Chapter 1

CATALYSIS OVERVIEW
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1.1 INTRODUCTION

This overview chapter gives a broad-stroke account of the role of heterogenous catalysis in future energy technology. The sections in this chapter address the societal impact of catalysis, its current evolution as a science and technology, and the role of heterogeneous catalysis in the energy industry, a role aimed at achieving energy savings either in production or in ultimate utility as fuel. New challenges and directions for advanced catalysis are also discussed The final section lists recommendations for short and long-range priorities with a focus on catalysis fundamentals and science.

1.2 HISTORY AND SOCIETAL IMPACT

Industrial catalysis received its largest initial impetus from the discovery of ammonia synthesis at the beginning of our century. From the 1930s, petroleum refining technology has been mainly developed in the U.S., driven by a chain of major discoveries in hydrocarbon catalysis made in industrial laboratories, aided by pioneering scientific fundamentals emerging from our leading universities. Successful industrial technology emerged in almost every case by combining catalyst chemistry and reactor process engineering in a creative way. Heterogeneous catalysis, more than other areas of chemical synthesis, requires creative engineering solutions to cope with catalyst-reactant interaction (fixed bed, fluid bed, slurry bed, moving bed), reaction heat transfer, and catalyst regeneration related problems. Successful engineering solutions of these problems are critical for competitive process economic performance in all areas of advanced catalytic processing. Present petroleum technology, with its key catalytic process steps used worldwide, became mainly a product of U.S. industry, with enormous economic benefit to our economy. The sales of proprietary catalytic technologies under license and proprietary catalysts became one of the largest and most profitable worldwide businesses in U.S. industry, providing high quality employment for skilled workers.

We will briefly review the societal impact of catalysis with data provided for the fuels and combined fuel and chemical industrial segments.

How important is catalysis to industry and, more broadly, to humanity? A recent report (Creek, 1989) sets the value of the worldwide catalyst market at $5 billion, with $1.9 billion alone in the United States; by the year 2000 it will grow to $6.5 billion worldwide and to $2.4 billion in the U.S. The cost of catalysts is estimated to be about 0.1 percent of the value of the fuels produced and about 0.22 percent of the petrochemicals produced *via* catalysis (*Chem Week*, 1979). This cost translates to worldwide catalysis product values for fuels and chemicals of $2.4

trillion. This amount is more than the gross national product (GNP) of some major industrial nations and is about half of the U.S. GNP. In the U.S. the value of fuels and chemicals derived ..om catalysis in 1990 was $891 billion or 17% of GNP. Since in process economics the value-added contributions by catalysts far outweigh the cost of the catalysts, the impact of catalysis must be measured by the impact of its products, not only by the cost of the catalyst itself (Roth, 1991). In the last decade, catalysis has also become the key technology for the protection of our environment, in addition to its role in the fuel and petrochemical industries. Here, part of the challenge is to reduce pollutants emitted in the processing of fuels and chemicals; another challenge is to help produce new, environmentally friendlier fuels and chemicals. An additional and ever-growing role is to reduce undesirable emissions from power plants and automobiles. In the latter field alone, the yearly catalyst market in the United States was about $650 million in 1989. In Europe, the total catalyst market was $900 million in the same period, and growth was projected to $1.8 billion by 1993, with auto-emission catalysts being the fastest growing component.

The societal impact of the fuel and petrochemical industries, in which catalysis is a critical component, also needs to be considered. According to a recent study of U.S. industry, the chemicals and fuels industry was the largest of all U.S. industry segments, with yearly sales of $210 billion, compared for example with $127 billion for automobiles (M.I.T., 1990). In 1990, employment in the petroleum industry in the United States was 750,000 compared to 1.04 million in the automobile industry. The pivotal role of catalysis is best displayed in a study reporting that of the 63 major product and 34 process innovations made between 1930 and 1980 in the chemicals and fuels industries, more than 60% of the products and 90% of the processes were based on catalysis (Bennett et al., 1988, 1990). This information clearly points to the critical role of catalysis not only in the chemical and fuel industries but also to economic progress in our whole society (Cusumano, 1992).

Beyond the many contributions of catalysis measurable in numbers, our human society has been immeasurably enriched by the improved quality of life and comfort provided by the products of catalytic processes.

Catalysis has also been absolutely critical to the economic success of the U.S. chemical industry. As discussed in Chapter 6, most major products of this industry are manufactured by catalytic processes. Continued innovation in catalysis and process engineering has made the U.S. chemical industry one of the strongest in the world. In contrast to many other domestic industries, the chemical industry is a very successful exporter of its products. It has consistently maintained a large positive balance of trade with other nations ($18.8 billion in 1991), which illustrates the importance of technology for the competitiveness of the U.S. manufacturing economy.

1.3 ROLE OF HETEROGENEOUS CATALYSIS IN THE ENERGY INDUSTRY

Heterogeneous catalysis plays a profound role in the energy industry. The ability of catalysts to facilitate difficult hydrocarbon transformations, and to guide chemical reactions toward desired reaction paths at high selectivity, permits the energy industry to produce the full range of quality

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motor fuels from the changing feedstocks available worldwide. The amazing flexibility of catalytic chemistry also allows the refiners to respond not only to differences in feedstock but also to changes in market needs, without penalty in quality. These characteristics of catalysis technologies are essential for the production of high quality fuels at a cost affordable to the public.

All liquid feedstocks used in the energy industry contain sulfur and often additional heteroatoms which are considered undesirable if released to the environment. Therefore, there is a need to remove these undesirable components either from the feed, from the product, or from the combustion effluent. These environmentally important operations involve fuel manufacturing processes, powerplants, automobile engines, exhausts, *etc*. Heterogeneous catalysis is the only feasible technology that can be applied in this wide ranging field with the desired high degree of efficiency and relatively low cost. The ability of heterogeneous catalysts to function in an extremely wide range of temperatures permits their application both at low temperatures required in certain fuel synthesis steps (isoparaffin alkylation) and at higher temperatures required in catalytic cracking, and even at very high temperatures existing in automobile exhaust manifolds. The techno-economic significance of catalysis rests on the following factors: a) ability to produce quality fuels from varying feedstocks, b) flexibility to produce a changing slate of fuels to respond to changes in demand, and c) high catalytic selectivity to desired products resulting in large value-added gain in most catalytic process steps. In some cases even the replacement of existing catalysts with new, more efficient catalysts also causes large economic benefits. For example, the replacement of the amorphous silica-alumina catalyst with zeolites in the catalytic cracking process gave rise to a value-added gain amounting to several billion dollars yearly in the U.S. alone. For these reasons, development of superior catalysts remains a valid technological objective as long as the limits of technology leave room for either environmentally or economically significant improvements.

The role and full impact of catalysis in energy related technology is best displayed by the scope of the chemical transformations it facilitates. Today, the principal source of motor fuels is petroleum. Its conversion to gasoline, turbine, and diesel fuels critically depends on catalytic action. Catalysts must convert the extremely broad range of hydrocarbons (decorated with both sulfur and nitrogen heteroatoms) found in various petroleum feedstocks into sulfur and nitrogen free hydrocarbons of well defined boiling range, hydrocarbon type and structure. Catalysis technology available at present has the capability to convert distillate petroleum feedstocks or gaseous hydrocarbons ($\geq C_3$) to hydrocarbon motor fuels of almost any specification. Production costs, the nature of available feedstocks, and changing needs give rise to preferred processing schemes in the overall petroleum refining or

These amazingly wide-ranging chemical transformations in petroleum refining are based mainly on two types of catalytic transformations: hydro-dehydrogenation and acidic hydrocarbon catalysis. The first controls the distribution of hydrogen among hydrocarbon products while the acid catalysis controls the carbon number and boiling range, the skeletal structure, as well as the types of hydrocarbons produced. Advanced catalysts available today combine these two catalytic functions with highly specific catalyst structure features, called shape selectivity, to control the size of molecules produced and other chemical features. Using an appropriate choice and

mixture of catalyst functions for catalytic processing, the carbon and hydrogen content of a petroleum feedstock can be redistributed to a fuel of almost any desired specification. Of course, raw material availability and production costs limit industrial applications to the most cost-effective technology schemes.

Catalytic efficiency, in terms of activity, selectivity, and operating costs, including that of a catalyst, are the key to superior technology in this field. It should be noted that in petroleum refining, the value-added advantage provided by advanced catalysts usually far outweighs the cost of the catalyst itself. The economic benefits justify, for example, the broad use of noble metals in refining catalysts. Since current hydrocarbon transformations in motor fuel production mainly rest on hydrogenation/dehydrogenation and on acid catalysis, the most important catalyst components are transition metals, often noble metals, and solid acids. In the latter category zeolites achieved particular prominence because of their outstanding acid type activity coupled with "molecular sieve" selectivity.

As a result of recent advances in petroleum refining catalysis, the transformation of hydrocarbon feedstocks, substantially free of solid inorganic components, can be converted to any desired motor fuel chosen within thermodynamic limitations, using chemically inert, solid catalysts, with few exceptions. The most notable exceptions are reactions requiring super acid catalysts, for example, the alkylation of isobutane with butene to produce the alkylate gasoline component. Here, the efforts to replace the corrosive and environmentally undesirable hydrogen fluoride or sulfuric acid catalysts with environmentally friendly solid catalysts has not succeeded as yet.

It should also be noted that the outstanding flexibility and selectivity achieved in catalytic hydrocarbon transformations is limited to the conversion of hydrocarbon feeds to hydrocarbon fuels of other specifications. The conversion of hydrocarbon feeds to products containing heteroatoms has been successfully developed only for unsaturated hydrocarbons, but not for paraffins and naphthenes which are most abundant both in petroleum and in natural gas. This limitation in catalysis technology poses great challenges to future energy technology, as will be discussed later.

