

Chapter 4

High Surface Area Materials

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INTRODUCTION

The trend to smaller and smaller structures, that is, miniaturization, is well known in the manufacturing and microelectronics industries, as evidenced by the rapid increase in computing power through reduction on chips of the area and volume needed per transistor (Roher 1993). In the materials area this same trend towards miniaturization also is occurring, but for different reasons. Smallness in itself is not the goal. Instead, it is the realization, or now possibly even the expectation, that new properties intrinsic to novel structures will enable breakthroughs in a multitude of technologically important areas (Siegel 1991; Gleiter 1989).

Of particular interest to materials scientists is the fact that nanostructures have higher surface areas than do conventional materials. The impact of nanostructure on the properties of high surface area materials is an area of increasing importance to understanding, creating, and improving materials for diverse applications. High surface areas can be attained either by fabricating small particles or clusters where the surface-to-volume ratio of each particle is high, or by creating materials where the void surface area (pores) is high compared to the amount of bulk support material. Materials such as highly dispersed supported metal catalysts and gas phase clusters fall into the former category, and microporous (nanometer-pored) materials such as zeolites, high surface area inorganic oxides, porous carbons, and amorphous silicas fall into the latter category.

There are many areas of current academic and industrial activity where the use of the nanostructure approach to high surface area materials may have significant impact:

- microporous materials for energy storage and separations technologies, including nanostructured materials for highly selective adsorption/separation processes such as H₂O, H₂S, or CO₂ removal; high capacity, low volume gas storage of H₂ and CH₄ for fuel cell applications and high selectivity; high permeance gas separations such as O₂ enrichment; and H₂ separation and recovery
- thermal barrier materials for use in high temperature engines
- understanding certain atmospheric reactions
- incorporation into construction industry materials for improved strength or for fault diagnostics
- battery or capacitor elements for new or improved operation
- biochemical and pharmaceutical separations
- product-specific catalysts for almost every petrochemical process

In catalysis the key goal is to promote reactions that have high selectivity with high yield. It is anticipated that this goal will be more closely approached through tailoring a catalyst particle via nanoparticle synthesis and assembly so that it performs only specific chemical conversions, performs these at high yield, and does so with greater energy efficiency. In the electronics area one may anticipate manufacture of single electron devices on a grand scale. Manufacture of materials with greatly improved properties in one or more areas such as strength, toughness, or ductility may become commonplace. In separations science new materials with well defined pore sizes and high surface areas are already being fabricated and tested in the laboratory for potential use in energy storage and separations technologies. In addition, many laboratories around the world are actively pursuing the potential to create novel thermal barrier materials, highly selective sensors, and novel construction materials whose bonding and strength depend upon the surface area and morphology of the nanoscale constituents. Many are also engaged in developing molecular replication technologies for rapid scaleup and manufacturing.

The nanoscale revolution in high surface area materials comes about for several reasons. First, since the late 1970s the scientific community has experienced enormous progress in the synthesis, characterization, and basic theoretical and experimental understanding of materials with nanoscale dimensions, i.e., small particles and clusters and their very high surface-to-volume ratios. Second, the properties of such materials have opened a third dimension to the periodic table, that is, the number of atoms, N (for a recent example see Rosen 1998). N now becomes a critical parameter by which the properties for “small” systems are defined. As a simple example, for metals

we have known for decades that the atomic ionization potential (IP) is typically about twice the value of the bulk work function (Lide 1993). It is only relatively recently that experiments have shown that the IP (and electron affinity) for clusters containing a specific number N of (metal) atoms varies dramatically and non-monotonically with N for clusters containing less than 100-200 atoms. (For examples see Taylor et al. 1992; Rademann et al. 1987; and Rohlfing et al. 1984.) Other properties such as chemical reactivity, magnetic moment, polarizability, and geometric structure, where they have been investigated, are also found to exhibit a strong dependence on N . Expectations for new materials with properties different from the atom or the bulk material have been realized (e.g., see Jena 1996 and reports therein). The opportunity is now open to precisely tailor new materials through atom-by-atom control of the composition (controlling the types as well as the numbers of atoms) in order to generate the clusters or particles of precision design for use in their own right or as building blocks of larger-scale materials or devices—that is, nanotechnology and fabrication at its ultimate.

Such precision engineering or tailoring of materials is the goal of much of the effort driving nanoscale technology. Scientists and engineers typically have approached the synthesis and fabrication of high surface area nanostructures from one of two directions:

1. The “bottom up” approach in which the nanostructures are built up from individual atoms or molecules. This is the basis of most “cluster science” as well as crystal materials synthesis, usually via chemical means. Both high surface area particles and micro- and mesoporous crystalline materials with high void volume (pore volume) are included in this “bottom up” approach.
2. The “top down” approach in which nanostructures are generated from breaking up bulk materials. This is the basis for techniques such as mechanical milling, lithography, precision engineering, and similar techniques that are commonly used to fabricate nanoscale materials (see Chapter 6), which in turn can be used directly or as building blocks for macroscopic structures.

