nanoporous Adsorbents

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## Abstract

Molecular probes can be employed in three different ways for the characterization of nanoporous adsorbents. The simplest approach is to use a range of globular nonpolar molecules of different diameter in order to assess the effective size of the pore entrances in a molecular sieve. For this purpose, conventional gas adsorption (static or dynamic measurements) or gas chromatographic techniques can be used. The aim of the second approach is to characterize the nanopore structure with the aid of nitrogen adsorption at 77 K together with isotherm and adsorption energy measurements with a variety of adsorptives of different molecular size, shape and polarity. The third approach is to make use of polar probe molecules (notably water and alcohols) to investigate the surface chemistry and stability of the adsorbent.

**Keywords:** adsorption, molecular probes, nanopores, physisorption, sorption

## 1 Introduction

As early as 1916 Langmuir [1] pointed out that in charcoal 'There are some spaces in which a molecule would be closely surrounded by carbon atoms on nearly all sides' and therefore 'there is no definite surface, which can be covered by a layer one molecule deep'. Confirmation that many activated carbons do contain pores of molecular dimensions was provided by the early molecular probe studies by Dubinin [2]. However, it became evident that most activated carbons contain a wide range of pores of different size and shape.

Various forms of molecular sieve carbon (MSC) were developed in the 1960s [3]. It was found, for example, that the slit-shaped pores of a carbonized form of PVDC were able to accommodate benzene, naphthalene and other aromatic molecules, but not more bulky molecules such as neopentane (2,2-dimethyl propane). Carbonized Saran, another well-known MSC, appeared to have a pore entrance of around 0.6 nm since it permitted the separation of isobutane (2-methyl propane) and neo-pentane (molecular diameters being taken, respectively, as 0.50 and 0.62 nm).

Early work on dehydrated chabazite (a natural zeolite) revealed that it possessed an assemblage of very fine pores and McBain came to the conclusion that it was a 'molecular sieve', in which the pore width was no larger than ca. 0.5 nm [4]. The importance of molecular probe measurements for characterizing synthetic zeolites was demonstrated by Breck et al. [5]. For example, it was reported that the 'apparent' pore size of the synthetic zeolite type A was ca. 0.42 nm and that this could be either increased or decreased by ion exchange (e.g. $Ca^{2+}$ for $Na^+$). For the assessment of the apparent pore size, it was of course necessary to use a range of molecules of different 'critical dimensions'. Since 1956, many other synthetic zeolites and related crystalline pore structures have been characterized in this manner [6, 7].

Considerable interest has been shown over the past twenty years in the development of shape selective catalysts and tailor-made adsorbents for *inter alia* respiratory protection, gas separation and storage. Pore dimensions are of great importance in the design of such advanced materials, but it is now understood that the nature of the adsorbent-adsorbate and adsorbate-adsorbate interactions must also be taken into account. In this review our aim is to illustrate the different ways in which gaseous molecular probes have been employed to provide

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useful information on the structure of some representative nanoporous adsorbents. Although adsorption measurements at the solid/liquid interface are also important, they are outside the scope of the present review.

In the classification of pore size proposed by the IUPAC [8], micropores, mesopores and macropores are defined, respectively, as pores with effective widths, $w < 2$ nm, $w = 2 - 50$ nm and $w > 50$ nm. In this review, we also follow other authors in using the term 'nanopores' to mean pores within the micropore and narrow mesopore range. Without giving a precise definition, we take the upper limit of nanopore dimensions to be $\sim 2 - 3$ nm so that we are, of course, mainly concerned with the micropore range.

There is a certain advantage in adopting this flexible approach since we can concentrate on the behavior of each adsorption system rather than be constrained by any fixed scale of pore size. At the same time we take the liberty of referring to the filling of molecular sized pores as 'ultramicropore filling' [9], but it should be understood that this process is dependent on the pore width/molecular size ratio and not simply on the pore size alone.

## 2 Methodology

### 2.1 Adsorption Isotherm Measurements

It is remarkable that for over 50 years nitrogen adsorption at $\sim 77$ K has remained the most widely used technique for determining the surface area and pore size distribution of porous adsorbents [10]. However, it is necessary to keep the advantages and limitations of the method under review. In fact, the particular shape of a nitrogen isotherm often gives a first indication of the nature of the pore structure [9 – 11]. Thus, nanoporous adsorbents with very narrow pores (i.e. molecular sieves) exhibit ultramicropore filling, which is associated with high-affinity, Type I nitrogen isotherms [9].

All the traditional computational procedures used for mesopore size analysis from nitrogen isotherms are based on the application of the Kelvin equation, which fails completely in the micropore range and is of doubtful validity for narrow mesopores [9, 10]. The modern approach, which involves the use of density functional theory (DFT), provides a more elegant treatment of both micropore and mesopore size analysis [12, 13]; but difficulties are encountered with some industrial adsorbents, which do not have well-defined adsorbent structures or surface compositions.

