Nanostructural Tailoring: Opportunities for Molecular Engineering in Catalysis

Jackie Y. Ying
Dept. of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

Introduction

Our ability to engineer novel structures at the molecular and supramolecular levels has led to unprecedented opportunities in materials design. It has fueled rapid development in nanotechnology for the past decade, leading to the creation of nanoporous and nanocrystalline systems with a wealth of potential applications. *Nanoporous materials,* characterized by well-defined pores or cavities in the nanometer-size regime and controlled pore diameter and structure, give rise to unique molecular sieving capabilities and ultrahigh internal surface areas. Nanoporous structures also act as hosts and templates for the fabrication of quantum dots and quantum wires. *Nanocrystalline materials* possess unique hybrid properties characteristic of neither the molecular nor bulk solid-state limits and may be confined in nanometer-sized domains in one, two or three dimensions. They exhibit unusual size-dependent behavior, such as quantum confinement effects and superparamagnetism.

The latest advances in nanotechnology have generated materials and devices with new physical characteristics and chemical/biological functionalities for a wide variety of applications. This new field of research is truly interdisciplinary. Chemical engineers are uniquely positioned to play a pivotal role in this technological revolution with their broad training in chemistry, processing, systems engineering, and product design. Active efforts in this burgeoning field will directly impact how we tailor novel materials in such areas as catalysis and separations, and how we integrate such miniaturized systems as microreactors, fuel cells, sensors, and batteries. Research in this exciting frontier will also lead to new devices for optical, electronic, magnetic, thermoelectric and biomedical applications. Significant efforts are devoted to this field by an increasing number of academic, industrial and governmental research laboratories in the U.S., Europe, and Asia.

This article describes some unique facets of nanostructure processing and the usefulness of this approach for catalysis. Catalysis is taken as the case study since it has a tremendous impact on the core chemical engineering businesses, such as chemicals and fuels production, environmental protection and remediation, and processing of consumer products and advanced materials. Central to a successful catalytic process is the development of an effective catalyst, which is often a complex system in both composition and functionality. The ability to better control its microstructure and chemistry would allow for the systematic manipulation of the catalyst's activity, selectivity, and stability. For a given catalytic reaction network, insights on the rate-limiting steps would provide valuable intuition concerning the rational design of catalytic properties. Using materials science and surface chemistry as the basis, a preferred list of chemical compositions can be selected for the catalyst system. The materials of interest can then be processed via nanostructure synthesis, which provides for structural control at the nanometer scale with regard to pore opening, crystallite size, and component dispersion. Nanoporous and nanocrystalline materials both possess an ultrahigh surface-to-volume ratio, which would offer a greatly increased number of active sites for carrying out catalytic reactions.

Nanoporous materials

It is important in catalyst design to tailor pore structures for excellent surface areas and product selectivity. Materials with pores <2 nm, 2–50 nm and >50 nm are classified by IUPAC as microporous, mesoporous, and macroporous, respectively. Microporous materials include zeolites, which have a crystalline (alumino)silicate-based framework with a well-defined pore structure. These materials are typically derived through templating with individual molecules. The resulting zeolitic structures consist of pore openings <1.5 nm that will allow only small molecules to enter and react, thus providing shape and size selectivity in separations and catalytic reactions.

