Perspective

Molecular Sieves in the Nanotechnology Era

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Introduction

Precise manipulation of matter at the nanometer scale is not a recent goal. Only recently, however, intensified research, expressed under the term nanotechnology, has been directed toward this ultimate goal. This effort, arguably enabled by technological advances in instrumentation and computing, is stimulated by past developments in physics, chemistry, and engineering.

For chemists and chemical engineers specializing in the interdisciplinary field of zeolites and molecular sieves, the nanotechnology era, albeit not articulated as such, has been ongoing for several decades generating nanoporous materials capable of molecular recognition at the nano- and subnanometer level. In the midst of nanotechnology initiatives by funding agencies worldwide, it is easy to lose sight that major petrochemical and catalyst companies, among others, are generating wealth based on investments made decades ago in the synthesis, structure and function of nanostructured materials (Figure 1). The current impact of molecular sieve materials is indisputably significant, with applications ranging from petroleum refining for fuels and petrochemical processes for various chemicals to air separation and nuclear waste management (Sherman, 1999).

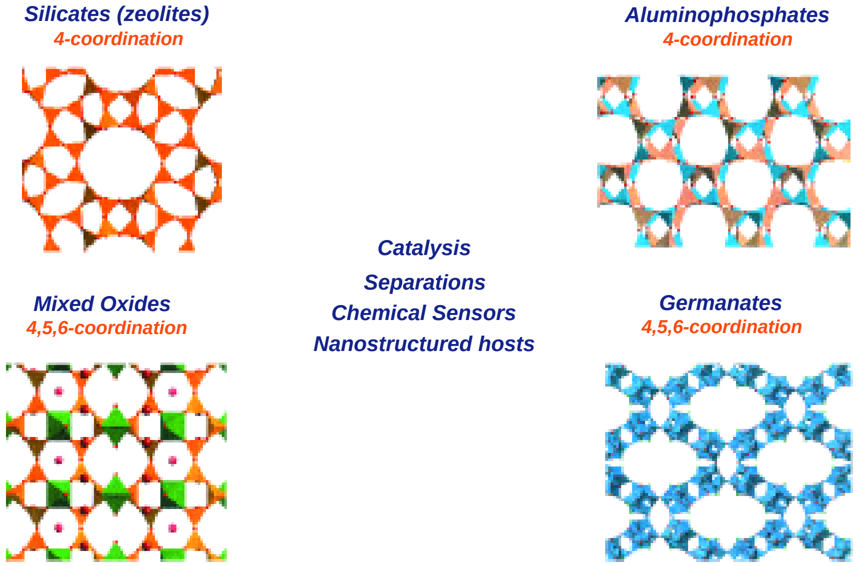

Figure 1. Molecular sieve materials.

The current research and development methodology in the field of structured nanoporous materials evolved over the years to an interdisciplinary blend of Edisonian approaches in synthesis and functionality, accompanied by rigorous structure elucidation/documentation, and, more recently, molecular modeling aided interpretation/prediction of structure-property relations. The existing knowledge base in the synthesis, structure and function of nanoporous media made possible a wealth of applications: fine chemical catalysis/separations (Davis, 1998; Martinez-Triguero et al., 1999), enantioselective synthesis (Joy and Ramamurthy, 2000; Beller, 1999), new ion-exchange uses (Bedard, 1999), and applications like dessicant cooling and heat pumps (Sherman, 1999). Based on past and recent accomplishments, it could be argued that the field of molecular sieves provides a paradigm to emulate in emerging nanotechnology areas.

However paradoxical it may appear, sustained research interest in the field is becoming increasingly difficult. For example, there is diminishing interest in new or improved catalytic, ion-exchange or adsorbent materials that provide moderate performance improvements for existing processes, because often the potential benefits rarely counterbalance the material uncertainties and associated development costs. Synthesis of new structures, considered a major driving force a decade ago (Davis and Lobo, 1992; Freyhardt et al., 1996; Camblor et al., 1992) is often criticized as having led to numerous new materials in search of application (Bedard, 1999). On the other hand, materials that can be claimed to be tailor-made for a specific problem are harder to come about as the remaining problems in catalysis and separations for new materials are extremely challenging, being the remnants of decade-long intensive research.

