Chapter 2

CATALYST PREPARATION - DESIGN AND SYNTHESIS
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2.1 INTRODUCTION

The purpose of this chapter is to examine the basic notions and premises of catalysis preparation as a science, to delineate the likely driving forces for new catalyst development, and to specify important topical research thrusts for catalyst design and synthesis over the next ten years.

2.2 GLOBAL OVERVIEW OF CATALYST DESIGN AND SYNTHESIS RESEARCH

> "Nevertheless, the importance to both theory and the practice of catalysis warrants a sustained experimental attack on the specification of active centers in heterogeneous catalysts. This requires a theoretical framework ... its construction calls for imagination and a willingness not to be confined by current concepts. Not until we can say for many catalyzed reactions that the mechanisms are known will heterogeneous catalysis finally pass from an art to a science."—G.C. Bond (1974)

Under ideal conditions catalysis science is the science of the "steady state". Heterogeneous catalysts by their very nature are non-equilibrium structures, or at best they are metastable states of a material. In most cases the solid surface of the catalyst and, often the product and reactant matrix above it, may be quite far from equilibrium. Examples of metastable and non-equilibrium structures of catalysts include dispersed metal particles on a high surface area support, a metal oxide in contact with a hydrocarbon reactant, or a highly hydrated zeolite located *in vacuo*. For each case the identifiable structure is dependent upon the pathway that led to its creation. In actuality the full structural development of the catalytically active material may not be complete even after pretreatment, but the interfacial structure will continue to evolve until the reactant and product matrix reach a steady state with the solid surface.

This aspect of catalytic materials preparation has been recognized, but only implicitly, in terms of the dependence of catalytic activity and selectivity upon pretreatment method. Conditions for calcination and reduction of supported metals control their activity and to some extent their selectivity. Now, however, a deeper recognition of the time-factored nature and path dependence of the development of a catalyst's interfacial, and in some cases bulk, structure must be included as a part of ongoing research aimed at the synthesis of new catalytic materials. A portion of this research should be focussed on developing an understanding of the transient phenomena associated with differences in structural attributes that lead to the catalytically active phase.

New research in catalyst design and synthesis should seek to reduce total complexity by increasing structural uniformity and specificity of working catalysts. Highly structured materials with uniform sites are inherently more easily "defined" than those that have a distribution of

active sites. With higher structural definition comes a higher degree of predictability and hence better opportunity for *ab initio* design. The long-range goal of *ab initio* catalyst design, to start at the molecular level of the active site and to extend through to the long-range structure of the solid, can be reached eventually, but only by embracing even more science in heterogeneous catalysis. Success will require an ongoing integration of the key-enabling sciences of inorganic, organometallic, and computational chemistry, with chemical reaction engineering and materials science. It can be argued that catalysis design and synthesis defines the intersection of chemistry, chemical reaction engineering, and materials science (Burton and Garten, 1977) (Figure 1).
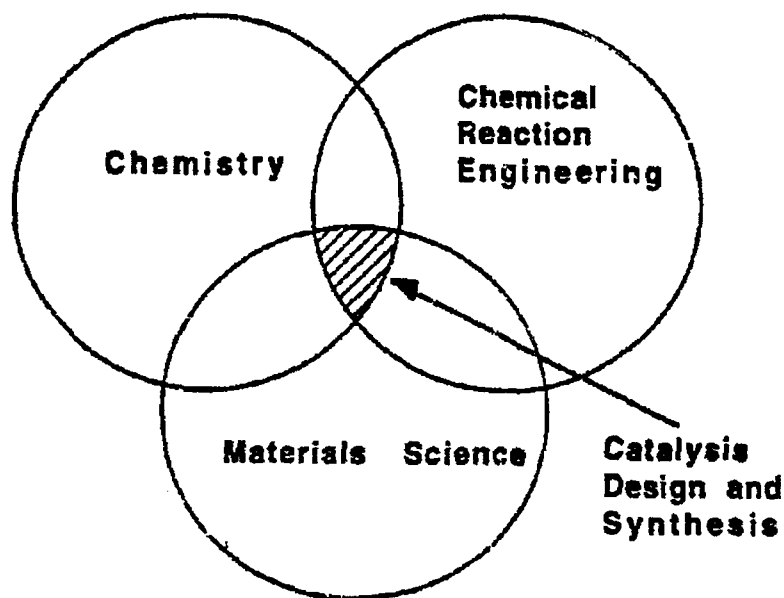

Figure 1. Catalysis Design and Synthesis Defines the Intersection of Chemistry, Chemical Reaction Engineering, and Materials Science.

The research thrusts in the design and synthesis of new catalytic materials must strike a balance between an emphasis on the short-range structure of the active site and the longer-range structure of the solid that constitutes the environment surrounding the active site. Advances in zeolite catalysis teach us that design and synthesis of new catalyst materials must include consideration of the full range of molecular phenomena that make up the process of heterogeneous catalysis, and not just those steps associated with bond-making and bond-breaking at the active site. Diffusion of molecules or ions to and from the vicinity of the active site, as well as energy transfer processes, must be provided for in the design and synthesis. The active site and the bulk structure surrounding it are physically and functionally inseparable. Creative new approaches that force coupling between physical processes and chemical reactions in well-defined ways through control of catalyst structure offer excellent prospects for entirely new processes with lower energy requirements and low to zero waste production.

Equally important will be research aimed at developing a molecular-level understanding of catalytic materials that are inherently non-uniform, that is complex, but well-suited for applications. For example, in petroleum refining, complex mixtures of reactants must be processed efficiently. These complex mixtures can be represented as distributions of different structural attributes. For these systems catalytic materials must present complementary distributions in their physical and chemical properties in order for efficient reaction to proceed. At the global level these materials appear amorphous or disordered, but at the local level these same materials have microstructures that provide the necessary "active sites" for specific reactions. Then, in a very real sense, these materials may be considered to be comprised of distributions of different active sites. This nonuniformity is advantageous for technology, but it complicates the science by frustrating attempts to fully elucidate structure and function, especially under real process conditions. However, progress has been made. A good case in point, perhaps the best, is that of ammonia synthesis, for which fundamental research has built a depth of understanding that is probably unrivaled by any other subfield of heterogeneous catalysis (Jennings, 1991), even though the industrial catalysts are complex solids.

Building on past efforts, the elucidation of complex, industrial catalyst structures must be pursued with renewed vigor. This will require an integration of experimentation and computation. Computation, or simulation, provides a means for expressing the extent of understanding that has been developed at any given point in time. Computation also provides a necessary guide for further experimentation and interpretation of new results. It seems possible, and even probable, that by focusing new research that couples the real surges in the power of computing with breakthroughs in instrumental methods, such as atomic force microscopy, more rapid progress will be made on the problem of structural and functional elucidation of complex catalysts.

At the other end of the spectrum, the synthesis and fabrication of interesting new materials that are either mimics of technical catalysts, or prototypes of new catalysts, can be conducted in ultrahigh vacuum using the methods that have been developed for electronic materials processing. More specifically, by using methods like molecular beam epitaxy (MBE), atomic layer epitaxy (ALE), or low pressure chemical vapor deposition (LPCVD), surface and materials scientists can begin to prepare more complex and more relevant materials that are still quite well-suited to their analysis methods. Some research has begun along these lines and the results appear to be quite interesting in prospect (Zuburtikudis, 1992).

As mentioned earlier in this section it will be necessary also to develop new and better probes of industrial catalysts, especially in their working state, a regime that is as yet largely inaccessible to analysis by spectroscopy. This problem is one that is at least as old as the field of catalysis research, and yet remains unsolved. So, it seems reasonable to focus some research on the development of new methods that address this problem. In the next chapter of the report, this topic is taken up in more detail, however, it is worth considering at this point as a trend in catalyst preparation science that is likely to advance a partial solution to this problem.

