Research Needs Assessment on Nanostructured Catalysts

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Abstract. Nanocrystalline and nanoporous materials with unique characteristics have attracted a great deal of research interest in the past decade. This paper discusses the latest advances in nanostructure processing which enable us to better control surface area, cluster size, grain morphology, pore structure, component dispersion, phase distribution, and defect concentration to engineer advanced catalysts with significantly improved reactivity and selectivity. Areas deserving further research to explore and realize the full potential of nanostructured catalytic materials are presented.

Keywords: nanocrystal, nanoporous, molecular sieve, catalysis, materials synthesis

1. Introduction

Both heterogeneous and homogeneous catalysis have made major impacts to chemicals and fuels production, environmental protection and remediation, and processing of consumer products and advanced materials. A survey of U.S. industries [1] revealed that the annual revenue from chemical and fuel production topped all other industrial sectors at $210 billion. Bennet et al.'s [2] survey showed that over 60% of the 63 major products and 90% of the 34 process innovations during 1930–80 involved catalysis, illustrating the critical role of this field in fuel and chemical industries. It is also noteworthy that the wholesale value of chemical manufacturing catalysts has been exceeded by that of environmental catalysts since the late 1980s [3], and the latter is projected to grow even faster in the future in response to the increasing environmental awareness and the more stringent government regulations. The significance of catalytic processes can be further demonstrated by the value of their products, which amounted to $1 trillion in the United States alone in 1989 [4]. Catalysis has had and will continue to have an important impact to the global economy, the environment, and our daily life.

2. Heterogeneous Catalysis

Heterogeneous catalysis is involved in more industrial processes than homogeneous catalysis because of its ease in handling and separation in continuous operations. Reactions on heterogeneous catalysts are complicated in nature, and are categorized into two classes: structure-insensitive reactions and structure-sensitive reactions [5]. The catalytic activity in structure-insensitive reactions depends only on the total number of active sites, the electronic structure of active species, and the chemical composition of the catalyst, and not on the crystal phase and grain size of the catalyst. Examples for this class of reactions are benzene or ethylene hydrogenation on Pt/SiO_2 and cyclopropane hydrogenolysis on Pt/Al_2O_3. The activity for structure-sensitive reactions is not only closely related to the number of active sites, but also to the crystal structure, interatomic spacing and crystallite size of the catalytic material. Some examples of structure-sensitive reactions are ethane hydrogenolysis on Ni/SiO_2-Al_2O_3 and Rh/SiO_2, neopentane hydrogenolysis and isomerization on Pt/Al_2O_3, and hydrogenation of benzene on Ni/SiO_2. In both classes of reactions, more active sites are required to obtain a higher catalytic reactivity or turnover frequency (TOF). Since surface area and the number of exposed active sites for a given quantity of material increase with a reduction in crystallite size, substantial efforts have been devoted to dispersing and stabilizing catalysts of small cluster or crystallite sizes on support materials to improve catalytic

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performance. Conventionally, clusters are dispersed on support structures via ion-exchange or impregnation [6,7]. Such preparation is extensively used in preparing supported metal catalysts, such as Pt/Al$_2$O$_3$ [8,9] and Pt-Re/zeolite L [10,11]. The focus of this report is to assess the research needs on novel sythesis, characterization, modeling and catalytic applications of nanostructured materials, which may be nanocrystalline or nanoporous in nature.

3.   Synthesis of Nanocrystalline Catalysts

Nanocrystalline materials consist of nanometer-sized crystallites that have a high surface-to-volume ratio. In a compacted assembly of nanocrystallites, a structure is obtained whereby a significant number of atoms are located at the grain boundaries (Fig. 1). The volume fraction of interfacial atoms varies with the grain size [12,13]. Nanostructured materials possess many properties that distinguish them from conventional polycrystalline or amorphous materials [14], which are associated with size-dependent effects or high surface/interfacial reactivity.

Over the past decade, research on nanocrystalline materials was greatly accelerated by the advances in our ability to manipulate structures on the molecular or atomic level. Nanocrystalline materials have been
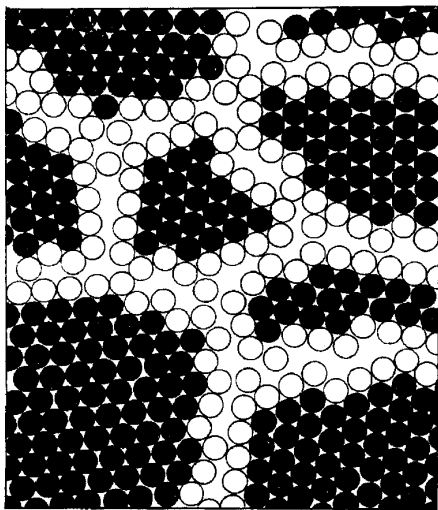

Fig. 1. Atomic structure of a two-dimensional nanocrystalline material [4]. The atoms in the centers of the ''crystals'' are indicated in black. The ones in the grain boundary core regions are represented by open circles.

synthesized with unique functional characteristics such as optical and electronic quantum confinement, giant magnetoresistance, and superparamagnetism. In advanced ceramic applications, nanocrystalline materials are noted for their high ductility and low-temperature sinterability, giving rise to attractive structural characteristics and the possibility of super-plastic net-shape forming. Although research in nanocrystalline materials has grown exponentially in the past decade, most of the studies have been limited to synthesis, characterization and application of these systems for mechanical and electronic applications. As catalysts, nanometer-sized active clusters have been examined for a long time, but they are mainly limited to supported metal systems. Direct synthesis and successful stabilization of nanocrystalline metallic and non-metallic materials have only recently been investigated in detail for catalytic applications [15].

3.1.   Sol-Gel Processing

Sol-gel processing is a wet chemical synthesis approach that can be used to generate inorganic oxides flexibly via gelation, precipitation, or hydro-thermal treatment [16]. It involves the creation of a loosely polymerized oxide/oxyhydroxide sol that contains a large amount of water in its structure, slow aging to generate a more condensed gel, followed by drying with appropriate methods to remove the volatiles in the gel structure to produce porous or condensed oxides [17]. In contrast, the traditional chemical precipitation process involves rapid generation of particulates as condensed crystal-line materials, with special attention paid to avoid gel formation. Sol-gel processing allows for a great deal of flexibility in parameters control in its relatively slow hydrolysis/polycondensation process to tailor the desired structural characteristics, such as compositional homogeneity, grain size, particle morphology and porosity [18–20]. Though more costly than simple chemical precipitation due to the expensiveness of some precursors (e.g., metal alkoxides), sol-gel processing allows nanocrystalline materials to be generated with little capital equipment cost compared to gas phase synthesis.

