Tailored Porous Materials

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Tailoring of porous materials involves not only chemical synthetic techniques for tailoring microscopic properties such as pore size, pore shape, pore connectivity, and pore surface reactivity, but also materials processing techniques for tailoring the meso- and the macroscopic properties of bulk materials in the form of fibers, thin films, and monoliths. These issues are addressed in the context of five specific classes of porous materials: oxide molecular sieves, porous coordination solids, porous carbons, sol–gel-derived oxides, and porous heteropolyanion salts. Reviews of these specific areas are preceded by a presentation of background material and review of current theoretical approaches to adsorption phenomena. A concluding section outlines current research needs and opportunities.

Contents

Introduction 2633
Background 2634
Molecular Modeling of Adsorption Phenomena 2635
Oxide Molecular Sieves 2637
Porous Coordination Solids 2641
Porous Carbons 2642
Sol–Gel-Derived Oxides 2644
Porous Heteropolyanion Salts 2650
Research Needs and Opportunities 2652

Introduction

Porous materials have attracted the attention of chemists and materials scientists due to commercial interest in their application in chemical separations and heterogeneous catalysis as well as scientific interest in the challenges posed by their synthesis, processing, and characterization. Application of basic scientific principles to the key technological issues involved has been difficult, however, and much more progress has been achieved in tailoring porous materials through manipulation of processing parameters than through understanding of the chemical and physical mechanisms that influence porosity. As a result, the tailoring of porous materials has proceeded largely in an empirical fashion rather than by design.

The present review is the product of a study panel convened under the auspices of the United States Department of Energy Council on Materials Research to assess basic research needs and opportunities in the area of tailored porous materials. Five classes of porous materials were selected for study that offer opportunities for tailoring their properties through rational
design: oxide molecular sieves, porous coordination solids, porous carbons, sol–gel–derived oxides, and porous heteropolyanion salts. In oxide molecular sieves, porosity can be tailored using either molecular or supramolecular templates to define both pore size and pore shape. Porous coordination solids offer the potential for a different type of tailoring, namely, the control of reactivity along pore walls through incorporation of different organic and inorganic functional groups. Unlike oxide molecular sieves and coordination solids, porous carbons are not crystalline materials and thus offer distinct advantages in terms of processibility, that is, tailoring on a macroscopic size scale to form membranes, monoliths, and fibers. Sol–gel-derived oxides are also processible in this sense and can in addition be tailored on the molecular size scale. Porous heteropolyanion salts are unique relative to the other materials selected for study in that they are true molecular materials. Moreover, certain heteropolyanion salts have well-defined primary, secondary, and tertiary structures and as a result, porosity can be tailored on several different size scales in one and the same material. Treatment of these five systems is preceded by more general discussions of how porosity is defined and measured and how it can be understood and modeled on a fundamental level. A final section is also provided that outlines some of the challenges currently facing researchers in this area.

Background

Historically speaking, porous materials are defined in terms of their adsorption properties. The term adsorption originally denoted the condensation of gas on a free surface as opposed to its entry into the bulk, as in absorption. Today, however, this distinction is frequently not observed, and the uptake of a gas by porous materials is often referred to as adsorption or simply sorption, regardless of the physical mechanism involved. Adsorption of a gas by a porous material is described quantitatively by an adsorption isotherm, the amount of gas adsorbed by the material at a fixed temperature as a function of pressure. The uptake of fluids into a porous material could be intuitively viewed simply as the filling of an existing vacuum (“Nature abhors a vacuum”), but adsorption has long been recognized as a far more subtle phenomenon. J. W. Gibbs expressed the concept of adsorption on a general thermodynamic basis as follows. For the system of a fluid in contact with an adsorbent, he defined the amount adsorbed as the quantity of fluid that is in excess of that which would be present if the adsorbent had no influence on the behavior of the fluid. The concept of adsorption as related to an area of exposed surface was developed by Irving Langmuir in his work on the “condensation” of gases on surfaces. From these studies emerged the concept of adsorption as a dynamic equilibrium between a gas and a solid surface resulting in a surface layer that is only one molecule thick, a concept that quite naturally led to the Brunauer, Emmett, and Teller (BET) treatment of multilayer adsorption. The BET equation is still commonly used for the determination of surface areas of porous solids.

Porous materials are most frequently characterized in terms of pore sizes derived from gas sorption data, and IUPAC conventions have been proposed for classifying pore sizes and gas sorption isotherms that reflect the relationship between porosity and sorption. Pores are classified according to pore diameter as follows: micropores have diameters less than about 2 nm; mesopores have diameters between 2 and 50 nm; and macropores have diameters greater than about 50 nm. Adsorption by mesopores is dominated by capillary condensation, whereas filling of micropores is controlled by stronger interactions between the adsorbate molecules and pore walls. It is noteworthy that this nomenclature addresses pore width but not pore shape, and pore shape can be important in some circumstances, such as when dealing with shape selective molecular sieve behavior. The IUPAC classification of adsorption isotherms is illustrated in Figure 1. The six types of isotherm are characteristic of adsorbents that are microporous (type I), nonporous or macroporous (types II, III, and VI) or mesoporous (types IV and V). The differences between types II and III isotherms and between types IV and V isotherms arise from the relative strengths of the fluid–solid and fluid–fluid attractive interactions: types II and IV are associated with stronger fluid–solid interactions and types III and V are associated with weaker fluid–solid interactions. The hysteresis loops usually exhibited by types IV and V isotherms are associated with capillary condensation in the mesopores. The type VI isotherm represents adsorption on nonporous or macroporous solids where stepwise multilayer adsorption occurs.

Reliable experimental methods are essential for characterizing tailored porous materials. Gas adsorption methods are commonly used, as is mercury porosimetry, small-angle X-ray scattering, fluid flow methods (permeation and diffusion), and thermoporometry. Optical and electron optical methods are used for qualitative characterization and increasingly for quantitative analysis using image analysis methods. The advantages and limitations of the major characteriza-
tion methods have been discussed elsewhere,1,7–9 and a thorough discussion is beyond the scope of this review. Three important points should be emphasized, however. First, most methods for obtaining pore size distributions model pores as arrays of nonintersecting cylinders or slit pores, whereas porous solids usually contain networks of interconnected pores. These methods assume that all pores are connected to the surface of the adsorbent and can drain in order of size, whereas in reality percolation effects play a key role in pore drainage.10 Second, microporous materials must be approached with caution: classical adsorption isotherms such as the BET equation are not applicable because of the strong adsorption forces in micropores resulting from the overlap of force fields from opposite pore walls. Consequently, adsorption in micropores occurs at very low pressures by a pore-filling mechanism. Exploration of this regime of the isotherm requires precise measurements of pressure and of amounts of fluid adsorbed, often at pressures less than 10$^{-6}$ atm. In addition, microporous networks are often constricted, as in active carbons, and constrictions can cause molecular sieve action and activated diffusion at low temperatures. Activated diffusion poses problems when using N$_2$ adsorption at 77 K to characterize microporous solids. In such cases, adsorption of carbon dioxide at higher temperature has been used.11Finally, highly porous materials can be quite compliant, and this can present problems during characterization of the pore size distribution. Techniques such as mercury porosimetry, thermodesorption, and nitrogen desorption all exert stresses on the porous body, and in some cases, the body contracts significantly during measurement such that pore size and volume are underestimated. For example, nitrogen desorption is a drying process where the pore liquid is nitrogen, and since the surface tension of liquid nitrogen at 77 K is 8.85 ergs/cm$^2$,12 this results in large capillary stresses that can compress the solid network and cause the gel to shrink severalfold upon nitrogen desorption.13,14 The magnitude of the contraction can be calculated if the mechanical properties of the network are known, and the initial (undeformed) pore size and pore volume can be estimated.14,15 Low-pressure adsorption hysteresis has also been linked to the dimensional changes in porous solids that follow adsorption.16

**Molecular Modeling of Adsorption Phenomena**

Molecular modeling of fluid behavior in porous materials has been a very active area in recent years and substantial advances have been made.17 This has come about through a combination of progress in the fundamental statistical mechanics of inhomogeneous fluids and the widespread availability of high-speed computing at low cost. A number of goals can be identified for the molecular modeling of adsorbed fluid behavior in the context of tailoring porous materials. These include: (i) formulation of microscopic mechanical models which give a physically correct description of the behavior of fluids in porous materials at the molecular level; (ii) development and application of methods for calculating equilibrium properties such as adsorption isotherms and/or dynamic properties such as diffusivities; and (iii) development of insights into microscopic behavior of fluids in porous materials and how this is reflected in experimental measurements of equilibria and dynamics as well as in the performance of the porous material in specific applications. Molecular models start with a picture of the microstructure of the porous material. This is then combined with a description of the intermolecular forces through which adsorbed molecules interact with the porous material and with each other. For some materials such as zeolites, a firm foundation for the microstructure is provided by experimental crystal structure determination. Zeolites are generally treated as collections of atoms and/or ions. The fluid–solid interactions are modeled with atom–atom potentials, possibly including electrostatic interactions in ionic materials. For other materials such as carbons and silica gels there is much more uncertainty in the microstructure, since these materials are intrinsically disordered. Porous carbons can be modeled as collections of slit pores with graphite-like surfaces with the pore–fluid potential treated with atom–atom potentials or integrated forms.3,18 Silica gels can be modeled as an agglomerations of microspheres of amorphous silica with the fluid–microsphere interactions treated with atom–atom potentials or integrated forms.19

**Intermolecular Forces in Adsorption.** Accurate determination of intermolecular forces in complex systems such as fluids in pores remains a largely unsolved problem. While it is true to say that we have a good qualitative understanding of these forces, accurate quantitative information is scarce. For bulk fluids, the most accurate intermolecular pair potentials are based on multiparameter functions with parameters obtained from experimental data from several different sources including second virial coefficients, molecular beam scattering, dilute gas transport properties, and spectroscopy.20 Far less information of this type is available for fluids in pores, where there is much more uncertainty in the functional form of the potential and values of the parameters involved. An important source of information about the fluid–solid interaction potential is experimental determination of the Henry's law constant which gives the limiting slope of the adsorption isotherm at low pressure.3,18 However, this property is very sensitive to nonuniformities in the adsorbent sample, and for microporous adsorbsents, the Henry's law regime often lies at extremely low pressures where adsorption measurements are especially difficult.