A fundamental driving force towards efforts to exploit the nanoscale or nanostructure is based upon two concepts or realizations: (1) that the macroscopic bulk behavior with which we are most familiar is significantly different from quantum behavior, and (2) that materials with some aspect of quantum behavior can now be synthesized and studied in the laboratory. Obviously, quantum behavior becomes increasingly important as the controlling parameter gets smaller and smaller. There are numerous examples of quantum behavior showing up in high surface materials: the fact introduced above that clusters are found to exhibit novel (compared to the

bulk) electronic, magnetic, chemical, and structural properties; the fact that the diffusivity of molecules through molecular sieving materials cannot be predicted or modeled by hard sphere molecule properties or fixed wall apertures; and the fact that catalysts with one, two, or three spatial dimensions in the nanometer size range exhibit unique (compared to the bulk) catalytic or chemical activity.

OPPORTUNITIES FOR CLUSTERS AND NANOCRYSTALLINE MATERIALS¹

Clusters are groups of atoms or molecules that display properties different from both the smaller atoms or molecules and the larger bulk materials. Many techniques have been developed to produce clusters, beams of clusters, and clusters in a bottle (see Chapter 2) for use in many different applications including thin film manufacture for advanced electronic or optical devices (see Chapters 3 and 5), production of nanoporous structures as thermal barrier coatings (Chapter 3), and fabrication of thin membranes of nanoporous materials for filtration and separation (see Chapters 3 and 7). Figure 4.1 depicts an apparatus developed at the University of Göteborg to measure cluster reactivity and sticking probability as a function of the number of metal atoms in the cluster.

The unique properties of nanoparticles make them of interest. For example, nanocrystalline materials composed of crystallites in the 1-10 nm size range possess very high surface to volume ratios because of the fine grain size. These materials are characterized by a very high number of low coordination number atoms at edge and corner sites which can provide a large number of catalytically active sites. Such materials exhibit chemical and physical properties characteristic of neither the isolated atoms nor of the bulk material. One of the key issues in applying such materials to industrial problems involves discovery of techniques to stabilize these small crystallites in the shape and size desired. This is an area of active fundamental research, and if successful on industrially interesting scales, is expected to lead to materials with novel properties, specific to the size or number of atoms in the crystallite.

¹ For examples see conference proceedings such as: ISSPIC 1, *J. Phys.* **38** (1977); ISSPIC 2, *Surf. Sci.* **106** (1981); ISSPIC 3, *Surf. Sci.* **156**, (1985); ISSPIC 4, *Z. Phys. D.* **12**, (1989); ISSPIC 5, *Z. Phys. D.* **19**, (1991); ISSPIC 6, *Z. Phys. D* **26**, (1993); ISSPIC 7, *Surf. Rev. and Lett.* **3**, (1996); ISSPIC 8, *Z. Phys. D.*, (1997). For background information, see Prigogine and Rice 1998; Averbach et al. 1991; Jena et al. 1996; and Chapter 2 of this report.