1.4 HETEROGENEOUS CATALYSTS AND CATALYSIS PHENOMENA

Catalysts facilitate chemical reactions to proceed at greatly enhanced rates. While catalysts always benefit reactivity and reaction rates, they also control, or at least influence, selectivity. Catalytic effects are usually based on chemical phenomena; however, physical characteristics of the catalyst are also important, and in most cases they are critical to optimum performance, because the physical features control the distribution of catalytic sites and the diffusion of both reactants and products.

Catalysts, while participating in the catalytic process, do not undergo change following typical catalytic reaction cycles. Thus, a catalytic site can carry out the catalyzed reaction cycle thousands or millions of times without losing activity. Ultimately, depending on reaction conditions, particularly the temperature and the chemical environment, catalysts lose activity or selectivity as a result of slow chemical change or deposition of coke or other debris, causing

interference either with the chemistry or with diffusion related transport phenomena. Following deactivation, catalysts are often regenerated by oxidative burn-off of carbonaceous deposits. In other cases, the spent catalyst must undergo chemical treatment called rejuvenation, usually aimed to reconstitute the original active sites such as fine metal dispersions. Ultimately, spent catalysts have to be replaced with fresh catalysts. Noble metals and other valuable components are usually recycled from the spent catalyst onto the fresh catalyst, depending on the economic incentive, while other components are discarded or may have to be managed, depending on their environmental effect and value.

Heterogeneous catalysts are solids, usually consisting of one or several catalytically active materials and one or more catalyst supports or solid additives aimed to provide fine and stable dispersions for the catalytically active materials (metals, oxides, etc.) and supporting particles. Supports provide a porous framework to permit access to the active sites for the reactants and free exit for the products from the catalyst particles. Specific control of access to and from catalytic sites on the basis of the molecular sieve effect is used sometimes to serve as a basis for catalytic selectivity. For these reasons, both chemical and physical characteristics play important and inseparable roles in the catalytic process. Therefore, beginning with the initial concept of a practical solid catalyst through the research and developmental steps of catalyst evolution, both chemical and physical features have to be optimized together to find the best interplay between these characteristics with the overall catalytic process in mind. Catalyst life and deactivation are additional important characteristics affecting process design and economics.

In catalyst synthesis, and in the ultimate catalyst manufacturing process, the catalytic active sites usually develop step by step. Catalyst supports may be utilized first in order to support precursors of the catalytic sites with desired concentrations and distributions. The active form of catalysts is usually achieved following optimized thermal and chemical treatments. Often, catalysts attain their active form only in the reaction environment in the catalytic process. In order to prepare catalysts with maximum efficiency, the synthesis process must follow synthetic steps carefully optimized in research programs.

As a result of the importance of the specific details of catalyst synthesis steps, it is necessary to establish specifications for the catalyst following each successive synthesis step. Therefore, the characterization of catalysts covers the whole range of intermediates as well as the finished, and even the spent catalysts.

In addition to the characterization of the catalytic solid, an additional important role of characterization is the elucidation of the chemistry of the catalytic reaction. This includes the catalytic active sites and the reaction intermediates formed between active sites and reactants, leading to product formation. This information is important to recognize the sequence of catalytic reaction steps with sufficient chemical and structural information, to enable the catalysis chemist to apply our existing science base, for example, organic or inorganic chemistry, material science or surface chemistry, to correct the observed catalyst deficiencies, and ultimately to develop advanced catalysts efficiently. In-depth information on catalytic sites and on the reaction mechanism at atomic/molecular level provides the most effective, thus the most valuable,

predictive scientific tools for the efficient development of advanced catalysts. This consideration places high value on *in situ* investigation of catalysts in the reaction environment.

Heterogeneous catalysis is an interface phenomenon. The catalytic sites formed on the surface of the catalyst interact both with the matrix of the solid catalyst and with the reactants. The interaction with the solid mainly involves atoms adjacent to catalytic sites. However, in some important cases the interaction between active sites and large segments of the catalytic phase, particularly crystals, results in long range effects which dominate catalytic performance (acidic zeolites).

Our knowledge of the structure of solids, particularly crystals, is highly developed by the use of X-ray crystallography and other quantitative tools which can be also applied, to a more limited extent, even to microcrystalline materials found in solid catalysts. By comparison, our knowledge of the surface of solids, including crystals, is much more limited. The available information here mainly rests on progress in surface science which has been developed to a great extent through the study of large single crystals, and results have been obtained with ligated and unligated metal clusters. In spite of great recent progress in surface science, the atomic structure of the surface of microcrystalline materials, often representing the anchor of the catalytic active sites in practical catalysis, is less understood. This deficiency in our knowledge places large emphasis on a future need to focus fundamental research on a direct characterization of catalytic active sites and reaction intermediates at the atomic/molecular scale. This information is crucial in order to achieve a higher predictive power for the science used in the conduct of research in the evolution of advanced catalysts.

Catalysis is an interdisciplinary science and technology. The catalytic reactions take place in the solid-gas interface. Therefore, the study of catalysis phenomena involves the solid matrix, the surface of solids, gas diffusion, reaction kinetics, and process engineering. The topic of the catalyst solid itself is a wide-ranging, complex science which embraces substantial portions of solid state chemistry as well as new, growing areas of synthetic inorganic chemistry, such as zeolites, clays, metals, and alloys. As a result, catalysis is an interdisciplinary field with large areas common with other fields of science and technology, and with others specifically related only to catalysis.

At present, heterogeneous catalysis is rapidly moving from a mainly experimentally driven endeavor in energy and chemical technology to a scientifically deeper rooted discipline of enormous industrial and economic potential. In the past decades progress depended mainly on intuition and on broad experimental scoping of the envisioned chemistry. The rate of progress was limited by the absence of precise models of active sites and of the path of catalytic reaction chemistry. In the absence of this fundamental knowledge, the feedback information guiding the next experiment for improvements was often absent, incomplete, or inaccurate. As a result, the time and cost required for the development of new, successful industrial catalytic processes has been very large, effectively limiting new catalysis technology to a few world leaders in the chemical and energy industries.

It is envisioned that progress in catalyst characterization and theoretical modeling will grow rapidly in the next 10-15 years. The anticipated future progress in computer technology will greatly facilitate theoretical modeling and data analysis in all experimental work. *Such events should, in the not too distant future, facilitate an operative linkage between the catalyst conception → synthesis → characterization and theoretical modeling → practical catalytic test → catalyst improvement steps.* This should bring about information feedback to improve development of advanced catalysis processes efficiently. To be on the leading edge of this development, to improve the predictive power of the knowledge base in heterogeneous catalysis would be an important advantage.

1.5 CURRENT STATE OF EVOLUTION IN CATALYSIS SCIENCE

The amazing concept of catalysis, that a foreign material can greatly accelerate chemical reactions without itself changing in the process, has inspired many theoreticians and experimentally inclined chemists and chemical engineers. This field offers opportunities of great scientific and enormous economic significance. As a result, catalysis, which began as a mainly experimental endeavor in chemistry, substantially broadened in the last 40 years to include, among its researchers representatives of a wide array of disciplines, such as chemistry, engineering, material science, and surface science. The totality of these disciplines reflects the multidisciplinary character of the field of catalysis. The amazing chemical concept of catalysis inspired the birth of numerous early "theories" many of which required modifications or did not survive a careful check of their general applicability. Problems usually centered on a lack of adequate limitations given for the applicability of the proposed hypotheses.

To conceive the best future strategy for heterogeneous catalysis in energy technology, first it is necessary to recognize the state of evolution in catalysis science. The important questions are whether the whole scientific basis of catalytic phenomena has been uncovered and whether catalysis phenomena have been adequately described to render catalyst development tractable using present day science. To answer these questions we shall briefly examine the two areas most important in energy related catalysis: metal catalysis and acid catalysis with zeolites.

1.5.1 Metal Catalysis

Science in *metal catalysis* has been greatly aided by several factors. Studies on metal alloys and on metal complexes provided basic information on the implication of atomic geometry and electronic structure on chemisorption and catalysis. Fundamental concepts such as the *ensemble effect* and the *ligand effect* in heterogeneous catalysis are based on these results. Studies of metal single crystals were of great help to further substantiate such concepts; this includes results on *microcrystals* exhibiting a variety of crystal faces studied by means of the field electron and the field ion microscope, and *macrocrystals* exhibiting only one single crystal face and studied, e.g., by LEED, AES, or XPS. The evolution of an amazing array of surface science techniques provided both *ex situ* and *in situ* investigative tools, such as surface crystallography using low-energy electron diffraction (LEED), for the study of metal surfaces. In addition, the structure of ligands, such as carbon monoxide and olefins, has been defined together with the metal atom or cluster with which they are associated. In this field, ^{13}C nuclear magnetic

resonance (NMR) spectroscopy, electron energy loss spectroscopy (EELS), and other spectroscopic techniques have been particularly effective.

Since industrial metal catalysts usually contain one or two metals and an oxide in addition to a variety of additives, much attention has been given to alloy chemistry, particularly on the metal surface, on metal-oxide interaction, and on adsorbate-adsorbent interaction. The complexity raised by these phenomena induced attempts to generalize the chemistry by taking into account concepts from both organometallic chemistry and solid-state chemistry. The significance of electronic versus structure effects has been debated at length.

In spite of the enormous growth of information on the surface chemistry of noble metals, some important aspects of metal catalysis remain unexplained, and the apparent complexity of catalysis phenomena seems to have grown. This suggests a balancing act between the organometallic complex formed between surface metal atoms and the reactant molecule and the whole metal crystal, based on the thermodynamic preference of each species. Quantitative evaluation of the energy balance between the short-range effects in the organometallic "molecule" and the long-range effects in the metal crystal is difficult, and such calculations can be handled only by using approximations, particularly regarding the long-range effect. For example, the phenomena of "corrosive chemisorption" and "chemisorption induced surface reconstruction" that were first reported in the 1960s illustrate the dynamic nature of the chemisorption process which usually involves multiple relocations of the atoms of the chemisorbing surface. The activation energy for these reconstructions is lower for the small particles in supported metal catalysts that are typical for industrial applications, than in macroscopic single crystals exhibiting close-packed crystal faces. There are also several new, unexplained phenomena. In hydrocarbon catalysis on noble metals, a carbonaceous overlayer covers a significant amount of the metal, affecting or even templating the surface metal layer with important involvement in surface chemistry and in catalytic mechanism. The specific role of this carbon overlayer is unknown. In another recent case, it was found that under certain conditions carbon monoxide and oxygen on platinum produce a dynamic cycle, forming a carbon-monoxide-rich overlayer followed by an oxygen-rich overlayer, in a cyclic manner. Both the carbon-monoxide-rich overlayer and the oxygen-rich overlayer display a long-range order, which suggests a long-range directing effect of unknown source. Again, the problem of reconciliation between short-range and long-range effects emerges.