Treatments of intermolecular forces for fluids in pores start with atom–atom potentials between sites in the adsorbate molecule and sites in the adsorbent.3,18 In most cases these potentials are chosen to have the Lennard-Jones 12–6 form, following the widespread use of the site–site 12–6 potential as an effective pair potential in bulk fluids.20 In addition, electrostatic interactions of the charge distribution in the adsorbent with permanent and/or induced charge distributions in the adsorbate molecules can be included. In the case of zeolites, for example, partial charges are often placed on the silicon, aluminum, and oxygen atoms of the framework in addition to the charge-balancing cations. For the adsorbate–adsorbate interactions, effective pair potentials from bulk fluid studies are usually used.

**Statistical Mechanical Theories.** Recent progress in the statistical mechanics of adsorption in pores has come principally from the recognition that the adsorbed...
fluid is inhomogeneous and from the development of techniques for treating such inhomogeneous fluids. Foremost among these are the density functional theories.21 Such theories have provided a wealth of information about the nature of fluid behavior at free solid surfaces and in simple models of pores such as slit pores and cylinders. Density functional theories have been especially successful in describing the nature of phase transitions of fluids in pores. Phenomena such as capillary condensation, wetting transitions, and layering transitions are now much better understood through applications of density functional theory. These applications are well reviewed in articles by Evans.21 Since it provides a more accurate picture of fluid behavior in single pores than traditional methods such as the Kelvin equation, density functional theory has recently been used in conjunction with molecular simulations and pore size distributions as a characterization tool for porous materials.22 Density functional theory has also been used to show that the slit pore model can generate all six classes of adsorption isotherm in the IUPAC classification, as well as a seventh class of behavior called capillary drying in which the capillary transition occurs at a bulk pressure higher than the saturated vapor pressure. The variation of the adsorption isotherms with the strength of the fluid–solid interaction and wall separation in the slit pore model is illustrated in Figure 2.

Other recent applications of density functional theory include selective adsorption from mixtures and the effect of confinement on liquid–liquid equilibrium.25 Extension of the method to chain molecules in pores has also been made.26 Most applications of density functional theory have been on simple pore geometries where the calculations involved can be reduced to one-dimensional integrals. Recently, however, an application to adsorption of xenon in zeolite NaA has been made27 and work on more complex pore structures should be anticipated.

Molecular Simulations. Molecular simulation using the Monte Carlo and molecular dynamics techniques is now the most widely used tool in the molecular modeling of fluid behavior in porous materials. This is especially true for complex materials such as zeolites where statistical mechanical theories are more difficult to apply.

Monte Carlo simulation in the grand canonical ensemble is the method of choice for studying equilibrium properties of fluids in porous materials and particularly for calculating adsorption isotherms. As an illustration of the kinds of calculations which are possible, we focus on recent studies of adsorption in zeolites and related molecular sieve adsorbents. The focus of these studies has been the development of intermolecular potentials as discussed above, calculation of the adsorption isotherm and heats of adsorption, and the development of insights into the molecular level behavior of the system. Two good examples are provided by calculations of adsorption of simple molecules in silicalite and some aluminophosphates.31 Interestingly, experimental data for argon in silicalite show a step in the adsorption isotherm indicative of a phase transition. This transition does not appear in the simulation results. The transition is thought to be a change in the silicalite structure

Figure 2. Types of adsorption isotherms obtained from slit pore model using density functional theory. The three large diagrams shown on the left qualitatively indicate which types of adsorption isotherms are obtained as a function of fluid–solid interaction strength $\varepsilon_{\text{sf}}/\varepsilon_{\text{ff}}$ and pore wall separation $H^*$ at three different temperatures, $T^* = 0.5, 0.8,$ and 1.4, corresponding to low temperature, intermediate temperature, and supercritical regimes. The actual isotherms are shown on the right, labeled according to the IUPAC classification shown in Figure 1. (Reprinted with permission from ref 23. Copyright 1993 American Chemical Society.)

induced by the presence of the argon, a conclusion supported by neutron diffraction studies33 of the adsorbent structure at different points on the isotherm.

Monte Carlo simulations have also been used to study adsorption of mixtures in porous materials. The focus of this work has been to understand the origins of selective adsorption and the nature of solution thermodynamics in porous materials. These studies are of fundamental importance in understanding the molecular basis of adsorption separations. Other areas where progress is being made in Monte Carlo simulations include more efficient sampling of high density states of fluids in the grand canonical ensemble via augmented/enlarged ensemble methods and configurational bias methods for studying chain molecules.

Molecular dynamics methods can be used to calculate transport properties in addition to thermodynamics. An important issue in adsorption is the nature of diffusive transport of molecules in porous materials.37 Molecular dynamics makes it possible to track the details of the
molecular motion in the system so that the mechanism of diffusion can be studied. Equilibrium molecular dynamics can be used to calculate the self-diffusivity from the mean square displacement or the velocity autocorrelation function. A recent example of such a calculation is the work of June et al. who calculated the self-diffusivities of methane and xenon in silicalite and obtained good agreement with the results from NMR measurements obtained for methane.\(^{39,40}\) The self-diffusivity is a measure of the diffusive motion of single molecules in the system at equilibrium. The transport diffusivity on the other hand is a measure of the collective motion of the fluid molecules in the presence of a concentration gradient. It is this quantity which is of importance in understanding transport effects in catalysis and separations. Maginn et al.\(^{41}\) have used nonequilibrium molecular dynamics to calculate the transport diffusivity for methane in silicalite. Other nonequilibrium molecular dynamics methods have been developed which allow the calculation of the transport diffusivity in the presence of large chemical potential gradients.\(^{42}\) Such methods hold considerable promise for improving our understanding of transport mechanisms in porous materials.

### Oxide Molecular Sieves

Natural zeolites are crystalline aluminosilicate minerals that can be reversibly dehydrated without any apparent change in their crystalline forms.\(^{43}\) The dehydrated minerals reversibly sorb water and methanol vapors, but largely exclude others, such as ether and benzene vapors. McBain regarded the zeolite mineral chabazite as an example of a “nearly perfect molecular sieve or a semi-permeable membrane of extremely regular structure,”\(^{44}\) and today, the family of oxide molecular sieves includes a wide variety of man-made microporous and mesoporous inorganic materials characterized by large internal surface area and pore volume.

Microporous zeolites constitute the largest known class of crystalline molecular sieves. These materials are composed of negatively charged aluminosilicate host frameworks that are sufficiently porous to accommodate a variety of different counterions plus, in many cases, guest molecules that can be reversibly desorbed. Zeolites have had enormous impact as catalysts and adsorbents in the chemical and petroleum industries.\(^{45}\) The now classical example is the fluidized catalytic cracking (FCC) of hydrocarbons to gasoline by supported, rare-earth modified faujasite catalysts which have replaced the amorphous acid clay and synthetic alumina gel materials used previously.\(^{46}\) It has been estimated that the use of this new technology has reduced the need for imported oil by 200 million barrels a year.\(^{46}\) More recent major innovations have been in the use of ZSM-5-based catalysts for the conversion of methanol to gasoline and also for the selective disproportionation of toluene into benzene and p-xylene.\(^{47}\) Zeolites also have found large-scale application as adsorbents and ion exchange agents. Most notably, certain lithium and calcium faujasites exhibit N\(_2\)-selective adsorption properties and are useful for the separation of air.\(^{48}\) and Zeolite 4A is widely used as a detergent builder.\(^{49}\)

Microporous zeolites and related crystalline oxides having a variety of micropore sizes and shapes are available, but crystalline mesoporous analogues are unknown. Two classes of ordered but noncrystalline mesoporous oxide molecular sieves are known, however. The first class, pillared layered solids, have been prepared from layered oxide materials by first separating the layers and then partially filling the space between the separated layers with inorganic pillars and finally removing the organic molecules thermally.\(^{50-53}\) Although many pillared layered oxides have been prepared for use as catalysts and adsorbents, these materials have failed to exhibit the narrow pore size distribution demonstrated by zeolites.\(^{54-57}\) More recently, a second class of mesoporous molecular sieves has been reported that contains uniformly sized, cylindrical mesopores arranged regularly in an amorphous aluminosilicate matrix.\(^{58,59}\) This class of materials is discussed in more detail below.

Microporous and mesoporous oxide molecular sieves, characterized by large internal surface area and pore volume, form the backbone of many heterogeneous catalysts and separations media. The ability to tailor the pore size and shape of these porous materials would allow for control of the diffusion of both reagents and products in and out of the porous medium as well as control over the possible reaction intermediates that might form within the pore system. In short, tailoring of oxide molecular sieves implies control of size and shape selectivity in catalysis and separations. Tailoring of porosity in oxide molecular sieves in terms of a priori structural design has proven to be extremely difficult, however, due to the inherent complexity of the synthetic procedures employed. In general, oxide molecular sieves are prepared by hydrothermal synthesis methods which involve both chemical and physical transformations within an amorphous oxide gel, often in the presence of a template species.\(^{60}\) The gel eventually crystallizes to form a material in which the template species and/or solvent molecules are guests within the channels and cages of an oxide host framework. A porous material is obtained upon removal of the guest molecules from the oxide framework. By varying the chemical composition of the gels, the reaction conditions, and the templating agent, it has been possible to arrive at the remarkable range of sieve compositions. The challenge of tailoring is largely the challenge of relating the initial synthesis conditions to the porosity of the molecular sieve material ultimately obtained.

### Molecular Templates in Molecular Sieve Synthesis

The role of organic templates or structure-directing agents in zeolite synthesis has been widely discussed in the recent literature,\(^{61}\) and even though major strides have been made in the past decade toward understanding the self-assembly process, the goal of “synthesis by design” still remains largely elusive. Two factors complicate the understanding of zeolite synthesis. First, zeolites are often metastable products formed under kinetic rather than thermodynamic control, and different crystalline materials are often obtained under the same reaction conditions when different reaction times are employed.\(^{62}\) Recent experimental\(^{63}\) and computational\(^{64}\) studies have shown that microporous silica frameworks are less stable than quartz by only 7–14 kJ mol\(^{-1}\). Second, molecular templates are only one of many factors that control the structure of synthetic
zeolites. Even though some clear examples of templating and structure-directing have been demonstrated, other systems show no such relationships and additional factors such as the influence of the temperature, pH, concentration, stirring rate, and the composition of the reaction vessel can be important.65

Gies and Marler66 were the first to investigate comprehensively the influence of the structure and chemical properties of organic and inorganic guest species on the synthesis of pure silica materials. Molecules with similar shapes and volumes, regardless of their differences in chemical properties, formed the same types of silica framework structures in that globular guest molecules yielded cage frameworks, linear chain guest molecules yielded one-dimensional channel frameworks, and branched chain guest molecules yielded intersecting channel frameworks. Moreover, a linear correlation between the size of the guest and the size of the cages formed was observed. Gies67 also showed by 13C solid-state NMR that the molecules were undergoing rapid reorientation within the cavities. This accounts for the insensitivity of the structures to the similarly sized, but chemically different, guest molecules. The kinetics of crystallization were affected by the basicity of the guest, but this was thought to be associated with the enhanced rate of silicate hydrolysis at higher pH's.