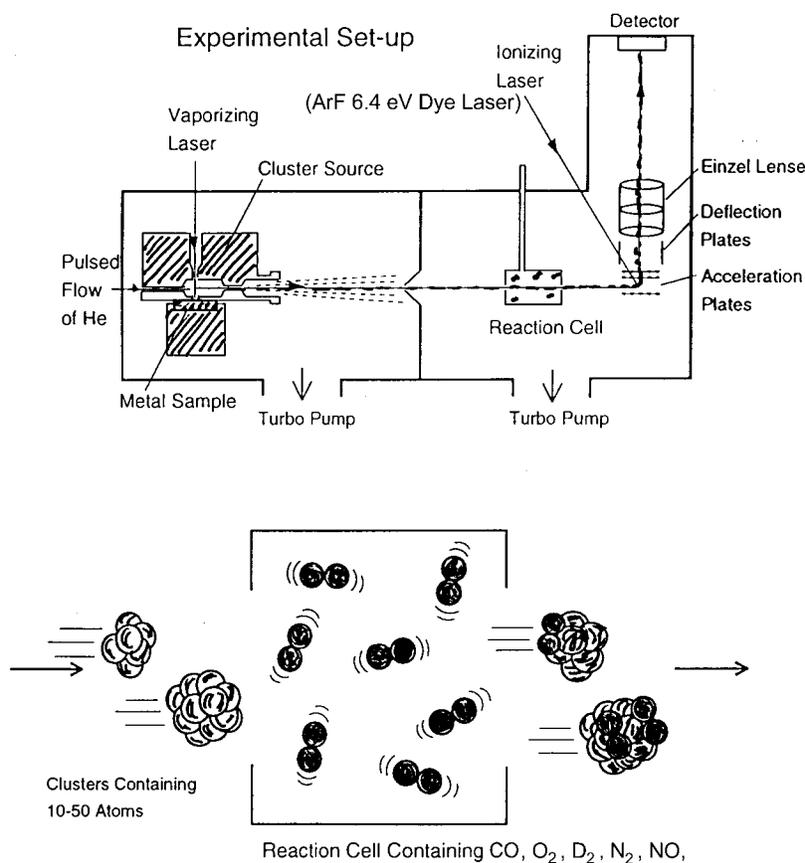


Figure 4.1. Schematic drawing of the experimental setup used in Göteborg for studies of chemical reactivity and/or sticking probability of various molecules with the clusters. The production of clusters is via laser vaporization of metal substrates and detection via photoionization time-of-flight mass spectrometry (A. Rosen, University of Göteborg, Sweden).

A typical objective of nanoscale catalyst research is to produce a material with exceedingly high selectivity at high yield in the reaction product or product state, i.e., chemicals by design, with the option of altering the product or product state simply by changing the surface functionality, elemental composition, or number of atoms in the catalyst particle. For instance, new catalysts with increasing specificity are now being fabricated in which the stoichiometry may be altered due to size restrictions or in which only one or two spatial dimensions are of nanometer size.

Five recent examples where nanocrystalline metallic and ceramic materials have been successfully investigated for catalytic applications are discussed below (Trudeau and Ying 1996).

Novel Catalytic Properties of Nanostructured Gold Catalysts

In the study of transition metal catalytic reactions the group at Osaka National Research Institute has discovered that nanoscale gold particles display novel catalytic properties (Haruta 1997). Highly selective low temperature catalytic activity is observed to switch on for gold particles smaller than about 3-5 nanometers in diameter. Accompanying this turn on in catalytic activity is the discovery that these nanoscale gold particles (crystals) also have icosahedral structure and not the bulk fcc structure, again a nanoscale phenomena not available with bulk samples.

In fabricating these novel catalytic materials several issues appear to be crucial. For instance, the Osaka group has shown that (a) the preparation method plays a crucial role for generating materials with high catalytic activity and selectivity; that (b) the catalytic activity, selectivity and temperature of operation is critically dependent on the choice of catalyst support, and that (c) water (moisture) even in parts per million (ppm) levels dramatically alters the catalytic properties. Figure 4.2 shows the effect of moisture on the conversion profiles for CO oxidation for nanoscale gold catalysts supported on cobalt oxide.

Examples of novel catalytic behavior of nanoscale gold particles include the following:

- CO oxidation at temperatures as low as -70°C , as illustrated in Figure 4.2
- very high selectivity in partial oxidation reactions, such as 100% selectivity at 50°C for oxidation of propylene to propylene oxide as well as near room temperature reduction of nitric oxide with H_2 using alumina-supported gold nanoparticles

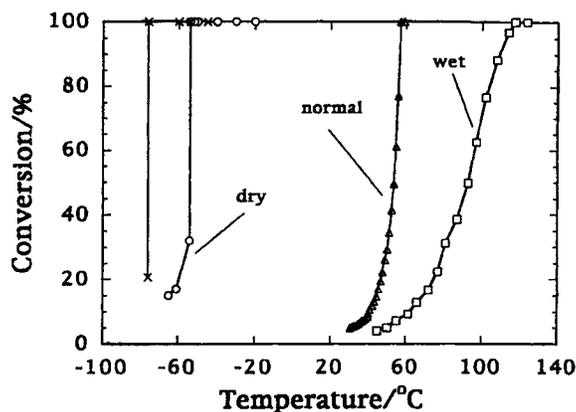


Figure 4.2. Effect of moisture on conversion profiles for CO oxidation over Co_3O_4 and $\text{Au}/\text{Co}_3\text{O}_4$.

The fundamental work on gold catalysts has led to “odor eaters” for the bathroom, based on nanoscale gold catalysts supported on $\alpha\text{-Fe}_2\text{O}_3$, a recent commercialization from Osaka National Research Institute in Japan.

Demonstration of the Importance of Controlling at Least One Dimension in the Nanoscale Size Range for the Industrially Important HDS Reaction²

For catalysts based on the layered compound MoS_2 , maximum hydrodesulfurization (HDS) activity is obtained only on well-crystallized nanosized materials, while HDS selectivity is determined by the number of layers or “stack height” of the nanocrystalline MoS_2 . In the hydrodesulfurization reaction, illustrated in Figure 4.3, cyclohexylbenzene occurs only on the MoS_2 “rim sites,” or those around the edges of the stack, whereas the pathway to biphenyl requires both “rim” and “edge” sites. Thus, the reaction selectivity can be controlled by controlling the aspect ratio of the nanoparticles of MoS_2 . Such control of one- and two-dimensional nanostructures for selective chemical advantage is an exciting new area of research. Of course, a major industrial challenge will be to fabricate such nanocrystals in a commercializable form (Chianelli 1998).