Clearly, even when using the whole array of surface science techniques available today, the study of noble metal single crystals still reveals new, unexplained phenomena. Recently interest has grown in the modeling of catalytic phenomena on noble metals using both *ab initio* methods and a variety of approximations in the computations for the long-range effects that cannot be handled today by rigorous, *ab initio* methods even with the use of supercomputers. However, recent work in theoretical modeling shows promise to explain and possibly to predict the changes in specific surface ligand formation, for example, the formation of ethylidine *vs.* ethylene pi complex on platinum, affected by changes in valence of the metal.

Compared with single crystals, industrial metal catalysts are vastly more complex. Instead of having well-grown crystals, they usually contain a variety of supported metal clusters or alloy

particles. Industrial catalysts are usually multifunctional, that is, they serve more than one role in chemistry and technology. The result is a complex catalyst composition and chemistry with chemical interactions between various ingredients. Research on zeolite supported metal clusters is revealed an important interaction between metal atoms and zeolite protons. The metal-proton adducts not only stabilize small clusters against agglomeration and concomitant loss of active sites, they also appear to combine the catalytic functions of separate metal sites and Brønsted acid sites as visualized in the classical model of bifunctional catalysis. The apparent "electron-deficiency" of these hybrid sites has been claimed to be a major cause for their enhanced catalytic performance. More research will be needed to substantiate these novel concepts. For these reasons, in the past, chemical intuition and experience has played as large a role as science in developing new and better industrial catalysts. Thus, in spite of a great enlargement of knowledge, researchers are still searching for the "light at the end of the metal-catalysis tunnel".

1.5.2 Acid Catalysis with Zeolites

In catalysis with metal oxides, the elucidation of catalytic phenomena has been aggravated by a lack of techniques available to define the structure of the surface with the precision required to construct useful theoretical models for reaction intermediates. This troublesome uncertainty about surface structure was to be absent in *acid catalysis with zeolites*. At the time of the discovery of zeolite catalysis, researchers hoped that X-ray crystallography would provide precise information on all atoms in the zeolite crystal, and thus catalytic sites would be well defined. Now, 35 years after the discovery of crystalline H-Y zeolite and after three decades of great success in industrial applications, researchers may finally be close to explaining, with some precision, the structure and chemistry of protonic catalytic sites in zeolites.

In this case, the problem of characterizing protonic sites rests on the fact that these sites are usually introduced by a proton attack on an oxide ion *via* thermolysis of the NH_4^+ cation. The proton, with its large electron affinity and minuscule size, affects not only the lone electron pair of the adjacent oxide ion, but also the bonds surrounding the newly formed acidic hydroxyl group. The result is a dislocation in the Si-OH-Al linkage that evaded precise characterization until recently.

The experiments with H-X and H-Y zeolites over 35 years ago showed that with aluminosilicates, crystallinity is critical for strong acid catalytic action. Early hopes to define the protonic catalytic sites were hampered by the chemical instability of the primary protonic sites in zeolite crystals. This instability caused various degrees of framework aluminum hydrolysis. Whether the partially hydrolyzed aluminum, or possibly its combination with the nonhydrolyzed protonic site, is the strong acid catalytic site has been a recurring question all through the years. Numerous IR spectroscopic investigations involving protonic zeolites provided little more than fingerprint-type characterization (Creek, 1989). H MAS NMR spectroscopy also offered hope for fundamental information on protonic acidity; however, the small range of the proton chemical shift limits the observation of differences between acidic hydrogens in solid acid to a small range. Furthermore, the acid catalytic action in catalysis should correspond to the deprotonation energy of the solid, that is, the energy needed to transfer

the proton from the catalyst to the reactant, more than to the mere polarity of the O-H linkage which is traced by static spectroscopic observations. The actual transfer of the proton to the reactant molecule involves substantial changes in the bond structure all around the protonic site. These changes depend on many material factors, including the polarity of the O-H linkage and the polarizability of the surrounding bonds, as well as on some long-range effects.

Theoretical modeling has been applied to elucidate the case of zeolite acidity by using $R_3Al-OH-SiR_3$ type molecules and, more recently, by using larger model segments of the zeolite crystal. The most important result of the theoretical modeling work is the conclusion that the bond structure of the Al-OH-Si group controls the ionic character and the acidity of the O-H linkage. According to this model, the deprotonation energy of zeolites decreases; consequently, the acid strength increases with increasing Si-OH-Al bond angle. Thus, the intrinsic strength of acid sites must also increase with increasing Si-OH-Al bond angles. This conclusion, drawn from theory, finds good corroboration with the relationship between Al-O-Si bond angles of zeolites, such as Y, mordenite, and ZSM-5 and their acid catalytic activity.

The precision of theoretical modeling becomes questionable when it has to reconcile the results bet short- and long-range effects in zeolite structures. The problem is centered on a recently proposed interpretation regarding the cause of the great difference in acid catalytic activity and acid strength between H-zeolite crystals and amorphous silica-alumina gels of comparable chemical composition. The interpretation rests on the idea that, without the influence outside factors, the protonated Al-OH-Si groups prefer to form strongly covalent O-H bonds by forming relatively low (sp^3-type) Al-O-Si bond angles. In zeolites, and particularly in silicon-rich zeolites, the Al-O-Si bond angles range between 135° and 170°; thus, they are higher than sp^3-type bond angles. It was suggested that lowering these high angles for the Al-OH-Si units, without affecting the nonprotonated Si-O-Si linkages also present in the zeolite crystal, is prevented or at least minimized by the zeolite crystal in order to maintain long-range order in the lattice. Thus, if long-range order in the crystal prevails over the short-range bonding preference of the Al-OH-Si group, then the original, large bond angles will be retained. In this case, the zeolite retains its crystallinity and displays strong acidity. On the other hand, in cases where the local bonding preference prevails (adjacent to OH group), the crystal may collapse, and the OH groups will be of much weaker acidity. Indeed, H-zeolites with high aluminum and consequently high H-content (Si/Al ≤ 2) all lose crystallinity, and crystalline H-zeolites all require the presence of stable Si-O-Si linkages in the zeolite crystal. The observed structural loss is probably the result of the reduction of the bond angle in the Al-OH-Si groups. This new theory suggests that the maintenance of crystallinity and the consequent strong acidity found in silicon-rich zeolites (Si/Al > 2) depend on an energy balance between the favored bond formation of a single Al-OH-Si group and the bond formation favored by the crystal. The latter favors retention of long-range order and symmetry. Here again, the issue is the balance and reconciliation between the short- and long-range effects.

The arguments outlined above attribute the lower acidity of amorphous silica-alumina gel to lower Al-OH-Si bond angles relative to those found in crystalline H-zeolites. However, most recent experimental evidence suggests a new and unanticipated chemical step. ^{1}H MAS NMR evidence taken following dehydration of amorphous silica-alumina gel and H-Y zeolite indicates

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that upon removal of the last H_2O molecule, the amorphous material responds by actually breaking the Si-O linkage in the Al-OH-Si unit while the dehydrated H-Y zeolite maintains its original Al-OH-Si linkages. These distinctly different chemical steps presumably occur because when the stabilizing H_2O ligand is removed, the Al-OH-Si unit prefers to form a strong O-H bond in the silica-alumina gel by cleaving the Si-O bond and forming a strongly covalent Al-OH linkage. In silicon-rich zeolite crystals this step is prevented, probably because of the stabilizing effect of the long-range atomic order and related lattice energy of the crystal.

1.5.3 Conclusions

These two short and sketchy excursions into metal and acid catalysis certainly do not portray the depth of science in these fields. They were only intended to exemplify the point that catalysis researchers are still "digging deep in the tunnel". Although some light is filtering through, the basic problem remains the same as before: to search for the precise characterization of the catalytic site and for the chemistry of the catalytic reaction mechanism.

Past research in catalysis fundamentals, however, was not in vain. Our enhanced knowledge in metal and acid catalysis resulted in better planning and higher efficiency in all stages of R&D. The highest predictive value of information is related to precise definition of the catalytic site and reaction mechanism. In metal catalysis, such information is still limited to metal single crystals and does not extend to practical, multicomponent catalysts containing microcrystalline metal particles. In the case of acidic zeolites, however, our knowledge base is rapidly approaching that of homogeneous catalysis. While many details will be reinterpreted and debated for many years to come, the present concept of the catalytic site together with a more or less firm knowledge of the crystal structure surrounding the active sites provide powerful predictive value to researchers experienced in the field. This knowledge base has been utilized to direct research to the synthesis of new zeolite-type materials. It has been also used recently to develop several new, fuel technology related processes for the processing of hydrocarbon feedstocks. With these highly structured crystalline catalysts, the catalytic capabilities display unique effects and product selectivities previously only known for enzyme catalysts.

Beyond the important, intrinsic characteristics of zeolites, such as strong acidity and molecular sieve character, the growing predictive power of our knowledge base with these crystalline catalysts has been also responsible for their commercial success: today between 30-50% of all catalysts sold worldwide are zeolite-based materials. The conceived higher probability of success in a chemical manipulation using a crystalline material such as a zeolite, resulting from higher predictive power of knowledge, renders zeolites attractive as research topics both in catalysis and in other fields of material science.