Zones, Olmstead, and Santilli68,69 have shown both the scope and limitations of a priori design in their studies of SSZ-26 synthesis. Their aim was to produce a novel zeolite, having a multidimensional channel system with large, 12-ring intersections. Realizing that the dication a was used to synthesize ZSM-12, they introduced a fused cyclohexane ring into the structure to form the propellane b, a dication too large to be contained within the one-dimensional ZSM-12 channel system, but potentially suited for occupying the junction of intersecting channels. By using this organic cation in a slightly aluminous reaction medium, a high silica zeolite (Si/Al = 20–50), SSZ-26, was produced. The framework architecture of this zeolite consisted of intersecting 10- and 12-ring channels, with a propellane molecule trapped at each intersection.70 SSZ-26 was not obtained, however, in the presence of monocationic propellane c or the structurally related trication d.

Clearly, the geometry of the organic molecule is only one of many factors determining the oxide framework structure in zeolites.

In theory, layered intermediates formed during zeolite synthesis could serve as precursors for pillared layered materials. These novel materials would be composed of layers having zeolitic microporosity and/or activity separated by mesoporous galleries. The first successful application of this concept was demonstrated by researchers at Mobil in the form of a material named MCM-36.71–73 Transmission electron micrographs of MCM-36 show that zeolite layers can be separated and pillared, using a silica source, to produce a pillared zeolite hybrid. Changes in the X-ray diffraction patterns, pore size distribution, and hydrocarbon sorption capacities support this proposed structure. The X-ray diffraction pattern of MCM-36 exhibits a low angle peak with a d spacing of ~50 Å consistent with the interlayer separation observed in the transmission electron micrographs. In addition, those peaks assigned to the interlayer ordering are significantly broadened while those peaks assigned to the intralayer structure remained sharp and unaffected by the pillaring procedure. Pore size distribution measurements of MCM-36 exhibit an expected microporous component of 6–7 Å, consistent with the zeolite pore structure as well as pores in the mesopore range between 30 and 35 Å. Surface areas and hydrocarbon sorption capacities increase by almost a factor of 2 compared to the parent unpillared molecular sieve. Dynamic sorption data of a bulky hydrocarbon, 2,2-dimethylbutane, suggest the presence of a mesoporous channel system that makes the micropores more accessible.73 The combination of the microporosity and activity of the zeolite layers and the mesoporous pillared structure should lead to applications involving larger molecules than those associated with traditional zeolitic materials.74

Supramolecular Templates in Molecular Sieve Synthesis. A new class of mesoporous molecular sieves, M41S, has been discovered by extending the concept of zeolite templating with small organic molecules to longer chain surfactant molecules.58,59 Rather than individual molecular directing agents participating in the ordering of the reagents to form the porous material, assemblies of molecules, dictated by solution energetics, are responsible for the formation of these pore systems. This supramolecular directing concept (illustrated in Figure 3) has led to a family of materials whose structure, composition, and pore size can be tailored during synthesis by variation of the reactant stoichiometry, nature of the surfactant molecule, or by postsynthesis functionalization techniques.

The formation mechanism of this mesoporous family of molecular sieves is dictated by two features. The first is the dynamics of surfactant molecules to form molecular assemblies which lead to micelle and, ultimately, liquid crystal formation. The second is the ability of the inorganic oxide to undergo condensation reactions to form extended, thermally stable structures. The initial discovery involved the formation of silicates using alkyltrimethylammonium cationic surfactants in a basic medium. Subsequent efforts have shown these structures can also be formed in acid
media, and by using neutral normal amines, nonionic surfactants, and dialkyl(dimethylammonium) cationic surfactants. In addition, several mechanistic studies have expanded the initial pathway studies to a more generalized view of an organic/inorganic charge balance driving force for the formation of these structures.

The initial members of the M41S family consisted of MCM-41 (hexagonal phase), MCM-48 (cubic Ia3d phase), and MCM-50 (a stabilized lamellar phase). MCM-41 exhibits an X-ray diffraction pattern containing three or more low angle (below 10° 2θ) peaks that can be indexed to an hexagonal h00 lattice. The structure is proposed to have an hexagonal stacking of uniform diameter porous tubes whose size can be varied from about 15 to more than 100 Å. An example of the characteristic X-ray diffraction pattern and proposed structure are shown in Figure 4. MCM-48, the cubic material, exhibits an X-ray diffraction pattern, shown in Figure 4, consisting of several peaks that can be
assigned to the la3d space group. The structure of MCM-48 has been proposed to be bicontinuous with a simplified representation of two infinite three-dimensional, mutually intertwined, unconnected network of rods as initially proposed by Luzzatti. A more sophisticated and perhaps more realistic model would be based on the concept of an infinite periodic minimal surface of the gyroid form, Q proposed for water–surfactant systems. A proposed structure is also shown in Figure 4. MCM-50, the stabilized lamellar structure, exhibits an X-ray diffraction pattern consisting of several low angle peaks that can be indexed to h00 reflections. This material could be a pillared layered material with inorganic oxide pillars separating a two-dimensional sheet similar to that of layered silicates such as magadite or kenyaite as illustrated in Figure 4. Alternatively, the lamellar phase could be represented by a variation in the stacking of surfactant rods such that the pores of the inorganic oxide product would be arranged in a layered form.

Other M41S type mesoporous materials are SBA-1 (cubic Pm3n phase) and SBA-2 (cubic p6/mmc phase). Further materials have been synthesized that are not as readily classified. These materials generally exhibit limited X-ray diffraction information (one peak) and may contain a random array of pores as shown in transmission electron micrographs. All of these mesoporous materials are characterized by having narrow pore size distributions comparable to microporous materials and extraordinary hydrocarbon sorption capacities (up to and equal to their weight).

The initial forms of the M41S family were synthesized as silicates and aluminosilicates. Subsequent synthesis efforts have produced materials having heteroatom substitution as well as nonsiliceous products. The initial nonsiliceous materials included oxides of W, Fe, Pb, Mo, and Sb. Many of these materials exhibited very poor thermal stability and upon the removal of the template, the structures collapsed. Mesoporous zirconia and titania materials have been prepared, however, that exhibit satisfactory thermal stability and thus are believed to be composed of extended and complete oxide nets of the elements.

One of the unique features of the M41S family of materials is the ability to tailor pore size. The pore size can be varied from about 15 Å to more than 100 Å by varying the length of the alkyl chain of the template molecule or by the use of auxiliary solubilized molecules. A series of transmission electron micrographs of MCM-41 materials having pore diameters from 20 to 100 Å is shown in Figure 5. The approach taken to varying mesopore size in a regular, systematic fashion stands in stark contrast to the inability to accomplish such goals for traditional microporous zeolitic materials.

Finally, it should be noted that postsynthesis methods such as functionalization of pore walls can also affect the pore size in M41S materials. MCM-41 samples contain a large concentration of silanols which can be functionalized via simple elimination reactions. This postsynthesis technique can be used to alter the pore size or affect the hydrophobicity of the pore wall. Alternatively, others species can be used to anchor...
Atoms. Thus the addition of tetrahedral [Cu(CH₃CN)₄]³⁺ with organic ligands containing nitrogen donor moieties having specific catalytic or adsorptive properties.⁹³

**Porous Coordination Solids**

The construction of porous materials by linking transition metal ions with bridging ligands other than oxygen is an approach that offers much potential for the synthesis of new types of tailored porous materials.⁹⁴ The synthetic conditions and conceptual approach employed in their preparation differ from those usually employed in the synthesis of oxide molecular sieves. Porous coordination solids are prepared by combining solutions containing the appropriate organic ligands and metal ions at or near room temperature, and an attempt is made when designing their synthesis to exploit the directional nature of metal–ligand interactions for the construction of specific framework topologies. For example, Cu(I) ions are known to form tetrahedral complexes with organic ligands containing nitrogen donor atoms. Thus the addition of tetrahedral [Cu(CH₃CN)₄]³⁺ as a PF₆⁻ salt to 4,4′-bipyridine (4,4′-bpy), e, a bifunctional building unit, yields Cu(4,4′-bpy)₂PF₆ as illustrated in Scheme 1.⁹⁵ Here, the cationic Cu(4,4′-bpy)₂³⁺ framework defines a three-dimensional channel system in which PF₆⁻ counteranions reside. As is possible for many coordination solids, the structure of this framework can be related to that of cubic diamond by alternately replacing the C atoms and the C–C bond in the diamond structure with Cu(I) ions and the 4,4′-bpy ligands, respectively. In this fashion, an open framework is produced as a consequence of the large metric difference (8–8.5 Å) between the C–C bond and the 4,4′-bpy ligand. The use of molecular ligands for the construction of porous materials offers two important features favorable for tailoring both the porosity and the reactivity of coordination solids. First, the coordination chemistry of metal ions is extensive and well-established. This allows for numerous combinations of metal and ligand building blocks that can be manipulated at the molecular level in order to direct the assembly of a given target compound.⁹⁶ Second, the molecular building units tend to have good solubility and assembly reactions often proceed at room temperature. Consequently, the integrity of the component molecules is maintained in the coordination solid, and a close connection can frequently be established between molecular and solid-state properties.