In view of the shortcomings of low-temperature nitrogen adsorption and for other reasons, there is much to be gained by studying the adsorption of a number of carefully selected gases. The molecular sieving of mol-

ecules of different diameter, $\sigma$, can be used to investigate their entry into pores of width, $w$, in the range $\sim 0.3 - 0.7$ nm. In addition, it is possible to increase the upper limit by a detailed analysis of each isotherm in relation to the corresponding $w/\sigma$ ratio [9].

An alternative procedure [14] is to determine the isotherms of several adsorptives (e.g. carbon dioxide, argon and nitrogen) at various temperatures. By increasing the temperature, one can often overcome the energy barrier associated with the 'activated entry' of molecules through constrictions or narrow pore entrances [15]. A completely different application of molecular probes involves the use of certain highly polar molecules (e.g. water and methanol) in order to characterize the location of cations or functional groups within the nanopore structure [9].

### 2.2 Adsorption Calorimetry

Calorimetry can be used in various ways to study the energetic interaction of probe molecules with nanoporous solids. Here we are concerned with gas adsorption calorimetry for determining differential enthalpies of adsorption over the range of pore filling. With the aid of refined Tian-Calvet microcalorimetry Rouquerol and his co-workers have been able to study [16] the energetics of nitrogen and argon adsorption on a variety of nanoporous carbons, zeolites and oxides. Comparison of the behavior of argon and nitrogen has turned out to be an excellent way of distinguishing between the initial stages of molecular pore filling and specific adsorbent-adsorbate interactions.

### 2.3 Miscellaneous Techniques

A novel method for the evaluation of microporosity was based on the pre-adsorption of n-nonane [17]. The aim was to fill the micropores with n-nonane, whilst leaving the open surface and wider pores still available for the adsorption of nitrogen at 77 K. The molecule n-nonane was chosen as the pre-adsorptive because of its small minimum dimension and relatively large adsorption energy. There is consequently a high energy barrier for the desorption of the n-nonane molecules, which at low temperature remain trapped in the narrow nanopores. The pre-adsorption method was successfully used to evaluate the micropore volume and external surface area of an activated sample of carbon black [17]. However, more recent work [9] has revealed that the results given by most activated carbons are not so easy to interpret since they depend on the nature of the pore network as well as the pore size distribution.

The transport of molecules into pores of molecular dimensions is often so slow that it is virtually impossible to attain thermodynamic equilibration. Various empirical procedures have been designed to overcome this problem. For example, the amounts adsorbed after a given time (e.g. 15 minutes) have been determined for vapors such as n-hexane and 2,3-dimethylbutane [7]. Obviously, the amounts adsorbed are not true adsorption capacities, but rather give an indication of relative rates of adsorption. Empirical investigations of this kind can be used to assess a so-called 'pore constraint index' or an effective pore size profile for a molecular sieve sample. A number of more rigorous techniques are available for measuring the rates of adsorption or the transport of probe molecules in (or through) nanoporous media [18]. A convenient approach is to make use of commercial gas chromatographic (GC) equipment. The GC measurements (e.g. elution or frontal analysis) can be designed to yield either equilibrium or dynamic data. In the former case it is advisable to undertake retention time measurements (i.e. inverse GC) under conditions of very low loading in the Henry's law region of the isotherm. From the corresponding specific retention volumes, as determined over wide ranges of temperature, it is then possible to derive differential energies of adsorption at 'zero–coverage' and thus investigate specific and non-specific gas-solid interactions [16, 19].

## 3 Molecular Dimensions and Sieving

Before discussing the size of probe molecules, we must briefly consider the question: how should the pore width be defined? In the context of the molecular modeling of pore filling, it has been customary [13, 14] to define the pore width, $H$, as the distance between atomic centers (e.g. of atoms in the opposite walls of a slit-shaped pore). From a practical standpoint, however, it is more convenient to take an *effective* pore width, $w$, which is defined as the available internal pore width. If a nanoporous structure is assumed to be rigid, this definition should be consistent with the manometric determination of the 'dead space' volume around an adsorbent.