In contrast to microporous zeolites, synthetic mesoporous materials such as aerogels are characterized by ill-defined pore morphologies and broad pore-size distributions. A major breakthrough in the synthesis of well-defined mesoporous materials came about in 1992 with the development of supramolecular templating, which involved the use of molecular aggregates, instead of individual molecules as the framework-directing agents. Supramolecular templating was first reported by Mobil researchers, who used surfactants to guide the formation of mesostructures from solubilized silicate precursors (Kresge et al., 1992). The anionic silicates were deposited around the positively charged surfactant templates to form inorganic-organic mesostructures via electrostatic interactions (Beck et al., 1992; Chen et al., 1993; Huo et al., 1994). The charge density distribution between the inorganic precursors and the surfactant head groups has been used to create different mesostructures (e.g., with hexagonal, cubic and lamellar ordering) based on possible liquid-crystalline phases. Figure 1 illustrates that hexagonally packed rod-shaped micellar templates were used to derive a mesostructured silicate-surfactant composite. Upon removal of the surfactant species, silicates with hexagonally packed cylindrical pores (designated MCM-41) were obtained with ultrahigh surface areas of >1,000 m^2/g. By using surfactants with longer hydrocarbon tails and by adding polar compounds (e.g., trimethylbenzene) that can cause swelling of the micellar templates, the diameter of the mesopores can be systematically varied between 2 and 10 nm.

To create a broad range of structural and chemical characteristics, much effort has been devoted to incorporating metal dopants within the silicate MCM-41 framework and deriving nonsilicate-based MCM-41-like mesostructures (Ying et al., 1999). The ability to introduce compositional variation into mesoporous structures presents exciting opportunities for attaining a great variety of molecular sieves well beyond the current synthetic flexibility associated with silicate-based zeolitic systems. For instance, alumina is one of the most commonly used catalyst supports, but it is typically generated with irregular pore structures. As another example, transition metal oxides play an important role as industrial catalysts in petrochemical production, pollution control, and fine chemical synthesis, but they are commonly available with low surface areas and ill-defined pore structures. Using a neutral templating method, Bagshaw and Pinnavaia (1996) have successfully derived well-defined mesoporous alumina. To synthesize mesoporous transition metal oxides, Antonelli and Ying (1996) have developed a ligand-assisted templating approach that established a strong chemical bond between the inorganic precursor and the surfactant head group throughout the self-assembly process. This strategy has led to the generation of a family of stable transition metal oxide molecular sieves (termed TMS or *Tech Molecular Sieves*) with surface areas in excess of 500 m^2/g. It has further allowed us to systematically synthesize structures that bridge the mesoporous (2–10 nm) and microporous (0.5–2 nm) regimes for the first time (Sun and Ying, 1997). This is important since zeolites cannot be synthesized with intentionally tuned pore sizes to cover the entire microporous regime. The transition metal-based composition further offers chemical flexibility in tailoring mixed oxidation states, electronic interactions, surface modification, and thermal stability. A wide variety of reactions and processes may profit from the dual microstructural and chemical functionalities of these new materials.

More recently, polyethylene oxide-polypropylene oxide-polyethylene oxide copolymers have been used to derive silicates with ultra-large pores (Zhao et al., 1998). Upon self-assembly, the amphiphilic triblock copolymer systems give rise to larger-size supramolecular aggregates than surfactant micelles, thus achieving uniform mesopores ≥6 nm (see the right side of the front cover). The molecular weight or chain length of the polymer blocks may be used to fine-tune the pore size. Particularly noteworthy is the possibility of creating mesocellular foams using this approach in combination with swelling agents such as trimethylbenzene (Schmidt-Winkel et al., 2000). The resulting materials are composed of uniformly-sized, large spherical cells up to 35 nm, which are interconnected by windows to create a continuous three-dimensional pore network (Figure 2). They are particularly attractive for use as catalyst supports in pharmaceuticals synthesis, because they will permit the diffusion of large substrates through their large, open-pore architectures. These porous matrices can also be utilized to host active metal or oxide clusters and to fixate organometallic ligands, offering new possibilities for creating heterogeneous catalysts useful in selective fine chemicals synthesis and asymmetric catalysis (Mehnert and Ying, 1997; Zhang et al., 1999). This is an exciting prospect for catalysis since these two areas of application currently involve mostly homogeneous catalysts, which are expensive organometallic complexes that are difficult to separate from the liquid-phase reactants/products. The availability of ultralarge-pore supports would enable the development of heterogeneous catalysts, which would make it easy to recover and reuse, and offer more flexibility in reactor design and reaction conditions.