Sol-gel derived zirconia-silicate has been shown to be an excellent 1-butene isomerization catalyst [21]. By prehydrolyzing tetraethyl orthosilicate to match the reactivity of zirconium n-propoxide [22], mole-

cularly mixed Zr-Si oxides were derived. Nanocrystalline aerogels with ultrahigh surface areas and tailored pore structures were further obtained by supercritical drying. It was found that the 95 mol% zirconia-5 mol% silica aerogels were more active for isomerization than poorly mixed multicomponent materials or single-component zirconia. This example illustrates the effectiveness of sol-gel processing in creating unique active centers such as Zr-O-Si linkages for solid acid catalysis.

The grain size of nanocrystalline materials can be manipulated by controlled sol-gel precipitation and dopant introduction. It was shown that the grain size of ZrO_2 could be decreased from 15 to 5 nm as the Y_2O_3 dopant concentration was increased [23]. The high-temperature cubic crystal phase of ZrO_2 could be attained at a substantially lower temperature of $450°C$ for nanocrystalline samples. The nanostructured Y_2O_3-doped ZrO_2 compact also has substantially higher oxygen ion conductivity than conventional Y_2O_3-stabilized ZrO_2. As the activity of a variety of reactions is closely related to the oxygen conductivity and crystalline structure, such doped nanocrystalline oxides offer potential advantages towards tailored catalytic characteristics.

Subsequent to precipitation, the oxyhydroxide gel obtained typically requires calcination to crystallize to a pure oxide phase. This process gives rise to some grain growth as well as surface area reduction from aggregation of particles during the thermal treatment. In the case of TiO_2 synthesis by sol-gel precipitation, for example, the finest crystallites obtainable from calcination are ~ 15 nm. Wang et al. [24] showed that hydrothermal treatment can effectively crystallize oxides at temperatures below $100°C$, such that ultrahigh surface area TiO_2 nanocrystallites with grain size ≤ 5 nm can be generated for photocatalysis. The concept of controlling particle nucleation and growth via the heating of an aqueous sol has also been combined with rapid quenching in a process known as RTDS [25,26]. The RTDS method involves a brief hydrothermal treatment that allows for the rapid thermal decomposition of precursors in solution, resulting in the formation of insoluble oxide particles. The fast heating is followed by an abrupt pressure drop and thermal quench to inhibit further grain growth. RTDS has generated nanocrystalline Fe_2O_3, TiO_2, and ZrO_2 with grain sizes ranging from a few nanometers to tens-of-nanometers depending on the hydrothermal treatment temperature. This continuous

flow process presents an attractive potential for large-scale powder production.

Currently, sol-gel processing is examined extensively for the nanostructure tailoring of metal oxide systems. Research in wet chemical processing is needed to generate metallic or alloy nanocrystalline catalysts. The conventional sol-gel route cannot be employed to produce the metallic nanocrystalline materials important for hydrogenation and reforming catalysis, except by post-reduction. It was found recently that metal cations could be reduced *in situ* to form metal atoms and hydrosols with uniformly dispersed nanoparticles by introducing reducing reagents into a sol of metal salts or alkoxides [27,28]. To stabilize these metallic nanocrystals, large surfactant molecules were added to prevent oxidation. The challenge in deriving metallic nanocrystals lies in the effective extraction of surfactant molecules without particle growth or structural changes. This may be accomplished by applying an oxide protective coating onto the metallic nanoclusters prior to or during surfactant removal.

The sol-gel approach can be developed as an even more flexible and powerful processing technique when combined with external fields, such as hydrodynamic cavitation or high-energy ultrasound. In a typical cavitation process, nanoparticles are generated through the creation and release of gas bubbles inside gel precipitates to destroy the massive oxyhydroxide network. The key factor is to rapidly synthesize and separate nanoparticles. In hydrodynamic cavitation, a freshly precipitated mixed metal oxyhydroxide sol is suddenly pressurized in a supercritical drying chamber through a small diameter tubing, and exposed to cavitational disturbance and high temperature heating [29]. The sol-gel solutions are remixed very effectively and the erupted hydrodynamic bubbles from inside the gels are involved in further cavitation. The resulting nanocrystallites are rapidly quenched to terminate grain growth. The grain size can be tuned by the pressure and the solution retention time in the cavitation chamber.

In a different approach from hydrodynamic cavitation, high-energy ultrasound has been employed to create acoustic cavitation. The acoustic cavitation process can generate a transient, local pressurized hot spot of 5000 K and 1800 atm with a cooling rate of 10^{10} K/s. Such sudden changes in temperature and pressure assist the destruction of large particles and the formation of high surface area nanocrystallites

[30,31]. Organometallic molecules are often the precursor of choice for this sonochemical process. The solvent can also be altered to suit the individual requirements in applications. For example, nano-crystalline Mo_2C was obtained by irradiating molybdenum hexacarbonyl in hexadecane with high-intensity ultrasound at $90°C$ in argon [32]. This material has a very high surface area of $\sim190\,m^2/g$, and shows good catalytic activity for cyclohexane dehydrogenation. The catalyst yields 100% selectivity towards benzene conversion without the undesired hydrogenolysis to methane.

Efforts in sol-gel research have focused mainly on demonstrating successful synthesis of nanocrystallites. Fundamental knowledge of the sol-gel synthetic parameters for controlling grain size distribution is still limited. Future studies are needed to elucidate the mechanisms of nucleation and grain/particle growth. Means of dispersing agglomerates and handling nanoparticles need to be established for effective powder processing. Economical continuous processing is still awaiting to be developed for commercial production. Potential bottlenecks that need to be addressed in large-scale processing include the availability of raw materials, cost of precursors, and recycling of solvents.