This brief assessment suggests that the best long-range strategy in energy related catalysis, just like in other fields of catalysis, is twofold: to carry out research for the discovery of new, advanced catalysts and catalytic materials and to focus fundamental research on the elucidation of catalytic sites and catalytic reaction mechanisms at the atomic/molecular level.

1.6 FUTURE CHALLENGES FOR CATALYSIS IN ENERGY TECHNOLOGY

The major challenges for new and more flexible catalysis technology come from new and changing feedstocks, markets, and from environmental considerations.

1.6.1 Changes in Petroleum Feedstocks

At present the principal feedstock for motor fuels is petroleum. This feedstock varies considerably, depending on its source. The principal variations are differences in distillate content, asphaltene and inorganic content in the distillation residue, and the heteroatom concentration (S,N) throughout the whole boiling range. Since the preferred feedstock is one with high distillate and low S, N content, these feeds have been used at a high rate, leaving feedstocks with higher residue and heteroatom contents for future use. The expected result is a gradual increase in the use of heavier feeds in future years. Since the principal products of petroleum refining are distillate motor fuels, a trend to heavier feedstocks will increase the conversion of both heavy distillates and residual feeds to motor fuels. There are, at present, several commercial processes for the conversion of heavy/residual feedstocks to motor fuels.

The conversion of heavy distillates and residual feeds to motor fuels is mainly carried out by the catalytic cracking and hydrocracking processes. The catalytic cracking process, FCC, has been converting residual feeds to gasoline either by using its conventional vacuum distillate feedstock with 10-20 percent admixed residue content or by using pure residual feeds. The processing of residual feeds requires more complex catalyst technology because of the high inorganic (V, Ni) and heteroatom (S,N) content. Because of the relatively lower hydrogen content of the residue, the yield of gasoline is low and the coke formation on the catalyst is much higher. For this reason, the catalyst usage and its cost is substantially higher. New catalysts and new process technologies have been developed in recent years to protect the cracking catalysts from rapid deactivation caused by the vanadium and nickel present in residual feeds.

An increasing future trend toward heavier feedstocks, particularly the use of the residue itself, poses great challenges to future catalyst technology in the catalytic cracking process. At present, the deleterious vanadium and nickel content of residual feeds is either removed in a preprocessing step on sacrificial sorbents or cheap catalysts, or it is deposited directly on the cracking catalyst. The latter application increases catalyst usage threefold, with substantial added cost and added technological complexity. For these reasons, there is a need to discover selective and cheap methods for the removal of vanadium and nickel from residues. In addition, future catalysts used for the efficient treatment of residual feedstocks need higher durability and fuel product selectivity. Higher durability is needed, first, to cope with the more demanding regenerator conditions (high temperature and steam) caused by the increased coke formation and, second, for the tolerance of vanadium and nickel in the feed. Major improvements in any one of these areas would have major economic significance. Desire for higher fuel product flexibility in the catalytic cracking of residual fuels stems from the fact that the hydrogen content increases in the following order: residue < diesel oil < turbine oil < gasoline. Therefore, most effective hydrogen economy and highest fuel yield would conceptually favor the production of the relatively hydrogen-poor diesel oil.

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To maximize the production of the valuable, hydrogen-rich motor fuels (gasoline, turbine, and diesel oil) from heavy distillates and residual feedstocks, the industry developed hydroprocessing to combine conversion to lower boiling range with hydrogen enrichment. Several proven commercial processes have been developed and are used worldwide for the hydroconversion of heavy distillates and residues. The addition of hydrogen allows a great increase in motor fuel yields ranging around 110-120 volume percent for heavy distillate feeds. The economic benefits of such greatly enhanced motor fuel product yields are partially compensated for by higher capital and operating costs and by the use of high pressures and the consumed hydrogen. In addition to higher motor fuel yields, the hydrocracking technology has broad flexibility to produce either gasoline, turbine, or diesel oil as markets and economics demand. In contrast, in the catalytic cracking process the principal product is gasoline.

A trend toward heavier petroleum feeds in the future projects a need to remove larger amounts of the sulfur and nitrogen heteroatoms *via* hydrotreatment process. The removal of sulfur is necessary from both motor fuels and heating fuels because of environmental considerations, while the removal of nitrogen is needed because it is a poison for cracking catalysts. Future improvements in this field will be directed to development of superior catalysts to permit higher selectivity and milder process conditions (lower pressure) in the hydrodesulfurization and hydrodenitrification processes. Future trends toward heavier petroleum feedstocks will result in increased demand for hydrogen in petroleum refining. Processes with the ability to cogenerate hydrogen, instead of consuming it, will be welcome in future refinery schemes (cyclar process).

1.6.2 Natural Gas, Syngas

Natural gas plays a pivotal role as an energy source in the generation of electricity, heat, and as a raw material for hydrogen and syngas in fuels and chemicals production. The availability of large natural gas resources in the U.S. and abroad, together with the declining supply of petroleum in the U.S., raises interest in the role of methane as feedstock for motor fuels. The main interest is to convert methane at its production location to useable motor fuels or at least to a liquid product that can be easily converted to motor fuels. The primary conversion to liquid is essential to enable cheap transportation *via* pipeline or ship from remote natural gas locations to the use areas.

At present, there is no industrial technology available for the direct conversion of methane in a single step to high quality motor fuels. The process schemes available at present either require several steps, show low thermal efficiency, or produce motor fuels of inadequate quality. Research for the conversion of methane is conducted using the following chemical paths:

methane → syngas → methanol → gasoline
methane → C_2-C_4 olefins → gasoline
methane → syngas → alcohol mixtures
methane → methanol.

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Potentially, every one of these process schemes has a chance of success if catalysts are discovered to operate at high selectivity at economically attractive conditions. Ultimately, one should grade these new processes both by process economics and by their thermal efficiency. The latter consideration should favor the chemically most efficient, direct catalytic conversion to motor fuels. The assessment of the favored route of methane to motor fuels also requires careful consideration regarding the integrated use of methane and petroleum in the overall refining operation and the wide scale application of methanol alone or in mixture with gasoline as motor fuel.

It should be noted here that in contrast to the great flexibility available for the catalytic conversion of hydrocarbon feeds to hydrocarbon products of different specification, using hydro-dehydrogenation and acid type catalysis, *vide infra*, the conversion of hydrocarbons to products containing oxygen is limited. Efficient and selective conversion of hydrocarbons to oxygenates is well developed for unsaturated hydrocarbons, but not for the paraffins abundant in both petroleum and natural gas. In the latter case, commercial success is limited to chemically stable molecules (butane to maleic anhydride). Therefore, direct oxidation of paraffins to the corresponding oxygenates such as alcohols and ethers from paraffins is one of the principal challenges for catalyst chemists in future energy technology. The reaction of paraffins with oxygen is thermodynamically favorable, therefore it offers the possibility to carry out the conversion at low temperatures and pressures in a single step. The direct conversion of methane to methanol and of light paraffins to corresponding alcohols or ethers are key objectives for future fuel technology.

So far, the results of research on direct oxidation of paraffins to alcohols and ethers show high selectivity only at low conversions and limited catalyst life. However, some of the recent results in paraffin oxidation using enzyme-like catalysts show that new advanced catalysts here will probably require a departure from traditional petroleum refining catalysts to new catalytic materials with uniform and highly structured catalytic sites, such as enzyme-like molecules. These catalytic molecules may be fixed or encapsulated in zeolites or other solids. Uniformity of catalytic sites and very high catalytic specificity, such as displayed by encapsulated catalytic molecules, will require new approaches to catalyst synthesis, in order to attain and to maintain the chemical and thermal stability required for these chemically fragile catalysts in practical use. Beyond discoveries in catalyst synthesis there is also a need for effective, innovative heat removal from the catalyst bed in the oxidation process to permit high conversions without unacceptable temperature rise in the catalyst.

One of the roles of growing importance in the use of syngas and natural gas is the production of hydrogen both for the energy industry and for chemicals manufacturing.

1.6.3 Liquid Transportation Fuels from Coal and Biomass

Declining petroleum resources and the availability of large coal resources in the U.S. render coal a strategically desirable feedstock for both solid and liquid fuels. The diverse and complex composition of coal, containing substantial amounts of noncombustible solids and a host of environmentally undesirable components (S, N), renders the conversion of coal a complex and

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expensive technological problem. In spite of major sustained efforts and considerable discoveries in coal liquefaction catalysis in the last seventy years, to date no economically and environmentally satisfactory solutions exist which would render coal competitive with petroleum or with natural gas. So far, the indirect liquefaction of coal *via* syngas intermediate deserves higher attention because of the flexibility it provides for choice of fuel and because it limits the handling of inorganic solids and the nitrogen and sulfur bearing compounds to the syngas producing step. These benefits simplify the fuel producing steps; however, they render the syngas production expensive, particularly because of the large cost of plant equipment needed in syngas generation and purification. Clearly, in this technology catalyst chemistry and process engineering must be applied synergistically with an eye on both technology and on process economics. The conversion of syngas to fuels (methanol, mixed oxygenates, diesel oil) is highly exothermic, requiring creative reactor design to remove reaction heat efficiently and at acceptable equipment cost (slurry-bed reactor).

While the catalytic conversion of syngas to liquid fuels offers certain flexibility to produce hydrocarbons or alcohol type fuels, both approaches need further improvements before practical applications can be implemented. Among other problems, the primary hydrocarbon fuel produced from syngas needs further processing steps to meet needs for use in combustion engines. In the conversion of syngas to alcohol fuels, substantial progress has been made both in catalyst selectivity and in reactor technology to achieve efficient heat removal at low equipment cost. Regarding the production and catalytic conversion of syngas, there are several opportunities for the integration of syngas into process schemes involving the production of electricity, motorfuels, or chemicals. In the conversion of syngas it is preferable to produce oxygenated fuels/chemicals with a value exceeding that of the corresponding hydrocarbon products, in order to increase thermal efficiency, to lower the exothermic heat of reaction, and to provide products with properties specifically responsive to future needs in high product selectivity and environmental concern.