Sustained research interest in the area of nanoporous materials in the nanotechnology era relies on three interrelated requirements, as explained by the following excellent examples that satisfy one or more of these requirements:

1. It enables their use in chemical or physical processes that cannot be addressed by existing materials (Bedard, 1999; Ying, 2000).
2. It introduces them as possible solutions to application problems dictated by expressed needs in nanotechnology (Caro, 1992; Hillhouse and Tuominen, 2001; Calzaferri et al., 2002; Pokropivny, 2000; Bordiga et al., 2000; Marlow et al., 1999; Giraldo et al., 2000; Lu et al., 1997).

3. It makes fundamental advances in understanding their synthesis, structure, and property interrelations combining modern experimental techniques, modeling, and simulation departing from the Edisonian approaches of the past (Yamamoto and Okubo, 2000; Jones et al., 1998; Nikolakis et al., 2000; Zhao et al. 1998; Czaplewski et al., 2001; Clark et al., 1998; Sholl, 1999).

This article discusses recent experiences on rewarding academic chemical engineering research in the field of nanoporous materials to provide possible directions for short- and long-term academic research opportunities. The development of a new selective adsorbent that can be fine-tuned by manipulating its framework flexibility is described as an example that, despite all the accumulated knowledge, there is still room for scientific breakthroughs and enabling technologies based on nanoporous materials in traditional fields like adsorption and gas separation. The synthesis and commercialization of molecular sieve membrane technology are also discussed as a distinct chemical engineering contribution to the field. Both examples underscore the requirement for academic researchers to work with industrial partners and vice versa, and the need for process design methodologies to not only take full advantage of new materials, but also guide their development. There is a unique opportunity for molecular sieve technology to contribute to nanotechnology needs: molecular sieves for device applications. Such applications that will bring crystalline porous oxides in industries like the microelectronics have been envisioned (Ozin et al., 1991) and few have proven possible. However, it is apparent that their implementation, beyond scientific curiosity, requires major scientific and engineering advances. These include breakthroughs in understanding and manipulating nanoporous materials growth for interfacing with other device components and for structural perfection not required by their current technological use. I believe that progress in this area relies on the ability to combine traditional chemical engineering background in nanoporous materials growth and structure with expertise in the applied physics of devices, through training or collaborations.