In the early work [4] on molecular sieve zeolites the van der Waals molecular diameter was taken as the appropriate 'yardstick' for the evaluation of the pore size. By 1974, however, when Breck's book 'Zeolite Molecular Sieves' [6] was published, it was considered that a more rigorously defined kinetic diameter, $\sigma$, should be adopted – provided that the probe molecule was globular and nonpolar. For simple molecules of this type, the Lennard-Jones 12:6 potential was used to calculate $\sigma$, which can be defined as the intermolecular distance of closest approach of two molecules of zero kinetic energy. How-

Table 1: Dimensions of some probe molecules.

| Molecule | $\sigma$/nm | MIN-1/nm | MIN-2/nm |
|---|---|---|---|
| $H_2O$ | 0.27 | 0.29 | 0.32 |
| $CO_2$ | 0.33 | 0.32 | 0.33 |
| Ar | 0.34 | 0.35 | 0.36 |
| $O_2$ | 0.35 | 0.29 | 0.30 |
| $N_2$ | 0.36 | 0.30 | 0.31 |
| $CH_4$ | 0.38 | 0.38 | 0.39 |
| $C_3H_8$ | 0.43 | 0.40 | 0.45 |
| n-$C_4H_{10}$ | 0.43 | 0.40 | 0.45 |
| iso-$C_4H_{10}$ | 0.50 | 0.46 | 0.60 |
| $SF_6$ | 0.55 | 0.49 | 0.53 |
| $CCl_4$ | 0.59 0.63* | 0.57 | 0.58 |
| $C_6H_6$ | 0.59 0.41* | 0.33 | 0.66 |
| Cyclohexane | 0.60 | 0.50 | 0.66 |
| Neopentane | 0.62 | – | – |

$\sigma$ Kinetic diameter [6]
MIN-1 Smallest dimension of the molecule [21]
MIN-2 Intermediate dimension perpendicular to MIN-1 [21]
* Critical diameter [23]

ever, with long-chain or complex molecules it was necessary to take the minimum cross-sectional diameter. A selection of Breck's recommended values of $\sigma$ is given in the second column of Table 1. Over the past 30 years, these values have been widely used although it has become increasingly apparent that in the context of molecular sieving their significance must be questioned [7].

Several efforts have been made to allow for the inadequacy of a single molecular dimension. For example, in their investigation of the adsorption of various hydrocarbons by high silica zeolites, Wu et al. [20] used Courtald space-filling models to estimate the 'critical dimensions' of each molecule along its $x$, $y$ and $z$ axes. As would be expected, with aromatic and aliphatic molecules this procedure has revealed significant differences. For example, the estimated critical dimensions for benzene, p-xylene and o-xylene are, respectively, $0.34 \times 0.62 \times 0.69$ nm, $0.37 \times 0.62 \times 0.86$ nm and $0.41 \times 0.69 \times 0.75$ nm, in comparison with the corresponding n-hexane values of $0.39 \times 0.43 \times 0.91$ nm. It was claimed [20] that such differences are consistent with the adsorptive properties of the zeolites.

In the work of Webster et al. [21, 22], a more elegant concept of effective minimum dimensions is advanced. Molecular orbital calculations give the dimensions along the $x$, $y$ and $z$ symmetry axes of an adsorptive molecule, but the critical dimension is dependent on the pore shape. Thus, the ability of a molecule to enter a slit-shaped pore is dependent on its smallest dimension, MIN-1, while the corresponding intermediate dimension, MIN-2, is the critical dimension for entry into a cylindrical pore. The representative values of MIN-1 and MIN-2 shown respectively in columns 3 and 4 of Table 1 are taken from the work of Webster et al. [21, 22]. For

comparison, a few of the 'critical dimensions', used by Stoeckli et al. [23] are also included in column 3.

Cook and Conner [24] and Traa and Weitkamp [7] have drawn attention to the unsatisfactory nature of any fixed list of critical dimensions. Strictly, allowance should be made for the nature of the complete adsorption system, including the flexibility of larger adsorptive molecules and the non-rigidity of many pore structures. In principle, a quantum mechanical treatment of each adsorption system is desirable. However, in spite of its drawbacks, the simple hard-sphere approach still has a useful role, provided that allowance is made for its limitations. In addition, caution must be exercised in the interpretation of experimental data, particularly when thermodynamic equilibration has not been attained. Some examples of the applications of molecular probes illustrating the various types of approach are to be found in the following section.

## 4 Some Applications of Molecular Probes

### 4.1 Nitrogen, Argon and Carbon Dioxide

The molecular dimensions of nitrogen, argon and carbon dioxide are similar (see Table 1), but in some respects the three adsorptives behave in quite different ways. Thus, the interaction of the nonpolar argon molecule is essentially non-specific with all types of adsorbent [19]. Nitrogen and carbon dioxide are quadrupolar, however, and we would expect these molecules to undergo certain specific interactions with a variety of surface functional groups and exposed ions.

