Perspective

Functional Materials Design for the New Millennium: Updating the Rational Strategy and Enabling Tools

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Today's industrial materials researcher faces many challenges—from escalating technical and commercial competition to proliferating sources of information. In addition, the business environment of the 90s and into the new millennium is far less patient in waiting for new discoveries. The temptation to "schedule" inventions to fit preset timetables continues to grow.

Earlier in this decade, the industrial R&D environment underwent significant changes to improve its innovation and effectiveness. Close collaboration among commercial technology specialists, applications engineers, solid-state chemists, and characterization experts has for some years been formalized in the "self-directed" project team concept of technology delivery. Many companies in our industry have adopted this collaborative concept, often with mixed success. In practice, the realities of commercial timetables sometimes bias the collective thoughts of a team in the direction of incremental modification of existing materials (base hit) rather than toward truly novel concepts and materials (home run). A team's willingness to risk the stretch goal can be increased by judiciously using molecular modeling, by diligently studying the patent and open literature, and by adopting discovery tools in the search for new materials. Theoretical insights, coupled with an awareness of the most up-to-date developments in materials science and applications technology, can enhance the ability of a team to venture into new territory.

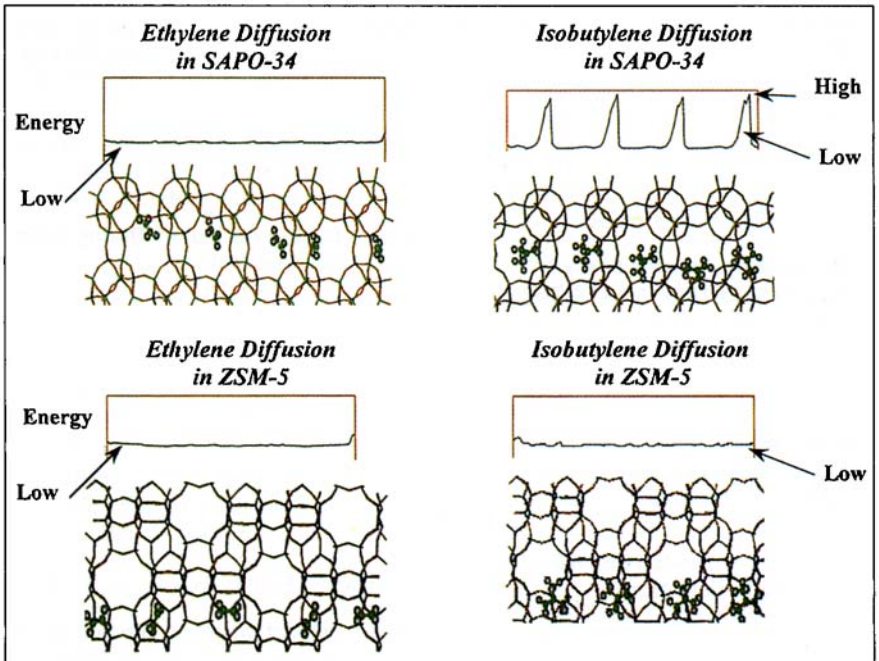

Figure 1. Structures models of SAPO-34 (top) and ZSM-5 (bottom) with graphs of diffusing hydrocarbon-framework interaction energies.

Inorganic materials breakthroughs are often the first step in the life cycle of chemical process innovations, particularly when a catalytic reaction, an adsorptive separation, or an ion exchange step is integral to the process. The synthesis of functional materials to fill these roles is a challenging enterprise, even without the new commercial realities. A new or substantially revised model for the rational design and synthesis of useful materials is necessary to assure success.

Of the many rapidly advancing fields that will affect the way inorganic materials are discovered in the future, the three fields—computational, combinatorial and supramolecular chemistry—will have profound significance.

Evolving materials discovery model: molecular modeling comes of age

There are many examples of successful integration of molecular modeling into the R&D process. Simple techniques for diffusion modeling of various molecular species in molecular sieve materials can lead to useful insight and identification or perhaps elimination of potential candidates for a given catalytic reaction. Such calculations, using software from Molecular Simulations Incorporated (InsightII), have been used to "screen" materials for possible use in the acid-catalyzed methanol-to-olefins process (Wilson and Barger, 1999) by sampling the interaction energies as a potential product molecule is moved through the candidate chan-

nel system (Gatter, 1999). Clearly, SAPO-34, a small-pore silicoaluminophosphate molecular sieve, would be more selective for product ethylene than isobutylene from this example calculation in Figure 1. Adsorption measurements and pilot-plant activity tests agree with many of these simple diffusion-modeling calculations.