As catalyst preparative methods become increasingly more sophisticated, in other words as catalyst preparation becomes catalyst synthesis, industrial catalyst structures will become more

uniform, less difficult to rigorously analyze, and hence more well-defined. Next, with this drive toward more uniformity in catalysts and the advantages it confers, will come the deeper involvement of synthesis specialists trained in inorganic and organometallic chemistries in heterogeneous catalysis. Their involvement will come as a response to the challenges in new "supramolecular syntheses" of materials mandated by specific needs in heterogeneous catalysis technology. In particular, increased interest in materials that can provide both catalysis and separation, shape selectivity, and even molecular recognition will drive research in supramolecular syntheses. By necessity in pursuit of these goals one will carry out characterization as a natural part of synthesis. With time, as this group comes to dominate heterogeneous catalysis as it already dominates homogenous catalysis, the artificiality of divorcing analysis and characterization from preparation and synthesis will tend to disappear. Innovations in developing structural information on the active site during catalysis will be driven by the same group. The continuing development of new and increasingly powerful spectroscopic methods, such as nuclear magnetic resonance, for the analysis of solids that parallel those available for the analysis of solutions, will make it easier to develop molecular level insights into catalyst systems in their working state. It is anticipated that in the next ten years advances in mechanistic understanding of heterogeneous catalysis rivaling those in homogeneous catalysis can and will be made.

2.3 HETEROGENEOUS CATALYST: DESIGN AND SYNTHESIS

2.3.1 Computation and Catalyst Design

Computation will be required in order to shorten the time and to lower the expense traditionally required to move from process conceptualization to implementation (Cusumano, 1992). To carry out process design that simultaneously starts at both the level of the catalyst and the macroscopic level of the reactor will require unprecedented levels of coordination between experimental research and engineering development, that can only be achieved through implementation of emerging computational methods (van Santen, 1987; 1989; 1990). At the current level of computational sophistication in process simulation and chemical kinetics, it is possible to explore the impact of a prospective new catalyst on an optimal process flow sheet given experimental data on rates and selectivities. In this way, preliminary results from experimental research can be extended, computationally, to answer questions of technical feasibility. With this, the best and worst case evaluations of economic and environmental efficiency for new, would-be processes can be done early. In the future, with more powerful computational methods, it may be possible to specify the requirements of the catalyst in terms of the process constraints and then to connect these directly to an optimal set of catalyst structural attributes (Boudart, 1987; 1992). These attributes will form the specific targets of catalyst synthesis. In this way experimentation will not be replaced, but rather it will be assisted and enhanced by computation with a reduction in the time and expense required for development, and in so doing risk will be reduced and profitability enhanced. In the meantime, catalysis research and development must seek to deepen and integrate the functional relationships between conceptualization, theory, synthesis, characterization, and experimental testing of new materials.

2.3.2 Molecular Design and Synthesis of Heterogeneous Catalysts

If computing capability at the molecular level continues to accelerate during the next ten years at the pace at which it has over the last ten years, then it is possible to envision teams of industrial chemists and chemical engineers working together in parallel, rather than in series, to do new process design and development from the level of the catalyst up to the level of the units. Currently, this scenario is still not possible, largely because of the severe limitations on computing the kinetics of catalytic reactions based solely on the structures of solids and the molecules that they are interacting with in the reaction/product matrix. Yet, it is not implausible to expect that the kind of technical progress that must be made in order to do this in catalysis science and technology will be made. For this to become a realization, catalysts must be structurally uniform, highly characterizable and hence "well-defined," so that clear connections can be established between the local structure of the active site and its reactivity.

For enzymatic and homogeneous catalysts, uniformity of active sites is nearly axiomatic. Manifestations of this in the case of homogeneous catalysts are evident (Collman et al., 1987; Parshall and Ittell, 1992). Changes in the identity of the metal center in an octahedral or square planar ligand array produce gross changes in catalytic chemistry required to span the plethora of different process needs, and for any given process chemistry subtle changes in activity and selectivity can be brought about through adjustments in the structure of the ligands. Phosphine ligands in particular can be used to control the steric as well as electronic factors at a low valent metal center. Alkyl groups attached to a phosphorous nucleus distribute in space in a way that diminishes nonbonded repulsive interactions. As the alkyl groups grow in size, they spread further apart, increasing their "cone angle" and thereby shielding the metal center to which the phosphine ligand is attached, like an open umbrella, from attack. At the same time, inductive effects of the alkyl or alkoxy groups on phosphorus can amplify its basicity and in turn increase electron density at the transition metal center. Nature has gone even further in that the macromolecular environment around the active site confers a high degree of substrate specificity and even molecular recognition. Currently, chemists can do a good job of building mimetics for the active sites in some enzymes, for example of the Blue Copper Proteins (Karlin and Zubieta, 1986), but the full effect of the active site combined with its macromolecular environment is difficult to fully analyze, let alone imitate. Yet, it is just this coupling between the uniform active sites and their highly specific molecular environments that we seek to emulate with heterogeneous catalysts, the synthetic analogues to enzymes. Shilov (1992) has championed this approach and refers to it as "catalysis with organized molecular systems". These organized molecular systems are multicomponent systems designed along the lines of enzymes.

To achieve the goal of producing catalysts with high active site uniformity and well-defined structures, catalyst preparation must be raised to the level of synthesis. The problem is one that is more germane to a synthetic specialist, such as an organometallic or inorganic chemist, than it probably is to any other chemical professional. Synthetic chemists routinely design and assemble molecules with uniform and "well-defined" structures. This already is done for zeolitic catalysts. Despite this it is not appropriate to expect classical synthetic chemists to produce the next revolution in heterogeneous catalysis design and synthesis. Instead, this must be done by catalysis chemists and engineers, the applied scientists who know the field, what the major

questions are, and what are significant new problems worthy of pursuit. It is expected that professionally trained inorganic and organometallic chemists, in addition to chemical reaction engineers and materials scientists, will cross over from their traditional fields of expertise into the arena of heterogeneous catalysis to pursue interdisciplinary research themes. Hence the real challenge for the next twenty years is to bring the most powerful methods and approaches of supramolecular synthesis and characterization into heterogeneous catalysis, and this must be done by those chemists and engineers who identify themselves with catalysis and seek to define it as a true discipline.

Since heterogeneous catalysis is a discipline that necessarily resides at and defines the intersection of chemistry, chemical reaction engineering, and materials science, the interdisciplinary nature of the field will become even more evident in the future Catalysis is concerted molecular phenomena that goes beyond bond-making and bond-breaking processes and into the transport of heat and mass between the gas liquid and solid phases. The solid catalysts are not simply two-dimensional solid surfaces, as some would represent them, but are richly structured, highly textured, complex phases that lie between two and three dimensions. Because of this the catalyst scientist cannot work effectively within the normal confines of local molecular structure that form the core of interest for the traditional chemist; nor can the catalyst scientist be a traditional reaction engineer, since a full appreciation of catalytic reaction networks and elementary steps must include the structure of the catalyst and some conceptualization of its active site or sites. Neither can the materials scientist examine only the static structure of the solid, since a catalyst is not a catalyst until it is dynamically interacting with a reactant and product matrix. So catalysis pushes at the envelopes associated with each of these fields as disciplines in their own right and forces the practitioner to expand his or her field of interest and expertise.

As such, catalysis scientists are applied scientists working very close to technology, but they must seek to integrate even more fully the enabling aspects of the pure sciences of inorganic and organometallic chemistry with chemical reaction engineering, surface, and materials science. With the future goal of *ab initio* design of catalysts from the microscopic level of the site up to the macroscopic level of reactors as a driving force, a new discipline and science can emerge. If *ab initio* design of uniform active sites in supramolecular architectures is the raison d'être of catalysis research, then the integration of the pure and applied sciences must proceed expeditiously, but in an earnest, scholarly as well as applied fashion.

2.3.3   Application of Solid State Electronics Technology for Catalysis Design and Fabrication

Nanoscale devices and machines are an emerging frontier of engineering science (Drexler, 1992). Catalysts are truly nanoscale devices that deserve to be mentioned in the same "high-technology" context as electronic devices. In contrast to solid state electronics, the role they play in technology is more hidden and removed from everyday experience and so they are less apt to be considered in the context of recognizable high technologies. Despite this difference, there are parallels and similarities between heterogeneous catalysts and solid state electronic devices that are worth considering.

Transistors, the microscopic components of integrated circuits, epitomize solid state technology. The degree to which microstructure and composition can be controlled, especially with silicon VLSI microfabrication methodologies, is impressive (Ghandi, 1983). Features that are on the order of 0.1 microns are routinely fabricated, and emerging methods allow for the feature size to be reduced to a few tens of nanometers or less. Silicon substrates are prepared with bulk purities meeting or exceeding 99.999%, and doping can be done at the level of a few parts per million with high reproducibility. Furthermore, during the last decade silicon microfabrication methods have transformed the micromachining of other three-dimensional structures including sensors, accelerometers, and capacitors. Even a gas chromatograph column has been fabricated on a chip of silicon! (Angell *et al.*, 1983).