Generation of Nanocrystalline, Non-Stoichiometric CeO_{2-x} by Controlled Post-Oxidation of Cerium Nanoclusters Produced Via Inert Gas Condensation Synthesis³

The cerium oxide (CeO_{2-x}) materials have been found to possess a significant concentration of Ce^{3+} and oxygen vacancies, even after high temperature (500°C) calcination. Such nanoclusters give rise to a substantial reduction in the temperature of selective SO_2 reduction by CO and exhibit excellent poisoning resistance against H_2O and CO_2 in the feed stream compared to that for conventional high surface area cerium oxide.

Electrochemical Reduction of Metal Salts⁴

Electrochemical reduction of metal salts is yet another option available to control the size of nanoscale catalyst particles. This has been successfully used to prepare highly dispersed metal colloids and fix the metal clusters to the substrate. Control of the current density during the electrochemical

² Chianelli et al. 1994

³ Tschope and Ying 1994; Tschope et al. 1995

⁴ Reetz et al. 1995

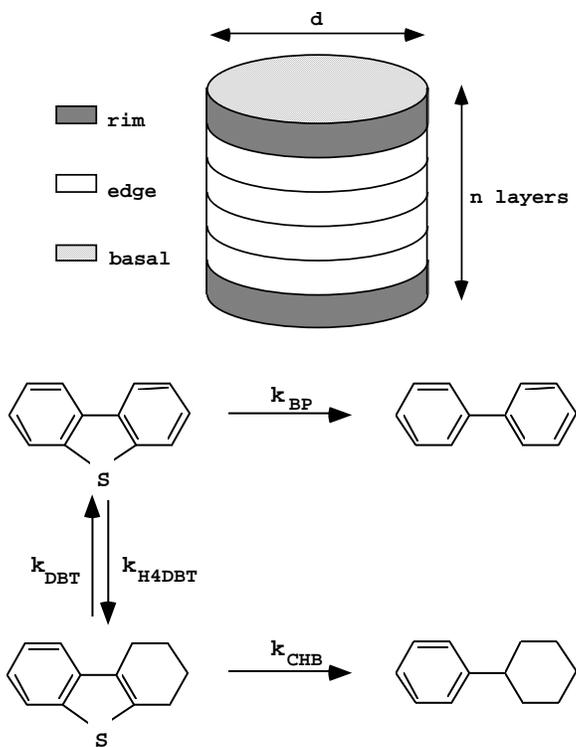


Figure 4.3. Hydrodesulfurization reaction. Selective catalysis is controlled by either the edge or rim of MoS₂ (Chianelli 1998).

synthesis process allows one to control the size of nanoscale transition metal particles. A combination of scanning tunneling microscopy (STM) and high-resolution transmission electron microscopy (TEM) has allowed surfactant molecules to be visualized on nanostructured palladium clusters.

Energy Storage Enhanced by Catalytic Dissociation of H₂

Materials with higher hydrogen storage per unit volume and weight are considered by many to be an enabling technology for vehicular fuel cell applications. Scientists at Los Alamos National Laboratories have developed an approach that enables materials such as Mg to be used for hydrogen storage (Schwartz 1998). Magnesium is of interest because it can store about 7.7 wt % hydrogen, but its adsorption/desorption kinetics are slow, i.e., the rate of charge (hydrogen dissociation and hydride formation) is much slower than in metal hydrides. At Los Alamos, high surface area mixtures of nanoscale Mg and Mg₂Ni particles are produced by mechanical means, ball milling. The addition of Mg₂Ni catalyzes the H₂ dissociation

such that the rate of hydrogen adsorption increases to a rate comparable to that of LaNi_5 . Once a hydride is formed, the hydrogen “spillover” leads to magnesium hydride formation.

Figure 4.4 illustrates the hydrogen adsorption/desorption characteristics of the mixture of Mg with 23 atomic % Ni. As can be seen, a low pressure plateau at about 1500 torr is obtained for this particular sample. Experiments show that the pressure plateau can be tailored through such alloying. Studies with other nanoscale materials, including other catalysts such as FeTi and LaNi_5 , are presently ongoing to further improve both the capacity and the rate of hydrogen storage.

OPPORTUNITIES IN SELF-ASSEMBLY

In self-assembly large molecular structures are obtained from the organization of a large number of molecules or atoms into a given shape, typically through specific interactions of the molecules among themselves and with a template. The interaction of the different bonding mechanisms is an area of strong fundamental research interest. Only two areas will be highlighted here: zeolites and carbon materials. Both of these materials exhibit characteristics of self-assembly, namely novel and reproducible structures that can be fabricated in industrially significant quantities.