The first stages of ultramicropore filling (in the narrowest accessible nanopores) take place at very low $p/p^0$. With the aid of nonlocal density functional theory, Ravikovitch et al. have calculated [14] that carbonaceous slit-shaped pores of around 0.5 nm are filled by nitrogen at $p/p^0 \sim 10^{-7}$ (i.e. at pressures $\sim 10^{-4}$ Torr). Indeed, experimental work has confirmed that significant amounts of nitrogen are adsorbed at $p/p^0 < 10^{-5}$ in the nanopores of molecular sieve carbons and zeolites [25]. High-resolution adsorption (HRADS) measure-

ments [26] are required to obtain accurate adsorption data in this low-pressure region. In practice, such measurements are difficult to undertake with commercial adsorption equipment and an alternative approach is evidently desirable.

Carbon dioxide adsorption at 273 or 298 K has been found [27] useful for probing the very narrow nanopores in activated carbons (of $w \sim 0.35$ nm). The higher operational temperature is important for two reasons: first, the adsorption of carbon dioxide can be measured at very low $p/p^0$ (e.g. at 298 K, 1 bar $a \sim 0.02 p^0$); secondly, the rate of molecular diffusion through narrow pore entrances is considerably increased [15]. Carbon dioxide adsorption has been exploited by Rodriguez-Reinoso and his co-workers [27] in their systematic studies of activated carbons of low burn-off, which may adsorb relatively small amounts of nitrogen at 77 K.

It is well known that high physisorption energies are produced by the overlap of the adsorbent-adsorbate interactions in pores of molecular dimensions [17]. In the slit-shaped pores of a molecular sieve carbon the maximum enhancement is expected to be about twice that given by the interaction of the same adsorbate with the corresponding nonporous surface. The results of microcalorimetric and isotherm measurements [28], shown in Table 2, confirm that enhancement of the initial adsorption energy is about two-fold for both nitrogen and argon adsorbed in the narrowest pores of molecular sieve carbons (i.e. with carbon cloth samples JF005 and JF142).

It is of interest that the nitrogen isotherms on nanoporous carbons in Figure 1 are of two types. The two molecular sieve carbons, JF005 and JF142, give typical high-affinity Type I isotherms, but the isotherms on PX21 and JF516 do not have the same well-defined Type I shape. It is not surprising to find that the differential adsorption enthalpies given by PX21 and JF516 are relatively low (see Table 2). Since the nitrogen and argon adsorption energies undergo similar changes, we can conclude that specific adsorbent-adsorbate interactions do not appear to make a major contribution to the pronounced energetic heterogeneity revealed in Table 2.

Table 2: Differential enthalpies of adsorption for $N_2$ and Ar at 77 K [28].

| Carbon | $\Delta h_0$-$N_2$/kJ mol$^{-1}$ | $\Delta h_{0.01}$-$N_2$/kJ mol$^{-1}$ | $\Delta h_0$-Ar/kJ mol$^{-1}$ | $\Delta h_{0.01}$-Ar/kJ mol$^{-1}$ |
|---|---|---|---|---|
| PX21 | 15.9 | 10.0 | 14.5 | 10.5 |
| JF516 | 18.2 | 10.8 | 16.1 | 11.4 |
| JF142 | 19.7 | 11.9 | 18.7 | 12.1 |
| JF005 | 20.8 | 13.3 | 19.7 | 12.8 |
| Graph C | 9.8 | – | 10.0 | – |

$\Delta h_0$-$N_2$ and $\Delta h_0$-Ar, initial enthalpies of adsorption for nitrogen and argon
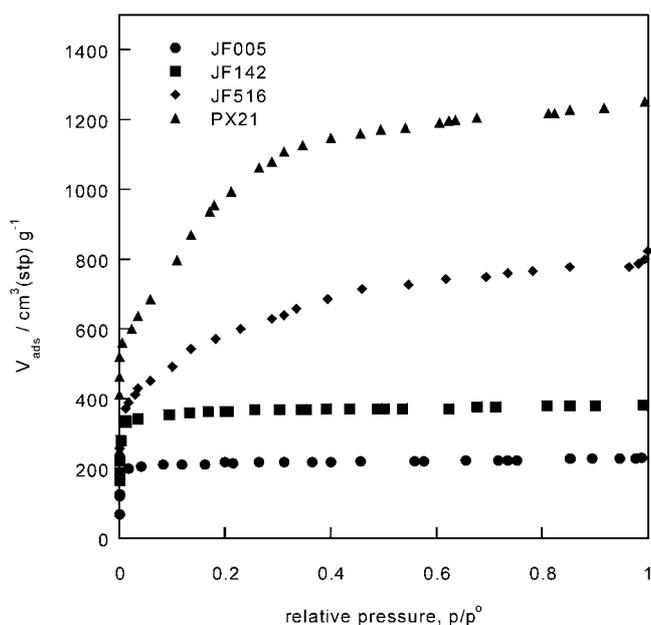$\Delta h_{0.01}$-$N_2$ and $\Delta h_{0.01}$-Ar, corresponding values at $p/p^0 = 0.01$

Fig. 1: Nitrogen isotherms on a superactive carbon, PX21, and carbon cloth samples JF516, JF142, JF005 [28].