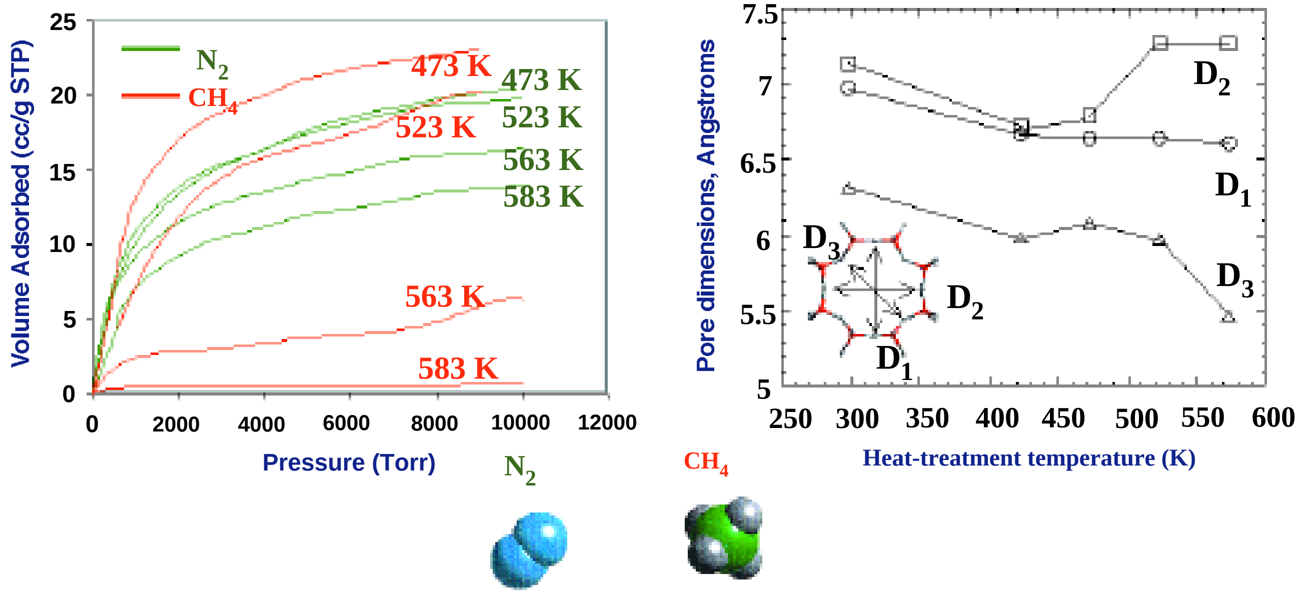

Figure 2. ETS-4 as a flexible molecular sieve.

Its structure can be tuned by heat treatment, and the heating-induced structural changes can be kept on cooling to room temperature. The pore-size reduction is commensurate with adsorption selectivity for N_2 over CH_4. The amount of methane (red) and nitrogen (green) adsorbed at room temperature after 20 min in Sr-ion-exchanged ETS-4 samples heated at the indicated temperatures (left). For heat treatments up to 523 K, the amounts of nitrogen and methane adsorbed are similar. After heat treatment above 563 K, a large reduction of methane adsorption is observed, which coincides with a reduction of the limiting dimension of the pore opening of ETS-4 and increased Sr-ion migration to the pore's center. Oxygen-to-oxygen distances (center to center) as determined by analysis of neutron diffraction data at room temperature after heat treatments at the indicated temperatures (right). The pore opening can be estimated by subtracting an estimate for the oxygen diameter (2.7). The decrease of the smallest distance (D3) from above 6 to about 5.5 clearly coincides with the onset of selectivity for nitrogen over methane.

Developing New Adsorbent: Engelhard-UMASS Collaboration on Molecular Gate Technology

Approximately a decade ago, Dr. Steven Kuznicki (at the time with Engelhard Corp.) and his group performed synthesis at an unexplored composition domain to incorporate titanium in the framework of silicate molecular sieves. This work resulted in microporous oxides containing silica tetrahedra and titania octahedra and paved the way for the synthesis of other mixed octahedral/tetrahedral molecular sieves (Rocha and Anderson, 2000).

The most studied of Engelhard's titanosilicates is ETS-10 (Engelhard TitanoSilicate Ten) (Kuznicki, 1989; Anderson et al., 1994), a large pore molecular sieve. More than 200 studies have been published addressing the structure, adsorption, and catalytic properties of ETS-10, and limited commercialization attempts have been initiated. A less studied, small pore material related to ETS-10, ETS-4 drew my attention about five years ago. It had been largely ignored by the academic molecular sieve community due to its poor thermal stability in the synthesized form. However, Engelhard Corp. was developing modification procedures that indicated the potential for increased thermal stability along with interesting and unexpected adsorption properties.

Powder neutron and X-ray diffraction studies revealed pronounced 3-D crystallographic lattice contraction, accompanied by continuous changes of the pore opening and cation relocations by simple dehydration at elevated temperatures. It was quickly realized that these changes of the anionic framework and extra-framework cations could be sustained at ambient conditions suggesting that the framework flexibility of ETS-4 could be used to fine-tune its adsorption properties (Kuznicki et al., 2001; Nair et al., 2001). Figure 2 shows an example that clearly demonstrates this point.