3.2. Gas Phase Synthesis

Inert gas condensation was first developed in the early 1980s by Gleiter and co-workers for high-purity synthesis of nanocrystalline materials [14]. In this process, an aerosol of particles is generated by evaporation, and cooled by collisions with inert gas atoms to condense as crystallites [33]. To increase the yield, a forced flow reactor design has been developed to allow rapid evaporation of metallic sources while suppressing particle growth [34]. Beside Joule heating, sputtering, electron beam, plasma and laser ablation have been developed to offer greater compositional flexibility and homogeneity in generating nanocrystals of refractory materials and multicomponent alloys [35]. The possibility of *in situ* post-treatment further allows the generation of nanocrystalline oxides, nitrides and sulfides. In particular, controlled post-oxidation of metallic clusters has been successfully used to create nano-crystalline nonstoichiometric oxides with a high concentration of oxygen vacancies for use as active redox catalysts [36].

Defect centers in metals, alloys, and metal oxides have been shown to be important as active catalytic sites in many reactions [37]. Oxygen vacancies, for example, are critical in oxidation catalysts. Nanocrystalline nonstoichiometric CeO_{2-x} produced by post-oxidation of Ce nanoclusters possessed a significant concentration of Ce^{3+} and oxygen vacancies even after calcination at $500°C$ in an oxidizing atmosphere [36]. The abundance of surface adsorbed O_2^- species associated with the quasi-free electrons of oxygen vacancies enabled this catalyst to achieve selective SO_2 reduction by CO at a low temperature of $460°C$ with excellent poisoning resistance against CO_2 and H_2O in the feed stream [38]. It would be of interest to generate selective oxidation catalysts such as molybdates and vanadates by similar gas phase approach. These materials are conventionally synthesized by wet chemical approaches that require calcination for sample purification and crystallization. Compared to wet chemical synthesis, gas phase synthesis of nanoclusters provides superior flexibility and control in tailoring defect structures. It is an attractive approach since it produces the nanoparticles directly in a pure, crystalline form, and thereby allows unique metastable structures to be isolated and utilized.

The large numbers of atoms residing at the surface and grain boundaries of a nanostructured material typically possess unsaturated dangling bonds that may be unusually reactive towards forming the desirable intermediates in a catalytic reaction. Where two or more metal cations are present in a mixed oxide nanocrystalline catalyst, phase segregation can further lead to effective dispersion of the components as an ideal supported catalyst or nanocomposite catalyst. An example of surface segregation was demonstrated by [39] for a Cu-Ce nanoalloy system generated by sputtering from a mixed metal target. Following an oxidative heat treatment, the two metals lost their miscibility in their respective oxide forms, and copper oxide became segregated and highly dispersed on cerium oxide nanocrystallites. Chemical and electronic synergisms between the intimately mixed components in the resulting nanocomposite catalyst greatly enhanced reactivity in CO oxidation [38,40]. Full conversion of this reaction was achieved at $80°C$, a remarkably low temperature considering that expensive noble metals were not employed. Exploitation of synergistic effects achievable in nanocomposite systems deserves further studies in a

wide variety of applications currently employing multicomponent catalysts or supported catalysts.

Beside gas condensation, efforts have been devoted to adapting conventional diffusion flame burners for the synthesis of nanocrystalline mixed oxides. Using a hydrogen-oxygen flame, [41] have generated nanocrystalline vanadium phosphorus oxide powders from $VOCl_3$ and PCl_3 liquid precursors. The formation processes were monitored by *in situ* laser light scattering and emission/absorption spectroscopy, as well as by transmission electron microscopy. It was found that VPO particles nucleated and agglomerated to form chain-like structures. As the flame temperature increased, the chain-like structures would collapse to produce nanometer-sized spherical particles. The crystalline phases of the powders derived were also strongly influenced by the flame temperature. By varying the process parameters, high surface area VPO powders of controlled structure and morphology could be obtained. These novel materials would be of interest for the selective oxidation of C_4 hydrocarbons to maleic anhydride.

Chemical vapor deposition (CVD) represents another gas phase synthesis which is unique for its ability to epitaxially grow active components in the form of multilayered nanostructure. This may be useful towards anchoring catalytically active sites to a specific environment for attaining highly selective catalytic activity. The CVD process can also accomplish site isolation in a uniform fashion, such as in cluster-encapsulated, zeolite catalysts. Combining zeolite chemistry with metal carbonyl cluster chemistry, a $[HOs_3(CO_{11})]^-$ catalyst located in the supercages of zeolite Y has been prepared by CVD for CO hydrogenation [42]. Uniformly distributed metal sulfide clusters in the supercages of zeolite Y have also been successfully achieved by reacting $(CH_3)_2M$ with $H_{44}Na_{11}$-Y, followed by exposure to H_2S vapor [43]. The aggregation of the small clusters was prevented because of (i) the strong chemical bonding between the metal cations and the sulfides, and (ii) the charge interaction between the metal cations and the anionic zeolite framework. Although this system was not designed specifically for a catalytic purpose, it provides useful basis for future catalyst design and synthesis with CVD.

Gas phase synthesis has been commercialized for manufacturing nanocrystalline materials. This technology involves high capital equipment investment, but offers excellent control on grain size distribution.

Nanocrystalline powders are typically dispersed in a liquid suspension or consolidated as a solid compact to facilitate further handling and utilization. Stability of nanostructures against grain growth, aggregation, sintering and phase transformation in liquid dispersion, pressure application and thermal treatment needs to be addressed for different applications of interest. Stabilization of reactive metallic clusters has been shown to be possible with inert silica encapsulation [44]. This approach involves deriving metal/silicon heteronuclear clusters from a gas aggregation source, followed by oxidation of the structured particles with exposure to air. The resulting minimum energy clusters have a ''fish-eye'' morphology, with a core consisting of metals such as Au and Ag, and a skin consisting of the lower surface free energy silica. Alternatively, it has been shown that metallic clusters can be captured as a colloidal suspension in an organic solvent whereby a support oxide can be introduced for cluster adsorption [45]. Upon removal of the solvent and surfactant, a supported metal catalyst such as Ag/SiO_2 can be derived for oxidation catalysis. These two examples illustrate the possibilities of stabilizing and handling ultrafine metallic clusters via intelligent processing.

3.3. High-Energy Ball Milling

High-energy ball milling has been employed to produce mechanically alloyed systems, highly strained amorphous structures, as well as nanocrystalline materials. During the plastic deformation of the ball milling process, dislocation cell structures are produced within shear bands. Crystalline nanostructures may result when the dislocation cells disappear upon further milling. Mechanical milling has been used to obtain homogeneous mixed oxide catalysts for a long time. However, generation of nanocrystalline catalysts by this approach has not been pursued till recent years. The simplicity of this approach lends it great potential for mass production without complex capital equipment, provided that the impurity from the milling vial/balls does not pose a concern. It has also been found that supersaturated solid solutions can be easily created at low temperatures by high-energy ball milling [46]. Combined with the highly strained interfacial component, there are tremendous opportunities for providing unique compositional control and creating active defects in the milling approach.