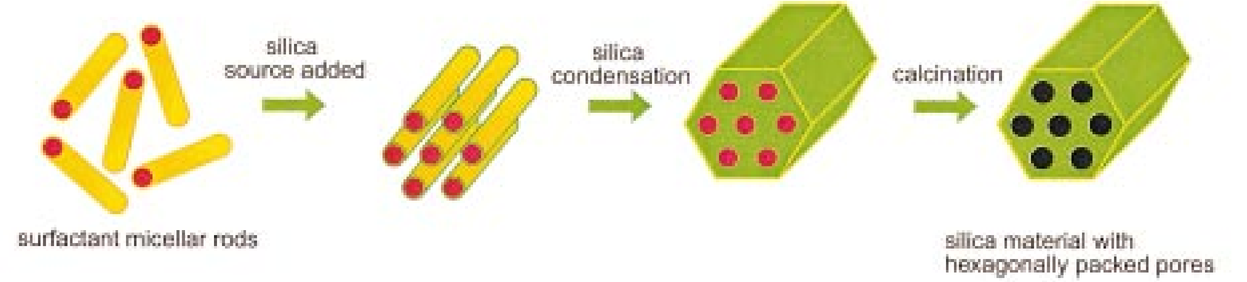

Figure 1. Supramolecular templating of mesoporous silicates.
Surfactant templates are used to form hexagonally packed micellar rods around which silicate precursors are condensed. Upon removal of the surfactants via heat treatment, silicates with hexagonally packed cylindrical pores are attained. Courtesy of J. S. Lettow and J. Y. Ying, MIT.

Nanocrystalline materials

Nanocrystalline materials offer unique characteristics useful for controlling the catalytic reactivity. In this section, a few examples of my group's research are presented to illustrate the advantages of nanocrystalline processing, which include the tailoring of size-dependent electronic properties, defect chemistry, homogeneous multicomponent systems, and excellent phase dispersion. These features provide nanocrystalline catalysts with greatly improved catalytic activity over conventional systems and multifunctionalities necessary for complex applications.

Catalytic reactions may be classified as structure-sensitive or structure-insensitive. In structure-insensitive reactions, catalytic activity is related directly to the number of active sites, thus the high surface-to-volume ratio in nanocrystalline catalysts gives these materials a distinct advantage. In contrast for structure-sensitive reactions catalytic activity depends not only on the number of active sites, but also on the crystal structure, interatomic spacing and crystallite size of the catalytic material. By varying crystal size and phase through molecular engineering it was possible to manipulate and optimize the catalyst design. An example of a structure-sensitive reaction is photocatalysis over titania. Photocatalysis represents an attractive low-temperature, nonenergy-intensive approach for decomposing chemical wastes using photon-generated electrons and holes. The pair of charge carriers produced in the semiconductor photocatalyst upon solar irradiation would migrate to the particle surface to serve as redox sources for adsorbed reactants. An ideal photocatalyst should provide for fast charge transfer rate and prevent charge carrier recombination on the surface or within the volume of the catalyst particle. In the search for an optimal system, titania crystals of controlled size (4–100 nm) and phase were systematically synthesized by sol–gel hydrolysis-precipitation, followed by hydrothermal treatment (Wang and Ying, 1999). This new wet-chemical approach allowed for materials of the appropriate crystallinity and phase to be achieved without going through the usual high-temperature treatments that often lead to crystal growth and phase transformation. In the photodecomposition of chloroform and trichloroethylene, anatase crystallites were found to outperform rutile crystallites due to their greater redox potential. Specifically, 10-nm anatase crystallites presented the best photonic efficiency (Zhang et al., 1998). Larger crystallites were associated with reduced surface reactivity and volume recombination effects. Nanocrystallites provided high surface areas and an increased bandgap from quantum size effects. The enhanced surface reactivity and redox potential, however, would be compromised by the significant surface recombination effects in crystallites smaller than 10 nm. Thus, through engineering of crystal size and phase, the photonic efficiency of titania semiconductor was substantially increased and successfully optimized for photocatalytic applications.