Catalytic phenomena and catalysts are even more challenging to treat than electronic phenomena and solid state electronic devices. In contrast to electronic devices that rely upon the phenomenon of solid state electron transport, catalysts rely upon phenomena that consist of several simultaneous molecular-level processes. Until recently electronic devices with micron to tenth-micron feature sizes could be treated and designed on the basis of sound theoretical models for the electronic structures of solids. In contrast, the treatment of catalysts demands that more specific molecular level considerations be taken into account, on length scales that are below the limits of continuum level models. As a result, there is no one overarching theory to guide catalytic materials design.

In the broadest general terms, catalytic phenomena consist of processes of energy and mass transport, and bond making and breaking. At the level of transport phenomena good advances have been made in theory, particularly in the treatment of molecular diffusion through porous solids. If the global rate of a catalytic process is controlled by Fickian or Knudsen diffusive transport to an active site where reaction occurs, then it can be described adequately by a continuum level analysis and *ab initio* design can be accomplished. However, even for some transport-limited problems, accurate, continuum level descriptions break down as the operative physics approach the molecular level. An example is the problem of simulating molecular transport in ultramicropores that have dimensions similar in size to the transporting molecules. With zeolites theoretical advances have been made in simulation of transport, especially for materials with high silicon to aluminum ratios for which good potential functions are available, and at low adsorbate loadings (Cook *et al.*, 1992; van Santen *et al.*, 1992).

It is suggested that there is an analogy between the physics of solid state electronic devices and heterogeneous catalysts. It is further suggested that advanced techniques used for solid state electronic devices, coupled with modern theoretical transport calculations can be a fruitful area to be investigated for design and fabrication of new and improved heterogeneous catalysts.

2.4 RESEARCH THRUSTS FOR CATALYST DESIGN AND SYNTHESIS

In this section are described new thrusts for heterogeneous catalysis research over the next twenty years. These new thrusts are described first in terms of new "effects" or "concepts" that have been identified as important to the advancement of the field, but which are not fully explored scientifically, and the degree to which they can be exploited for new catalyst

technology, as yet, has not been fully defined. This section motivates the next section in which new thrusts in heterogeneous catalysis are given in terms of the traditional disciplines or enabling sciences of inorganic and organometallic chemistry, chemical reaction engineering and computation, and materials and surface science. The two sections are coupled in that the exploration of new catalysis "effects" will demand advances that can only be brought to fruition through new research using the methods and techniques of these disciplines.

2.4.1   New Catalysis Effects and Concepts

"It is proposed that major progress in catalysis occurs in a stepwise manner. Breakthroughs which revolutionize technology occur every five to ten years. After such a breakthrough, there are extended periods during which fundamental research investigating the underlying phenomena leads to better understanding and gradual improvement of the new technology. During such periods, it may appear that a field or even the whole of catalytic technology is relatively mature. This is, however, a misconception because history teaches us that fields which appear mature are suddenly revitalized by a major discovery." (Heinemann, 1988).

Over the last two decades tremendous strides have been taken in catalysis as science and catalysis as technology.· In the past, especially in the first half of this century, catalysis science naturally and necessarily followed technology. Discovery guided by intuition ran well ahead of logical analysis and synthesis. This can be documented for many cases, including ammonia synthesis, reforming, hydrotreating, cracking, and Fischer-Tropsch syntheses. With these technologies in the lead, catalytic science was advanced in specific areas such as promoted bulk metals, catalysis by supported metals and alloys, non-metal catalysts, solid acids, zeolites, and other molecular sieves. From these research thrusts came deeper understanding, which in turn led to new concepts and the identification of effects in catalysis, such as electronic versus textural promotion, metal-support interactions, surface organometallic chemistry, structure sensitivity and insensitivity, and kinetic coupling, to name a few. Over time, these concepts and effects have been raised to the highest levels of scientific rigor and now constitute the foundation of catalysis as science. At this point in time the science of catalysis, it can be argued, does not lag behind the technology. With the science, embodied in synthesis and analysis, in the lead, new catalyst technologies can be developed more rapidly than through the slower processes of empiricism. This is not to suggest that unexpected, fundamentally new catalytic phenomena will not be discovered or invented; they will be, but even for these cases the process of discovery and the implementation of such discoveries should be accelerated by the science.

Over the past ten years a few new concepts and effects have emerged from catalysis technology and science, that define the frontier for the next ten years. An exploration of these concepts and effects is motivated by the promise that they offer for major advancement of the field, both as science and as technology. In particular these new concepts include the following:

- ► Combined catalysis and separation

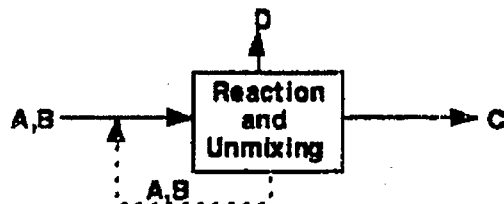- ► Shape selectivity and molecular recognition

2.8

- Site isolation

- Multifunctionality

- New solid acids and bases

- Numeric and heuristic computing for design.

2.4.1.1 Catalysis and Separation

Combining *catalysis and separation* into one unit operation (Figure 2) has many appealing, potential advantages for selected problems in catalytic technology. At the macroscopic level one example of this integration of two unit operations into one is catalytic distillation in which the plates of a distillation tower are loaded with catalyst, reactants are fed to the column, products are formed at the catalyst, and the components of the reactant and product matrix are distilled away from each other to be taken off the column in pure form at different points along its height. The potential advantage of this particular approach is that capital costs may be lower, but more importantly, closed system equilibrium-limited conversions may be overcome with substantial savings in energy.
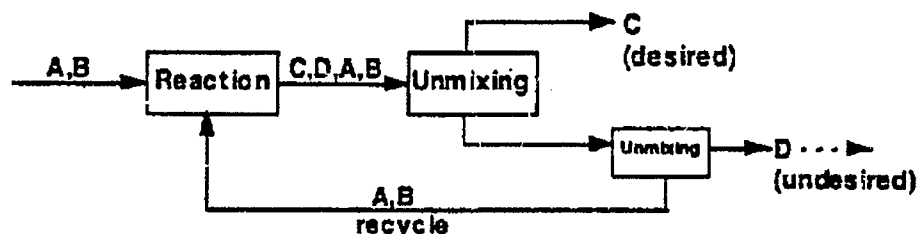

Figure 2. Classical Sequential Processing Versus Simultaneous Processing with Integrated Reaction and Separation.

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As interesting as the integration of distillation and reactor technology is, the integration of membranes and catalytic reactors is even more interesting (Armor, 1989; 1992) (Figure 3). As in the case of the reactive distillation, the same incentives exist for integrated reactor and membrane technology: potentially lower capital costs and release of the closed system, equilibrium constraints. However, with the integrated membrane-reactor approach an additional, very important incentive is the potential to substantially lower the total energy requirements for the conversion of reactant to pure, unmixed products. In conventional catalytic process technology, which includes an upstream reactor and downstream distillation train, major costs are tied up in the capital and energy expenditures that are necessarily associated with distillative separation. In principle, the energy costs for a well-defined and efficient membrane reactor unit should be substantially lower than those for conventional technology.