A drawback in ball milling is the low surface area

of the as-prepared samples due to problems in dispersing the nanoparticles during synthesis. The milling medium may be used as a means to control particle aggregation in mechanical milling. Zielinski et al. [47] has found that milling γ-Al$_2$O$_3$ powder in air could lead to nanocrystalline alumina powders with a substantial surface area ($\sim$100 m^2/g), while milling in an inert argon atmosphere produced samples with a lower surface area (26 m^2/g). Surfactants and polyelectrolytes may be helpful in achieving a monodispersed nanocrystallite suspension via wet-milling. The relationship between milling conditions (e.g., deagglomeration medium, milling temperature and energy input) and nanostructure tailoring needs to be established in future research.

High-energy ball milling is noted for creating crystalline phases by mechanical energy instead of thermal energy. This is particularly attractive for deriving nanocrystalline materials of certain high-temperature phases without going to extreme heat treatments that induce significant grain growth and surface area loss. For example, it has been found that a significant amount of α-Al$_2$O$_3$ seeds can be generated by high-energy ball milling of γ-Al$_2$O$_3$ for well less than an hour [48]. This mechanical seeding approach avoids the impurity introduction from prolonged milling, and allows the full transformation to the α-phase at relatively low temperatures, such that a surface area of over 35 m^2/g could be achieved. This thermally stable non-acidic Al$_2$O$_3$ phase cannot be obtained conventionally with a surface area greater than 5 m^2/g. The novel nanocrystalline α-Al$_2$O$_3$ with high surface area and excellent thermal stability presents an attractive potential as an inert catalyst support for partial oxidation and high-temperature combustion applications.

4.   Synthesis of Nanoporous Catalysts

4.1.   Microporous Molecular Sieves

There has been significant interest in the past decades on the manipulation of the pore structure, composition, and chemical properties of molecular sieves. In particular, silicate-based zeolites have been widely examined for catalytic applications. However, chemical synthesis of tailored porous structures has relied mainly on trial-and-error. In some cases, the crystal structures of zeolites are thought to be controlled by templating agents, such as inorganic cations and organic molecules. The relationship between templating agents and zeolite structure development is not entirely well understood. Nevertheless, recent advances in synthesis have resulted in the successful derivation of specially designed pore structures, such as SSZ-26 [49]. By deliberately adding a third ring to a fused two five-membered ring of diquaternary organocation (which has been used to synthesize ZSM-12 with a one-dimensional channel structure), the polycyclic organocation templating agent prevented the formation of straight channels during the nucleation of the zeolite synthesis, and created a two-dimensional pore structure in which two channels intersect.

Zeolites with large window sizes will provide more opportunities for developing catalysts for new and existing processes, such as the processing of heavy petroleum residual to produce gasoline. All silicate-based zeolites have a window size distribution ranging from 3 to 8 Å, and no success has been reported for increasing beyond the 12-membered ring window size in this system until recently. A 14-membered ring UTD-1 silicate-based zeolite with a straight channel pore structure was synthesized using an organometallic complex as a templating agent [50]. Breakthroughs in deriving huge 18- and 20-membered ring window were achieved with phosphate-based zeolites, such as VPI-5 [51] and cloverite [52], respectively. Cloverite has a face centered cubic structure (Fig. 2) that consists of α-cages (similar to the body-centered supercage in zeolite A). Each of the cages sits at the corner of a cube, and the cubes are connected along the edges through eight double-rpa-cages (as found in AlPO$_4$-22) by sharing tetrahedral phosphorus atoms in the eight-membered rings of the α-cages. The four-leaf-clover-shaped window structure led to its nickname, cloverite. The largest open dimension (30 Å) in this molecular sieve is given by the body diagonal of the center supercage. However, the largest window is still limited to 6.0×13.2 Å which is not large enough for processing polyaromatic molecules. More research is needed for establishing larger templating agents, developing appropriate precursors, and understanding the nucleation mechanism of molecular sieve structures.

The window opening of zeolites offers exceptional size and shape selectivity in catalytic applications. In addition, these molecular sieves also provide an ideal matrix for the derivation of metallic nanoclusters. For
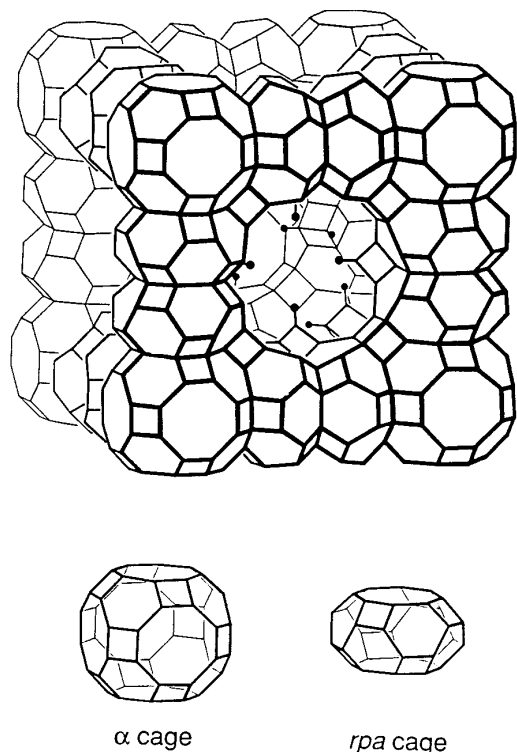
α cage   rpa cage

Fig. 2. Crystal structure of cloverite [52].

example, 5 Å Pt clusters can be stably dispersed within the cages of BaKLTL zeolite. Such small clusters uniquely provide highly selective conversion of naphtha to aromatics [53,54]. The steric limitation imposed by zeolites provides an unusual opportunity to examine structure and chemistry of nanoclusters, which are catalytically unique for a variety of structure-sensitive reactions.