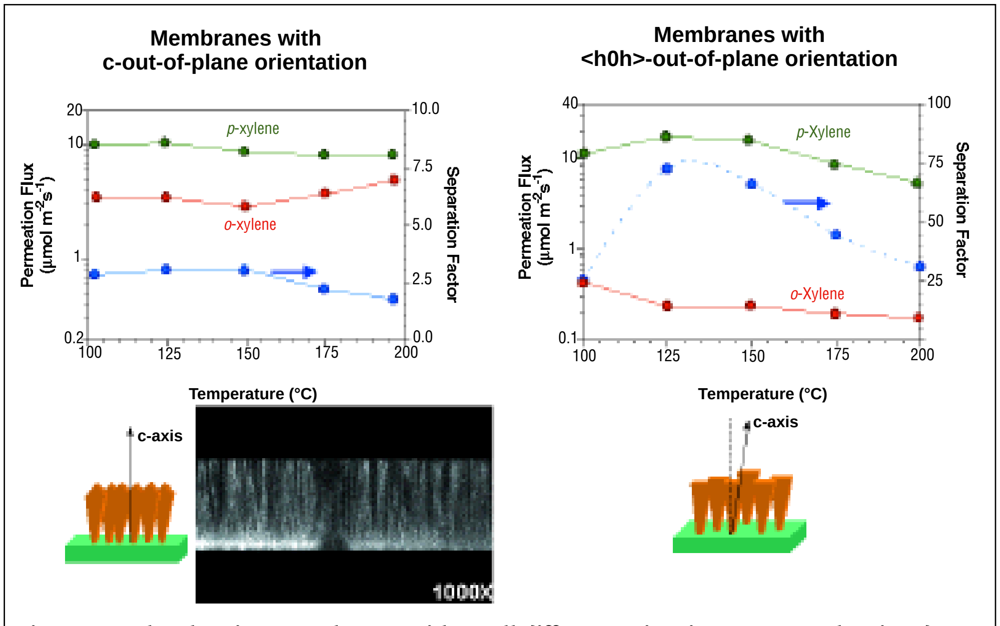

Figure 3. Molecular sieve membranes with small differences in microstructure showing drastically different performance.
Membranes of the high silica molecular sieve MFI with c-out-of-plane preferred orientation show small selectivity for p-/o-xylene (left top) due to the presence of grain boundary defects. The defects are detected by first impregnating a fluorescent dye that is too large to fit in the molecular sieve pores followed by nondestructive imaging by fluorescence confocal optical microscopy (left bottom inset). The bright lines spanning the thickness of the membrane show the presence of grain boundaries with pores large enough to accommodate the fluorescent dye and therefore larger than the zeolite's pores. MFI membranes with a small difference in preferred orientation (c-axis inclined by about 35 deg on the right bottom) show no evidence for the presence of similar defects at the grain boundaries. These membranes show excellent selectivity (right top) for p-xylene.

After dehydration at approximately 300°C, ETS-4 essentially excludes methane while still allowing for substantial adsorption of nitrogen, a smaller molecule. This separation has been of commercial potential since it allows for purification of nitrogen contaminated natural gas by pressure swing adsorption at well-head pressures. A field demonstration has been in operation for about two years. Although it is still early to judge the commercial impact of the nitrogen methane separation by the finely-tuned ETS-4 adsorbent, the underlying phenomena are intriguing and stimulating. There is certainly interest for academic research to develop predictive capabilities for framework flexibility. Moreover, from the applied standpoint, there is potential for using the knowledge on ETS-4 in synthesizing or discovering other highly flexible frameworks tunable to specific applications of commercial significance. I expect that extension of these phenomena to large pore materials is feasible and possibly much more rewarding commercially.

Molecular Sieve Membranes with Many More Possibilities for the CPI

The idea to fabricate molecular sieve membranes goes back to the beginnings of zeolite and membrane science. However, it took decades for this early vision to become a marketable reality. Despite the recent commercialization of zeolite membranes by Mitsui Co. (Morigami et al., 2001) and others, many challenges remain for this technology to be established in the chemical processes industry (Yan et al., 1995; Jia et al., 1994; denExter et al., 1996). One example may be high-temperature uses such as membrane reactors (Xomeritakis et al., 2001). Many of these challenges are particularly well suited for academic research in nanotechnology related areas.

The indisputable advantage of zeolite membranes is the subnanometer precision of pore structure architectures provided by the crystalline nature of these materials. However, the crystallinity also poses enormous challenges when one attempts to prepare continuous polycrystalline zeolite films (Dong et al., 2000). Issues of grain orientation and grain boundary structure are of paramount importance not only for determining the expected transport properties, but for ensuring mechanical integrity and stability (Figure 3). In this regard, there is a need for developing quantitative understanding of crystal growth mechanisms in hydrothermal systems to allow for reproducible and scalable synthesis of zeolite films. More specifically, increased attention should be directed toward controlling molecular sieve crystal size and shape at the nanometer level. Major breakthroughs in the near future may come by identifying, isolating, purifying, and eventually using, in controlled deposition schemes, nucleation and growth precursor nanostructures. The existence of such nanostructures has been confirmed by various investigators during the last decade (de Moor et al., 1999). However, isolating these supermolecular species in nonaggregated, pure form amenable to synthetic manipulation remains elusive.