**Anionic Frameworks.** Metal cyanide compounds comprise a large family of coordination solids having anionic frameworks. The most thoroughly studied of these are the hexacyanometalates, often referred to as Prussian blue analogues.⁹⁷,⁹⁸ Here, octahedral metal centers are linked together by the rodlike, doubly bridging CN ligands, f, to generate three-dimensional, cubic, anionic networks that are sufficiently porous to accommodate countercations and/or additional neutral guest molecules. These guest molecules are in some cases coordinated to metal centers as in Mn₃[Co(CN)₆]₂·xH₂O, which contains both uncoordinated “lattice water” and coordinated “ligand water”.⁹⁹ Many analogous materials have zeolitic properties in that they desorb water without degradation of the cyanometalate framework structure, and the resulting porous materials can reversibly sorb a variety of small organic and inorganic molecules.¹⁰⁰ Related hexacyanometalates such as M₂Zn₃[Fe(CN)₆]₉·xH₂O, M = K⁺, Na⁺, and Cs⁺, display similar behavior.¹⁰¹

**Cationic Frameworks.** Reaction of AgNO₃ with 4,4′-bipyridine (4,4′-bpy) under hydrothermal conditions yields colorless crystals of Ag(4,4′-bpy)NO₃. This cationic framework compound is composed of linear silver bipyridine chains that are cross-linked by Ag–Ag bonds, dAg–Ag = 2.98 Å, to form 3-fold interpenetrating, three-dimensional, three-connected α-ThSi₂-like networks (see Figure 6).¹⁰² The nitrate counteranions occupy 23 × 6 Å channels within this framework, and weak interactions between the nitrate anion and the cationic framework, dAg–O = 2.78 and 2.83 Å, allow for anion exchange with ions such as PF₆⁻, MoO₄²⁻, BF₄⁻, and SO₄²⁻.¹⁰² This exchange process is completed rapidly, without destruction of the metal–organic framework.
In the diamond-like, 4-fold interpenetrated Cu(4,4′-bpy)2+ framework of Cu(4,4′-bpy)2PF6, the PF6− anions occupy a channel system nearly 6 Å in diameter and can be exchanged with SCN− ions.95b Ion exchange is accompanied, however, by deformation of the cationic framework due to strong anion–framework interactions. A diamond-like network is also observed for the copper-tetracyanotetraphenylmethane framework in Cu[C6H4CN)4]BF4·xC6H5NO2.103 Here, framework interpenetration is not observed despite the presence of large, 22-Å diameter channels in the Cu[C6H4CN)4]+ framework. These channels are occupied by stable clusters of BF4− anions and nitrobenzene solvent molecules that act as guests in the cationic framework and presumably inhibit interpenetration. Unfortunately, the orientation and number of guest species could not be determined X-ray crystallographically. A similar situation prevails in Cu(tpp)(BF4)3DMF, Li3Co(CN)5•1.42DMF•0.48DMAC (DMF = N,N-dimethylformamide and DMAC = N,N-dimethylacetamide), and (Bu4N)2[Co(CN)4(NC5H5)] which are selective, high-capacity, reversible sorbents for O2.105−107 The first material shows a striking pressure reversible uptake of as much as ~55 cm³ O2 per gram. Surprisingly, the compound is not microporous: O2 is taken into the solid since it can bind to the coordinatively unsaturated Co(II) centers, but helium does not enter the crystal. Apparently, the Li3Co(CN)5•3DMF structure is sufficiently flexible to accommodate the passage of O2 to the Co(II) binding site.

Selective sorption of organic molecules containing specific functional groups has been observed for Zn2−(BTC)(NO3)2-(H2O)(C6H5OH)3, BTC = 1,3,5-benzenetricarboxylate (h), prepared by diffusing triethylamine into a solution of 1,3,5-benzenetricarboxylic acid and zinc(II) nitrate hexahydrate in ethanol.108 In this material, the Zn2(BTC)(NO3) framework forms channels 14 Å in diameter that are occupied by water and ethanol. The nitrate ion is strongly bonded to the framework and cannot be exchanged. All of the neutral guest molecules can be exchanged at ambient temperature, however, including the three ethanol molecules that are coordinated to Zn(II). Exchange is quite selective for alcohols, and potential guest molecules such as tetrahydrofuran, methycyclohexane, methyl ethyl ketone, acetonitrile, and acetone are excluded.109 This selectivity appears to result from binding selectivity at the Zn(II) coordination site.

Selective sorption of aromatic organic molecules has been observed in a different type of BTC coordination solid, Co(C6H3(COOH)2/3)(NC5H5)2/2NC5H5. As shown in Figure 7, this material has a layer structure where two pyridine molecules are coordinated to each cobalt center in a two-dimensional, planar Co-BTC network, with one pyridine molecule extending above the plane and the other below the plane.96c These “anchored” pyridine molecules fail to fill the interlayer space, and as a result, uncoordinated pyridine molecules are intercalated between the Co-BTC layers. These guest molecules can be exchanged or even removed from the solid material with retention of the Co(C6H3(COOH)2/3(–NC5H5)2 host framework structure; this framework is stable up to 300 ºC. Competitive sorption experiments performed using guest-free material show high selectivity for benzene derivatives. For example, benzonitrile is sorbed selectively from benzene–acetonitrile mixtures. The probable origin of this selectivity is evident in Figure 7: favorable π–π stacking interactions between aromatic guest molecules that intercalate between the benzene rings of BTC units in adjacent layers.

**Figure 7.** A perspective drawing of the solid-state structure of Co(C6H3(COOH)2/3)2(–NC5H5)2/2NC5H5 perpendicular to the crystallographic z-axis. The Co(C6H3(COOH)2/3)(NC5H5)2 layers are shown as ball-and-stick models, and the intercalated pyridine guest molecules are shown as space-filling models. Cobalt atoms are represented by filled spheres, carbon atoms by shaded spheres, nitrogen atoms by partially shaded spheres, and oxygen atoms by unshaded, open spheres.

**Porous Carbons**

Because of their disorganized microstructure, porous carbons cannot be tailored by control of crystal structure, as is the case, for example, with zeolites and coordination solids. However, enough is known about the influence of processing on porosity in carbons to enable them, with care, to be tailored on a molecular level. This is best illustrated by the molecular selectivities of carbon molecular sieve membranes described below. An additional advantage of porous carbons is their processibility, that is, their ability to be fabricated into a variety of macroscopic forms more easily than many other porous materials.

Most industrial carbon materials are derived from organic precursors by heat-treatment in an inert atmo-
sphere. During this carbonization process, a carbon residue is formed by condensation of polynuclear aromatic compounds and expulsion of side chain groups. However, industrial carbons retain a significant concentration of heteroelements, especially oxygen and hydrogen, and may also contain mineral matter. Carbons are broadly classified into graphitizing carbons that have developed three-dimensional graphitic order, and non-graphitizing carbons that inhibit the development of a pre-graphitic structure. By contrast, cross-linking reactions occur during carbonization of non-graphitizing carbons that have not. A liquid phase is formed during carbonization of most graphitizing precursors in which polynuclear aromatic hydrocarbons are stacked into parallel arrays. This pregraphitic, liquid crystalline material is called the carbonaceous mesophase. By contrast, cross-linking reactions occur during carbonization of nongraphitizing carbons that have developed three-dimensional graphitic order. Therefore, industrial carbons retain a significant concentration of heteroelements, especially oxygen and hydrogen, and may also contain mineral matter. The most important class of porous, nongraphitizing carbons is active carbons that have a high open porosity and high specific surface area, up to 1200 m² g⁻¹ in commercial active carbons. The major sources of active carbons are coals (lignites, bituminous coals, and anthracites), peat, wood, and a wide range of organic byproducts of industry and agriculture. The adsorptive capacity of the carbonized materials is usually too low for practical applications, so porosity in the carbon is developed by activation during or prior to carbonization by reaction of the precursor either with oxidizing gases such as H₂O or CO₂ or with other inorganic chemical activating agents such as H₃PO₄ or ZnCl₂. About 90% of active carbons are produced in granular or powder form, with most of the remainder in pelleted form. About 80 wt % of active carbons are used for liquid-phase applications such as water treatment, decolorization, and gas separation. The remainder are used for gas-phase applications in solvent recovery, air purification, catalysis, gas separation, cigarette filters, and military and nuclear applications. Mechanisms of activation by reaction with oxidizing gases during carbonization have been extensively studied. In the initial stages of activation, new open micro pores are created, possibly by removal of secondary carbon formed by cracked volatiles from pore entrances. In the later stages of activation micropore widening is the dominant process so that the pore size distribution extends into the mesopore size range. Much less is known about mechanisms of chemical activation although there has been recent work on the chemical activation of woods and coals by phosphoric acid. Measurements of open porosity develop upon heat treatment of wood with phosphoric acid at 200 °C, increases to a maximum of ~2000 m² g⁻¹ at 350–500 °C, and decreases at higher heat-treatment temperatures. Studies by ¹³C NMR have shown that phosphoric acid promotes cross-linking reactions and dehydration at low temperatures, thus bonding otherwise volatile material into the structure and leading to increased carbon yield. Partial depolymerization of lignin and hemicellulose also occurs, cellulose being more resistant to depolymerization. It is inferred that generation of accessible porosity results from dilatation following depolymerization. At higher temperatures (~450 °C) there is repolymerization and a sudden growth in the average size of aromatic clusters, indicating that bond cleavage and structural rearrangement occur, causing contraction and the observed reduction in porosity. Table 1 shows how the distribution of different pore types in active carbons varies with the nature of the precursor. By judicious choice of the precursor and by careful control of carbonization and activation it is possible to tailor active carbons for particular applications. Carbons used for gas-phase applications require significant mesoporosity as provided by the lignite-based active carbon (see Table 1) and also by phosphoric acid-activated wood-based carbons. Highly microporous carbons are required for gas-phase applications. Nongraphitizing carbons such as active carbons have a very disordered structure as revealed by high-resolution electron microscopy and various model structures have been proposed. Although the models differ in detail, the essential feature of all of them is a twisted network of defective hexagonal carbon layer planes, cross-linked by aliphatic bridging groups. The width of layer planes varies, but typically is about 5 nm. Simple functional groups (e.g., C=O, C=O) and heteroelements are incorporated into the network and are bound to the periphery of the carbon layer planes. Functional groups can have an important influence on adsorption. In active carbons the layer planes occur singly in small stacks of two, three, or four with variable interlayer spacings typically in the range 0.34 to 0.8 nm. There is considerable microporosity in the form of an interconnected network of slit-shaped pores formed by the spaces between the stacks. Thus the widths of pores formed by interlayer spacings are significantly less than 2 nm, the upper limit for micropore widths. Constrictions in the microporous network are particular features of the structure that control access to much of the pore space. Constrictions may also occur due to the presence of functional groups attached to the edges of layer planes and by carbon deposits formed by thermal cracking of volatiles. The high adsorptive capacity of active carbons used in gas adsorption mainly results from the presence of small micropores (ultramicropores or nanopores) of width commensurate with adsorbate molecules. In such pores there is overlap of the force fields from opposite pore walls leading to strong adsorption.