Fig. 2: Nitrogen and water isotherms on zeolite HZSM-5 [30].

With oxides or zeolitic adsorbents, the use of a combination of polar and nonpolar probes is more rewarding and determination of isotherm and adsorption energies can now reveal some striking differences. A well-known example of the difference between the adsorption of argon and nitrogen is on silica [29]. Thus, on a fully hydroxylated silica surface the corresponding values of the initial differential adsorption enthalpy are $>20$ kJ $mol^{-1}$ for nitrogen and ca. 15 kJ $mol^{-1}$ for argon. After surface dehydroxylation, the nitrogen value is reduced to ca. 17 kJ $mol^{-1}$, while the argon value remains unchanged. This reduction in the nitrogen energy of adsorption is consistent with a significant change in shape of the nitrogen isotherm [29], which is reflected in a decrease in the value of the BET $C$ parameter.

The characterization of the pentasil zeolite ZSM-5 and its pure silica form, Silicalite-I, has involved *inter alia* the application of argon and nitrogen adsorption [30]. In the case of Silicalite the differential enthalpies of adsorption of both argon and nitrogen remain almost constant over a fairly wide range of pore filling, which is indicative of a high degree of surface uniformity and little adsorbate-adsorbate interaction. Small sub-steps appear in the isotherms of both argon and nitrogen on Silicalite at loadings of ca. 22 molecules per unit cell.

With nitrogen (but not argon) a second and more pronounced sub-step is located at $p/p^0 \sim 0.1$: this is associated with a well-defined hysteresis loop (see Figure 2). Various explanations have been give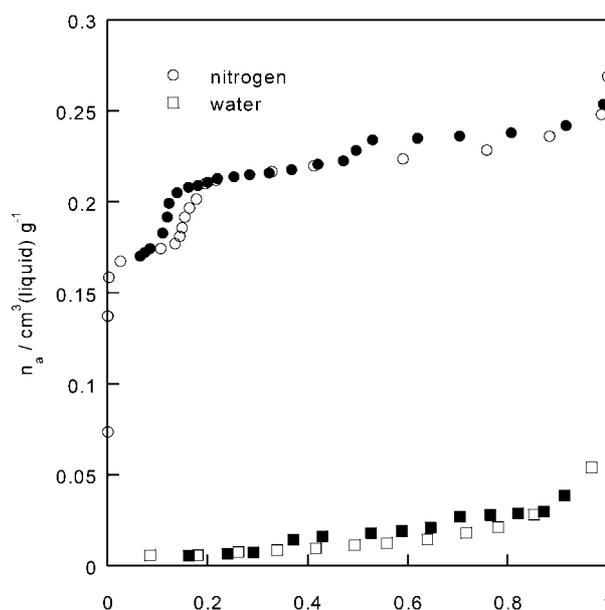n [30] for the appearance of this hysteresis loop in an unexpected region of the isotherm. However, it seems likely that it originates through the reorientation of nitrogen molecules to allow an increase in packing density and a more favorable quadrupole-quadrupole interaction.

It turns out that the highly distinctive features of the nitrogen isotherm in Figure 2 provide a useful basis for the characterization of different preparations of Silicalite and ZSM-5 [30]. Thus, the sub-steps become less distinctive as the Al content is increased or the crystal structure more disordered. Furthermore, the hysteresis loop located in the normal range of higher $p/p^0$ is associated with capillary condensation and can be used to characterize the porous agglomerated assemblage of small zeolite crystals.

In his pioneering work on zeolites, Barrer studied the adsorption of a wide range of polar and nonpolar probe molecules by various natural and synthetic zeolitic structures. In the present context it is appropriate to refer briefly to certain aspects of Barrer's work on the energetics of carbon dioxide adsorption [31]. It was first established that for the adsorption of the quadrupolar molecules $N_2$, CO and $CO_2$ by chabazite there was a linear correlation between the initial adsorption enthalpy and the permanent quadrupole moment of each molecule. Barrer therefore selected $CO_2$ as the probe molecule most likely to exhibit strong interactions with the exchangeable cations. The experimental results, which were broadly in agreement with theoretical predictions, confirmed the importance of the cation size and valency in determining both the magnitude of the adsorption enthalpy and the scale of the energetic heterogeneity.

## 4.2 Organic Vapors

By using organic probes of different molecular size, shape and polarity, we are able to characterize a wide range of nanoporous adsorbents. The following examples should serve to illustrate how various techniques and combinations of probe molecules can be effectively exploited.