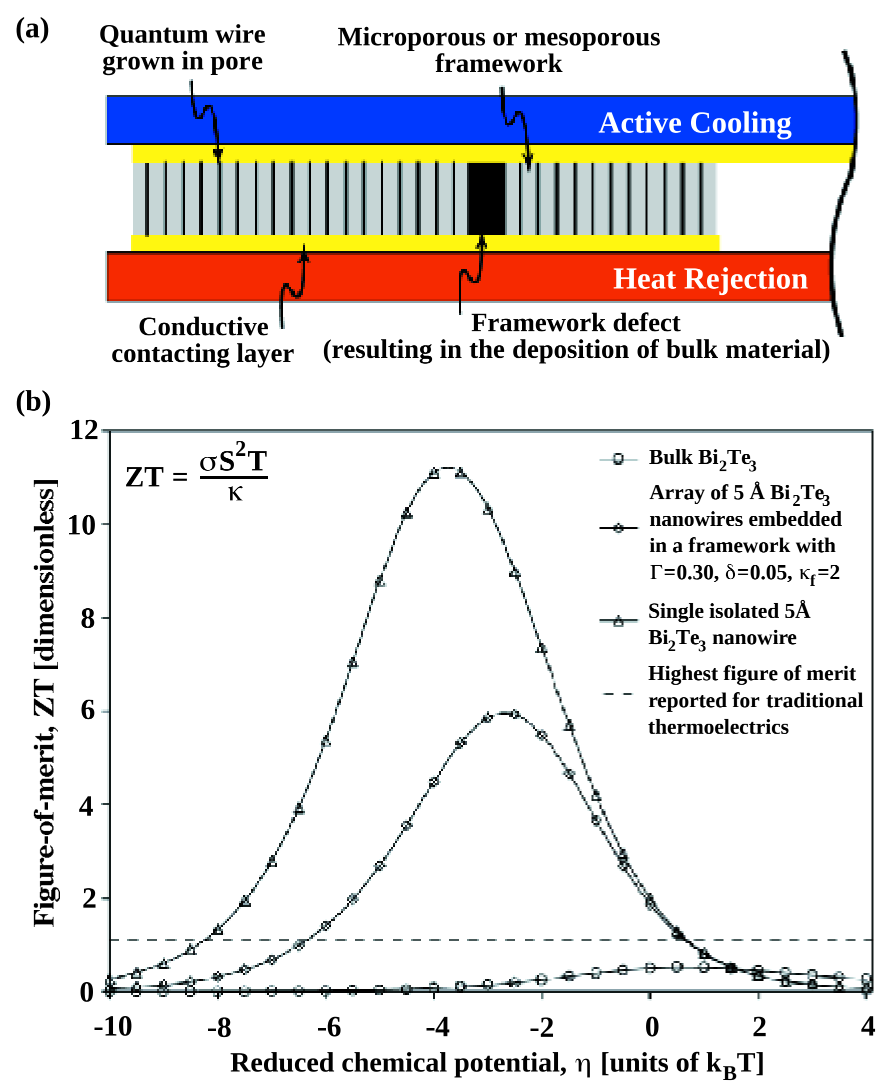

Figure 4. Molecular sieves used as hosts to stabilize nanostructures with desirable functionality.

Thermoelectric cooling devices perform superiorly if nano- and subnanometer wires could be fabricated and incorporated in appropriate devices. A molecular sieve film can play the role of the host in a thermoelectric device. Figure 4a, such a device with wires hosted in a nanoporous medium; 4b, corresponding calculated figures of merit and comparison with performance of currently available materials. Courtesy of HW Hillhouse (Hillhouse and Tuominen, 2001).