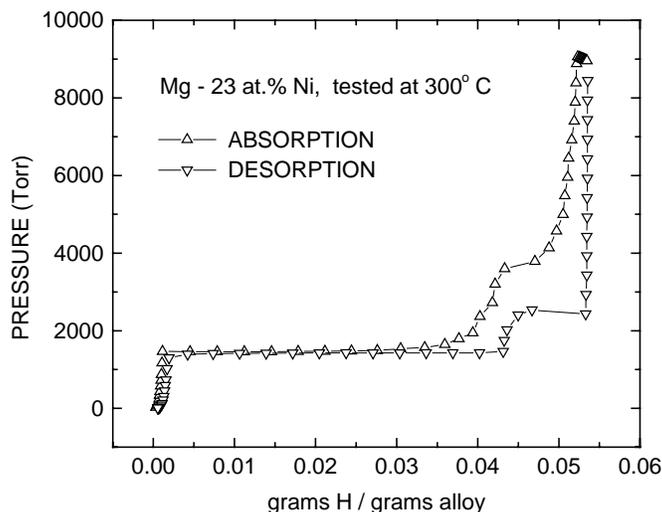


Figure 4.4. Hydrogen absorption-desorption characteristics for mixture of Mg and Mg_2Ni prepared by mechanical alloying.

Zeolitic Materials

Aluminosilicates (e.g., zeolites) are crystalline porous nanostructures with long range crystalline order with pore sizes which can be varied from about 4 Å to 15 Å in conventional zeolites. Figure 4.5 shows a 3-dimensional (e.g., MFI) zeolite cage structure together with a depiction of the straight and ziz-zag channels and a 2-dimensional zeolite with channels only in 2 directions. The vertices in the stick drawing denote position of the O atoms in the crystalline lattice. This particular zeolite has 10 atoms in the zeolite “window.” The size of the window is determined by the number of oxygens in the ring. Table 4.1 gives approximate window dimensions for zeolites as a function of the number of oxygens in the ring.

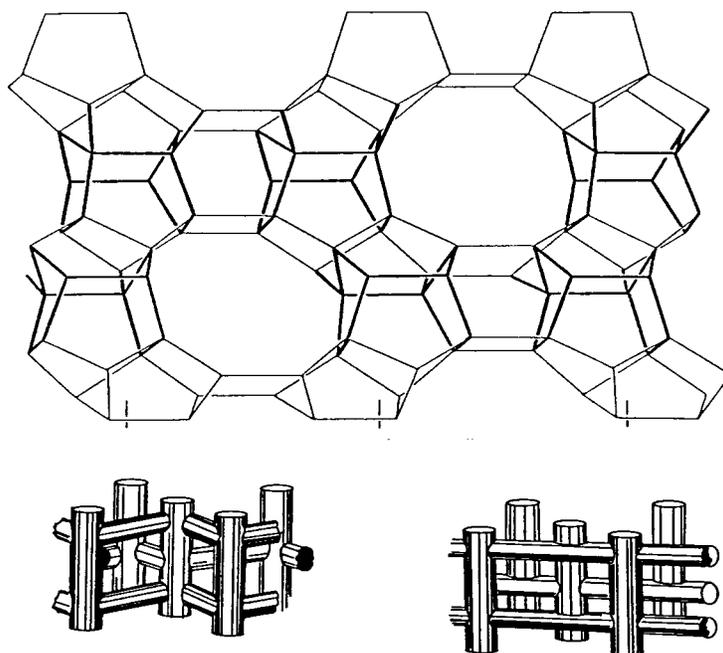


Figure 4.5. Typical zeolite structures together depicting the positions of the O atoms (vertices in upper figure) and two different zeolitic structures one (lower left) with a three dimensional structure and (lower right) a zeolite with a two dimensional channel structure.

TABLE 4.1. Zeolite Channel "Window" Dimension for Number of Oxygens in Ring

Number of Oxygens in Ring	Ring Diameter (Å)
4	1.2
5	2.0
6	2.8
8	4.5
10	6.3
12	8.0

As can be seen by examination of Table 4.1, molecules can pass through or be blocked from transport through or into the zeolite depending on the zeolite. For example normal hexane with a kinetic molecular diameter of about 5.1 Å can pass through a 10 ring or larger, whereas cyclohexane with a kinetic molecular diameter of 6.9 Å would be hard pressed to pass through a 10 ring. Thus all other things being equal, a 10-ring zeolite could be used to separate mixtures of normal hexane and cyclohexane. It is this property together with the ability to chemically modify the acidity of zeolitic materials that makes them extremely valuable as selective sorbants, as membranes and for use in selective catalytic reactions.