Carbon molecular sieves, CMS, can be prepared by deposition of carbon from the vapor phase. CVD can be used to prepare CMS in tonnage quantities to separate N₂ from air by pressure swing adsorption. The separation is...
larger molecule $N_2$ progressively reduces $O_2:N_2$ selectivity. The authors show that reduction in particle size of CMS by grinding microporous network by CVD. However, recent work selectivity results from constriction of apertures in the $O_2$ molecule kinetic, depending upon faster adsorption of the smaller hydrogen and $C_1$ hydrocarbons. The processes involved are illustrated in Figure 9 and Table 2, selectivity in the smallest pores results from size exclusion. In larger pores of width $>5$ nm, nonselective viscous flow is the principal transport mechanism. However, Knudsen diffusion dominates transport processes at high temperatures. Clearly, there is much scope for developing CMS membranes with different pore sizes and operating them at different temperatures in order to achieve a wider range of selectivity than is possible today. Modeling these complex processes is also a rich field for molecular simulation studies.

Active carbon fibers, ACF, can be prepared by carbonization and activation of a range of polymer fibers (e.g., phenolics, acrylics, and vinyls) and isotropic pitch fibers. ACF are usually microporous, although mesoporous fibers are also known. They are characterized by rapid diffusion of adsorbates in to and out of the fibers. Textile technology has been adapted to produce a range of flexible woven and nonwoven forms of ACF that have found a diverse range of applications such as water and air purification, military clothing, surgical dressings, and high-capacity double-layer capacitors. Rigidized monolithic forms of ACF called carbon-bonded carbon fibers, CBCF, have been produced from a slurry of chopped carbon fibers and a resin powder that is filtered to produce a mat. This is followed by carbonization of the resin binder and activation of the fiber. One form of CBCF has exhibited molecular sieve character, showing selectivity between $CO_2$ and $CH_4$. An interesting aspect of this study is the use of an electric field across the CBCF to assist desorption of $CO_2$. ACF and related materials are promising materials for electrosorption and thermal swing processing using resistive heating, although their potential has not been fully explored.

There is much current interest in the development of porous carbon anodes for Li ion batteries. The capacity of commercial carbon anodes is 200–250 mA h g$^{-1}$, but laboratory studies have shown that carbons with capacities in the range 500–900 mA h g$^{-1}$ can be prepared. The nature of the interaction of Li$^+$ ions with carbons depends on microstructure. Lithium intercalates into graphitic carbons, the extent of staging increasing with graphitic character. For nongraphitizing carbons, lithium is bound close to carbon layer planes, possibly in micropores. For carbons heat treated to less than 1000 °C, Li is bound close to residual H in the carbon structure. An interesting form of porous carbon anode of high capacity (925 mA h g$^{-1}$) has been produced by carbonizing organics inserted into the pores of a pillared clay.

**Sol–Gel-Derived Oxides**

Amorphous silica can be prepared by acidification of basic aqueous silicate solutions as in reaction 1, and

$$Na_2SiO_3 + 2H^+ \rightarrow SiO_2 + H_2O + 2Na^+$$

when reaction conditions are properly adjusted, porous silica gels are obtained. Two types of chemical reactions are involved: silicate neutralization producing silicic acids, reaction 2, followed by condensation polymerization of the silicic acids, reaction 3.

If water is evaporated from the pores of silica hydrogels prepared in this fashion, porous xerogels (dried...
gels) are obtained. Porous, amorphous oxides of silicon and other elements are produced in this fashion commercially on a very large scale and have found widespread application as high surface area catalysts, catalyst supports, chromatographic stationary phases, and gas sorbents.\textsuperscript{134,135} As hydrophilic materials, their sorption properties complement those of porous carbons, since carbons are hydrophobic and tend to selectively adsorb hydrocarbons.

An alternative route to porous, amorphous oxides involves reaction of alkoxides with water as illustrated in reaction 4 for silica.\textsuperscript{136,137} Here, silicic acids are first produced by hydrolysis of a silicon alkoxide, formally a silicic acid ester, as in reaction 5. The silicic acids thus formed can then either undergo self-condensation, reaction 6, or condensation with an alkoxide as in reaction 7. The overall reaction therefore proceeds initially as a condensation polymerization reaction to form soluble, high molecular weight polysilicates (a sol), and these polysilicates then link together to form a three-dimensional network whose pores are filled with solvent molecules (a gel). Hence the name “sol–gel polymerization” of alkoxides and “sol–gel processing” of oxides.

Both sol–gel-derived oxides and oxide molecular sieves are usually prepared from oxide gels, and in a certain sense both can be regarded as sol–gel-derived oxides differing only in their degree of structural ordering. In sol–gel-derived oxides, neither the oxide framework nor the pore structure are ordered. Mesoporous oxide molecular sieves resemble sol–gel-derived oxides in that they have noncrystalline, amorphous oxide frameworks but differ in that their mesopores are uniform and ordered. Microporous oxide molecular sieves also have uniform, ordered pore structures but in addition have crystalline oxide frameworks. Ordering is achieved in the synthesis of oxide molecular sieves by heat treatment of an oxide gel in the presence of an organic or inorganic “structure-directing” species. This heat treatment promotes reversible dissolution of the solid oxide gel framework into pore fluid solution and subsequent nucleation and growth of ordered materials. In short, heat treatment allows the system to approach metastable equilibrium. Note that the true equilibrium state for most oxides is a dense, nonporous phase and that oxide molecular sieves as well as sol–gel-derived oxides are thermodynamically metastable phases. In both cases, optimized processing conditions represent a balance between kinetic and thermodynamic factors.

Sol–gel-derived oxides have yet to receive widespread application as porous materials, but they have nonetheless been investigated extensively due to the versatility of sol–gel processing techniques. Sol–gel processing conditions can be employed in the fabrication of oxide monoliths, fibers, thin films, and monodisperse powders.\textsuperscript{136,137} Moreover, the chemical properties of sol–gel-derived oxides can be manipulated by incorporating organic, organometallic, and inorganic functional groups into the gel framework.\textsuperscript{138} The discussion that follows is restricted almost exclusively to sol–gel-derived silica, but the principles involved are quite general and can be applied to the processing of many other main group and transition metal oxides. In the first section, the

\begin{equation}
\text{Si} - \text{O}^{-} + \text{H}^{+} = \text{Si} - \text{OH}
\end{equation}

\begin{equation}
\text{Si} - \text{OH} + \text{HO} - \text{Si}^{-} = \text{Si} - \text{O}^- - \text{Si}^- + \text{H}_2\text{O}
\end{equation}

\begin{equation}
\text{Si(OR)}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{ROH}
\end{equation}

\begin{equation}
\text{Si} - \text{OR} + \text{H}_2\text{O} = \text{Si} - \text{OH} + \text{ROH}
\end{equation}

\begin{equation}
\text{Si} - \text{OH} + \text{HO} - \text{Si}^{-} = \text{Si} - \text{O}^- - \text{Si}^- + \text{H}_2\text{O}
\end{equation}

\begin{equation}
\text{Si} - \text{OH} + \text{RO} - \text{Si}^- = \text{Si} - \text{O}^- - \text{Si}^- + \text{ROH}
\end{equation}
influence of processing conditions on porosity is considered in terms of the distinct processing steps involved. The two sections that follow are concerned with tailoring the porosity of sol–gel-derived oxides not through manipulation of processing conditions but instead through manipulation of precursor composition and geometry.

**Sol–Gel Processing.** The initial stages of sol–gel processing proceed in solution, and the porosity of the final product is most easily tailored during these initial stages by introducing acids such as hydrochloric acid or bases such as ammonium hydroxide into the reaction solution. Silica xerogels processed under relatively acidic conditions display type I nitrogen sorption isotherms characteristic of microporous materials, whereas those processed under basic conditions display type IV isotherms characteristic of mesoporous materials (see Figure 1). These types of isotherms represent exotherms characteristic of mesoporous materials and characteristic of microporous materials, whereas those processed under acidic conditions display type I nitrogen sorption isotherms reflecting the presence of both micro- and mesoporosity. Transmission electron microscopic studies show that the microstructure of xerogels varies from homogeneous to particulate as the processing conditions are varied from acidic to basic. Studies of particulate silica xerogels obtained from aggregated aqueous silica colloidal sols and studies of silica nanoparticles prepared by controlled hydrolysis of tetramethyl orthosilicate both show that mesoporosity arises from interstitial pore space in particle aggregates and as a result, the average mesopore radius increases with increasing particle size. This observation supports the idea that porosity in sol–gel-derived oxides depends on the internal structure of the primary particles, the size and size distribution of the primary particles, how these primary particles aggregate, and how the gel structure responds to the capillary stresses during drying (see below).

Quasi elastic light scattering (QELS) has proved to be a powerful tool for monitoring the course of sol–gel polymerization in solution since the Z-average hydrodynamic radius \( R_h \) of the polysilicates formed can be continuously monitored as a function of time. For sol–gel polymerization of dilute Si(OCH₃)₄ in basic methanol solution, an extended growth stage is observed where \( R_h \) varies exponentially with time. Exponential growth of this type is characteristic of particle aggregation processes controlled by chemical kinetics (reaction-limited cluster aggregation) as opposed to particle diffusion (diffusion-limited cluster aggregation). For sol–gel polymerization of dilute Si(OCH₃)₄ in basic methanol solution, this stage begins when \( R_h \) is about 5 nm. A comparison between sol–gel polymerization under basic and acidic conditions has been made in a slightly more concentrated system. Under basic conditions, exponential growth was observed once the hydrodynamic radius reached about 20 nm but under acidic condition, \( R_h \) was \(<2 \text{ nm} \) at the onset of the exponential growth stage. In both cases, the exponential growth stage was preceded by a shorter, faster initial growth stage and was followed by a critical growth stage. During this critical growth stage, \( R_h \) diverges as the gel time \( t_{gel} \) is approached according to \( R_h = (t_{gel} - t)^{-7} \). In summary, QELS studies have shown that the sol–gel polymerization of Si(OCH₃)₄ proceeds in three successive, possibly overlapping polymerization stages: (1) initial polymerization of the Si(OCH₃)₄ precursor into polysilicates that serve as monomers in the second stage, (2) exponential growth of polysilicate primary particles formed in the first stage into particle aggregates that serve as monomers in the final stage, and (3) critical growth of the aggregates formed in the second stage into a gel.