Keeping in mind that sound energy-technology strategy must lead to the highest possible utilization of the energy sources, it is necessary to rate the calorific efficiency of various reaction routes from feed to fuel, and even beyond, to the efficiency of the final combustion step (engine efficiency). Based on this consideration, all promising reaction schemes for the conversion of coal to gaseous or liquid fuels need to be examined. Among these alternative reactions the low-temperature conversion of carbon (carbonized coal) with steam deserves special attention

$$< 500°C$$
$$2C + 2 H_2O \leftrightarrow CH_4 + CO_2$$
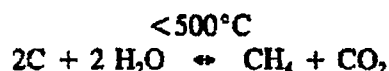
because of its high thermal and raw material efficiency to produce methane. A successful catalytic process here would require a movement of the active catalyst from the processed coal backward to the fresh carbon feed, a difficult chemical and engineering problem.

In the conversion of coal and biomass to motor fuels, one may encounter both catalytic and engineering problems of such magnitude that they may affect feasibility at any given level of available technology. Because of this, it is necessary to carry out reviews periodically to

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establish priorities based on overall strategy, promoting superior approaches in priority when their feasibility has been demonstrated.

1.6.4 Changes Resulting From Environmental Considerations

Interest in protecting the environment has increased and expanded greatly. The challenge is to preserve the benefits of modern technology without seriously contaminating the natural world.

Three strategies are available for reducing the impact of chemicals on the environment: waste minimization, emission abatement, and remediation. Waste minimization calls for the design and development of products and processes that are inherently low-polluting or non-polluting. The abatement of emissions can often be achieved by trapping harmful effluents or converting them to harmless substances, for example, conversion of nitric oxide to nitrogen. . Where an environmental lapse has occurred, effective means of remediation are needed. As shown by the examples in the following sections, catalysis can contribute to these three approaches.

Changes resulting from environmental considerations involve new specifications for gasoline resulting in the reformulation of this fuel, deeper desulfurization of distillate motor fuels, control of undesirable emissions in fuel production, powerplant and automobile exhaust control, and the replacement of corrosive catalysts with chemically inert catalysts.

1.6.4.1 Gasoline Reformulation

While the current understanding of how the individual components of gasoline affect various environmental issues is limited, several components in gasoline are now considered harmful to the environment if released into the atmosphere at high concentrations as either spills, vaporization losses, or the result of incomplete combustion. They include aromatics, notably benzene, which is a carcinogenic reagent; high-vapor-pressure hydrocarbons such as butane; and chemically reactive hydrocarbons such as olefins and sulfur compounds, which could promote the formation of smog and acids. The industry is responding to the environmental concern and the resultant environmental law by making changes in existing processes and by developing new catalytic processes needed to satisfy new gasoline specifications.

Among the petroleum conversion processes (cracking, hydrocracking), the hydrocracking will retain a vital role in producing motor fuels with environmentally desirable hydrocarbon compositions (low sulfur, low unsaturates) at high yields.

Innovations in catalytic cracking catalysts over the last 30 years, particularly the introduction of zeolite catalysts, have improved the conversion of the heavier components of crude oil to gasoline and diesel oil, allowing a reduction in crude imports to the United States of more than 400 million barrels a year. In the future, new types of cracking catalysts and additional process steps will be required to produce motor fuels that are environmentally more acceptable. To reduce the aromatics content of gasoline and at the same time provide higher octane, fluid catalytic cracking (FCC) catalysts must produce more olefins. The highly reactive olefins then can be isomerized, oligomerized, or alkylated with paraffins to produce high quality gasoline

components. Olefins can also be reacted with methanol to produce a variety of high-octane ethers. New generation, zeolite-type catalysts have also been proved active in isomerizing and oligomerizing olefins to a variety of liquid fuels.

Cracking catalysts will also have to become more rugged to endure the higher temperatures required to produce more olefins for subsequent processing into oxygenates for gasoline. The catalytic cracking process has been the workhorse of modern refineries for 30 years and, with improved catalysts, will continue to be an important process for converting the heavier end of crude oil into gasoline and to a lesser extent to diesel fuel.

The need to reduce the amount of aromatics and to introduce the mandated oxygenates in gasoline has created a need for oxygenated hydrocarbons as replacement octane enhancers. Today the two predominant oxygenates used as octane enhancers are methyl tertiary butyl ether (MTBE) and ethanol (EtOH). However, other oxygenates, such as methanol and higher alcohols, ethers, acetates, and carbonates are known octane boosters. Some of these compounds have been evaluated only partially for their performance characteristics and may represent major growth opportunities for oxygenated fuels. Currently, approximately 150,000 barrels per day of oxygenated compounds (MTBE and EtOH) are added to gasoline in the United States. By the year 2000, projections indicate that 750,000 barrels per day (the equivalent of roughly 10% of current U.S. production of petroleum) of oxygenates will be required in the United States for the gasoline pool. In the United States, the 1990 MTBE production capacity was 117,200 barrels per day. By 1993, it is targeted at 256,400 barrels per day. Iso-olefins (e.g., isobutylene) are now produced as a by-product of fluidized catalytic crackers in petroleum refineries. These quantities will support the production of ether at a rate of only 200,000 to 300,000 barrels per day.

The isomerization of nC_4 to C_6 olefins produced in the catalytic cracking process could greatly boost the production potential of gasoline oxygenates without substantial added cost to the refiner. The catalyst challenge here is to achieve high skeletal isomerization selectivity and particularly to attain adequate catalyst life, durability, and still to carry out the isomerization reaction. The production of olefins is expected to gain new flexibility in the choice of feedstock by the development of efficient and selective catalysts and processes for the oxidative dehydrogenation of both long and short chain paraffins, including methane.

The process technology leading to the majority of oxygenates now in use has been made efficient through catalyst modifications and engineering design. However, new processes leading to the same oxygenates may have cost advantages if cheaper feedstock sources (crude oil versus coal versus natural gas) are found.

If the reformation of gasoline proceeds, in order to provide oxygenated gasoline of sharply reduced olefin and aromatics content, there will be a need to find additional methods to maintain and to increase gasoline octane, and also to find new hydrogen production sources. While the current automobile engine design prevails, higher gasoline octane may translate into higher calorific efficiency, as long as the balance of efficiencies between combustion and "octane production" is positive. This consideration points to a need to carry out the skeletal

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isomerization of all gasoline paraffins to the maximum permitted by thermodynamics. Such conversion requires environmentally friendly solid, strong-acid catalysts with the ability to carry out isomerization of long paraffins and naphthenes without undesirable cracking. At present, the catalytic reforming process provides the high octane gasoline aromatics and a large part of the hydrogen needed in petroleum processing. If gasoline's aromatics content is reduced, then less hydrogen will be generated, thus the need for new hydrogen sources. Such new sources may be found in the catalytic conversion of C_1 - C_4 paraffins directly to aromatics, producing chemical feedstocks.

The environmental trend to reduce the S and N heteroatoms in fuels to lower levels and reduce the amounts of unsaturated hydrocarbons in all fuel categories places a growing burden on fuel production technology to find additional sources of hydrogen at an acceptable cost.

1.6.4.2 Replacement of Corrosive Refinery Catalysts with Chemically Inert Materials

The alkylation of paraffins with olefins is an important refinery operation. The process reacts isobutane with olefins, generally propylene and butenes, to produce highly branched C_7 and C_8 paraffins, respectively. They constitute a premium high-octane gasoline component (95 to 98 research octane number for C_4 alkylate). The alkylation process is assuming increasing importance with increased olefin production from modern FCC units and with the recent emphasis on lower olefin and aromatics content in the gasoline product.

Both of the currently used liquid acid catalysts, sulfuric acid and hydrogen fluoride, are corrosive. Acid waste disposal of sulfuric acid, and particularly of liquid hydrogen fluoride, is a potential health hazard. As a result of increasing concerns and possible legislative action addressing environmental and safety issues, current alkylation processes are facing increasing scrutiny.

The formidable challenge to the industry is the development of a new, solid catalyst for isobutane alkylation. The new process must have high yield of alkylate, selectivity to produce high-octane gasoline, long life cycle, regenerability, and greatly reduced environmental and safety risks. This challenge would benefit from broad-based fundamental studies of acid catalysis and from increased exploratory research for solid superacids. At the present time, no satisfactory solid motor fuel alkylation catalyst exists. An alternate, if temporary, solution in this field may be a combination of modifications such as the application of additives used in the chemistry of the currently used halide catalyst, resulting in substantial reduction of undesirable emissions and even the hazard of accidental emissions in the alkylation process.

1.6.4.3 Plant and Automobile Emission Control

Catalytic technology is playing an ever-increasing role in environmental protection. In 1989, for the first time in the United States, the market for emission control catalysts (largely for automotive emissions) exceeded the market for petroleum refining catalysts. In addition, the area of stationary emission control (e.g., from power plants) will also experience large (20% per year) growth in the years ahead. Many chemical production plants also need to reduce

emirsions. Thus, novel catalysis will in many cases be the critical technology that enables most of the benefits created by the chemical and petroleum industries to be maintained, but with improved preservation of the environment.

Catalysts for automotive emission control are now well developed in the United States and, in general, meet mandated standards for removal of hydrocarbons, CO, and NO_x. Recent Clean Air Act revisions will require significantly greater reductions in 1993 in the emissions of hydrocarbons. CO, and NO_x than those that are now mandated. In addition, stringent local automobile emission standards, as in California and Vermont, will require up to a tenfold reduction in emissions by the late 1990s. These reductions will require more active and more stable catalysts and new reactor designs that enhance low-temperature performance. Because of the rapidly escalating price of rhodium, which promotes NO_x reduction, the industry needs to develop lower-cost NO_x reduction catalysts or practical catalysts for NO_x decomposition. Cleaner gasolines may provide opportunities to develop lower-cost catalysts that contain a smaller amount of the expensive noble metals. Finally, substantially improved technology needs to be developed for the recovery and the recycling of noble metals, including rhodium because of its high cost and low natural abundance.