In 1992, a new family of aluminosilicates (M41S) with pores sizes between 20 and 100 Å in diameter were reported by Mobil researchers (Beck et al. 1992; Kresge et al. 1992). One of particular interest is MCM-41, which consists of hexagonal arrays of uniform 2 to 10 nanometer-sized cylindrical pores. Not only can such materials be synthesized, but novel structures such as "tubules-within-a-tubule" have been fabricated as mesoporous molecular sieves in MCM-41 (Lin and Mou 1996). Of particular interest is the possibility of expanding the so-called "liquid crystal templating" mechanism (Chen et al. 1993) to non-aluminum dopants within the silicate MCM-41 framework (Tanev et al. 1994) and to derive non-siliceous MCM-41 type of materials (Braun et al. 1996).

Another approach to synthesizing large pore and large single crystals of zeolytic materials is being pioneered by Geoffrey Ozin and his group at the University of Toronto, who have demonstrated that crystals as large as 5 mm can be synthesized (Kupperman et al. 1993). The ability to synthesize such large crystals has important implications for discovery of new sensors (selective chemical adsorbants) and membrane devices (selective transport of molecular species), since large single crystals can now be available to the laboratory researcher to carry out fundamental studies of adsorption and diffusion properties with such materials. These materials are expected to create new opportunities for applications in the fields of separations science, for use directly as molecular sieves or as new molecular sieving sorbant materials; in catalysis, as heterogeneous catalysts; and as supports for other

catalytic materials as well as other novel applications (Bowes et al. 1996; Brinker 1996; Sayari 1996). The ability to synthesize zeolitic materials of precise pore size in the range between 4 and 100 Å continues to expand the possibilities for research and technological innovation in the catalytic, separations, and sorption technologies (Ruthven et al. 1994; Karger and Ruthven 1992).

Carbon Materials

The carbon-based materials of interest from a molecular self-assembly point of view include fullerenes and their relatives, including endohedral fullerenes and metal-coated fullerenes, carbon nanotubes, carbon nanoparticles, and porous carbons. Since 1990 with the discovery of techniques to produce soluble carbon in a bottle (for examples, see Krätschmer et al. 1990 and references therein), research on and with carbon materials has skyrocketed (Dresselhaus et al. 1996; Dresselhaus and Dresselhaus 1995). Not only can the molecular forms of carbon (the fullerenes and their derivatives) be synthesized, characterized, and studied for applications, but many other new carbon materials such as multi- and single-walled carbon nanotubes can now be produced in macroscopic quantities. Figure 4.6 illustrates the broad variety of carbon nanotube structures whose properties are now being examined both theoretically and experimentally. A rich literature on these new carbon materials now exists. This report will only attempt to highlight a few important recent examples in the area of high surface area materials.

Of particular interest for future catalytic applications is the recent report that not only can C_{60} be coated with metal atoms, but that the metal coating can consist of a precise number of metal atoms. For example, $C_{60}Li_{12}$ and $C_{60}Ca_{32}$ have been identified mass spectroscopically (Martin, Malinowski, et al. 1993; Martin, Naher, et al. 1993; Zimmerman et al. 1995). C_{60} has been coated with a variety of different metals, including Li, Ca, Sr, Ba, V, Ta and other transition metals. Interestingly, addition of more than 3 Ta atoms to C_{60} breaks the C_{60} cage. Replacement of one carbon atom in C_{60} by a transition metal atom such as Co or Ir is being studied for possible catalytic applications. The future technological challenge will be to discover techniques to fabricate large quantities of such materials, so that such catalyst materials can be put in a bottle and not just in molecular beams.

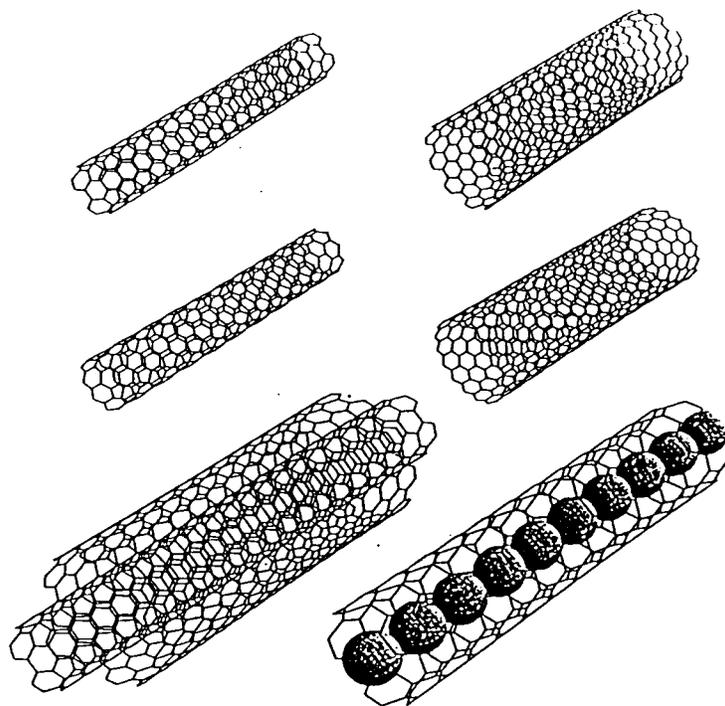


Figure 4.6. Examples of carbon nanotube structures, including multiwalled and metal-atom-filled nanotubes.