The synthesis of new molecules, especially pharmaceutical chemicals, requires highly selective catalytic processes to be developed. Frequently, only one enantiomer is desired in a mixture of chiral products. Porous materials with engineered chirality may offer an attractive alternative to the conventional expensive separation processes. They may also be directly used for asymmetric catalysis to preferentially produce the desired enantiomer. ETS-10 and zeolite beta are examples that have a chiral framework structure consisting of a helical 10-ring channel parallel to the (001) direction [55,56] It has also been shown that water molecules captured in the pores of VPI-5 are arranged amazingly in the fashion of a triple helix through hydrogen bonding [57]. This example illustrates that even a non-chiral crystal

structure may create an environment for hosting molecules in a chiral arrangement. The application of nanoporous structures towards asymmetric catalysis promises to be an exciting area for future research.

Utilization of the uniformly distributed channels and cages to mimic protein-surrounded active sites in enzyme catalysts would be very useful in the effective catalysis of numerous low-temperature reactions. Zeolitic materials offer robust, well-defined cavities suitable for hosting catalytically active sites and simulating the selective function of proteins. For example, iron-phthalocyanine incorporated into the supercage of zeolite Y was recently developed to mimic the P-450 cytochrome enzyme [58]. The catalyst demonstrated a 300-fold enhanced activity in alkane oxygenation with a much milder oxidant compared to traditionally prepared zeolite-encapsulated complexes, and was as active as a P-450 cytochrome enzyme. Application of microporous structures as enzyme-mimicking catalysts holds a great deal of promise, especially if a rational approach is adopted in the catalyst design of such systems; a series of successful nanostructured catalysts have, for example, been developed using ''imprinting'' or templating synthesis for this application [59].

The synthesis of redox porous catalysts has been of significant interest since the inability to incorporate significant amount of active transition metal cations has limited the use of zeolites in oxidation catalysis. Octahedral molecular sieves that are believed to have variable oxidation states in the framework atoms have recently been synthesized by a hydrothermal method. Termed OMS-1, the unique microporous manganese oxide material shows a 3×3 octahedral tunnel structure similar to that found in the mineral, todorokite [60]. However, no success has yet been reported in the synthesis of microporous transition metal oxides with two- or three-dimensional pore structures. The importance of this type of materials can be extrapolated from the impact of TS-1 on fine chemical processing [61] and of Cu-exchanged ZSM-5 on environmental catalysis [62,63]. TS-1 is a titanium-substituted silicalite with a MFI (ZSM-5-like) structure. It has significant activity in selective catalytic oxidation processes, such as hydroxylation of phenol to produce catechol and hydroquinone. Hydroxylation of other aromatics, epoxidation of alkenes, ammoxidation of cyclohexanone, and oxidation of alcohols and alkanes can also be catalyzed with TS-1. Cu-ZSM-5 was discovered to have stable high

activity for direct nitric oxide decomposition. The sustained decomposition over Cu-ZSM-5 probably results from the unique coordination of Cu cations imposed by the channel and cage structure of ZSM-5 since many other copper-exchanged zeolites and copper oxides do not have such high activity and longevity for NO decomposition.

Pillared lamellar solids represent another class of porous materials of interest to catalysis. The pore structure of the layered materials can be manipulated by expanding the interlayer spacing through the intercalation of large molecules or pillaring agents. The pillaring agents are cations or anions which interact with the layered hosts by charge compensation. Pillaring of silicate clays have been widely examined, but the non-uniform distribution of pillaring agents prevents a narrow pore size distribution from being readily achievable. Recently, reaction pathways were developed to chemically link the pillaring agent with the host structure [64,65]. Such an approach has successfully created a new family of layered transition metal molybdates (LTM) with not only compositional flexibility but also controlled oxide stoichiometry of interest to oxidative dehydrogenation of lower alkanes to alkenes [66]. It is also fruitful towards creating stable nanoporous clays [64], which are of interest as a low-cost family of materials for petroleum processing [67]. The current bottleneck in the utilization of pillared clays lies in their limited hydrothermal and thermal stability, except for rectorite which is a rare natural clay. Further research is needed to develop a synthetic rectorite for large-scale utilization of such systems.

Another class of microporous materials that has attracted much attention as catalysts is the carbogenic molecular sieves (CMS). Unlike zeolites, these carbon-based materials do not have a well-defined crystalline pore structure or acidic sites. They have a pore size distribution from 3 to 7 Å, and can be synthesized by pyrolysis of carbon-containing sources. Judicious selection of precursor materials and control of treatment conditions have led to precise tailoring of the CMS pore structure. Foley et al. [68] have found a composite of CMS and amorphous aluminosilicate to be very useful for selective production of mono- and dimethylamines. Other applications of CMS include gas separation of small molecules, such as oxygen vs. nitrogen and ethylene vs. ethane.

It would be of significant interest to establish new technology that would offer combined separation and catalysis. Such a membrane reactor system may utilize the size and shape selectivity of molecular sieves to shift chemical equilibrium towards increased conversion during catalytic reactions. The key to the development of such processes lies in the successful derivation of defect-free and mechanically stable membranes of tailored nanoporous structures [69].

4.2. Mesoporous Materials

4.2.1. Silicate-based mesoporous catalysts.

Extending the pore size of well-defined nanostructures to the mesoporous range (2–50 nm) was accomplished by Mobil researchers in 1992 via a liquid crystal mechanism [70,71]. Through charge interaction, silicate-based precursors were deposited onto hexagonally-packed rod-shaped micellar templating agents. Upon calcination, the organic surfactant molecules were removed to expose the hexagonally-packed cylindrical porous structures termed MCM-41. The inorganic framework of these mesoporous materials is not crystalline as in the case of zeolitic structures. However, the pore size of the materials derived by such approach can be uniformly varied between 2–10 nm through altering the surfactant chain length or adding swelling agents such as mesitylene (Fig. 3). These large pore openings overcome the configurational diffusion limitations of the zeolitic systems. Stucky's group has further developed a different type of surfactant as templating agents, and obtained a three-dimensional cage-structured mesoporous material, SBA-2 [72]. The MCM family of mesoporous materials is particularly attractive as catalysts that may provide high selectivity towards petroleum cracking or fine chemical processing involving large molecules that cannot be accommodated in the micropores of zeolite catalysts. A great deal of research has recently been devoted to refining and understanding the supramolecular templating synthesis of mesoporous systems [73–78], and interesting catalytic applications are also beginning to emerge for this new class of materials [79].