Power plant emission control is another major area of opportunity for catalysis. In particular, NO_x emissions need to be removed either *via* selective catalytic reduction (SCR) or, if achievable, *via* the preferable NO_x dissociation to produce nitrogen and oxygen, eliminating the need for reducing agents. The abatement of NO_x from power plants is important in efforts to control acid rain and photochemical smog, the latter being linked with harmful ozone production. Selective catalytic reduction removes NO_x in flue gas by reacting oxides of nitrogen with ammonia to form nitrogen and water. The catalyst is the heart of SCR technology, and it must provide both high activity and high selectivity (toward nitrogen formation). Major improvements in performance are desirable toward the conversion of nitrogen oxides directly to nitrogen and oxygen.

An important gas emission believed to affect the environment is CO_2. There is a need to develop a long range industrial/environmental strategy aimed at containment if not reduction of the air's CO_2 level. The primary goal is to develop competitive processes for the production of hydrogen, chemicals, and energy sources not involving CO_2 production or providing reduced CO_2 production.

1.6.4.4   Replacements for Chlorofluorocarbons

Chlorofluorocarbons play an important role at present as energy transfer agents (refrigerants) in industry and everyday life. Therefore, their environmental impact is of concern to the energy industry.

Chlorofluorocarbons (CFCs) are now believed to contribute to the seasonal ozone depletion over the Antarctic continent. However, because they are crucial to many aspects of modern society and have no available replacements, ceasing their production immediately is not practical. By 1988, the total CFC consumption worldwide had grown to 2.5 billion pounds per year for use

as refrigerants, foam-blowing agents for polystyrene and polyurethane, and industrial solvents and cleaning agents.

Ironically, the high stability and inertness of CFCs, which make them so valuable, have led to their downfall. Once released at ground level into the atmosphere, they rise slowly into the stratosphere, where they are degraded by high-energy radiation from the sun and release chlorine-containing free radicals that trigger a catalytic ozone depletion cycle. Following detailed, though not definitive studies, agreement was reached on a major global environmental treaty, the Montreal Protocol, to phase out CFC production by January 1, 1996. A race by all CFC producers then began to find suitable and environmentally acceptable substitutes. The strategy is to reduce its atmospheric lifetime by introducing hydrogen into the molecule so that it is removed from the atmosphere by reaction with hydroxyl radicals in the stratosphere. The commercially viable synthesis of these new compounds is a major challenge for catalysis because catalysts used for the production of CFCs lack the required selectivity and activity to be acceptable for the production of hydrogen-containing substitutes.

New catalytic processes have been developed to begin large-scale commercial production of hydrogen-containing chlorofluorocarbon replacements, both hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). The HFCs are satisfactory alternatives to the CFCs in many applications, but they are more expensive than the materials that they replace. Replacements must also be found for the HCFCs because they contain chlorine and can damage the ozone layer, although to a much lesser extent than the CFCs. Major advances in catalytic science and technology will be required to develop production processes for fully acceptable substitutes in applications such as refrigeration, air conditioning, insulating foams, and fire extinguishing fluids.

1.6.4.5 Recycle and Recovery of Catalytic Material

Catalysts, if released into the environment, often represent substantial health hazards. Therefore, the containment and/or recycle of relevant components of spent catalysts provide both environmental and economic incentives. In the case of noble metals there is a further incentive, namely the irreplaceability of these heavy elements which are critical for future energy and chemical technologies.

1.7 FEEDSTOCKS FOR THE CHEMICAL AND PETROCHEMICAL INDUSTRIES

The chemical and petrochemical industries draw their raw materials from petroleum and natural gas. The main chemical intermediates are hydrogen, olefins, and aromatics. Hydrogen is used widely in chemical syntheses, from the production of ammonia to the many products requiring hydrogen addition. Olefins are used both as short carbon chain (C_2-C_4) for polymerization and for the synthesis of a great variety of heteroorganic compounds, while long chain olefins (C_{12}-C_{18}) are used for both plastics and chemicals production. At present, there are several processes available in the petroleum/petrochemicals industry to produce desired chemical feedstocks from various raw materials. Feedstock for the production of C_2-C_4 olefins is provided from natural gas liquids, straut-run petroleum distillates, and distillates produced in the hydrocracking process.

Both short and long chain olefins are produced from the corresponding paraffins *via* selective oxidative dehydrogenation. Aromatics are produced by extracting the desired fraction from gasoline reformates or from the aromatic residue formed in light olefin production. New emerging technology is also available for the direct conversion of C_3-C_4 paraffins to mixed aromatics, producing hydrogen as a valuable by-product.

The most important future objective in the production of petroleum feedstocks is to increase the chemical efficiency of the catalytic processes used to produce chemical feedstocks in order to maintain the competitiveness of our petrochemical and chemical industries. These industries with their successful worldwide business provides an outstanding, positive trade balance for the U.S. Maintenance of our leadership position here is of highest strategic interest for the U.S. economy.

1.8   NEW APPROACHES TO ADVANCED CATALYSIS

1.8.1   Introduction

Great technological advances have been realized since the thirties in all areas of the energy industry. In this evolution, heterogeneous catalysis played the pivotal role to convert available feedstocks to quality fuel products. Most of the technological advances rest on the flexibility, efficiency, and durability of catalysts developed for the conversion of one hydrocarbon type to hydrocarbons of different specifications. Similarly, good progress has been achieved in the conversion of olefins to oxygenates, useful as motorfuels. Progress is evident in other areas of the energy industry as well. As a result of long sustained research, improvements have been realized in the catalytic conversion of syngas to methanol, mixed alcohols, or to mixed hydrocarbon fuel. A practical, industrial catalyst has also been developed for the direct conversion of retorted shale oil to quality turbine and diesel oil. The most important omission in this chain of success is the direct conversion of saturated hydrocarbons to oxygenates (and to other heteroorganic compounds). This reaction, if carried out efficiently, would allow the production of all oxygenates needed beyond those obtainable economically from FCC produced olefins. It would also allow the production of methanol from methane directly, leaving out the costly and energy inefficient syngas intermediate product. There are some encouraging recent research results on selective paraffin oxidation catalysis. The new catalysts applied here operate at near room temperature using enzyme-like catalytic molecules (porphyrin, phthallocyanine, *etc.*) either in solution, encapsulated in zeolites, or in other structured supports.

It is important to review critically what has been accomplished in the past, with a view to future challenges. Recognition of some of the general characteristics of our traditional heterogenous catalysts, as well all those we envision today, could lead to advanced catalysts of the future. For sure, no conceptual generalization will lead to success in every application. Nevertheless, such analysis may be useful to guide in the selection of alternate approaches.

It seems useful here to compare the main chemical and performance characteristics of current industrial heterogeneous catalysts with enzyme catalysts. Enzymes, as we know, are intermediate to large size molecules with multifunctional catalytic roles played by different

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segments of the molecule. Enzyme catalysts have identical active sites. These usually highly structured catalyst molecules are much more efficient (in turn-over number) than current industrial catalysts; however, they are much more fragile. They are readily destroyed by high temperatures or in a reactive chemical environment. The latter limits the practical applications of these materials, even though much has been recently accomplished to "fix" enzymes to improve their stability and technological applicability. In contrast to enzymes, traditional heterogeneous catalysts have a range of active sites. Lack of uniformity of active sites results in compromise in selectivity and in chosen process conditions. The ability of our traditional catalysts to operate in an extremely broad range of temperatures renders them practical, particularly in cases where limiting thermodynamics require high temperatures not suitable for large and sensitive feed molecules. However, in cases where thermodynamics or other process constraints are absent, it is worthwhile to consider the development of new types of catalysts with uniform catalytic sites for advanced catalysis in future energy technology.

Priority for choices in future energy technologies need to follow basic guidelines in future energy strategy and in competitive economics. Such consideration points to a need to analyze the economics and the calorific efficiency of alternative paths from fuel feedstocks through fuel production to ultimate combustion. Calorific efficiencies with attendant economics must be considered in the context of the whole life cycle of fuels. Comparative analysis of this type, as well as environmental considerations, should help to rank the value of new technology steps. This consideration makes it attractive to try to introduce advanced catalysts into the combustion step. Catalytic or nanometric treatment of combustion surfaces may lead to superior engine design, higher thermal efficiency (see discussion below on new materials), or superior environmental effect. In order to create the invention of such complex, novel approaches it is desirable to carry out feasibility studies by multidisciplinary teams of experts with proven track records in creative approaches to map out opportunities in this field.

1.8.2 New Catalytic Materials

In the last four decades the largest impact on heterogeneous catalysis was the introduction of new catalytic materials. Since the great success of zeolite catalysts in industry, catalyst synthesis adopted several synthesis topics and characterization methods from materials science. Catalyst synthesis, a critical subdiscipline of catalysis, has developed a methodology of its own. Today the objectives of catalyst synthesis are far-reaching. They include the whole variety of industrial oxide catalysts, supported metals, biocatalysts, and zeolites and other microporous or layered materials such as clays, with wide ranges of chemical compositions, pore sizes, and crystal structures. With zeolites, large pore size seems to be of premium value. Large-pore zeolites with pore sizes of about 8 Å are yearly bested by new microporous crystals with pore sizes of 12 Å and most recently with about 20 Å pores. The main incentive for catalysis in this field is that these large pores, acting as molecular sieves, may benefit catalytic selectivity in the treatment of heavy petroleum products. They may also act as receptors for immobilized, enzyme-like molecules. At present, this area of synthesis research is achieving a high rate of productivity worldwide.

As scientists look for guiding principles for strategy in future catalysis, they must contemplate the differences between biocatalysts and man-made catalysts. Biocatalysts have uniform catalytic sites, and they have high catalytic selectivity. Man-made heterogeneous catalysts, such as oxides, supported metals, and even acidic zeolite crystals, contain a range of active sites. With non-uniform active sites, the catalytic specificity to the desired product is lower. This simplistic comparison between biocatalysts and traditional heterogeneous catalysts points to catalytic-site uniformity as a desirable feature for future heterogeneous catalysts.