From the processing perspective, as commercialization of molecular sieve membranes for more demanding applications is emerging, deposition methods should be evaluated for potential in allowing reproducible control of nano- and microstructure in scale-up. Multistep methods, like secondary growth of zeolite nanocrystals, are preferable when such constraints are considered (Lovallo and Tsapatsis, 1996; Mintova et al., 1997). Recent developments in the preparation of closely packed, in certain cases oriented, nanocrystalline zeolite layers (Lee et al., 2001; Boudreau et al., 1999; Schoeman et al., 1999) suggest that reproducible and economic production of submicrometer molecular sieve films with controlled microstructures can be realized at a commercial scale in the near future.

Mathematical modeling of hydrothermal growth is still at a very primitive level to substantially contribute in the development of molecular sieve films in the near future. Its role will be limited to specific questions posed by experimental observations (Bonilla et al., 2001). In contrast, modeling of transport in molecular sieve films is at a level of sophistication that allows even quantitative predictions of separation performance (Sholl, 2000; Nelson and Auerbach, 1999; Sanborn and Snurr, 2001; Krishna and Paschek, 2000). These models, properly implemented, can play a pivotal role at the process design stage in the selection of zeolite membranes for specific separations by providing predictions of the expected (ideal) behavior in the absence of defects. Modeling efforts to account for the role of defects are also foreseeable contributors in commercialization efforts (Nelson et al., 2001).

For some applications, zeolite-polymer composite membranes (often called mixed matrix membranes) can potentially exhibit superior performance to polymer films (Zimmerman et al., 1997). Although mixed matrix membranes do not meet the thermal and chemical stability requirements for many of the desirable applications, they have considerable potential for use in gas separations and fuel cells (Takami et al., 2001). Challenging issues related to nanostructure control provide opportunities for academic chemical engineering research in this arena as well. These include development of processes that allow fabrication of composites with high zeolite loading and zeolite pore connectivity, engineering the zeolite-polymer interface, and developing proper transport models for high zeolite loading to guide polymer and zeolite selection.

Molecular Sieves for Device Applications: Sensors, Thermoelectrics, Ionic-Conductors, Superconductors...

Current synthetic procedures for molecular sieves reflect constraints imposed by their market value as ion exchangers, adsorbents, and catalysts. These prices often do not exceed several \$/lb. As a result, most zeolites and molecular sieves are made in bulk quantities, and issues of structural perfection (defect density), particle size and shape uniformity, external surface perfection, and purity are compromised. Device uses, on the other hand, can justify much larger material synthesis costs allowing a departure from the traditional view of molecular sieves as large quantity, low cost materials.

The regular porous structures of molecular sieves (Figure 1) have inspired suggestions for use not only in novel guest molecule recognition applications, like sensors and ion conductors, but also in guest organization to nanostructures with novel properties including optoelectronic and thermoelectric materials (Figure 4). In this regard, the synthesis of high quality single crystals or highly in-plane and out-of-plane oriented films (Okubo et al., 2001) with, for example, minimal internal defects and surface roughness, can be justifiable.

With the recent and foreseeable future advances in single crystal and thin film molecular sieve synthesis more intensive exploration of molecular sieves as hosts for organizing nanostructures should be expected. Moreover, the recent demonstrations of low dielectric constant properties of high silica molecular sieves open possibilities of exploiting the structural perfection of these materials in uses other than those requiring accessible porosity (Wang et al., 2001; Cheng et al., 2001). Finally, demonstrations of quantum confinement in the titania chains that are part of the framework of certain titanosilicate molecular sieves may pave the way toward new direct nanotechnology applications of framework oxides (Bordiga et al., 2000). It is worth reemphasizing that evaluating molecular sieve materials as candidates in device applications requires a combination of chemical engineering background with expertise in physics of nanostructured devices for predicting and measuring the corresponding properties.

Concluding Remarks

Traditional uses of molecular sieves will continue to play a major role in industry and drive academic chemical engineering research. In addition to the ever-present potential for unforeseeable breakthroughs there are many outstanding challenges like chiral frameworks, crystalline mesoporous molecular sieves, economic routes to functional hierarchical materials, catalyst design, and so on.

Fundamental advances in understanding and controlling growth and predicting their properties may enable the incorporation of these materials in devices, such as thermoelectric, and demonstrate novel functionalities like corrosion resistant coatings and microreactors.

These newer uses are more likely to be driven by academic research since drastic departures from the current synthesis and application paradigms will be necessary, and because these materials are not familiar to industries like the microelectronic.

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