Carbon nanotubes have the interesting property that they are predicted to be either semiconducting or conducting (metallic), depending on the chirality and diameter of the nanotube. Such materials are being studied as conductive additives to plastics and for use in electrochemical applications where the uniformity of the nanotube diameter and length is not overly critical (Dresselhaus 1998). Another approach is to use the carbon nanotube as a template for a nanotube of an inorganic oxide. Hollow nanotubes of zirconia and yttria-stabilized zirconia have been prepared by coating treated carbon nanotubes with a zirconium compound and then burning out the carbon template (Rao et al. 1997). Finally, large scale production of single-walled nanotubes has recently been demonstrated, so one may anticipate a strong upsurge in the characterization and potential usage of single-walled carbon nanotubes in the future (Jounet et al. 1997).

Porous carbons are of interest as molecular sieve materials, both as sorbants and as membranes, or as nanostraws for filtration. One of the major research objectives is to develop materials or structures with exceedingly high storage capacity per unit volume and weight for gases such as H_2 or CH_4 . H_2 or CH_4 could become an economic source of combustion fuel or a

means to power fuel cells for ultralow-emission vehicles or for electric power generation. Microporous hollow carbon fibers have exhibited high permeance and high selectivity as hydrogen selective membranes, and development is now underway to scale up these membranes to commercial levels (Soffer et al. 1987; Jones and Koros 1994; Rao and Sircar 1993). Carbon fiber materials produced via catalytic decomposition of hydrocarbon vapors have also recently been reported to exhibit exceptionally high hydrogen adsorption capacity (Baker 1998). More mundane uses of nanotubes are as nanometer reinforcing rods in polymers or even in concrete. Incorporation of conducting carbon nanotubes in construction materials such as concrete or structural plastics opens opportunities for real time monitoring of material integrity and quality.

Microporous and Dense Ultrathin Films

Research and development of microporous thin films for use as molecular sieving membranes using inorganic crystalline materials such as zeolites or porous silica is another area of active research around the world. For molecular sieving membranes, one critical challenge rests on discovering ways to create large scale, thin, nearly defect-free membranes. One recent example is the fabrication of mesoporous conducting thin films grown from liquid crystal mixtures (Attard et al. 1997). Transmission electron microscopy (TEM) reveals an ordered array of 2.5 nm diameter cylindrical holes in a 300 nm thick Pt film. The hole diameter can be varied either by changing the chain length of the surfactant molecule or by adding an alkane to the plating solution. It is interesting that this technique produces a continuous thin film with nanoscale porosity in an electrically conducting material.

Dense ultrathin films such as single monolayer films would be of significant importance in the semiconductor industry (see Chapter 3). Thin films of specialized coatings for corrosion, thermal, and/or chemical stability should be valuable for the chemical and aerospace industries. Novel chemical sensors may be anticipated through use of ultrathin films composed of specialized clusters. Typical techniques for production of thin films are physical vapor deposition, chemical vapor deposition, and Langmuir-Blodgett processes.

OPPORTUNITIES IN CHARACTERIZATION AND MANIPULATION AT THE NANOSCALE

Over the last two decades, the development and improvement of new techniques to fabricate and characterize nanoscale materials have fueled

much of the enormous growth in nanoscale science and technology, not only by making nanoscale materials relatively easily available for scientific study and characterization, but also in some instances, opening the door for large scale industrial use. For example, atomic force microscopy and scanning tunneling microscopy are two techniques that have become major workhorses for characterization of nanoscale materials. The strong upsurge in interest and funding in nanoscale materials must to some (large) degree be credited to the recent development of these two techniques. Combining X-ray structure, high resolution TEM and low energy, high resolution scanning electron microscopy (SEM), researchers now have the means to physically characterize even the smallest structures in ways impossible just a few years ago. Not only can a nanostructure be precisely examined, but its electronic character can also be mapped out.

Using the scanning probe devices, scientists can both image individual atoms and molecules and also manipulate and arrange them one at a time. This atomic manipulation to build structures is just in its infancy, but it does allow one to imagine a route to the ultimate goal of atomically tailored materials, built up atom-by-atom by a robotic synthesizer. The “abacus” of C₆₀ molecules produced at the IBM laboratories in 1997 is an excellent example of possibilities that may lie ahead for manipulation at the atomic scale. The Atom Technology project in Japan is now in its second five-year program to push the frontiers of atom manipulation closer to the commercial sector (see NAIR site report in Appendix D).