Several approaches have recently been used to develop solid catalysts with uniform catalytic sites. The "fixing" of enzymes on supports and, more recently, the immobilization of enzyme-like molecules in zeolites are good examples. In the latter case, catalytic molecules, such as porphyrin, phthalocyanine, or salen, each containing a variety of transition metals, have been immobilized in zeolite crystal cavities using ship-in-bottle synthesis. Recent data indicate synergistic phenomena between the zeolite structure and the occluded complex. These phenomena give rise to substantial stabilization of the complex. The result is higher catalytic turnover numbers achievable relative to the solution of the same complex. In addition, catalytic specificity is strongly influenced not only by the active complex itself, but also by the uniform spatial constraint around active sites. Such spatial constraint is provided by the intracrystalline environment (*regio* selectivity) of the zeolite support.

Microporous crystals may also offer several new strategies to provide uniform catalytic sites. Recent developments in the synthesis of microporous crystals, particularly in aluminophosphates, permit the synthesis of compositions containing a variety of transition metal ions in the crystal framework. These tetrahedral ions are on the intracrystalline surface. They can occupy identical crystallographic sites by the proper choice of crystal type, transition metal, and its concentration. Some tetrahedral cations have been observed to be capable of reversible change in coordination, from tetrahedral to octahedral, upon hydration-dehydration cycles. Therefore, these transition metal cations are probably accessible to varying degrees to catalytic reactants. They may also be suitable sites for the synthesis of larger, enzyme-like catalytic centers.

Uniform catalytic sites combined with shape selectivity offer new opportunities in catalysis. The substitution of aluminum or other small framework cations of microporous crystals such as zeolites with larger, transition metal cations must result in a distortion of the substituted crystal site that causes stretching and bending of adjacent bonds. This crystal-site distortion may result in a distortion of the local site symmetry, leading to stereospecificity or even chirality. Such changes may even form the basis for stereospecific catalysis.

In addition to three-dimensional crystalline microporous materials, near uniform porosity with variable micropores has been prepared with crystalline layer structures (pillared clays) and even with amorphous inorganic oxides. These materials, if provided with adequate thermal/hydrothermal stability and flexibility in choice of pore size, may find use in heavy oil processing as well as other energy related applications.

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Beyond the advanced, highly structured catalytic materials there is a need to improve the synthesis of traditional catalytic material such as oxide type supports and catalysts, sulfides and supported metals, particularly noble metals.

In the past, acid catalysis has been the key catalytic reaction in all motor fuel production technologies. Acid catalysis, using environmentally friendly catalysts, is also essential to achieve future goals in energy technologies. The environmental constraints and the need to treat heavy oils and new feedstocks place high priority on the discovery of superior solid acid catalysts. Improvements are needed to achieve all ranges of acid strength from moderate to super acid strength, to display uniform or near uniform acid strengths of active sites, and adequate thermal and chemical stability for practical applications. These materials may be crystalline or amorphous. They may also be surface decorated with suitable activating groups (ZrO_2 - SO_4). High acid strength is needed to carry out reactions at ambient temperature in cases where high temperatures produce undesirable thermodynamic or other chemical limitations.

In other fields of catalyst synthesis, a particularly important breakthrough in catalysis would be the synthesis of thin, continuous layers of microporous crystals that are usable as *catalytic membranes*. This development, when combined with inventive reactor/process design aimed to overcome mass transfer limitations of membranes, would probably revolutionize not only catalyst synthesis but also catalytic reactor design because of its large potential applications in combining molecular-sieve type separations with catalysis. In spite of its large potential impact, no new, inspiring approaches that are comparable in novelty and creativity to those used in the synthesis of new molecular sieves are apparent.

Aiming at the formation of uniform surfaces and uniform catalytic sites, it is conceivable that the atomic force microscope or a mechanical system of similar design may be used not only to monitor the surface layer of crystals, but also to modify them. Ultimately, scientists may devise a mechanism to imprint or replicate uniform surface structures on metals or oxides so that they become uniform catalytic sites.

Combustion engines designed today have limited thermal efficiency, based on the spherical propagation of the pressure wave generated by the fuel combustion. An examination should be made to see if combustion engine efficiency could be improved by the application of nanometrically engineered combustion surfaces, possibly zeolite-type membranes, to create oblong pressure waves with attendant enhancement in thermal efficiency.

1.8.3 Catalyst Characterization

Beyond the routine physical and chemical analyses used in catalyst synthesis, catalyst characterization is needed to define a catalyst beyond its chemical composition and crystalline components, so that its catalytic properties can be reproduced. Furthermore, in the development of new catalysts, chemical concepts regarding composition or structure are conceived. Following synthesis, the match between the envisioned chemical concept and the actual catalyst product must be confirmed. Catalysts also undergo changes in use. Industrial catalysts are usually used for several months or years before they are replaced, regenerated, or rejuvenated.

In this period, the catalyst degrades in performance to a certain extent, and characterization is needed to indicate the change in the property most relevant to catalytic performance. Successful industrial catalysts are often multifunctional, that is, they contain several catalyst components. Their manufacture requires meticulous characterization following each significant catalyst synthesis step. Regeneration or rejuvenation of used catalysts also requires a proof of restoration of catalytic properties, as well as both physical and chemical characteristics. Therefore, characterization involves a long list of physical and chemical methods and usually also includes an actual catalysis test. Clearly, catalyst characterization serves many needs, from research to manufacture. The characterization may relate to the catalyst support, to the precursor phases of the catalyst, to the catalytic site, or to the catalytic reaction itself.

Any experimental plan developed for the creation of a better catalyst requires a description of the catalytic site and its catalytic function that is as accurate as possible. Superior knowledge of the active site obviously translates to a better plan for catalyst improvements. This consideration leads to the most important future objective in catalysis characterization: the *characterization of catalytic sites at the atomic level*, with sufficient detail in chemistry and structure to allow the planning of modifications, leading to desired changes in chemical and catalytic characteristics. This objective requires a depth of knowledge similar to that existing today in homogeneous catalysis. Since the catalyst surface and particularly the catalytic active sites are usually sensitive to the chemical environment, the characterization should be carried out in an environment consistent with the reaction environment, and preferably it should be carried out *via in situ* experiments.

Beyond the atomic and molecular description of the catalytic site itself, scientists must also seek to understand the relationship between the chemistry of the active site and long-range effects exerted by the crystalline base or other long-range phenomena, such as ordered overlayers. Long-range effects can be important, and in some cases they are the key to catalytic phenomena. The formation of a catalytic site or reaction intermediates tends to distort the crystal, causing disorder. The direction of the long-range effect is generally the maintenance or restoration of lattice order to increase thermodynamic stability of the whole crystal. The quantitative assessment of the preferred bond structure at the catalytic site (short-range effect) of the whole crystal (long-range effect) is difficult because of the large size of the computational terms related to the long-range effect. Therefore, scientists need to search for some traceable spectroscopic evidence to monitor long-range stress in catalyst crystals.

Since catalysis is a surface phenomenon and since the active ingredients in supported metal catalysts are small metal clusters, relevant information on sites and adsorbed molecules on metal particles is provided by FTIR, NMR, EXAFS, and Mössbauer spectroscopy. For macroscopic surfaces, *e.g.* of single crystals, information can be obtained by LEED, elemental analysis (ISS), and XPS. Opportunity to monitor valence and atomic surface structure may be provided by advanced ESCA equipment furnished with a high intensity, monochromatized X-ray source. This may become an effective method to characterize the chemistry and the atomic structure of the surface of both metal and oxide-type catalysts in the near term.

Characterization of catalytic active sites at the atomic scale received a great boost from the development of the electron tunneling, ETM, and atomic force, AFM, microscopes. These methods have the potential to reveal the surface structure of both metals and oxides and to show atomic dislocations. They can even map the atoms and molecules of the chemisorbed overlayer. In addition, these techniques may also have the potential for indicating the bonding characteristics of surface atoms by applying perturbations. Such measurements may be developed in the future to characterize the chemistry of surface atoms. Today, however, the electron tunneling and atomic force microscopes are only designed to monitor the surfaces of single crystals. To render these revolutionary, atomic-level characterization techniques useful to catalysis, there is a need to redesign the delicate mechanical control system to allow monitoring of microcrystalline material. Such redesign would involve the development of improved mechanics and computer software to allow the mapping of small crystal surfaces and the automatic reorientation of the sample to find the next crystal surface. The development of electron tunneling and atomic force microscopic techniques for microcrystalline catalysts would be an important step in achieving catalytic site characterization of practical catalysts at the atomic level.

Future progress in catalysis science also needs expanded knowledge of the reaction chemistry so that scientists can contemplate modifications for catalyst improvement. With this long-range objective in mind, the determination of the catalytic reaction steps and reaction intermediates is essential to future progress. Recent years have seen excellent progress in this field from a variety of sophisticated techniques, including ^{13}C NMR, EELS, and FTIR, for the identification of chemisorbed molecules and catalytic reaction intermediates on noble metals. The next step in this field is to extend the application of these techniques to industrial catalysts, including supported metal catalysts, oxides, and acidic zeolites, under practical reaction conditions. In this field, methods with adequate response time are also needed to identify relatively unstable reaction intermediates as well.

The ultimate purpose of gaining detailed knowledge about catalytic sites and catalytic reaction intermediates is to bring catalysis, as a branch of chemistry, to the level where the predictive scientific quality of the experimental plan compares to that used today in inorganic or organic synthesis.

In order to improve the effectiveness of catalysis R&D in future years, to grade the quality of available choices, and to rank the experimental options based on relevant scientific considerations, appropriate theory is needed in the modeling of catalytic sites and catalytic reaction intermediates. Quantum-mechanical modeling should be applied with a critical attitude in the application of assumptions used to abbreviate the computation of the short-range and, especially, the long-range effects. The development of scientifically reliable theoretical modeling is a challenging and difficult task. Today, *ab initio* calculations are still limited to small atom clusters or they require the use of generalized or simplified expressions for long-range effects. The future direction in theoretical modeling is almost obvious. If current trends in computer and software development continue, scientists cannot escape the conclusion that in the future computational modeling will probably be one of the fastest growing areas in catalysis science. For this reason, theoretical modeling will no doubt have an important place in future catalysis.