Having recognized the potential advantages of membrane reactor technology, it must also be recognized that it will probably have application in selected niches of process chemistry that can most benefit from the advantages it offers (Cicero and Jarr, 1990; Shu et al., 1991; David et al., 1992). Lower energy costs and the release of equilibrium constraints, offered by membrane-

- **Catalytic Membrane Reactors**
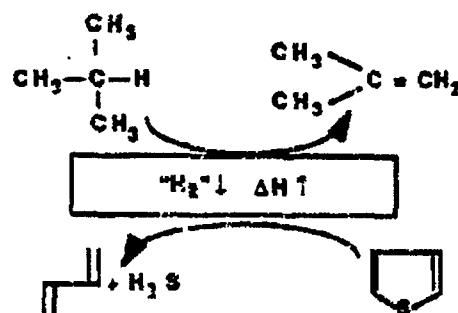
- **Adsorption and Catalytic Regeneration**
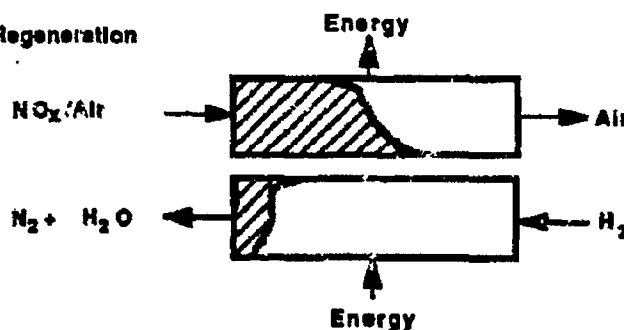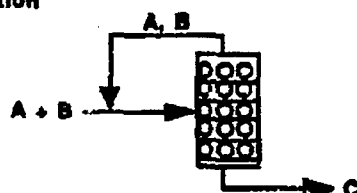
- **Catalytic Distillation**

Figure 3. Approaches to Catalysis and Separation by Three Distinct Methods.

reactor technology, are particularly important considerations for developing new approaches to endothermic reactions. Currently, the commercial use of saturated hydrocarbons, especially components of natural gas, as feedstocks for fuels, fuel additives, and chemicals is limited by the thermodynamics of dehydrogenation. A good example is ethane to ethylene (Tsotsis *et al.*, 1992), another is isobutane to isobutene. The latter is particularly interesting since isobutene is used to produce MTBE and the demand for it outstrips current capacity. Despite the fact that there are industrially practiced technologies for producing isobutene from isobutane, such as the Catofin[R] process, the increase in demand and the need for ever improving processes with higher efficiencies drives new research. New approaches to this and other hydrocarbon dehydrogenation motivate the fuller exploration of catalytic membrane-reactor technology in all its possible forms.

Enough early research into catalytic membrane-reactor technology has been done to be able to lay out the most important areas of topical research. First, at the level of the materials used as high temperature membranes, the options are metal alloys with exclusive permselectivity for hydrogen, ceramic membranes with Knudsen-like diffusional mechanisms, hybrid structures of the two, and new molecular sieving membranes based on zeolites, ultramicroporous carbons and other monolithic forms of molecular sieves (Burggsaaff *et al.*, 1991). New research needs to be done on the materials issues associated with each of these, especially with respect to synthesis of new structures and the mechanisms for deactivation and failure for both new and existing membrane systems (Wang *et al.*, 1992; Foley *et al.*, 1993). At another level the analyses of the dynamics of membrane reactors are not generally well described or understood, particularly for the systems that operate on the basis of the Knudsen mechanism, despite exceptions for a few specific cases that are more well-described. These two problems — materials and dynamical modeling—frustrate design and implementation. Finally, for the case of low to moderate temperature dehydrogenation, driven to high conversion by hydrogen transport through the membrane, catalysts must be able to withstand coking and other forms of deactivation which are expected to be somewhat accelerated at lower hydrogen fugacities in the reaction zone.

2.4.1.2 Shape Selectivity and Molecular Recognition

Zeolites have revolutionized catalysis and have provided a degree of control over reaction dynamics that was previously unattainable (Csicsery, 1976). Initially used as solid acid catalysts for hydrocarbon cracking, presently zeolites have demonstrated utility in a wide array of reaction chemistries including acid-catalyzed fine chemicals synthesis, Fischer-Tropsch synthesis, oxidations, and even base-catalyzed reactions. Not only are zeolites useful catalysts for a wide array of reaction chemistries, they also lead to markedly different selectivities when compared to non-zeolitic catalysts. As patterns of selectivity emerged and were analyzed, an effect termed *shape selectivity* was recognized to be caused by mediation of transport and reaction by the zeolite framework. Upon further analysis shape, selectivity was conceptualized to arise through one of three mechanisms in the zeolite pore structure — reactant transport, product transport, or transition state constriction. In essence, reactant and product shape selectivity, which constitute the bulk of examples of shape selectivity, are the ultimate forms of separation and catalysis. The zeolite catalyst is a nanoreactor device that combines the two unit operations into one on a microscopic level.

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An example of this coupling of reaction and separation at the microscopic level is given by the synthesis of para-xylene from methanol and toluene over a pore-mouth narrowed ZSM-5 catalyst (Haag and Chen, 1987) (Figure 4). Methanol and toluene transport into the core of the zeolite through the layer of narrowed pores and react to give an equilibrium distribution of products. At equilibrium the selectivity to para-xylene under standard process conditions is approximately 20%. For the treated zeolite catalyst the selectivity can rise to over 80%. The reason is that the equilibrium at the core of the catalyst is continuously and selectively bled in favor of the para-xylene. Para-xylene has a substantially higher diffusivity than that of either ortho- or meta-xylene, presumably because of its more streamlined shape. Taken from another point of view, this example of zeolite product shape selectivity and preferential transport is one of the few cases in which a heterogeneous solid catalyst can begin to approach the level of selectivity and "molecular recognition" embodied in cellular enzymatic catalysis. Other microporous molecular
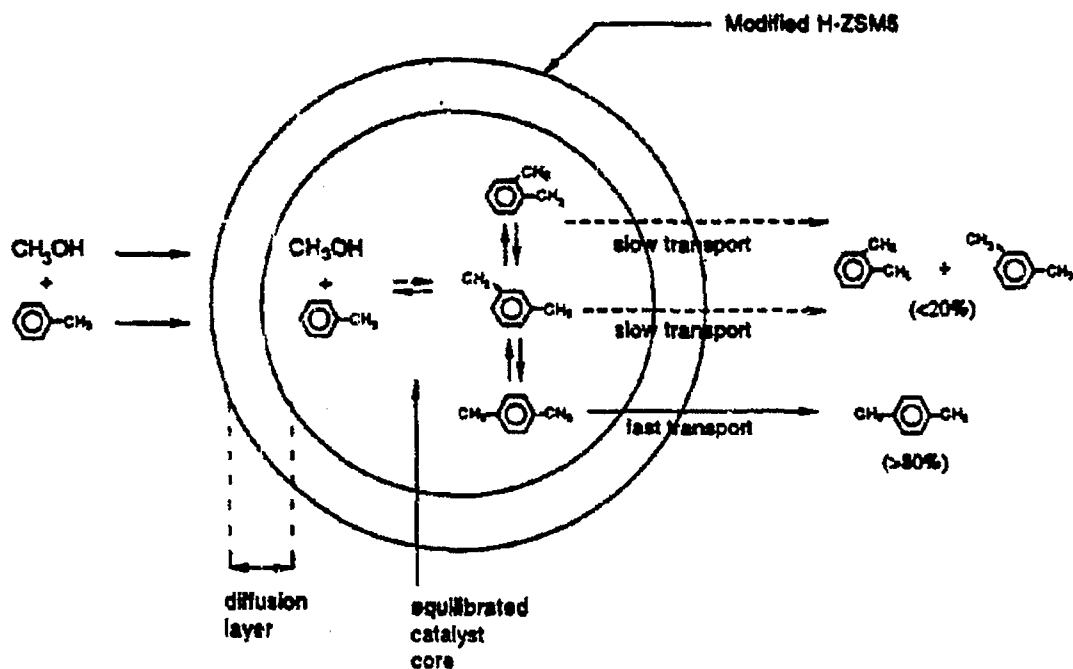

Figure 4. Product Shape Selectivity in the Synthesis of Para-Xylene from Methanol and Toluene Over a Modified H-ZSM5 Catalyst.

sieves with medium pore sizes, such as SAPO-11, also display this behavior. In fact, the AlPO$_4$ family of molecular sieves and their isomorphically substituted analogues are under intense scrutiny for application in both petroleum-related and chemicals-related catalysis (John et al., 1992). Hence the phenomenon may be far more generally exploitable than was once recognized.

The ultimate in "molecular recognition" will come about when chiral catalysis can be done with a zeolite or molecular sieve. David (1993) suggests that it should be achievable through a detailed consideration of molecular topography.

What is now accepted as shape selectivity has broadened the original view of zeolites as unusual solid acids to one of "nanoscale reactors" that control transport to and away from the active sites where bond-making and breaking occur. In the limit of zeolite framework effects, it can be shown that the pore structure actually constrains the transition state of certain reactions, thus altering selectivity. The restricted transition state phenomenon can prevent transalkylation during bimolecular alkylation of aromatics. It was not a long jump to realize that zeolites also could be used to confine and limit the growth of metal particles within their pores. This has been demonstrated in a number of cases and appears to have relevance not only for catalysis, but also for the synthesis of electronic devices based on quantum-dot principles. At the same time it has been realized that the basis for shape selectivity in zeolites is their molecular-sized pores and this is a feature that is not exclusive to zeolites but rather is a general property of any solid material with connected free-volume and molecular-sized pores.