It has been shown that MCM-41 materials can be functionalized with surface silanol groups to modify the pore size and hydrophobicity of these catalysts [71]. Such surface functionalization may also be very useful towards anchoring active catalytic sites in these large-pore materials to tailor specific activity and

shape selectivity. Beside alumino-silicate compositions, full alumina mesoporous MCM-41-like materials can also be prepared [80,81]. Doping of silicate-based or alumina-based MCM family of mesoporous materials can provide an excellent means of introducing acid sites and ion-exchange capabilities into the inorganic framework. The lack of crystallinity in the porous framework of MCM-41 materials gives it greater tolerance towards incorporating transition metal dopants than the zeolitic materials. The resulting mixed coordination and oxidation states is particularly useful for tailoring catalytic properties. For example, 1% Ti-doped MCM-41 has been found to be an effective catalyst for hydroxylation of benzene to phenol [82,83]. Compared to TS-1, this material is also unique for its ability to catalyze much larger aromatic molecules, such as 2,6-di-tert-butyl phenol to the corresponding quinone, because of its larger pore dimension.

In our ability to derive well-defined porous structures, there is currently a gap between the 3-dimensional crystalline microporous zeolitic materials and the noninterconnecting hexagonally-packed mesoporous MCM-41 systems. Long-range order in the inorganic backbone of porous materials has been found to be critical in catalytic selectivity of a variety of reactions. It would be of interest to investigate means of crystallizing the framework of MCM-41 materials, for example by increasing the wall thickness of the pore structure or incorporating the crystalline building blocks used in deriving microporous cage-like structures. It would further be of synthetic interest to derive a well-defined 3-dimensional mesoporous network.

Organic ion-exchange resins have played an important role in acid catalysis, such as the production of methyl tert-butyl ether (MTBE), because of their low cost and strong acidity. It is desirable, however, to create a better substitute for these materials with improved thermal stability, homogeneity, porosity, and ability to be regenerated. The development of polysiloxanes has made inorganic ion-exchange resins a potential competitor to zeolites as catalysts, although the former still suffer from drawbacks in pore structure control and active site creation. Recently, a silicon alkoxide precursor modified with an organic bromide functionality was used to prepare a cross-linked sulfonated silica [84,85]. The pore size distribution of this inorganic polymer can be controlled with sol pH, reaction temperature, and
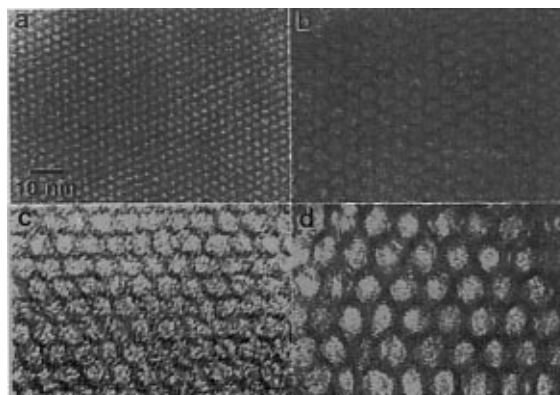

Fig. 3. Transmission electron micrographs of several MCM-41 materials having pore sizes of (a) 20 Å, (b) 40 Å, (c) 65 Å and (d) 100 Å [71].

drying/heat treatment. The SO_3^{2-} functionality provides a unique ion-exchange capability for introducing active metal cations and complexes within the stable inorganic oxide framework for catalytic and gas adsorption applications. Such a concept of surface functionalization awaits broader application to mesoporous structures for selective catalytic site generation.

For practical applications of mesoporous catalysts, it would be important to work towards increasing hydrothermal stability and mechanical/thermal robustness for handling/recycling. These issues may be addressed by improved processing and/or compositional control. It is also anticipated that the cost of surfactant template use and recovery may be a potential bottleneck in the processing of MCM-41-type mesoporous materials, and should be addressed in future research.

4.2.2. Transition metal oxide-based mesoporous catalysts. Transition metal oxides are widely used in heterogeneous catalysis [86], but they are limited to traditional wet chemical synthesis that does not present well-defined pore structures or ultrahigh surface areas. Typically, transition metals are dispersed as metals or oxides on high surface area supports, or introduced as dopants into silicate-based microporous or mesoporous framework. A direct synthesis of transition metal oxide-based porous structures will open up opportunities for designing advanced catalysts tailored in both surface reactivity and size/shape selectivity. It would be of interest to

reactions such as photocatalytic decomposition of organic compounds (TiO_2), solid acid isomerization and alkylation (sulfated ZrO_2), hydrodesulfurization (Ni/Co oxide), and partial oxidation (V_2O_5, MoO_3). Mesoporous transition metal oxides may further be useful as selective adsorbents for gas/liquid separation of olefins and aromatics from paraffins since the presence of unsaturated coordination on transition metal ions will preferentially adsorb bonding-unsaturated organic compounds. The presence of d electron orbitals in transition metal oxides also gives rise to lower energy gaps, facilitating electron or charge transfer. The possibility to create unique catalysts with designed oxidation states, coordination chemistry, electronic structure, and thermal stability can be expected with the advent of well-defined transition metal oxide-based porous structures.

Currently, a very limited number of transition metal oxide molecular sieves has been reported. OMS-1, a microporous manganese oxide [60], represents a rare example for this class of highly desired materials. Stable mesoporous transition metal oxide-based molecular sieves were not successfully synthesized until recently. Using a ligand-assisted templating approach, Antonelli and Ying generated a family of hexagonally-packed transition metal oxide molecular sieves termed TMS-1 [87]. Nb-TMS1, a niobium oxide analog of silicate-based MCM-41, was derived by first establishing a covalent bond between the niobium ethoxide precursor and an amine surfactant. The ligand formation ensures precursor-surfactant

interaction and micellar self-assembly prior to precursor hydrolysis (see Fig. 4). To delay the rapid hydrolysis of transition metal alkoxides, a modified sol-gel processing was also developed with steric hindrance provided by acetylacetone additives [88]. Between the two approaches, hexagonally-packed mesoporous oxides of Nb, Ta, Ti, Zr, etc. have been synthesized with ultrahigh surface areas and excellent thermal and hydrothermal stability. Mixed metal oxide molecular sieves can easily be achieved by these approaches to provide the fundamental chemical flexibility associated with compositional control and homogeneity. This, coupled with the possibility of tailoring pore sizes in the range of 2–10 nm, offers exciting new opportunities towards catalytic and gas adsorption applications. The full potential of this new class of mesoporous materials awaits further research. It would also be of interest to extend the supramolecular templating approach to derive more examples of microporous transition metal oxides. Sun and Ying [89] have recently demonstrated that pore size tuning of Nb_2O_5 (Nb-TMS5) is possible for the microporous regime (<2 nm) via ligand-assisted self-assembly of small templating molecules.