In catalysis, the active species are typically the surface and edge atoms, which are often associated with surface unsaturated bonds and a lower coordination number than in the bulk crystalline state. The high volume fraction of surface/interfacial atoms in nanocrystalline materials, therefore, presents a unique opportunity to control the surface chemistry and defect concentration. This can be exploited in a variety of catalytic processes, such as in the reduction of SO_2 by CO. The generation of oxygen vacancies and the mobility of oxygen ions represent the rate-limiting steps in this redox reaction. Therefore, ceria, a fluorite-structured oxide with high intrinsic oxygen mobility, was selected as the catalytic material. Cerium may exist in +3 and +4 oxidation states; the former is particularly active for catalyzing redox reactions. Reduction of CeO_2, however, conventionally requires high temperatures that would lower catalyst's surface area. Thus, it would be highly desirable to have a cerium oxide catalyst synthesized with a high surface area and a reservoir of oxygen vacancies. We have generated such a novel material with enhanced electrical conductivity through modified magnetron sputtering of cerium in argon, followed by controlled post-oxidation (Ying and Tschöpe, 1996). The resulting 6-nm CeO_{2-x} nanocrystals were found to be an excellent catalyst for SO_2 pollutant treatment. It enabled 100% selective conversion of SO_2 to S at 460°C, compared to 580°C needed by ultrafine stoichiometric CeO_2 powder (Tschöpe et al., 1995). This example illustrates the design of nanocrystalline materials with a flexible control of stoichiometry and electronic properties important for redox catalysis.

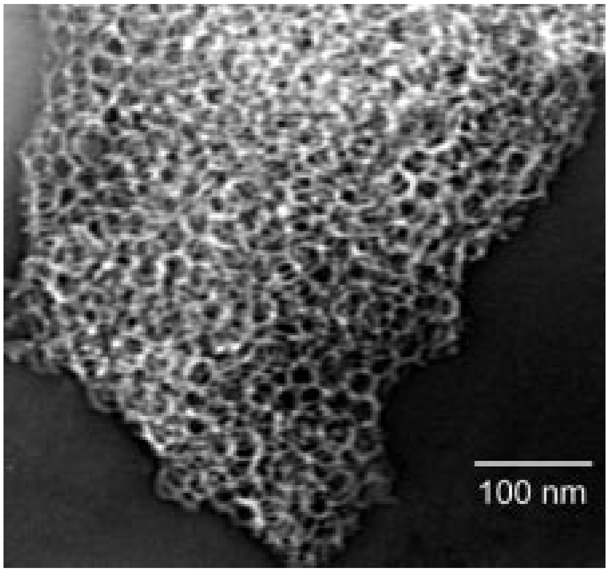

Figure 2. **Siliceous mesocellular foams.** Transmission electron micrograph of mesocellular foams produced by templating with triblock copolymers and trimethylbenzene. Courtesy of J. S. Lettow and J. Y. Ying, MIT.

Consider now the implications of tailored nanostructures for high-temperature catalysis, which is an area of great interest to many industrial processes, such as catalytic combustion, steam reforming, and selective oxidation of hydrocarbons. The catalytic materials involved must operate for extended periods without undergoing loss of activity at high temperatures and in the presence of water vapor and poisoning impurities. This presents a great challenge since substantial crystal growth and surface restructuring would likely occur under those severe operating conditions.