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The ultimate objective is to develop an operative linkage between catalyst conception → synthesis → characterization → theoretical modeling → catalytic test and catalyst improvement. Such linkage between these steps provides the most effective feedback for the evolution of the advanced catalysts needed in future energy technology.

1.8.4 Industrial Catalytic Process Development

The objective of industrial catalysis is to develop economically superior processes based on innovations that lead to the use of cheaper feedstocks, to higher product yield, or to other process efficiencies that translate to superior process economics. Industrial research organizations depend on their experience, which is based on both successful and unsuccessful experiments in catalyst synthesis or on the process side, to develop their favored research strategy.

Recent success in the use of bio-derived catalysts in a variety of pharmaceutical syntheses and specialty chemicals syntheses substantially broadened the spectrum of the knowledge base from which the research strategy for advanced catalytic processes should be conceived. Because of the differences in applicable catalyst types, such as enzymes, zeolites, superacids, and supported metal systems, the catalysts and the processes of competing approaches may be profoundly different. They may even require researchers of different disciplines for efficient, creative pursuit. Future industrial success for new catalysis technology will probably favor those scientists who can consider all potential options from the point of view of catalyst types and process approaches to develop the best conceptual research strategy. Developing new competitive catalytic process technology is indeed a complex job that requires a broad-minded research organization and people of excellence in a whole spectrum of disciplines, including chemical synthesis, chemical engineering, and materials science.

These considerations and the challenges discussed above lead to the following recommendations in the pursuit of industrial catalytic process work:

► Learn from biocatalysis and homogeneous catalysis and seek catalyst synthesis approaches that develop catalysts with uniform catalytic sites. Look for approaches for uniform catalytic sites not only in the use of enzyme-like species but also in seeking novel approaches of "surface synthesis", using both metals and oxides. Industrial catalysts are often multifunctional. Sometimes the functions relate to two interacting catalytic steps (bifunctional catalysts). However, in many cases only one or more catalyst additives are present to help correct a certain catalyst deficiency, such as rapid metal aggregation, or to aid catalyst burn-off. Based on past experience, if a new catalyst does not have sufficiently high catalytic selectivity or activity, fixing these initial problems requires using additives, dopants, or expensive catalyst regenerative or rejuvenation methods, often requiring large costs and long time periods. For these reasons, a strategy aiming from the start at uniform catalytic sites may be a rewarding principle.

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▶ Acid catalysis is the most common and important catalytic function in industrial hydrocarbon catalysis. All ranges of acidity, including mild, strong, and "super" acidity, are important for distinct areas of industrial applications. Environmental considerations place high priority on the development of chemically inert, solid superacids for a variety of manufacturing processes. This need focuses attention on the theory of solid acids. Theory is needed to elucidate the specific role and contributions of structural and chemical factors affecting strong and super acidity as well as of the interaction between protonic and Lewis-acid sites. The goal is to gain maximum acid strength and to control the reaction mechanism. A basic understanding here would provide a rich basis for new, superior synthesis approaches to solid acid catalysts in the whole range of acidity.

▶ Implementation of new environmental technology needs both improved and new catalysts. Among these, high priority should be given to the catalytic decomposition of nitric oxide to nitrogen and oxygen in order to eliminate the use of ammonia as reducing agent.

▶ Successful industrial catalysis technology requires the creative combination of catalyst chemistry and reactor/process engineering in order to solve problems in catalyst-reactant interaction (fixed bed, fluid bed, slurry bed, moving bed), heat transfer, and catalyst regeneration. Successful engineering solutions of these problems are critical for competitive process economic performance in every energy related application. Imaginative catalyst flow control, such as fluid, or moving bed applications, has revolutionized catalytic cracking, gasoline reforming, and ethylene polymerization, greatly increasing product quality and the feasibility of achieving these processes. Such process innovation can release the processes from reactor-size constraints and provide superior operational control and stability with added benefits in the optimization of operating conditions. In several areas, new creative engineering may benefit future catalysis technology. New imaginative process solutions may be similar to those successfully applied recently in sorption-separation processes with respect to countercurrent reactant-flow control, use of desorbents, etc. These ideas may find applicability in cases of multistep catalytic reactions conducted in a single catalyst bed, particularly in cases using multiple feeds. Catalytic sensors also have an important role in future technological advances.

1.9 THE DISCIPLINE OF CATALYSIS

The makeup of the catalysis discipline is continuously evolving. In the last forty years, researchers in surface science, material science, inorganic synthesis, and theory have given catalysis great scientific strength. The most important aspect of this change is the broadening of scientific topics and the focus toward more quantitative scientific methods. This trend will, no doubt, stay with catalysis in the future as well. The field will broaden to include biocatalysis and new areas of inorganic synthesis for new catalytic materials. Surface science will blossom, together with theory, particularly when theory can play a role as a predictive tool in an operational linkage between conceptual planning and catalyst synthesis.

Changes in the future makeup of the discipline of catalysis must be reflected also in the institutional training of future scientists. Therefore, efforts should be made to develop broad as well as scientifically sound curriculums at selected universities where catalysis programs are on the teaching agenda.

1.10 RECENT RESEARCH TRENDS

The direction and management of catalytic research for future applications have been examined critically in recent years. The 1985 National Research Council report 'Opportunities in Chemistry' selected chemical catalysis as one of only five topics to be given national priority. This report also recommended "New mechanisms and incentives should be sought for strengthening the links between industrial and academic research". Recent in-depth studies have provided further insight and recommendations for research for energy applications (DOE 1985, 1989). Research to provide for alternative fuels and environmental protection has been of particular concern.

However, in sharp contrast, industrial catalytic research has greatly decreased in the past decade, particularly research for synthetic fuels. The drastic reduction in oil prices led to the conclusion that synthetic fuels research is too long-term for industry. Other factors deemed to restrict manufacturing opportunities in the U.S. are the increasingly costly and uncertain environmental restrictions, restrictions that do not apply to manufacture overseas.

A different concern perceived to limit research progress is the recognition that there is insufficient collaboration between the science base and the engineering community on the practical application to process and reactor development.

Recognizing the opportunities and problems in conducting longer range catalytic research, many countries in Europe (Belgium, France, Germany, and the United Kingdom) and Japan have in the past five years created organizational structures to implement increased catalysis research and particularly to encourage effective industry/academia/government cooperative programs. It is no longer believed feasible to leave to chance the very intimate relationships that exist between scientific progress and industrial developments. There is only a limited amount of technical research available and choices of paramount importance must be made. This approach is being increasingly discussed internationally (Haggin, 1993).

1.11 RECOMMENDATIONS

This chapter lists recommendations focused on fundamentals and on new approaches in catalysis. Recommendations are given for short-term (up to 5 years) and for long-term (up to 20 years). All supported approaches must take into account future trends in environmental policy.

1.11.1 Short-Term Goals

1. Develop instrumental methods for the characterization of the chemistry and structure of catalytic active sites and catalytic reaction intermediates, applicable to commercial catalysts.

2. Develop durable catalyzed combustion system for turbines (and engines) aimed at substantial NO_x emission reduction.

3. Develop the theoretical basis of acid strength, from weak to superacid, for environmentally friendly solid acid catalysts.

4. Carry out preliminary study to evaluate the potential advantage and preferred applications for heterogeneous catalysts of uniform active sites.

5. Carry out a preliminary study to evaluate new approaches to advanced, high efficiency engines applying catalytic combustion surface. Among various options nanometrically engineered combustor surface creating oblong (rather than spherical) pressure waves should also be considered.

1.11.2 Long-Term Goals

1. Develop practical techniques for the characterization of the chemistry and atomic structure of catalytic active sites and catalytic reaction mechanism, preferably under reaction conditions.

2. Support fundamental research in catalysis aimed to develop functional linkage between catalyst synthesis, characterization, theoretical modeling, testing, and catalyst improvement.

3. Develop catalyzed combustion systems (turbines, engines) aimed at higher thermal efficiency and reduced emissions.

4. Develop techniques for selective, direct oxidation of paraffins, including methane, to corresponding oxygenates.

5. Develop advanced catalyst/reactor concepts aimed at complete conversion, minimized by-product formation and efficient heat removal.

6. Develop low temperature catalytic conversion of coal with H_2O.

$$< 500°C$$
$$2C + 2 H_2O \leftrightarrow CH_4 + CO_2$$
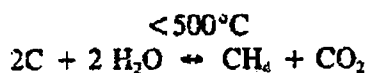
7. Develop techniques for catalytic desulfurization/denitrification of fossil fuel feedstocks below 1 ppm level at mild reaction conditions.

8. Develop solid catalyst compositions with uniform active sites aimed at energy saving technologies.

REFERENCES

Bennett, M. J., A. A. Boccone, and C. H. Vline. 1988. *Chemtech.* 18:162.

Bennett, M. J., A. A. Boccone, and C. H. Vline. 1990. *Chemtech.* 20(4):224.

Chem. Week. 1979. 124(14):47.

Creek, B. F. 1989. *Chem. Eng. News.* 67(22):29.

Cusumano, J. A. 1992. in *Chemistry for the 21st Century.* J. M. Thomas and K. I. Zamaraev, Eds., Oxford; Boston:Blackwell Scientific Publication.

DOE, 1985 Coal Gasification, DOE/ER-0326.

DOE, 1989 Coal Liquefaction, DOE/ER-0400.

Haggin, J. 1993. Chemical and Engineering News, May 31, pp. 23-27.

M.I.T. Commission on Productivity. 1990. *CHEMTECH*, April, pp. 224-229.

National Research Council. 1985. Opportunities in Chemistry. Washington:National Academy Press.

Roth, J. F. 1991. *Chemtech.* (June): 357.