5.   Characterization and Modeling of Nanostructured Catalysts

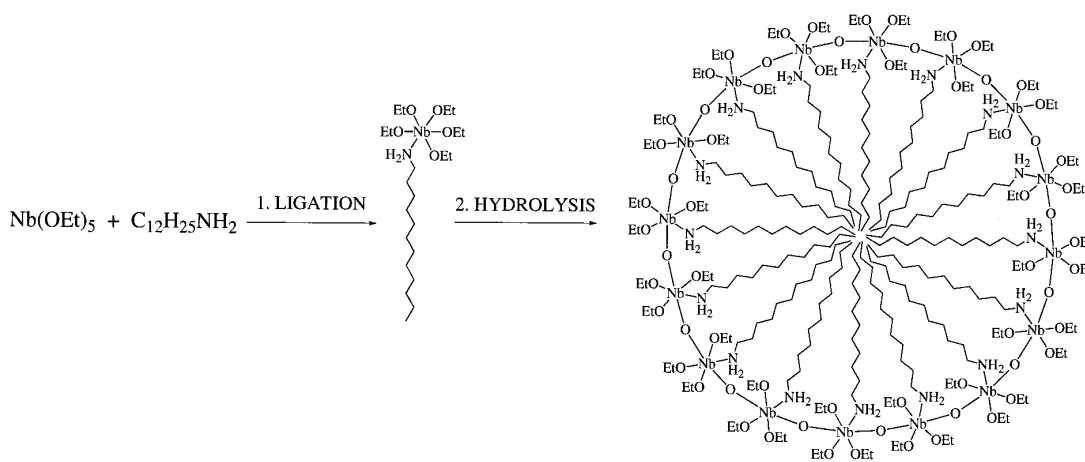Due to the ultrafine nature of nanostructured materials, it is critical that we develop better

Fig. 4. Ligand-assisted templating as a method of synthesizing transition metal oxide analogs of MCM-41, such as Nb-TMS1.

techniques to characterize them at the atomic level. Much more research should be devoted to relating the characteristics and properties of nanostructured catalysts. For example, it is highly desirable to identify and have information about the physical location of the catalytically active sites, the bonding environment of the transition metal ions in the mixed oxides, the distribution and the chemical states of elements in multicomponent systems, and the size distribution and morphology of nanostructured noble metal clusters [90]. Knowledge of these structural features of nanostructured catalysts under *in situ* conditions would be particularly useful.

Due to the size quantization effect and high surface-to-volume ratio of the nanocrystalline catalysts, it is difficult to extrapolate our knowledge of bulk polycrystalline catalysts to such systems. The lack of long-range order at the surfaces, edges and grain boundaries of nanocrystals will also affect their surface bonding characteristics in forming catalytic intermediate complexes. The lack of well-developed surface characterization techniques has restricted our ability to learn more about the surface structure of nanocrystalline materials. High-resolution electron microscopy (HREM) has been applied to study interfacial structure, such as atomic coordination, in well-defined bicrystal systems. This technique may be adapted to examine the surface structure of nanocrystals. The recent development of coupling scanning transmission electron microscopy (STEM) with energy dispersive X-ray spectroscopy (EDX) has provided excellent compositional mapping capabilities for examining doped conventional TiO_2 polycrystals [91]. This approach has been demonstrated to possess sufficiently high resolution to examine a Cu/CeO_{2-x} nanocomposite used as supported metal catalysts in SO_2 reduction and CO oxidation [39]. Investigation of the electronic structure of pure or doped oxide nanostructured catalysts may benefit significantly with the development of STEM coupled with electron energy loss spectroscopy (EELS). The atomic, chemical and electronic structures of surfaces represent an important frontier for future research, and will contribute directly to our ability to intelligently design catalysts for enhanced activity and selectivity. The grain size effects in structure-sensitive reactions will particularly benefit from such advances in characterization. It has been found that scanning tunneling microscopy (STM) and atomic force microscopy (AFM) (Fig. 5)

are very useful for illustrating the surface morphology of nanostructured materials [92,93]. Further development of such surface probe microscopy with *in situ* capabilities will serve towards understanding the surface structural changes and reconstruction of catalytic materials during actual reaction conditions.

X-ray powder diffractometry (XRD) has been widely used for analyzing grain size and lattice strain in nanocrystalline systems. Spectroscopic techniques, such as Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible optical spectroscopy (UV-VIS), electron paramagnetic resonance (EPR) spectroscopy and solid state nuclear magnetic resonance (NMR) spectroscopy should be very useful for examining the chemical bonding and adsorption characteristics of nanocrystalline catalysts. Further information about the surface/interfacial structure and chemistry can be obtained by extended X-ray absorption fine structure (EXAFS) and small angle neutron scattering studies. EXAFS provides information on the short-range coordination of elements of interest, which would be particularly useful in elucidating the active centers in bimetallic or mixed metal oxide catalysts with ultrafine grain sizes.