Qualitative comparison of the gas sorption data, electron microscopic information, and quasi elastic light scattering data just reviewed strongly suggest that micro- and mesoporosity in sol–gel-derived xerogels is ultimately derived from the size of primary particles formed during the early stages of sol–gel polymerization. Under more basic conditions where larger primary particles are formed, mesoporosity is obtained, and under more acidic conditions where smaller primary particles are formed, microporosity is obtained. Two points should be noted in this context, however. First, the preceding discussion has focused on the influence of acidic and basic conditions on porosity, but many other processing conditions play a subsidiary but important role. Second, acidic and basic conditions affect not only the sizes but also the structures of the primary particles formed in the course of sol–gel polymerization. The polysilicate primary particles formed under basic conditions are more cross-linked than those formed under acidic conditions and are therefore more dense as well.

At the moment of gelation, significant concentrations of soluble silicates are still present in the liquid phase. During the next stage of sol–gel processing, gel aging, these species become attached to the gel network, leading to an increase in its rigidity. In addition, condensation can still occur within the gel network according to reactions 6 and 7, resulting in stiffening and contraction (syneresis). This type of network stiffening can be enhanced by adding alkoxide monomer after gelation. Such treatments cause some modification of the pore structure in the wet gel, but their most important effect is a strengthening of the gel network that serves to reduce the amount of shrinkage that occurs during drying. The pore size distribution can be systematically altered by aging in a reactive liquid that promotes equilibration in the gel framework: dissolution/reprecipitation transfers material from the surfaces of larger pores to smaller ones, leading to coarsening. Aging by dissolution/reprecipitation raises the modulus of a gel initially, as material is deposited in regions of negative curvature. Longer aging can reduce the rigidity, however, probably owing to instability in long chains that breaks up the network.

Once gel aging is completed, steps are taken to remove the liquid phase from the solid gel framework. Drying of gels involves shrinkage, implying as much as an order of magnitude reduction in pore volume and a corresponding reduction in pore sizes. The final density depends on the balance between the capillary pressure that drives shrinkage and the rigidity of the network that resists shrinkage. If the connectivity of the network of the gel is low, the gel may be so compliant that the pores collapse. By minimizing the degree of cross-linking in the gel, the network can...
be made supple enough to collapse until the “pore” diameter is determined by the size of the solvent molecule.153 On the other hand, some gels undergo large contraction during drying, but then spring back completely. This is achieved by passivating the surfaces of the gel through trimethylsililation of hydroxyl groups with trimethylchlorosilane, so that branches of the network cannot bond to one another when they are forced into contact during drying.154,155

The final stage of sol–gel processing is a heat treatment stage. As a gel is heated in air, adsorbed solvent evaporates and by about 400 °C, most organics burn off. In some cases, when small molecules or substituents are removed from within the dried gel framework, micropores are created and the surface area increases.156 As the temperature approaches the glass transition temperature of the network, sintering results from viscous flow driven by the curvature of the solid/vapor interface.157 This causes the smallest pores to collapse first, followed by larger pores. Thus, micropores can be created by heating at low temperatures, and they can be eliminated by partial sintering. Many gels crystallize when heated, even at temperatures too low for significant sintering. In such cases, crystals grow within the porous network, and the pores engulfed within the crystal grains are very difficult to eliminate by subsequent heat treatment. However, the sintering rate accelerates monotonically with temperature, while the crystallization rate goes through a maximum at a temperature well below the melting point, so the competition between sintering and crystallization can be tilted in favor of sintering by using rapid heating.158 Quantitative prediction of the thermal history needed to obtain densification before crystallization requires knowledge of the nucleation and growth rates within the gel matrix; unfortunately, very little is known about the mechanisms of nucleation and growth in gels.

The Molecular Building Block Approach. Sol–gel-derived oxides can be tailored on a macroscopic size scale since gelation, aging, and drying can usually be achieved with retention of the overall macroscopic shape assumed by the material upon gelation, be it a fiber, a thin film, or a monolith. Tailoring on a microscopic size scale is far more difficult since these materials are structurally disordered on the molecular size scale. Oxide molecular sieves, on the other hand, can be tailored on the microscopic size scale in terms of micro- and mesoporosity (see above) but are virtually impossible to tailor on the macroscopic size scale due to their crystallinity. The molecular building block approach to sol–gel-derived oxides159,160 combines the advantages associated with traditional sol–gel-derived oxides and oxide molecular sieves by tailoring properties on both the microscopic and macroscopic size scales. In this approach, sol–gel processing techniques are employed to polymerize molecular oxide alkoxides designed to influence the properties of the sol–gel-derived material much in the same way that monomers employed in organic polymerizations are designed to influence the properties of the resin or polymer obtained. For example, porous materials require mechanically rigid framework structures, and precursor molecules containing mechanically rigid core structures are in principle suitable molecular building blocks for this type of extended framework.

Specifically, the \([\text{Si}_8\text{O}_{12}]\) precursor molecule161 has a rigid \([\text{Si}_8\text{O}_{12}]\) cage core structure, and the \([\text{Ti}_{16}\text{O}_{16}]\) \((\text{OC}_2\text{H}_8)_6\) precursor molecule162 has \([\text{Ti}_{16}\text{O}_{16}]\) core structure where oxygen atoms are closest-packed and titanium atoms occupy octahedral interstices. The influence of the molecular building block employed extends beyond the local structure of sol–gel-derived oxides, however, since the nature of the molecular precursor also influences the molecular growth pathway followed during sol–gel polymerization. In traditional sol–gel processing, porosity can be tailored by manipulating the size distribution and structure of the primary particles formed by hydrolysis/condensation of simple alkoxides, but since a variety of different primary particles is formed regardless of the processing conditions employed, pore size distributions and pore shapes can be only crudely tailored at the molecular level. In the molecular building block approach, a single molecular entity can serve as the primary particle during sol–gel polymerization, and as a result, the meso- and microstructural homogeneity of sol–gel-derived oxides can be tailored.

A necessary condition for successful implementation of the molecular building block approach is stability of the molecular building block employed under sol–gel processing conditions. If the molecular structure of the precursor molecule employed is to influence the porosity of the sol–gel-derived oxide ultimately obtained, the core structure of the precursor molecule must remain largely intact in the final product. The issue of molecular building block stability was first explored in a comparative study of \(\text{Si}(\text{OCH}_3)_4\) and \([\text{Si}_8\text{O}_{12}]\)(\text{OCH}_3)_6\) sol–gel polymerization. During the early stages of sol gel processing, hydrolysis of \(\text{Si}(\text{OCH}_3)_4\) and condensation of the resulting SiOH groups yields a family of low molecular weight polysilicates that have been identified using gas chromatography coupled with mass spectrometry (see Figure 10).163–165 None of these low molecular weight polysilicates were observed upon hydrolysis/
condensation of $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$, nor were any of the Si–O–Si siloxane bonds in the $[\text{Si}_8\text{O}_{12}]$ core of $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$ or its hydrolysis products attacked under these conditions. Comparative $^{29}\text{Si}$ MAS NMR studies of Si-(OCH$_3$)$_4$-derived and $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$-derived xerogels gave evidence for a barely measurable amount of cage degradation in the $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$-derived material, suggesting that the cubic $\text{Si}_8\text{O}_{12}$ core was largely intact in the final material. As expected, the properties of Si-(OCH$_3$)$_4$-derived and $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$-derived xerogels were quite different, with apparent BET surface areas of 510 and 919 m$^2$ g$^{-1}$, respectively, when the materials were processed under similar conditions. These differences in porosity could be interpreted structurally from transmission electron micrographs of platinum replicated xerogels of the type shown in Figure 11, where silica appears as a white image against a black background. Micrographs obtained from replicas of $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$-derived xerogels (see Figure 11a) show uniformly sized silica structures and pores relative to the broader size distribution of silica structures and pores in micrographs of replicas obtained from Si-(OCH$_3$)$_4$-derived xerogels (see Figure 11b). Moreover, the silica features observed in micrographs of $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$-derived xerogels are on average thicker than the corresponding features in micrographs of Si-(OCH$_3$)$_4$-derived xerogels. The electron micrographs therefore support a model for $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$ sol–gel polymerization where polymers of the structurally rigid cubic precursor are themselves rigid relative to Si-(OCH$_3$)$_4$-derived polymers and therefore undergo less cyclization and cross-linking during all stages of sol–gel processing, ultimately yielding more uniformly sized silica structures and pores in the xerogel. In the case of Si-(OCH$_3$)$_4$-derived xerogels, smaller silica structures are not observed as the result of using a smaller molecular building block. Instead, the conformational flexibility of Si-(OCH$_3$)$_4$-derived polysilicate chains allows for extensive cyclization and leads to the observed clustering of silicate chains into larger and more irregularly shaped silica structures.

The role played by molecular building blocks as primary particles during the exponential growth stage of sol–gel polymerization has been explored in the titania system, where stable molecular building blocks are available that are considerably larger than those available in the silica system and thus more amenable to study using dynamic light scattering. In the titania system, the course of titania sol–gel polymerization can also be monitored using $^{17}$O NMR spectroscopy in solution and the solid state due to the large, >400 ppm chemical shift range observed for oxygen nuclei in...
Organically Modified Oxide Gels. By replacing one of the four reactive groups on a silica precursor SiX₄ with an organic group R, an organosilicon monomer RSiX₃ (R = alkyl, aryl, alkenyl), is obtained in which the organic group is attached to the silicon atom through a Si–C bond that is stable under sol–gel processing conditions. Incorporation of the organic functionality offers the opportunity to modify the physical properties of the final xerogel both directly, by organically modifying the gel, and indirectly, through the influence of the organic group on the reaction pathways followed during sol–gel processing. In theory, hydrolysis/condensation of an organosilicon alkoxide precursor RSiX₃ as in reaction 8 should afford an organically modified silica gel under the same reaction conditions employed to form silica from the corresponding Si(OR)₄ precursor as in reaction 4. In practice, (RSiO₁.₅)ₙ polyorganosilsesquioxane gels are readily obtained only from the polymerization of methyltrialkoxyxilanes. Silsesquioxane monomers with more sterically bulky substituents rarely lead to gels under conventional sol–gel processing conditions. Instead, lower molecular weight, soluble materials known as organosilsesquioxane resins are formed. Polysilsesquioxane gels can be prepared, however, under emulsion polymerization conditions, i.e., heterogeneous polymerization of the monomers in aqueous dispersions. Under these conditions, gelation rates still decrease with increasing steric bulk of the organic substituent. Interestingly, mesopore size in the xerogels increases with increasing size of the organic functionality in the order methyl, vinyl, phenyl.