With this realization has come an explosion of new materials with unexpected molecular sieving properties. Examples include silico-aluminophosphates, carbogenic molecular sieves, transition metal-silicates, some transition metal oxides and new silica-aluminates with tunnel structures that can be synthesized with virtually a singular pore size but over a wide range of single values (Kresge et al., 1993).

In many ways these materials offer the ultimate in separation and catalysis since they can be depended upon to integrate the two at the molecular level. The frontiers for synthesis in this area of catalytic materials seem limitless and advances can be expected to accelerate. Modeling, particularly of reaction and molecular transport, in these structures has only just begun to be seriously attacked. Two primary problem areas need much deeper consideration: computation methods and potential functions. Even with the tremendous advances that have been made in computing power and efficiency, these computations are massive and even in simplified form they rapidly outstrip reasonable CPU times with the best available hardware and software. Today practical *ab initio* calculations are limited to about ten moderately heavy atoms. Excellent opportunities exist for attacking the problem with more effective computing strategies, for example parallel processing, or with more effective theoretical approaches to simplify the computation while maintaining the essential features of the problem — density functional analysis is one such approach. At another level even if the computing problem could be resolved instantly, the simulations of transport in molecular sieving media would still be frustrated, except for only the simplest cases, the lack of adequate potential functions to account for realistically complex interactions that account for the coupled electrostatic as well as van der Waal forces exerted by zeolite structures on adsorbates

Eventually, research in shape selective materials will lead to shape selective membranes providing the ultimate in membrane reactor technology, and hence catalysis and separation. MCM-40 from Mobil (Kresge et al., 1993) is a good example of the kind of new, highly structured microporous material that can be expected to emerge in catalysis over the next decade.

2.4.1.3 Site Isolation

With the synthesis of uniform active sites also goes the notion of *site isolation*. If parallel pathways leading to different products are catalyzed by different sites for the same reactants on a nonuniform catalyst, then in principle a particular pathway could be favored and selectivity increased by the extent to which one site can be synthesized over another. Hence, the motivation to explore the synthesis of uniform active sites. If active sites are in close proximity, then there is also the possibility that intermediates can diffuse between these sites opening up the potential for sequential and possibly deleterious reactions to occur. Isolation of these sites to prevent diffusive or reactive communication between them can provide increased selectivity, especially in favor of the early products in a series of reactions. This provides the driving force for exploring the synthesis of kinetically isolated uniform sites.

An example of site isolation and its effect on selectivity is provided by the case of allylic oxidation over uranium and antimony oxides (Grasselli and Burrington, 1981) (Figure 5). As in any selective oxidation, the objective is to develop a catalyst that will produce the highest yield possible of desired product, in this case acrolein. Over UO_3 and $USbO_5$, propene is converted at equivalent conditions primarily to carbon dioxide and water, the undesired deep oxidation products. However, over USb_3O_{10} propene is converted to acrolein with high selectivity. The different and substantially better behavior of USb_3O_{10} is attributed to site isolation (Grasselli and Suresh, 1972; Oyama, *et al.*, 1993) (Figure 6). Inspection of the crystal structures of UO_3 and $USbO_5$ shows that in the former, uranium oxide sites are surrounded by other uranium oxide sites, whereas in the latter, the lattice planes are comprised of rows of uranium oxide sites separated by rows of antimony oxide sites, so that in one dimension uranium sites are adjacent to antimony sites but in the other dimension they are still adjacent to each other. But with the USb_3O_{10} structure, uranium sites are islands surrounded by a band of antimony oxide sites, so that uranium oxide centers are only adjacent to antimony oxide centers and are never found adjacent to other uranium sites. This island-like structure led to the concept of site isolation and it is to this structural feature that the selectivity is ascribed.

This concept of site isolation may be useful in the design of new oxidation and oxidative dehydrogenation catalysts for other more demanding reactions. After all, the most selective oxidation catalysts are natural enzymes and these systems are completely site isolated. In fact, good progress has been made by mimicking the site isolation of enzymatic active sites with fluorinated metalloporphyrins (Ellis and Lyons, 1992). Site isolation in solids comparable to that achieved in the metalloporphyrins may be obtained through the use and occupancy of particular ion exchange sites in metal-containing zeolites. Zeolites are particularly attractive, especially since site isolation alone is not enough — one must also have optimal site densities per unit area of catalyst surface.

In acid catalysis by zeolites the effect of site isolation is well known. The catalytic activities of HZSM-5 and dealuminated Y-type zeolites are linearly related to their framework aluminum contents. This proportionality indicates that every active site is nearly equally active. The active sites in high Si-Al zeolites are not only homogeneous but are "in a state of an ideally