To develop improved materials for radioactive ^{137}Cs ion exchange (Bedard, 1999), crystallographic intergrowth structures were first modeled before the intergrowth materials were actually synthesized. The two structures, known as pharmacodsiderite (Ph) (Chapman and Roe, 1990) and sitinakite (Si) (Sokalova et al., 1989; Men'shikov et al., 1992), are titanosilicate compositions that are highly insoluble over a large pH range in aqueous solution and are, therefore, useful for nuclear waste remediation in a variety of aqueous applications. Sitinakite has a uniquely high selectivity for Cs (Anthony et al., 1993), but has one-dimensional cation diffusion because the large pores in the structure only go in one direction. Pharmacosiderite has significantly lower selectivity for Cs but has three-dimensional diffusion paths accessible to Cs because of the 3-D topology of the large pores of the structure. The two materials have an epitaxic relationship between their crystal structures, allowing intergrowths of the two with the potential for combining favorable properties of each material. Structural simulations (InsightII) coupled with X-ray diffraction simulations using the DIFFax program (Treacy et al., 1991) allowed a preliminary understanding of the expected diffraction properties of hypothetical ordered and random intergrowths. A simulated ordered structure alongside a high-resolution TEM picture of one of the synthesized disordered intergrowths is shown in Figure 2. The wide white stripes in the model and TEM photo correspond to single slabs of the 3-D porosity mineral structure, "Ph," while the narrow white stripes are slabs of 1-D porosity mineral, "Si."

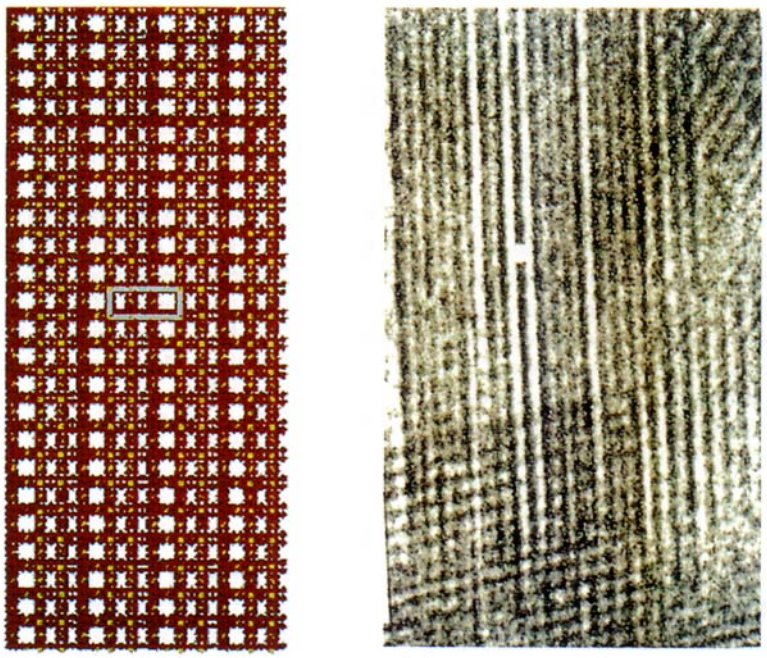

Figure 2. Ordered intergrowth structural model (left) and HREM image of synthesized material with disordered intergrowth (right) (TEM photo by Charles Bateman).

A group at BASF has recently reported another example showing the value of integrating modeling with careful experimentation and applications understanding (Breuer et al., 1999). In this study, embedded cluster DFT techniques were used to model the reaction of primary alcohols with alkynes on zinc silicate surfaces to produce vinyl ethers. The modeling provided insight into the mechanism and aided in the identification and synthesis of an active catalytic phase. BASF's proposed mechanism is supported by its similarity with the catalytic pathway for similar reactions with the enzyme carbonic anhydrase.