Some of the difficulties associated with sol–gel polymerization of simple organosilicon precursors RSiX₃ can be circumvented by using polyfunctional precursors in which two or more triethoxysilyl groups are bonded to a single arylene, alkenylene, or acetylene bridging group as shown in Scheme 2. In almost all cases, these monomers produce bridged polysilsesquioxane gels in minutes to hours under sol–gel processing conditions. For example, arylene-bridged gels form so readily at high monomer concentrations (> 1.8 M) that gelation occurs before the solution can be completely mixed. At lower monomer concentrations, 1,4-phenylene-bridged gels can be prepared in alcohols, tetrahydrofuran, toluene (using surfactants and phase transfer catalysts), and even in supercritical carbon dioxide. Longer gelation times are observed with alkylene-bridged 1,2-ethylene, 1,3-propylene, and 1,4-butylene precursors that form less reactive cyclic disilsesquioxanes under acidic conditions and with the sterically congested and unreactive 4,5-bis(triethoxysilyl)norborn-2-ene precursor.

Bridged polysilsequioxane xerogels based on rigid arylene, ethenylene, or acetylene bridging groups are high surface area, microporous materials. For example, 1,4-phenylene-bridged xerogels exhibit type I Ar adsorption isotherms and have apparent BET surface areas approaching 1000 m²/g, indicating significant microporosity. Arylene-bridged aerogels prepared by supercritical carbon dioxide extraction retain this microporosity but in addition have significant mesoporosity, leading
to apparent BET surface areas as high as 1865 m$^2$/g.\textsuperscript{182} The surface areas and porosities of bridged polysilsesquioxane xerogels based on flexible alkylene bridging groups are dependent upon the length of the bridging group employed. This effect has been examined in a series of alkylene-bridged gels with bridging groups, ranging from ethylene to tetradecylene, that were prepared under acidic and basic conditions and then dried both under supercritical conditions and evaporatively. The aerogels were all mesoporous materials with surface areas between 100 and 1000 m$^2$/g that exhibited significant shrinkage during drying despite the supercritical conditions.\textsuperscript{183} In contrast, mesoporosity was observed in xerogels prepared under acidic conditions only when alkylene bridging groups shorter than the butylene group were employed and in xerogels prepared under basic conditions only when alkylene bridging groups shorter than the tetradecylene group were employed.\textsuperscript{176a,184} In each case, longer alkylene bridging groups gave materials that were nonporous to nitrogen and, in the case of the hexylene bridging groups under acidic conditions, carbon dioxide. In addition, pore sizes determined for the base-catalyzed gels exhibited a direct dependence on length of the bridging group. The porosities of bridged silsesquioxane is most simply related to the nature of the bridging group in terms of the structural rigidity of the bridging group. Presumably, rigid arylene bridging groups not only inhibit the formation of small cyclic structures but also produce relatively noncompliant networks, such that collapse of porosity is inhibited during drying. In the case of the more flexible alkylene bridging groups, collapse of porosity during drying may be due to the greater compliance of the less condensed, acid-catalyzed materials employing linear alkylene bridging groups containing more than six carbon atoms. The gels prepared using base catalysts exhibit higher degrees of condensation such that longer alkylene bridging groups are needed to make the gels compliant enough for collapse of porosity during drying.

Several strategies have been used in attempts to modify the organosilsesquioxane gels using secondary chemical processes. One successful approach involves preparing a porous or nonporous xerogel and using the organic bridging group as a pore template. By taking advantage of the differences in thermal and chemical stabilities between the siloxane and organic components of these gels it is possible to selectively liberate part or all of the organic group. This strategy has been successfully applied to organosilsesquioxane polymers by thermally oxidizing pendant organic groups to generate microporous materials.\textsuperscript{185} Similarly, alkylene and arylene bridging groups can be selectively removed using a low temperature inductively coupled oxygen plasma to burn away the organic components and leave behind porous silica gels (Scheme 3).\textsuperscript{186} When nonporous alkylene-bridged xerogels are used, the mean pore size is proportional to the length of the bridging alkylene group. Not only can porous silica gels be generated with some degree of control over porosity, but information concerning the organic domain can be obtained through characterization of the pores.

Organic bridging or pendant groups can also provide platforms for attaching functional groups that can act as metal ligands and provide additional reversible, bonding interactions with which to organize the growing polymer before gelation occurs. Several groups have used amino- and mercapto-functionalized alkyltriethoxysilanes to bind metal centers and generate siloxane gels with homogeneously dispersed metal clusters.\textsuperscript{187,188} Formation of coordination complexes with a single metal or metal cluster using several precursor molecules potentially permits the self-assembly of a bridged silsesquioxane before or during the sol–gel polymerization. Complexation of metals using pendant or bridging groups containing olefinic\textsuperscript{188,189} or acetylenic\textsuperscript{190} functionalities is another successful strategy for changing the sol–gel chemistry. Corriu was able to show significantly faster gelation times with a 2-butenylene-bridged precursor in the presence of palladium(II) salts.\textsuperscript{189} Similarly, palladium salts have been shown to decrease gel times in ethylene-bridged systems by over 3 orders of magnitude.\textsuperscript{191} This chemistry is complicated by the reduction of palladium(II) salts to palladium(0) nanoclusters driven by the oxidation of ethanol liberated during the sol–gel polymerization. However, rhodium and ruthenium salts can also used to coordinately reduce gelation rates for the ethylene-bridged monomer while still in the mononuclear form.\textsuperscript{191}

**Porous Heteropolyanion Salts**

Heteropolyanions are large, anionic metal oxide clusters whose salts are often porous materials.\textsuperscript{192,193} Because certain heteropolyanion salts are thermally stable and chemically reactive, porous heteropolyanion salts have attracted much attention as heterogeneous catalysts.\textsuperscript{193,194} The structures of heteropolyanion salts are well-defined on three levels of organization: primary, secondary, and tertiary. As shown for the phosphotungstate anion [PW$_{12}$O$_{40}$]$^{3-}$ in Figure 12, the molecular structure of a heteropolyanion defines the primary structure, and the secondary structure is defined by the arrangement of the heteropolyanions, the countercations, plus any other constituent molecules in three-dimensional space. Small crystallites of heteropolyanion salts sometimes serve as primary particles that aggregate into secondary particles, and this arrangement defines the tertiary structure. With respect to the pore structure, the tertiary structure is important, since the polyanion framework (primary structure) is only 1–1.5 nm in size and usually nonporous. The secondary structure is as a rule also nonporous. Hence, pores are formed in the space between the primary particles of aggregates. Salts of the so-called Keggin-type heteropolyanions [$X$(Mo$_{6}$O$_{19}$)$^{3-}$ and Dawson-type heteropolyanions [$X$(Mo$_{10}$O$_{37}$)]$^{9-}$ are the most thoroughly studied heteropolyanion salts and the former have found large-scale industrial application as heterogeneous catalysts.\textsuperscript{195}

Heteropolyanion salts are known to display two fundamentally different types of adsorption and are classified accordingly as A-class and B-class salts.\textsuperscript{196} A-class salts are water-soluble compounds, containing
small monovalent or multivalent cations such as Na\(^+\), H\(^+\), or Ni\(^{2+}\), and are nonporous and low surface area solids in terms of their ability to sorb nitrogen. However, these solids exhibit unique “pseudoliquid” absorption behavior toward polar molecules that plays an important role in catalysis. B-class salts contain cations such as Cs\(^+\), K\(^+\), and NH\(_4^+\) and are water-insoluble. These materials have high porosity in terms of surface areas derived from nitrogen gas sorption isotherms.

**Pseudoliquid-Phase Behavior.** Large amounts of polar materials such as alcohols and amines are absorbed stepwise as a function of partial pressure into the solid bulk of A-class salts such as H\(_3\)PW\(_{12}\)O\(_{40}\)\(^-\), either reversibly or irreversibly, while only small amounts of nonpolar materials such as hydrocarbons and N\(_2\) are adsorbed, and these are adsorbed only on the surface of the heteropolyanion salt. This polarity- (or basicity-) selective sorption into the ionic heteropolyanion salt lattice sometimes results in expansion of the lattice dimensions. In the case of ethanol absorption by the polyacid H\(_3\)PW\(_{12}\)O\(_{40}\), NMR studies have shown that both the proton and alcohol mobilities as well as the rate of proton exchange between the polyacid and absorbed alcohol increase as the number of adsorbed alcohol molecules increases.\(^{198}\) In the case of pyridine (py) absorption by H\(_3\)PW\(_{12}\)O\(_{40}\), single-crystal XRD\(^{199}\) and infrared spectroscopic studies have shown that stable stoichiometric crystalline salts H\(_3\)PW\(_{12}\)O\(_{40}\)-6py are formed in which py-H\(^+\)-py groups are present.

**Pore Structure of Cs and NH\(_4\) Salts.** The surface areas of H\(_3\)PW\(_{12}\)O\(_{40}\) and its sodium salt are low and both materials show type II nitrogen adsorption isotherms, reflecting their nonporous nature. The B-class acidic cesium salts of H\(_3\)PW\(_{12}\)O\(_{40}\) or Cs\(_x\)H\(_3\)\(_3\)\(_x\)PW\(_{12}\)O\(_{40}\) or Cs\(_x\), display very different behavior.\(^{200}\) Here, surface area increases rapidly when x > 2 and reaches 150–170 m\(^2\) g\(^{-1}\) when 2.5 < x < 3.0. The isotherms for x > 2.3 show the presence of mesopores in the region of 3–6 nm in addition to increased porosity in the micropore region. The size of these pores changes with x, indicating that the pore size can be controlled. As a result, shape-selective adsorption and catalysis is observed for several liquid-phase reactions catalyzed by Cs\(_x\).\(^{200,201}\)

The adsorption of different gas phase probe molecules by Cs\(_x\) has also been used to demonstrate that the size of micropores in Cs\(_x\) increases gradually with increasing x.\(^{201}\) As shown in Table 3, the average micropore diameter is ~0.59 nm for Cs\(_{2.1}\), 0.62–0.75 nm for Cs\(_{2.2}\), and >0.85 nm for Cs\(_{2.5}\). BJH and HK analyses for meso- and micropores, respectively, are in semiquantitative agreement with these results. Phosphorus-31 NMR spectra of Cs\(_x\) display four resonances which have been assigned to the polyanions associated with 0, 1, 2, and 3 protons, respectively. As the relative intensities of the four lines agree with the statistical distribution in accordance with the x value, the salts are seen to be nearly uniform solid solutions of H\(_3\)PW\(_{12}\)O\(_{40}\) and Cs\(_3\)PW\(_{12}\)O\(_{40}\). Particle sizes estimated from surface area by assuming spherical primary particles were comparable with those estimated from XRD line widths only when x > 2.2; the first estimate greatly exceeded the second for x = 1 and 2.