O = Oxygen

● = Uranium

UO₆   SbO₆

UO$_3$ USbO$_5$ USb$_3$O$_{10}$

U—Sb—U	Sb—Sb—Sb	Sb—Sb—Sb	Sb—Sb—Sb
Sb Sb	U Sb	Sb Sb	Sb U
Sb U Sb	Sb Sb Sb	U Sb U	Sb Sb Sb
Sb Sb	Sb U	Sb Sb	U Sb
U—Sb—U	Sb—Sb—Sb	Sb—U—Sb	Sb—Sb—Sb
c = 0	1/4	1/2	3/4
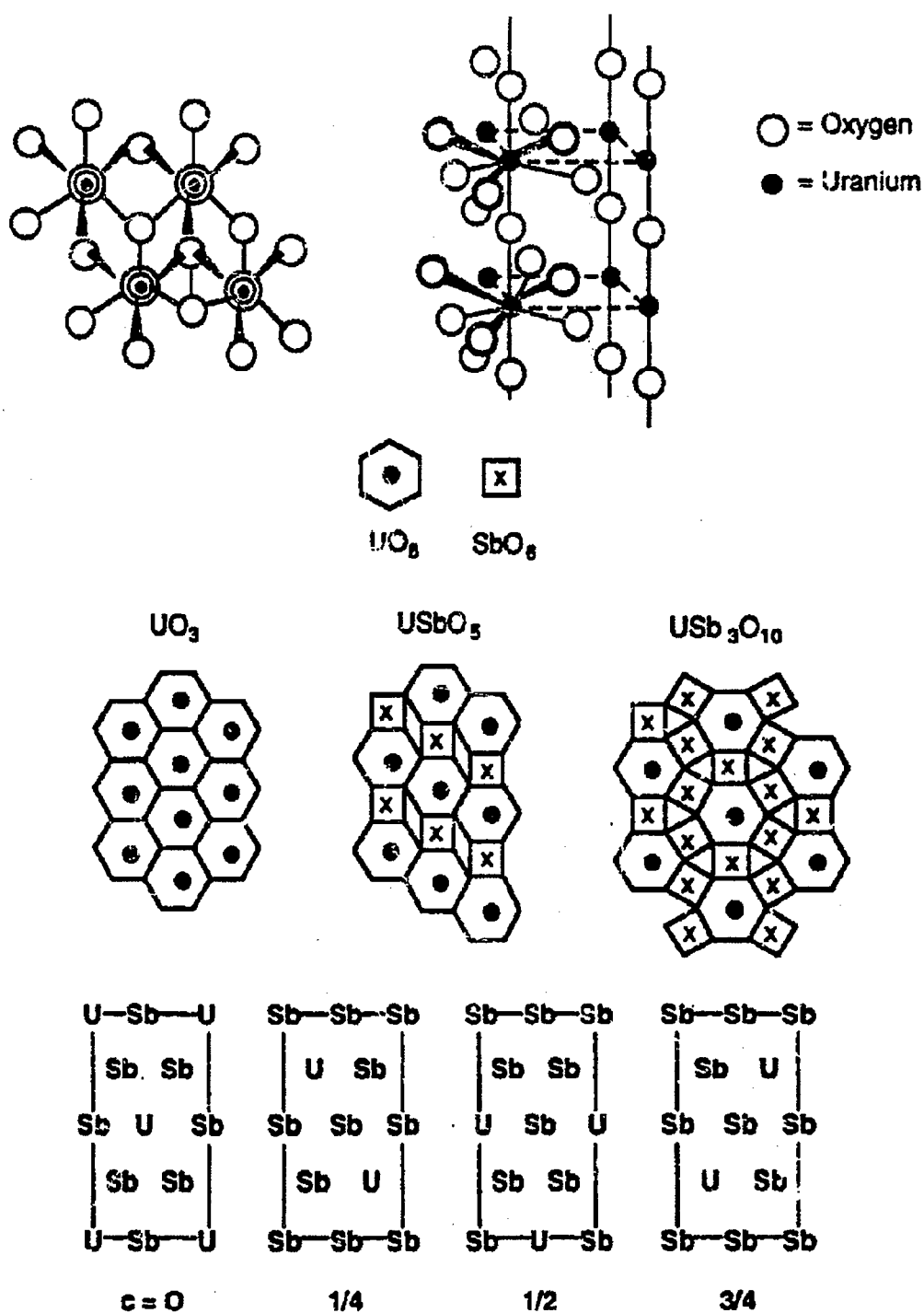
Figure 5.   Structures of UO$_3$, USbO$_5$, and USb$_3$O$_{10}$ and (bottom row)
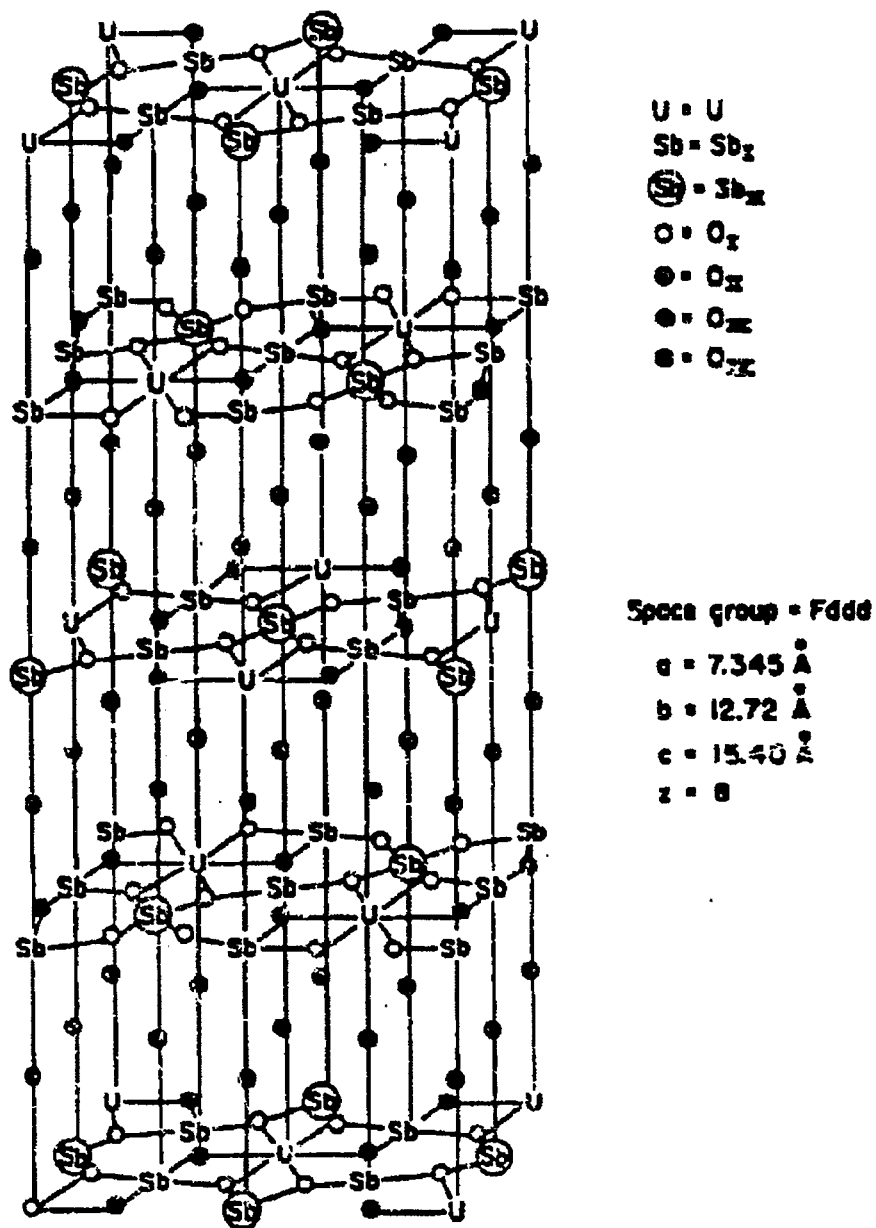Cation Positions in USb$_2$O$_{10}$. (Adapted from Grasselli and Suresh, 1972).

2.15

Figure 6. Unit Cell Structure of USb_3O_{18} Showing Cation and Anion Positions.
(Reprinted from Grasselli and Suresh, 1972, by permission of Academic Press).

dilute solution" (Haag and Chen, 1987; Rabo and Gajda, 1990). This is a classical example of site isolation in a solid catalyst.

Another feature of site isolation that is perhaps as crucial as the effect of physical separation from other sites is the ability to truly modify the electronic properties of the isolated metal. Isolated metals by their nature differ electronically from metal particles since they do not have a band structure. Instead, their atomic orbitals are mixed with those of their non-metallic, nearest neighbors into metal-ligand molecular orbitals. As a result, the electronic properties of the nearest neighbor atoms and their geometric disposition can have a marked and real effect on the reactivity of the site isolated metal. Metals confined to the ligation spheres of molecular catalysts are the epitome of site isolation. It is well known that in these systems the metal's reactivity, and hence the catalyst's activity and selectivity, is highly dependent upon the choice of ligands. This has been done already in metal-containing zeolites. Recently, small isolated clusters of palladium have been reported to form in NaY and 5A zeolites (Beutel et al., 1993).

Site isolation in solids is the best approach to reproducing the specificity and control offered by homogeneous molecular catalysts. The design of catalysts for specific reactions will require site isolation. It has been reported that for the reduction of carbon monoxide by hydrogen, supported bimetallic catalysts comprised of rhodium and an early transition metal oxide from Groups IV to VI or lanthanium oxide have higher selectivity toward methanol and other alcohols than do catalysts comprised of just rhodium, which tend to produce methane (Figure 7).

Several groups have considered this to be due to a textural promotion of rhodium by the early metal oxide rendering it ultra- or atomically dispersed. This is the ultimate in textural promotion, and when considered at the molecular level of the active site, may prove to be another example of site isolation, but in this case for a reduction step rather than for an oxidation step.

2.4.1.4   Multifunctionality

For complex reaction mixtures such as those encountered in petroleum refining multisite catalysts are useful and even preferred. In these systems, because of steric demands or other constraints associated with the complexity of the reactant matrix, different sites may be required to carry out generically the same chemical steps, for example, hydrogenation or desulfurization. In some instances even for simple, not complex reactant feeds, the reaction pathway from reactant to final product demands that several generically different reactions be coupled together. In these instances there is a need for multifunctional catalysts in which the different sites carry out generically different reaction steps. In fact, for some catalysts each functional type of site may actually be distributed, so these systems are both multifunctional, multisite catalysts. The classic example of an industrial catalyst that is multifunctional is the petroleum reforming catalyst. In this system two separate functions, one for dehydrogenation of hydrocarbons by supported metals and the other for skeletal isomerization of unsaturated hydrocarbons, are combined to work together (Mills et al., 1953). By working in concert, the rates of skeletal isomerization are markedly increased since the latter steps require a carbenium ion intermediate to proceed, and
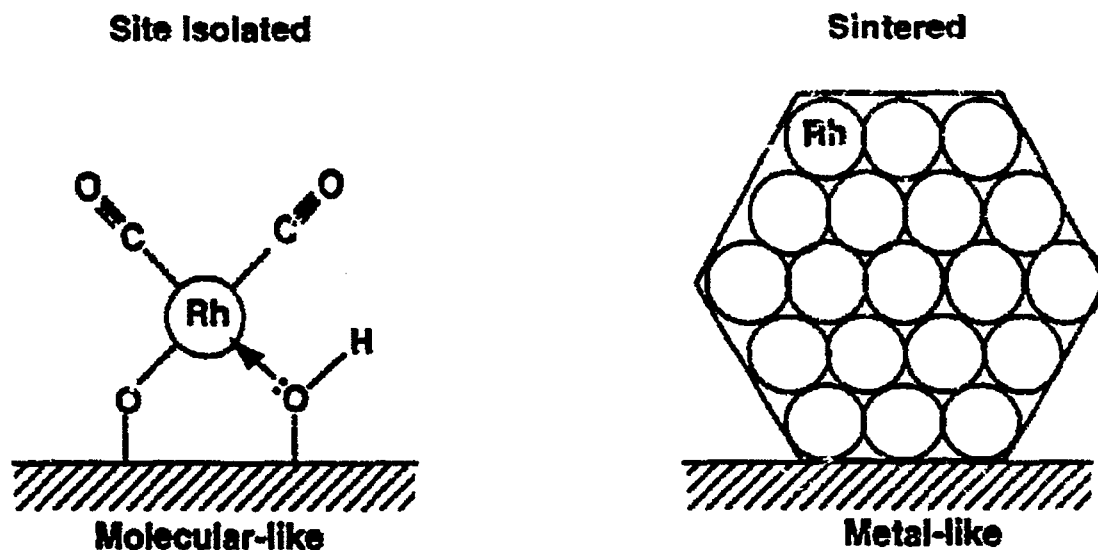
Figure 7.   Site-Isolated Versus Sintered Rhodium on an Oxide Support Surface.