It is instructive to compare the isotherms given by a number of adsorptives of different molecular size on a particular nanoporous adsorbent. For example, it is immediately obvious that of the four isotherms in Figure 3, which were all determined on the same sample of Carbosieve [32], only those of nitrogen and propane are reversible. It is evident that the large hysteresis loops given by isobutane (2-methyl propane) and neopentane (2,2-dimethyl propane) do not close at low pressure and that the two desorption isotherms remain almost flat over a wide range of $p/p^0$. These features are associated with 'activated entry' effects together with entrapment of adsorbed molecules at the operational temperature of 273 K [17].

Since the isobutane and neopentane isotherms in Figure 3 are not thermodynamically reversible, they cannot be subjected to any form of rigorous analysis. However, the uptake at the saturation pressure can be regarded as the effective adsorption capacity with respect to each adsorptive. It would appear, therefore, that around 40% of the available nanopore volume is contained within
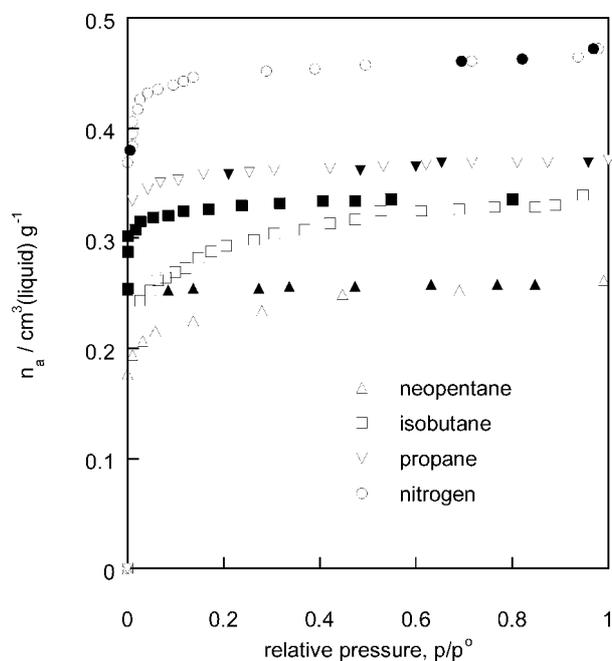
pores no wider than $\sim 0.6$ nm. By detailed analysis of these isotherms and other adsorption data, we may tentatively conclude that the effective nanopore volume of the sample of Carbosieve is ca. 0.43 cm$^3$ g$^{-1}$ with the effective size range of most pores $\sim 0.35 - 0.7$ nm [32].

Neopentane has been found a useful probe for characterizing the pore structure of partially decomposed inorganic hydroxides and oxide-hydroxides [16]. One example is the controlled thermal decomposition of magnesium hydroxide [33]. Remarkably regular slit-shaped pores are developed when small crystals of $Mg(OH)_2$ are carefully outgassed at $523 - 873$ K. Between 40% and 90% decomposition the mean pore width appears to remain nearly constant at ca. 0.93 nm and thereafter it increases up to ca. 1.8 nm. In pores of this size, nitrogen adsorption at 77 K takes place in two stages: surface coverage followed by cooperative nanopore filling. Because of its larger molecular size ($\sigma = 0.62$ nm), neopentane is adsorbed in the 0.93 nm pores by a primary micropore filling process – as is indicated by the high affinity nature of its Type I isotherm [16]. Carbon tetrachloride is another bulky molecule of relatively high polarizability, which is also useful for the characterization of nanoporous oxides [15].

Another illustration of the relation between isotherm character and molecular size and shape is afforded by the use of hexene isomers for studying the surface properties of ruthenium-doped MCM-41. The work of Singh et al. [34] has revealed a significant difference in the isotherms of 1-hexene and 3,3-dimethyl-1-butene at 303 K on a heat-treated sample of Ru-MCM-41. Both isotherms were of Type I character, in contrast to the well-defined Type IV isotherm given by nitrogen at 77 K, but the uptake of 1-hexene was considerably larger than that of 3,3-dimethyl-1-butene. The lower uptake of the more globular isomer ($\sigma = 0.70$ nm) strongly suggests that this molecule experiences a greater degree of steric hindrance than the straight chain isomer.

As indicated in Table 1, for entry into slit-shaped pores and voids between platy particles, the effective minimum dimension of aromatic molecules such as benzene, toluene and xylenes is ca. 0.38 nm. Benzene adsorption is still extensively employed for characterizing porous carbons and other nanoporous adsorbents [35, 36]. Indeed, the results of routine measurements on activated carbons are sometimes recorded in the form of a 'benzene index' [35].