Another interesting feature of B-class salts is the epitaxial self-assembly of primary particles leading to tertiary structure of the type shown in Figure 12. In the case of [PW\(_{12}\)O\(_{40}\)]\(^-\) precipitated as an ammonium salt or as a cesium salt at elevated temperatures, dodecahedra having similar size have been observed by

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**Figure 12.** (From left to right) Primary, secondary, and tertiary structures of heteropolyanion compounds. (Reprinted with permission from ref 193. Copyright 1996 Academic Press, Inc.)
SEM to be composed of primary particles 10–20 nm in size (see Figure 13). The BET surface areas measured for these materials were much greater than those estimated from the dodecahedra observed by SEM, showing that the dodecahedra are porous and the particles seen by SEM are secondary particles. However, the particle size estimated from the XRD line width was close to that observed in the SEM photographs and much greater than those calculated using BET theory. This is in contrast to CsX case, x > 2.2, described above, indicating that the crystal planes of the primary particles (crystallites) observed by SEM are aligned, making the secondary particles more or less like a porous single crystal. Electron diffraction patterns were in agreement with this idea. A possible explanation for the formation of an epitaxial interface between primary particles is that reorientation of the microcrystalline primary particles, accompanied by slight dissolution at the outer surface, can take place during the assembly of preformed microcrystallites. In this case, solubility is the key factor controlling the self-assembly process.

### Research Needs and Opportunities

The tailoring of porous materials poses a broad challenge that is perhaps best appreciated by considering the range of applications where specific types of new porous materials are needed for use in devices or systems that perform specific functions. Examples include shape-selective gas or liquid permselective membranes, catalytic membrane reactors, energy storage systems such as batteries, and on a longer time scale, molecular electronic and electrooptic devices as well as biomolecule separation, isolation, and delivery. These applications will require tailoring not only on the molecular size scale, the domain of chemical synthesis, but also on the meso- and macroscopic size scale, the domain of materials processing. For example, porous carbons are difficult to tailor on the molecular size scale, but they can be processed into the specific geometries required for different applications. In contrast, oxide molecular sieves with specific pore sizes and shapes are available for specific applications, but they are easily obtained only as micrometer-sized crystals. For the fabrication of truly shape-selective membranes, molecular sieve materials should ideally be available as very thin (0.1–10 µm) films over surface areas of one to several square meters where micro- or mesopores are all aligned in the direction of the permeating flow.

Many scientific and technological problems must be addressed before porous materials can be tailored to the same extent possible with other important classes of engineering materials such as semiconductors, dielectric ceramics, organic polymers, and metallic alloys. Historically, these problems have been addressed by focusing on specific types of materials such as molecular sieves or porous carbons or specific applications such as gas separation or catalysis rather than investigating the fundamental scientific issues involved. Research opportunities addressing these issues are the focus of attention in this section, since resolution of fundamental scientific issues will impact a broad range of materials and applications.

Perhaps the most fundamental issue involved in tailoring porous materials is the nature of adsorbent–adsorbate interactions and the relationship between these interactions and sorption kinetics and thermodynamics. The nature of relatively "simple" adsorbent–adsorbate interactions involving electrostatic forces in heteroatom-substituted zeolites is not well understood, and far more complex interactions must be considered in coordination solids that show chemical selectivity for specific types of molecules such as aromatics or specific molecules such as oxygen. The use of effective intermo-

### Table 3. Sorptive Properties of CsX, X = 2.1, 2.2, and 2.5

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Diameter ( \AA )</th>
<th>( \text{CsX} )</th>
<th>( \text{CsX} )</th>
<th>( \text{CsX} )</th>
<th>( \text{CsX} )</th>
<th>( \text{CsX} )</th>
</tr>
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<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>3.6</td>
<td>487</td>
<td>861</td>
<td>1648</td>
<td>0.30</td>
<td>0.52</td>
</tr>
<tr>
<td>( \text{C} - \text{C} - \text{C} )</td>
<td>5.9</td>
<td>10</td>
<td>124</td>
<td>232</td>
<td>0.04</td>
<td>0.53</td>
</tr>
<tr>
<td>( \text{C} - \text{C} - \text{C} )</td>
<td>6.2</td>
<td>5</td>
<td>179</td>
<td>390</td>
<td>0.01</td>
<td>0.46</td>
</tr>
<tr>
<td>( \text{C} - \text{C} - \text{C} )</td>
<td>7.5</td>
<td>-</td>
<td>11</td>
<td>237</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>( \text{C} - \text{C} - \text{C} )</td>
<td>8.5</td>
<td>-</td>
<td>15</td>
<td>236</td>
<td>-</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Figure 13. Scanning electron micrograph of \((\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}\) precipitated at 368 K.

SEM to be composed of primary particles 10–20 nm in size (see Figure 13). The BET surface areas measured for these materials were much greater than those estimated from the dodecahedra observed by SEM, showing that the dodecahedra are porous and the particles seen by SEM are secondary particles. However, the particle size estimated from the XRD line width was close to that observed in the SEM photographs and much greater than those calculated using BET theory.
Molecular potentials remains an important aspect of molecular modeling, and a careful assessment of the accuracy of such approaches along the lines of Pellonq and Nicholson should prove to be useful starting point. Improvements in quantum mechanical methods also offer promise in this area as do the development of new experimental techniques which directly probe adsorbent–adsorbate interactions. New molecular simulation techniques and new statistical mechanical theories are also emerging that allow for improved modeling of sorption kinetics and thermodynamics. Further development and application of nonequilibrium molecular dynamics techniques offer the prospect of better understanding transport processes known to be important in kinetics-based adsorption separations. This prospect is particularly relevant to multicomponent adsorption and surface diffusion in carbon molecular sieve membrane separations where the influence of pressure, temperature, and pore structure on selectivity is poorly understood and therefore difficult to control. Future progress in statistical mechanical theories such as density functional theory should lead to a better understanding of the behavior of complex adsorbates such as chain molecules as well as adsorbents having complex pore geometries and disordered structures. Further developments in molecular modeling techniques for adsorbents that behave as deformable solids or even undergo adsorbate-induced phase transitions should also be anticipated.

Zeolites, mesoporous molecular sieves, and sol–gel-derived oxides are all prepared from oxide gels, and advances in the processing of these materials will require a better physical understanding of how porosity evolves in gels and in porous materials that crystallize from gels. Most notably, the mechanism of nucleation and growth of ordered domains in gels has not been adequately explored. The challenge here is to develop effective in situ techniques that will allow systematic studies of local ordering and nucleation rates as a function of synthesis and processing conditions. There is a particular need to study the detailed role of templating agents, especially in nonsilicic systems. During sol–gel processing, the mechanical properties of a gel can also influence the evolution of its pore structure and these mechanical properties are controlled by the gel’s network structure. No methods are currently available, however, for measuring the connectivity of the network. Improved modeling and measurement techniques are also needed to understand the rigidity of gel networks. Several models exist that explain the power-law dependence of the modulus on the density, but they have not yet been adequately tested by obtaining data on the structure and the mechanical properties of the same samples. Improved models are needed to explore the mechanism of pore formation in such cases. These considerations are particularly important for the development of size-selective membranes.

Molecular design of noncrystalline, porous materials raises the general question of how porosity can be tailored through controlled polymerization of well-defined molecular building blocks. In general, the structural evolution of the inorganic polymers on the molecular level requires study beyond the oligomeric stages that are easily probed spectroscopically, possibly using mass spectrometry, chromatography, scattering techniques, and high field nuclear magnetic resonance techniques. Continued efforts to use new chemistry to preorganize monomers reversibly before cross-linking takes place may bring a higher degree of control over porosity in these materials and possibly provide improved mechanical properties by allowing the reversible bonds to rearrange and permit maximum connectivity to be achieved in the ultimate product. It may be possible in this fashion to achieve the goal of preparing tailored materials that are sufficiently ordered over short distances to serve as selective adsorbents but sufficiently disordered over long distances to avoid crystallization and thus remain processible.

Tremendous advances have been made in tailoring the porosity of oxide molecular sieves and porous carbons in terms of size and shape selectivity. Relatively little progress has been achieved, however, in terms of chemoselectivity, that is, selectivity for specific molecules or functional groups based on their chemical reactivity as opposed to their physical size or shape. The incorporation of active sites into these materials is therefore a high priority. Other classes of materials such as porous coordination solids, sol–gel-derived oxides, and porous heteropolyanion salts offer great promise in this regard since they can be prepared from well-defined molecular precursors containing a variety of metal and nonmetal centers under relatively mild conditions. To date, impressive results have been obtained with porous coordination solids by using π–π stacking interactions to achieve selective binding of aromatic hydrocarbons and metal–ligand interactions to achieve selective binding of oxygen molecules and organic alcohols. There is tremendous potential for expanding this type of chemoselectivity where coordinatively unsaturated metal centers, hydrogen bond acceptors, hydrogen bond donors, or virtually any type of active sites are incorporated into the framework of a porous material: incoming guest molecules must not only have the appropriate shape and size but also the required affinity for the active sites present. Analogous materials with charged frameworks capable of reversible ion exchange also offer opportunities for achieving chemoselectivity by tailoring cation or anion binding sites to create an affinity for specific anions or cations.

Given the wide variety of porous materials that are currently available, it is hardly surprising that most current research devoted to tailoring porous materials is concerned with development of known routes to porous materials rather than exploration of entirely new approaches. Nonetheless, there is a pressing need to reach beyond the traditional techniques generally associated with the synthesis and processing of porous materials, that is, hydrothermal treatment, gel crystallization, coordination polymerization, gelation, pyrolysis, and precipitation. Exploration of entirely new approaches to the preparation porous materials promises to open up new research opportunities for tailoring porous materials, both new materials and old materials.

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Chemistry

Comprehensive Supramolecular

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E.; Petroff, P. M.; Schüth, F.; Stucky, G. D.


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Over the years, MCM-41 has been used in various applications. For example, it has been used in catalytic processes like the conversion of ethylene into ethane and as a support for metal catalysts such as palladium. The porosity and surface area of MCM-41 make it an ideal material for many applications, including adsorption, separation, and catalysis. The mesoporous structure of this material allows for the easy access of reactants and products, which is crucial for efficient catalytic reactions.

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