this is efficiently produced from an unsaturated hydrocarbon (Figure 8). Transport and reaction between the two kinds of sites was probed explicitly by combining a dehydrogenation catalyst (Pt/SiO$_2$) with an acid catalyst (SiO$_2$-Al$_2$O$_3$) (Weisz and Swegler, 1957). It is irresistible to describe this multifunctional effect as synergy, since either function alone would lead to quite different ends at quite different rates. More recently, metal-containing zeolites also have been shown to be able to do this kind of coupled chemistry.

It seems logical that if the synthesis and control of separate uniform sites for generically different chemistries can be accomplished, then it also eventually should be possible to synthesize and assemble these sites on the same material to produce well-defined multifunctional catalysts that are true nanoscale devices.

2.4.1.5   New Solid Acids and Bases

Zeolite solid acids are ubiquitous as catalysts for a wide range of processes that lead either to carbon-carbon bond breaking or making steps. It is likely that further advances in this arena will come through more complete control of pore sizes especially at the large end of the range (> 7.4Å).
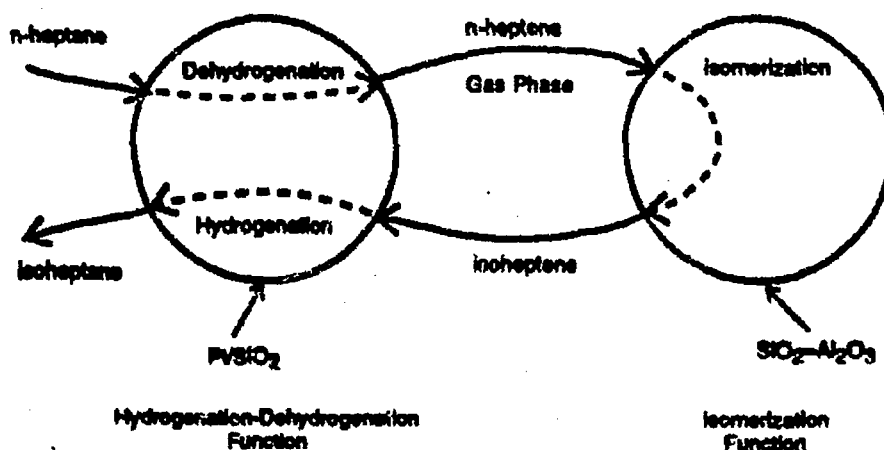
2.18

**Figure 8.   Transport and Reaction of n-Alkanes Between
Metal and Acid Functionalities and Example of Bifunctional Catalysts.**
(Adapted from Gates et al., 1979).

At the same time, many other molecular sieving materials are now available and will lead to new catalysts for acid catalyzed reaction. These systems will include the aluminophosphates with the full range of isomorphically substituted analogues, synthetic clays, and layer structures and heretofore unanticipated materials such as MCM-41.

Interestingly, much less has been accomplished in the area of solid-base catalysis (Pines, 1981; Tundo, 1992). Some reactions such as isomerizations and hydride exchanges have been reportea to occur. Most catalysts in this category have been prepared by supporting basic oxides or carbonates, liquid metals, or organic bases in suitable solids. More recently side chain alkylation of toluene to ethylbenzene has been investigated over alkali-metal excharged and phosphorous-doped zeolites (John et al., 1992).

Oxidative coupling of methane especially to produce ethane and ethylene can be carried out with lithium metal supported on MgO. Intercalated alkali metals in graphite also are catalytically active for various reactions but they suffer from short lifetimes, thermal instabilities, and oxygen sensitivity (Bartlett and McQuillan, 1982). New forms of carbon, particularly carbogenic molecular sieves with ultramicroporosity, like that of zeolites and other molecular sieves but with little or no inherent acidity, should be ideally suited for the dispersion and stabilization of alkali metals for base catalysis. Fullerene carbons offer the opportunity to prepare crystalline carbon structures with free volume and molecular sieving properties.

2.4.1.6 Numeric and Heuristic Computing for Design

Numerical models of catalytic phenomena that are well-described by continuum level analyses are proving to be exceptionally useful for the optimal design of catalyst structures. These models have been employed, for example, to optimize the pore structure of particular catalysts, used in SCR, HDM, and other applications (Beeckman and Hegedus, 1991; Hegedus and Pereira, 1990; Pereira et al., 1988a; 1988b) in order to squeeze out the highest efficiency possible. The processes captured by these numeric models are inherently deterministic and so can be handled explicitly. Thus the advantage of this approach is that it allows the catalyst design engineer to utilize the full power of modern computational methods to describe the problem with all its inherent complexity at a level previously unrealizable.

In contrast, even the simplest cases of molecular sieving or reaction phenomena defy complete analysis and simulation since they occur on length and time scales well below the continuum limit, as explained earlier in this chapter. Although good efforts are under way to bring higher level theory to these problems, they are still in the research stages and provide little help to the practitioner of catalysis faced with an actual design problem. Despite the lack of rigorous numeric models for reactions at active sites, catalysis experts have and do continue to design novel catalysts with new components and functions. This is done largely through the use of heuristics — design rules that are assembled through analogy and experience (Foley et al., 1992). The type and level of heuristics that any one expert or group of experts may employ depend upon their training, exposure to other disciplines, and experience base in heterogeneous catalysis. True experts are considered to be insightful because they are able to establish a path forward that can be implemented with high likelihood of success. The insights attributable to specialists derive largely from their ability to recast the problem at hand and to attack it heuristically, at least at the initial stages of the research. Their success is largely dependent upon the quality and sophistication of their heuristics which are both personal and cumulative over time (Figure 9).

The value then of an expert in the industrial setting is his or her ability to derive a solution to a problem creatively so that a novel result is produced expediently, so that the time and cost required to derive the result can be minimized. Two problems immediately come to mind. Despite similarities in training, some individuals are more effective than others. Yet in many cases this higher effectiveness or insight cannot be readily transferred to others with less experience. This raises the second problem. When the highly effective individual expert discontinues practice, the heuristics that led to higher effectiveness and deeper insights may be lost. A mechanism needs to be established to codify as much as possible, if it is possible, heuristics employed by experts so that they are transferable and not lost.