Take the case of catalytic combustion, which can proceed at high levels of excess air, leading to more complete oxidation and decreased hydrocarbon emissions. The catalytic process stabilizes flame at relatively lower temperatures than homogeneous combustion, thus minimizing nitrogen oxide production. Catalytic combustion of methane or natural gas makes it possible to generate power with reduced emissions of greenhouse gases compared to the burning of coal and higher hydrocarbons. It, however, requires a catalyst that can sustain activity and mechanical integrity at flame temperatures as high as 1,300°C. The catalyst must also be active at low temperatures for startup and transient periods. Noble metal catalysts exhibit excellent light-off behavior at 350–400°C, but suffer from deactivation by 700–800°C. To achieve high-temperature stability, one system considered is barium hexaaluminate (BHA), which is suppressed in particle growth and sintering once it is crystallized. Using a reverse microemulsion mediated sol–gel synthesis, molecular-level chemical homogeneity was achieved in multicomponent systems, so that the desired BHA spinel-like crystalline phase can be induced at relatively low temperatures. This minimizes subsequent particle growth at the high flame temperatures of catalytic combustion. The resulting discrete BHA nanoparticles preserved a remarkable surface area of >100 m^2/g at 1,300°C (Zarur et al., 2000). These materials of superb thermal stability were then used to support transition metal and rare earth oxides to create highly dispersed nanocomposite systems (see the left side of the front cover). The CeO_2 nanoclusters coated on the stable BHA nanoparticles successfully retained a crystal size of 20 nm even at 1,100°C and allowed methane light-off by 400°C (Zarur and Ying, 2000). This nanocomposite displays a low-temperature activity that is comparable to noble metal systems; it is also less expensive and presents superior thermal and hydrothermal stability. The example illustrates how one may combine components of different functionalities with nanoscaled dispersion to achieve unique structural and chemical synergistic effects.

Outlook

Vapor-phase and wet-chemical synthetic approaches have led to unprecedented control of material structures at the atomic and molecular levels, and brought about ensembles of such features in the form of nanocrystalline systems with crystallite-size tuning. Nanocrystalline materials created with unique surface and defect chemistry, complex compositions, controlled component dispersion, and excellent stability offered great flexibility in tailoring materials with a combination of specific functionalities for different catalytic applications. Now complex nanocomposite systems can be built to fulfill various roles required by the reaction mechanism and conditions. Nanocomposite processing also lends itself readily to intelligent combinatorial approaches in materials design and rapid catalyst screening (Davis, 1999; Beddard, 1999; Engstrom and Weinberg, 2000). The concept of nanocomposite particles with ultrahigh specific surface area and catalytic reactivity will facilitate the development of efficient, light weight/compact devices such as microreactors (Jensen, 1999). Beyond catalysis, nanoparticles can be dispersed in a liquid or an emulsion for use in coating applications, food processing, consumer and cosmetic products, etc. Of great interest for future research are organic nanoparticles for drug delivery and gene therapy systems, and quantum dots for medical imaging and diagnostics. Nanoparticles can also be assembled in the bulk form or as coatings to produce advanced materials with superior microstructural uniformity and mechanical reliability. One can further envision a great variety of ceramic-metal and organic-inorganic nanocomposites that provide for a unique combination of materials characteristics for novel chemical, biomedical, optical, electronic, structural and thermal applications.

Through supramolecular templating, nanoporous systems can now be derived with well-defined pore size and structure, as well as compositional flexibility, in the form of particles and thin films. Besides catalysis, these new materials are attractive for use in gas absorption, membrane separations, chromatography, microfiltration, sensors, electrochemical systems, and thermal/electrical insulation, as well as hosts for quantum dot and nanowire devices (Ying, 1999). Nanoporous structures hold many possibilities in materials applications, especially with further developments in molecular engineering such as surface functionalization of inorganic structures and extension of supramolecular templating to organic systems. Self-assembly of nanostructured building blocks (e.g., nanocrystals) in concert with porosities on different length scales would lead to interesting hierarchical structures. Such systems with multiple levels of intricacies and design parameters offer the possibility to simultaneously engineer molecular, microscopic and macroscopic materials characteristics. It will lead to the realization of such advanced systems as quantum electronic/photonic devices and biomimicking medical implants.

Acknowledgments

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