Whereas benzene adsorption by nanoporous carbons is to a large extent dependent on pore size and shape, it is the specific interaction of benzene molecules with surface hydroxyls or exposed cations, which must also be taken into account if benzene adsorption is used for characterizing nanoporous oxides [19]. In their work on phenyl-modified porous silicas, Bambrough et al. [36]



Fig. 3: Isotherms of nitrogen, propane, isobutane and neopentane on Carbosieve [32] (filled symbols denote desorption points).

found that the pore volume available to benzene at 293 K appeared to be significantly larger than that given by nitrogen adsorption at 77 K. The apparent discrepancy was attributed to an abnormal structure of adsorbed benzene.

It is noteworthy that in comparison with the surface area available for low-temperature nitrogen adsorption, the sorption of toluene vapor at 298 K by aggregated β-copper phthalocyanine crystals is surprisingly large [37]. It appears that the toluene molecules can penetrate into the void space between platy crystals to a much greater extent than nitrogen molecules. This difference in molecular accessibility is probably due to the more favorable molecular shape of toluene and the higher operational temperature.

Alcohol molecules undergo even stronger specific inter-actions (H bonding in this case) with exposed hydroxyls. On a nonporous oxide surface this can lead to a form of 'autophobicity' [16], which results in the appearance of a pseudo Type I isotherm (i.e. weak multilayer develop-ment). It is, of course, important to avoid confusion with the true Type I isotherms given by the filling of narrow nanopores.

Steric effects have been noted [38] in the adsorption of n-butanol and tert-butanol by certain phenyl-modified porous silicas. Whilst the paths of the two isotherms were almost identical on a mesoporous form of the modified silica, they were strikingly different on the chemically similar microporous material. In the latter case, the tert-butanol gave a well-defined Type I isotherm, whereas the lower level n-butanol isotherm appeared to be severely affected by partial pore blocking.

Next, we show how gas chromatographic (GC) retention measurements can be used for studying the interaction of organic probe molecules with nanoporous adsorbents. This is illustrated in Figure 4, where the 'zero' coverage energy of adsorption, $E_0$, is plotted against the carbon number, N, for each adsorbent [39]. As indicated in Table 1, the minimum dimension of all n-alkane mole-cules is ca. 0.4 nm and here the operational temperatures are high enough (373 – 473 K) to allow rapid diffusion into the nanopores – even with the molecular sieve carbon. However, the elution peaks are no longer sharp when more bulky probe molecules such as neopentane are injected into molecular sieve carbon or Silicalite columns. This is a clear sign that thermodynamic equilibrium is not attained since the molecular diam-eter of the probe molecule is too large to allow easy access to the complete pore structure.

With each adsorbent in Figure 4, a linear relation is given between $E_0$ and N: this is consistent with a regular increase in the dispersion energy as the molecular polarizability, α, is increased. The specific contributions to the interaction energies, which are revealed when $E_0$ is
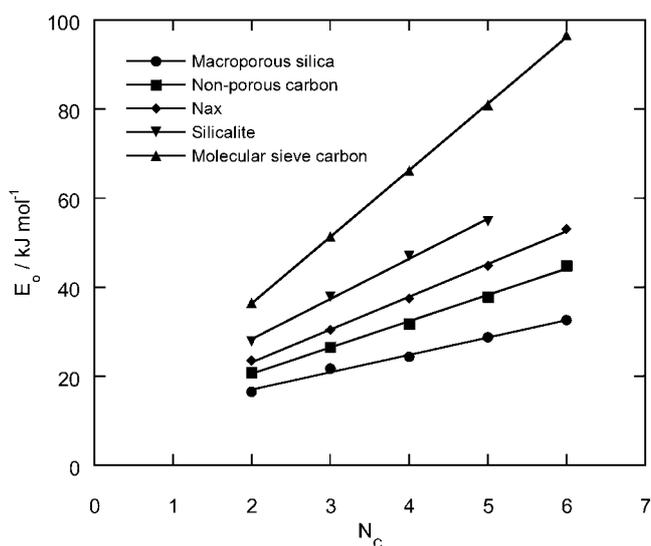


Fig. 4:  'Zero' coverage energy of adsorption of n-alkanes versus carbon number, $N_C$, on three nanoporous adsorbents (NaX, Silicalite-I and a molecular sieve carbon), a macroporous silica and a nonporous carbon [39].

plotted against α, are quite small for the adsorption of alkene molecules by activated carbons [19]. Much larger specific adsorbent-adsorbate interactions are registered, however, for the adsorption of alcohols and other polar molecules by activated carbons and zeolites.

### 4.3 Water Vapor

The water molecule is relatively small and of low polarizability, but it is also highly polar and reactive and has a propensity for strong hydrogen bonding. In view of these unusual properties it is hardly surprising that water has a unique role as a molecular probe. It can be used to characterize the surface chemistry and stability of the adsorbent as well as certain properties of the pore structure. It must always be kept in mind, however, that the 'sorption' of water may alter the surface chemistry (e.g. rehydroxylation of a dehydroxy-lated surface of silica) or even bring about low-temper-ature aging [16], which results in an irreversible loss of surface area and possibly the development of crystal-linity.