Combinatorial chemistry: enabling tool for rapid screening of synthesis strategies

The emergence of combinatorial chemistry techniques for solid-state inorganic materials synthesis represents a revolutionary advance in discovery tools (Briceño et al., 1995; Bein, 1999). The ability to synthesize hundreds or thousands of materials in short periods of time could save enormous amounts of synthesis resources. Combinatorial techniques could revolutionize the materials R&D process from the initial discovery of novel compositions of matter through product and process optimization. The technique, however, does not eliminate the effort needed to determine the best mode of materials synthesis for a particular application (Schlögl, 1998). There are often many ways to synthesize a given catalytic material. The surface structure sensitivity of many catalytic reactions makes synthesis methods and post-synthetic treatments critical issues. It is often the case that each catalytic composition attains its optimum performance under slightly or even significantly different pretreatment and/or catalytic process conditions. Some of these aspects of catalysis R&D may be difficult to address with combinatorial methods.

It is apparent that one of the biggest challenges in applying this new tool is the design of reliable parallel screening methods to measure quantities that rank materials in the desired functionality (Sankan, 1998; Holzwarth et al., 1998). The probability of success of combinatorial methods is likely to substantially increase with full integration of combinatorial tools into the industrial R&D process (Scott, 1999). Full knowledge of applications technology will likely be critical to those designing parallel synthesis, characterization and functionality screening experiments.

Combinatorial tools, when combined with theoretical insight into structure/composition and functionality interrelationships, will likely be a profitable approach to new materials design and discovery.

Material, assemble thyself: Supramolecular products

The phenomenon of self-assembly has occurred for millennia in biological systems for the formation of shells and membranes, and the replication of DNA, as well as in protein synthesis to name only a few examples. The discovery of supramolecular-templated

mesoporous silica (Kresge et al., 1992a,b), together with extensive research on the crystallization at organic-inorganic interfaces (Mann et al., 1993), has underscored the ability of soft, weakly aggregated assemblies of organic molecules to affect the structure, morphology and properties of inorganic materials at length scales spanning from 10's to 1000's of Angströms. Long-range structure of not only catalyst particles but also of the final engineered products may soon be manipulated in ways similar to that of the synthesis of organically templated molecular sieves. Properties such as diffusion and thermal conductivity may be incorporated into functional products by chemical synthesis, rather than by today's powder and colloidal processing techniques. The length scales accessible with chemistry will increase into the range historically associated with materials and chemical engineering, as self-assembly phenomena become understood and controllable.

Traditionally, the colloid science associated with forming of adsorbents and catalysts has been within the realm of chemical engineering because of its close connection with product manufacturing. Catalyst forms, such as extrudates, spray-dried particles, and monoliths, have been formed by mature technologies with relatively little change during the last decade. In the future, some catalyst and other product forms may be at least partially fabricated using self-assembly phenomena. Careful exploitation of these phenomena could result in positioning of vital catalyst components in optimal quantities and locations in the final catalyst forms. As we understand the interaction of organic species with inorganic surfaces better, molecular recognition phenomena may be used to control and perhaps engineer the defect structure and morphology of colloidal catalytic particles on a much smaller length scale than typically considered by production engineers. These engineered colloids ultimately become the components of catalysts and other functional composites, in effect bringing the length scale accessible by engineering to the range historically associated with chemistry.

The long tradition of industrial collaboration between chemists and chemical engineers will thus be strengthened, as supramolecular chemistry is applied to catalytic, adsorptive and ion exchange products.

Reengineering the laboratory bench

As computational, combinatorial and supramolecular chemistry are fully applied to inorganic materials, industrial research will experience renewed vitality and unprecedented productivity. Experiments will be carefully planned in the light of theoretical insights attained using molecular modeling and then will be rapidly carried out in a parallel fashion to quickly validate and refine those theoretical insights. Promising catalytic and other functional materials will be efficiently screened and optimized with combinatorial tools. Crystal, defect and morphological properties will be designed by controlling the organic-inorganic interface with supramolecular templates. Diffusion, heat transfer, and other important technological characteristics will be engineered into finished products. These new products will be produced by a combination of chemical syntheses using self-assembly phenomena and colloidal processing that has been updated with renewed understanding and application of molecular recognition phenomena. With these updated strategies and enabling tools, inorganic materials R&D will indeed meet the challenges brought by the commercial realities of the new millennium.