Another trend that needs to be dealt with is the crush of information that can be routinely produced in research programs. One need only follow the literature of heterogeneous catalysis to realize that with automation and better instrumentation, catalysis researchers are able to produce unprecedented amounts of new information. Information is not knowledge and information alone is difficult to apply; it must be reviewed and distilled for its key elements. At the same time, information storage and retrieval must be handled in new ways in order to
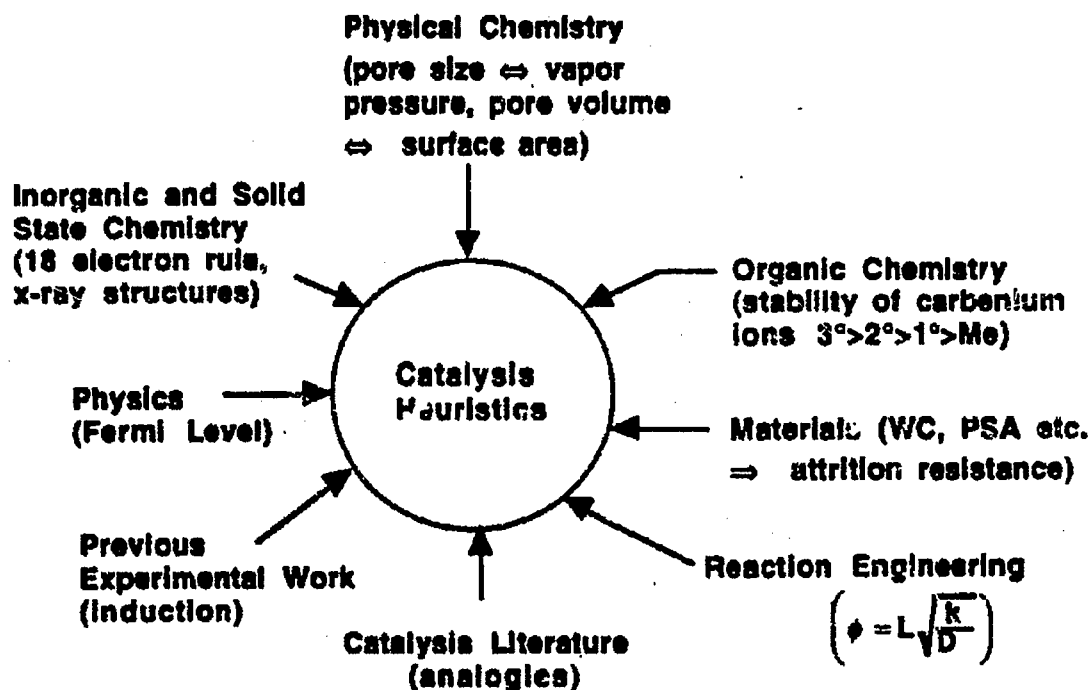
Physical Chemistry
(pore size $\Leftrightarrow$ vapor pressure, pore volume $\Leftrightarrow$ surface area)

Inorganic and Solid State Chemistry
(18 electron rule, x-ray structures)

Organic Chemistry
(stability of carbenium ions $3°{>}2°{>}1°{>}$Me)

Physics
(Fermi Level)

Catalysis Heuristics

Materials (WC, PSA etc. $\Rightarrow$ attrition resistance)

Previous Experimental Work
(induction)

Reaction Engineering
$$\left(\phi = L\sqrt{\tfrac{k}{D}} \right)$$

Catalysis Literature
(analogies)

Figure 9.   Sources of Catalysis Heuristics for Design.
(Adapted from Foley et al., 1993).

facilitate its usefulness and to ensure that it is not inadvertently lost, especially at the current costs of research.

With these trends in mind, it is reasonable to begin to carry out research aimed at the use of nonnumeric or heuristic computing in catalysis research and development. Knowledge bases and expert systems may provide new approaches to codifying the rules that experts use implicitly when considering problems in heterogeneous catalysis design and synthesis (Hu *et al.*, 1991). This seems even more imperative as the field becomes more interdisciplinary, since specialists with different backgrounds working in catalysis must know more than that provided by the limits of their traditional training. Hybrid systems that use heuristics to describe those phenomena that cannot be modeled explicitly and rigorous numeric models for those phenomena that are deterministic may be particularly useful and important (Dumesic *et al.*, 1987; Banares-Alcantara *et al.*, 1987; 1988; Kito *et al.*, 1984). In other disciplines heuristics and deterministic models are combined quite satisfactorily to describe real problems that are too complex to handle *ab initio*.

Transfer of expertise, assimilation of information, and higher productivity are all potential outcomes of this new approach to computing in catalyst research and design.

2.21

2.4.2 Enabling Sciences in Catalyst Design and Synthesis

Catalyst design and synthesis is necessarily interdisciplinary and it defines the intersection of three otherwise distinct and separate disciplines: chemistry, chemical reaction engineering, materials and surface science. The exploration and development of the new concepts and effects in catalysis described in the previous section will require the further implementation and application of methods and techniques developed by these enabling sciences.

2.4.2.1 Inorganic and Organometallic Chemistries

The development of new catalytic systems that can carry out separation and catalysis, or that provide uniform isolated sites will require that advances be made in materials synthesis. This can be accomplished partially by incorporating the latest advances in organometallic and inorganic synthesis, but these methods must be pushed beyond the current horizons and limits of the traditional discipline. Catalyst synthesis involves developing architectures on length scales uncommon in molecular syntheses. Therefore, new techniques based on conventional methods will need to be developed in order to synthesize supramolecular architectures. Hence, the challenge of catalyst synthesis can be a driver for the new field of supramolecular synthesis.

To the extent that supramolecular synthesis is aimed at the design of catalysts rather that sensors or nanoscale electronic devices it should be embraced as a legitimate part of catalysis research in the future. However, much can be learned from advances that will be made in supramolecular syntheses devoted to these other fields of application. Cross fertilization between research aimed at new materials that provide molecular recognition, molecular level logic, and catalysis is to be expected and encouraged.

2.4.2.2 Chemical Kinetics and Reaction Engineering

Pharmaceutical design and synthesis is facilitated by the use of computation chemistry methods from *ab initio* quantum methods to highly parametized molecular mechanics. As catalyst materials preparation becomes synthesized with the drive for supramolecular architecture, site isolation and multifunctionality, computational methods will be more relevant, applicable, and necessary for design. Hence it will be crucial to incorporate more computational chemistry in chemical reaction engineering. To do this will require a sustained and earnest effort or the part of those chemical reaction engineers in catalysis to become molecular reaction engineers.

Eventually, it is possible that molecular level models for individual reaction steps can be incorporated into models for reaction networks which in turn are utilized in the full description of a reactor in a particular process. Nesting of models from the molecular level up to the macroscopic level of the units will advance no faster than the hands employed to advance computing power, both in terms of hardware and algorithmic methods. However, research should be done on this frontier so that computing in catalysis can be as up-to-date as is technically feasible

2.4.2.3   Materials and Surface Science

Surface science has and will continue to advance the level of understanding of molecular interactions at well defined interfaces through experimental and theoretical analysis of structure. A frontier that is just beginning to open up is the use of materials science methods as employed in other technologies, such as electronic materials, in the synthesis of well-defined catalyst materials. High to low vacuum methods from molecular beam epitaxy to low pressure organometallic vapor deposition offer exciting new ways to prepare more complex model systems that are well suited to high vacuum and other emerging methods of analysis. These new synthesis techniques combined with new techniques for analysis like atomic force and scanning electron microscopy offer unparalleled opportunities for surface and materials scientists to begin to do rigorous syntheses that can lead to a deeper knowledge of the subtleties of structure and function in catalysis

2.7   SUMMARY AND RECOMMENDATIONS

The drive to new energy efficient and low cost, zero waste solutions to chemical process technologies is fueling he drive for new research in catalysis science and technology. The science of catalysis has overtaken the technology of catalysis, and future advances in technology are as likely to result from first principles application as they are from pure empiricism and discovery.

This trend brings with it the need for catalysis preparation to become a science in its own right, thus it is appropriate to consider catalysis materials preparation as a problem in supramolecular synthesis. In this way, catalysts can be viewed as nanoscale reactors with specifiable structures and functions.

As catalysis synthesis becomes more controlled and scientific, hence predictable and reproducible, it is natural to consider the problem to be one of materials design at the nanoscale. Along with this view comes the need for modeling in order to guide design, to streamline experimentation, and to accelerate innovation. Computation at all levels will be required to bring *ab initio* design to its full fruition in catalysis.

Surface and materials science have provided valuable new tools for the analysis of catalytic steps and for the characterization of interfacial systems. With the advances that have been made in the fabrication of nanoscale devices with materials synthesis techniques, the field is poised to make major strides in bringing these new approaches into catalysis. In this way, surface and materials methodologies can provide new routes to the synthesis of advanced structures and more complex model systems.

More specifically, it is recommended that research thrusts be aimed over the next ten years at new concepts and effects in catalysis especially:

> Combined catalysis and separation

- Shape selectivity and molecular recognition

- Site isolation

- Multifunctionality

- New solid acids and bases

- Numeric and heuristic computing for design

These topics are at the forefront of current catalytic science and technology and hold the promise for major advancements over the next ten years.

Beyond these topics, integration of the enabling sciences of inorganic and organometallic chemistries, chemical reaction engineering and computation, and materials and surface science must be integrated more fully into the science of heterogeneous catalysis.

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