A water isotherm on graphitized carbon black is of Type III character and since the dispersion interactions are weak the adsorption at $p/p^0 < 0.8$ is very low [19]. However, if the pure carbon is nanoporous its water isotherm will have the characteristic Type V shape, the adsorption capacity (i.e. the amount adsorbed at the plateau) being controlled by the effective nanopore volume [8, 9, 40].

If specific adsorbent-adsorbate interactions are brought into play by the presence of polar groups on an activated carbon surface, the adsorption affinity is enhanced and the water isotherm is changed from Type V to a weak Type IV isotherm [8]. In this case, localized adsorption is followed by water-water hydrogen bonding with the clustering of the water molecules around the hydrophilic sites and finally complete nanopore filling.

Returning to Figure 2, we may note that in comparison with nitrogen the level of water adsorption by Silicalite I is low over the complete range of the isotherm. Thus, even at $p/p^0 = 0.90$, the uptake of water is only about 10% of the equivalent nitrogen capacity. Furthermore, the similarity of the corresponding water and nitrogen hysteresis loops is a clear indication that most of the capillary condensed water is held within the secondary pores between the small zeolite crystals rather than in the zeolitic channel structure. This is confirmed by the fact that the total water uptake is appreciably reduced when the Silicalite crystal size is increased. Although the level of water adsorption is somewhat greater when the Al content of ZSM-5 is increased, the uptake at high $p/p^0$ is still considerably less than the total amount required for complete nanopore filling.

From these results, it would seem that in certain respects pure Silicalite is more hydrophobic than a molecular sieve carbon such as Carbosieve! Both adsorbents exhibit a low affinity for water, but only Silicalite has the relatively low adsorption capacity evident in Figure 2. In seeking an explanation for these findings, we must take account of the difference in pore shape. Thus, Silicalite has an interconnected tubular pore structure while the pores in molecular sieve carbons tend to be slit-shaped. It can easily be shown that slit-shaped pores are able to accommodate thin undistorted layers of hydrogen-bonded water molecules, which is not possible in the tubular pores of similar width in Silicalite [30].

Another example of the use of water as a molecular probe is for the characterization of the large-pore aluminophosphate VPI-5. A systematic investigation [16] of the adsorption-desorption isotherms has revealed three distinct steps at low $p/p^0$. Furthermore, the exposure of VPI-5 to water vapor at saturation pressure brings about rapid aging (loss of BET-area) and a partial and irreversible conversion to $AlPO_4$-8.

## 5  Conclusions

Nitrogen adsorption at 77 K should be regarded as only the first stage in the characterization of a nanoporous adsorbent. With the aid of a number of carefully selected probes of different molecular size, shape and polarity, it is possible to undertake a detailed exploration of the accessible pore structure and the nature of the available internal surface.

The simplest approach is to use globular nonpolar molecules of different size in order to investigate the molecular sieve properties of the adsorbent. For this purpose, it is convenient to employ either adsorption isotherm or gas chromatographic measurements. These procedures have been particularly useful for determining the accessible window size and adsorption capacity of synthetic zeolites and other intracrystalline nanopore structures. Furthermore, adsorption measurements with molecules of different shape (e.g. various aliphatic and aromatic hydrocarbons) have shown the importance of pore shape as well as pore size in determining the molecular sieve properties of nanoporous carbons.

It becomes more difficult to study the molecular sieving of gases if the size of the pore entrance is much larger than ∼0.7 nm. However, it is still possible to use gas adsorption to investigate the larger nanopores by the analysis of isotherm and adsorption energy data in terms of the pore filling mechanisms. For example, the filling of slit-shaped pores no wider than two molecular diameters takes place at very low relative pressures and is associated with enhanced adsorption energies. The filling of somewhat wider nanopores is dependent on a cooperative process (i.e. involving adsorbate-adsorbate interactions), while the filling of mesopores takes place in two separate stages: multilayer adsorption followed by capillary condensation.

The adsorption of water vapor is particularly useful for investigating the surface structure of nanoporous adsorbents (e.g. for characterizing their hydrophobic-hydrophilic nature). In addition, water sorption measurements can be used to study aging mechanisms, which may involve surface hydration, loss of surface area or even changes in solid structure.

Finally, it is necessary to bear in mind that any list of the 'absolute' dimensions of probe molecules is of limited value unless the intermolecular forces and statistical mechanical effects are also taken into account. Nevertheless, it seems likely that the hard-sphere approach will continue to play a useful semi-quantitative role in the characterization of nanoporous adsorbents.

## 6  References

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