Literature Cited

Anthony, R. G., C. V. Philip, and R. G. Dosch, "Selective Adsorption and Ion Exchange of Metal Cations and Anions with Silico-Titanates and Layered Titanates," *Waste Mgmt.*, **13**, 503 (1993).

Bedard, R. L., "Use of Crystalline Intergrowth Molecular Sieves for Removing Contaminant Metal Ions from Liquid Streams," *U.S. Patent* 5,858,243 (1999).

Bein, T., "Efficient Assays for Combinatorial Methods for the Discovery of Catalysts," *Angew. Chem. Int. Ed.*, **38**, 323 (1999).

Breuer, K., J. H. Teles, D. Demuth, H. Hibst, A, Schäfer, S. Brode, and H. Domgörgen, "Zinc Silicates: Very Efficient Heterogeneous Catalysts for the Addition of Primary Alcohols to Alkynes and Allenes," *Angew. Chem. Int. Ed.*, **38**, 1401 (1999).

Briceño, G., H. Chang, X. Sun, P. G. Shultz, and X.-D. Xiang, "A Class of Cobalt Oxide Magnetoresistance Materials Discovered with Combinatorial Synthesis," *Science*, **270**, 273 (1995).

Chapman , D. M., and A. L. Roe, "Synthesis, Characterization and Crystal Chemistry of Microporous Titanium Silicate Materials," *Zeolites*, **10**, 730 (1990).

Gatter, M. G., UOP, unpublished work (1999).

Holzwarth, A., H. Schmidt, and W. F. Maier, "Detection of Catalytic Activity in Combinatorial Libraries of Heterogeneous Catalysts by IR Thermography," *Angew. Chem. Int. Ed.*, **37**, 2644, (1998).

InsightII, Molecular Simulations Inc., San Diego, CA.

Kresge, C. T., M. E. Leonowicz, W. J. Roth, J. C. Vartulli, and J. S. Beck, "Ordered Mesoporous Molecular Sieves Synthesized by a Liquid Crystal Template Mechanism," *Nature*, **359**, 710 (1992a).

Kresge, C. T., M. E. Leonowicz, W. J. Roth, J. C. Vartulli, and J. S. Beck, "Synthetic Mesoporous Crystalline Material," *U.S. Patent*, 5,098,684 (1992b).

Mann, S., D. D. Archibald, J. M. Didymus, T. Douglas, B. D. Heywood, F. C. Meldrum, and N. J. Reeves, "Crystallization at Inorganic-Organic Interfaces: Biominerals and Biomimetic Synthesis," *Science*, **261**, 1286 (1993).

Men'shikov, Yu. P., E. V. Sokolova, Yu. K. Egorov-Tismenko, A. P. Khomjakov, and L. I. Polezhaeva, "Sitinakite $Na_2KTi_4Si_2O_{13}\cdot 4H_2O$. A New Mineral," *Zap. Vseross. Mineral. O-Va.*, **121**, 94 (1992).

Sankan, S. M., "High Throughput Screening of Solid State Catalyst Libraries," *Nature*, **394**, 350 (1998).

Schlögl, R., "Combinatorial Chemistry in Heterogeneous Catalysis: A New Scientific Approach or 'The Kings New Clothes'," *Angew. Chem. Int. Ed.*, **37**, 2333 (1998).

Scott, A., "BASF, UOP Invest in Catalyst Discovery Technology," *Chem. Week*, **7/14**, 26 (1999).

Sokalova, E. V., R. K. Rastsvetaeva, V. I. Andianov, K. Yu Egorov-Tismenko, and Yu. P. Men'shikov, "Crystal Structure of a New Natural Sodium Titanosilicate," *Dokl. Akad. Nauk SSSR*, **307**, 114 (1989).

Treacy, M. M. J., J. M. Newsam, and M. W. Deem, "A General Recursion Method for Calculating Diffracted Intensities from Crystals Containing Planar Faults," *Proc. R. Soc. Lond. A.*, **433**, 499 (1991).

Wilson, S., and P. Barger, "The Characteristics of SAPO-34 which Influence the Conversion of Methanol to Light Olefins," *Microporous and Mesoporous Mater.*, **29**, 117 (1999).