Of all fundamental properties controlling the stability of atoms, clusters, and particles on a surface or support, knowledge of the adsorption and adhesive energies of the metal atom or particle on the solid metal or oxide surface is critical to fundamental understanding of the stability of high surface area materials for materials applications that include oxide-supported metal catalysts, bimetallic catalysts, and metal-ceramic interfaces used in microelectronics. Knowledge of such parameters allows researchers to predict the relative strengths of the metal-metal and metal atom-support interaction energies, and to infer relative stabilities as a function of the composition and size of the metal cluster. Recently it has become possible to experimentally measure the metal atom-surface bond strength on a per-atom basis using adsorption micro-calorimetry on ultrathin single crystal metal or metal oxide surfaces (Stuckless et al. 1997). The direct calorimetric measurement of metal adsorption energies developed at the University of Washington is based in part on earlier work first developed by D.A. King and colleagues at Cambridge University (Yeo et al. 1995). A technique such as this capable of probing interactions on an atom-by-atom or molecule-by-molecule basis can be thought of as another “atomic probe” that can be expected to substantially advance our database and understanding at the ultimate nanoscale for materials, that is, single atom binding energies to surfaces.

Similarly, new techniques are being developed to allow chemical and catalytic reactions to be followed in situ in real time. As an example, an infrared and nuclear magnetic resonance spectroscopic technique is being developed at the Max Planck Institute in Mülheim (see the MPI Mülheim site report in Appendix B) to monitor kinetics of CO adsorption on 1-3 nm diameter metal colloid particles (typically Pt, Rh, or Pd) in liquids and to follow in real time the way CO organizes itself on the particles while in liquid suspension. Such techniques will allow one to begin to understand the metal particle properties in solution and thus infer what might occur in real reaction mixtures. Extension of such techniques to real catalytic reactions in solution for catalyst particles of various sizes and composition is likely in the not too distant future.

SUMMARY

The areas where nanoscale high surface area materials may have the greatest future impact are difficult to predict, but some signs point to the possibility of substantial advancement in the areas of adsorption/separations, particularly in gas sorption and separations and in novel chemical catalysis using nanoscale catalyst particles.

At least two major challenges must be faced before utilization and generation of high surface area nanoscale materials becomes a commonplace reality. First is critical dimensional control of the nanoscale structure over long times and varying conditions. In nanoscale catalyst materials the critical chemical selectivity is likely to be intimately associated with the local environment around what is termed the “active” site. This suggests that the size, type, and geometry of the atoms making up the active site will play a critical role in defining the conditions under which this active site will be able to carry out its designed function. Ability to fabricate materials with “exactly” the same structure and composition at each active site has been and will continue to be a major challenge to materials and catalytic scientists.

A second challenge involves thermal and chemical stability control of the fabricated nanostructure. It is generally accepted that the smaller the nanostructure (active site) the more likely it is that the structure may move, aggregate, be poisoned, decompose, or change its shape, composition or morphology upon exposure to thermal and/or chemical cycling. Identifying windows of stable operation in which the specific structure or material will be able to retain the desired (and designed) behavior is critical for commercial applications. On the other hand, the driving force is the fact that nanostructured materials typically exhibit unique properties that are expected to open windows of opportunity previously inaccessible with existing materials.

It is important to recognize that nanoscale science and technology is not a “stand alone” field of endeavor, but rather is more of a “generic” area that is expected to have a critical impact and overlap in many areas of science and technology. The breadth of issues covered in this report can be taken as proof of this principle. The fields that fall under the “nanoscale” umbrella are many and diverse, illustrating that nanoscale science and technology is a collection of many different disciplines and areas of expertise. Such science and technology offers both an opportunity and a challenge to the scientific and technological community. Researchers in some areas of science included under the broad umbrella of nanoscale science and technology in this report do not normally consider (or in some cases, want) their scientific efforts to be labeled as “nanoscale.” For this chapter, nanoscale science and technology broadly encompasses the science and technology that falls between that involving individual atoms or molecules at the one extreme and that involving “bulk” materials at the other extreme.

In summary, it is important to recognize that the use of nanostructuring or nanostructures to generate, fabricate or assemble high surface area materials is at an embryonic stage. The effect of the nanostructure and our ability to measure it will be increasingly important for future progress and development of materials for the marketplace. That said, it is apparent that so-called “mature” technologies such as catalysis, coatings, separations, etc., are already being impacted. Thus, one may eagerly anticipate exciting new advances in many diverse technological areas growing from our increasing understanding of nanostructuring and nanostructured materials.

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