Further research is also needed in the characterization and catalytic studies of the novel mesoporous materials. The nature and strength of acid sites [94] need to be investigated for potential applications as solid acid catalysts. The mesoporous aluminosilicates are of particular interest as cracking catalysts for large aromatic molecules. Studies have suggested that the amorphous silicate-based framework of MCM materials might provide more Lewis acid sites than the microporous zeolites. This may open the possibility for catalyzing some reactions which proceed via a radical reaction mechanism. Kinetics and diffusion characteristics of the mesostructures also await further examination and modeling. The flexibility of pore size tailoring associated with MCM-41 materials should make these structures very useful as matrices for anchoring large organometallic molecules. For example, porphyrins and metallocenes that provide high selectivity in homogeneous epoxidation and polymerization catalysis, respectively, may be fixated on mesoporous supports as novel heterogeneous catalysts. This will improve the long-term activity of these catalytic complexes through active site isolation, leaching prevention and ease of handling/recovery.
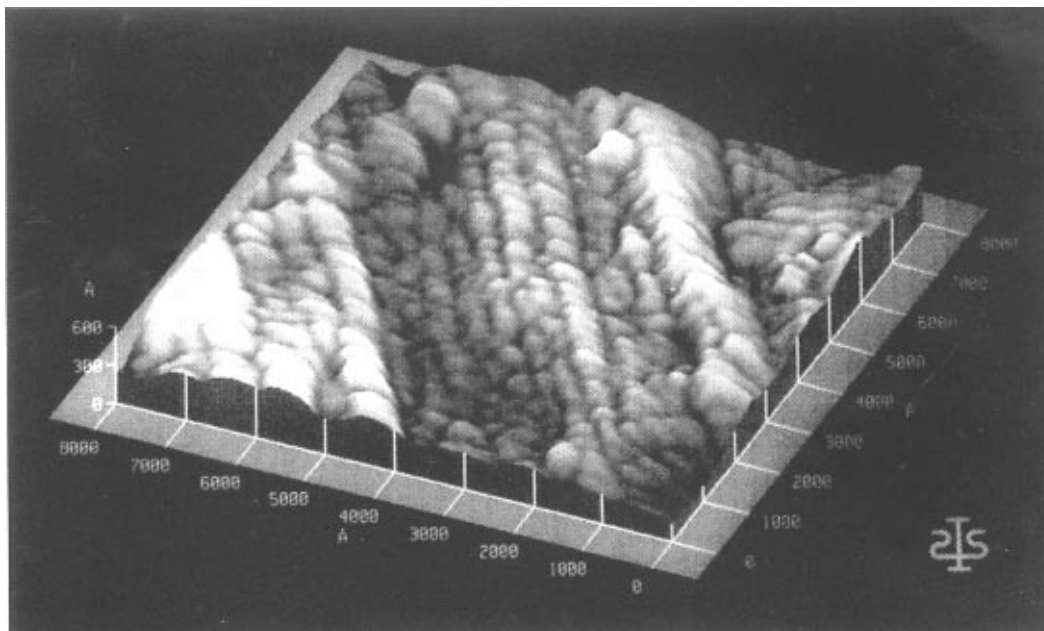
In general, the synthesis and processing of

Fig. 5. Atomic force microscopy surface image of nanocrystalline TiO_{2-x} green compact.

nanocrystalline and nanoporous materials will benefit greatly from the development of on-line monitoring/ characterization instrumentation. The nucleation and growth processes of nanoclusters and self-assembled molecular sieves need to be better understood on the fundamental level, as well as for improved process control and future scale-up. Techniques based on light scattering and laser dopler effects may be further developed to offer characterization capabilities in the size range of 0.5–50 nm. If morphological information can also be obtained, important insights into the directional crystal growth and micelle templating mechanism can be achieved, facilitating future synthetic breakthroughs. It would be important to combine experimental characterization with computational tools to model and predict novel nanostructures of interest to catalytic applications. Modeling of the synthesis process will be important to bring about better design of reactors for effective manufacturing of nanostructured materials. Of particular concern is the large amount of diluents and solvents that may be involved in the processing of nanostructured materials. Use of precursors, mixing of reactants, collection of nanoparticles, and recycling of solvents should all be effectively addressed with a systems engineering approach in the reactor design.

6. Opportunities for Nanostructured Catalysts in Fine Chemical and Fuel Production

The driving force behind catalysis research lies in the growing need for cheaper energy and chemical production, and greener manufacturing technologies. Nanocrystalline and nanoporous materials offer unique structural characteristics that may be tailored towards a wide variety of opportunities in innovating these processes.

6.1. Opportunities for Catalytic Production of Fine Chemicals

6.1.1. Oxydehydrogenation, oxyhydroxylation and ammoxidation catalysts.   There is a tremendous need to replace existing chemical processes that are highly energy-intensive and/or environmentally unfriendly (involving, for example, corrosive catalysts or waste generation). Processes such as oxydehydrogenation, oxyhydroxylation and ammoxidation represent innovative approaches that simplify multi-step reactions for energy savings. Oxydehydrogenation represents a process which is very attractive for the production of oxygenated organic chemicals, such as ethene oxide from ethane, propene oxide from propane, propanol

from propane, and 2-methyl-2-propanol from 2-methyl-propane. The conventional processes typically involve expensive olefin feedstocks, or paraffins that have to be dehydrogenated via an energy-intensive process followed by an intermediate olefin/paraffin separation. The development of a catalytic oxydehydrogenation process will allow highly demanded oxygenated chemicals to be produced directly from inexpensive paraffin feedstocks. Oxydehydrogenation is also an attractive alternative to high-temperature dehydrogenation reactions for the production of propene from propane and 2-methylpropene from 2-methylpropane.

Oxyhydroxylation could be applied to generate phenol and H_2O by-products by reacting benzene with hydrogen peroxide in the presence of Ti-containing silicalite. This type of economical process approach can be used to prepare oxygenated hydrocarbons from alkanes with inorganic mimics of enzyme catalysts. Also of great commercial interest is the direct oxyhydroxylation of benzene to phenol and of butane to butanediol with molecular oxygen.

Ammoxidation allows organic nitrogen compounds to be synthesized through a simple, energy-efficient process. An example is the ammoxidation reaction to produce acrylonitrile from three raw materials which are inexpensive and easily accessible,

$$NH_3 + 2O_2 + C_3H_8 \rightarrow 4H_2O + CH_2CHCN$$
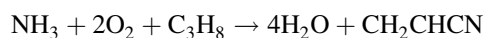
The development of oxydehydrogenation, oxyhydroxylation and ammoxidation processes will rely on successful novel catalytic technologies. Heterogeneous catalysts that can provide not only high activity, but also excellent selectivity for minimal by-product generation, will need to be developed. Nanocrystalline or nanoporous transition metal oxides may present attractive characteristics towards these applications.

### 6.1.2. Catalysts for natural gas conversion.
Research on new feedstocks for fine chemicals synthesis is an important direction for catalysis. The abundant natural gas supply is currently utilized in the form of synthesis gas (syngas) for the production of methanol, acetone, acetic acid, and mixed alcohols. Syngas generation via conventional steam reforming is an energy-intensive process. A more effective catalyst is needed to lower the reaction temperature and pressure for economic competitiveness. Recently,

Schmidt and co-workers developed a direct catalytic partial oxidation approach for selective conversion of methane and other alkanes to syngas [95,96]. A very high conversion was achieved over a Pt or Rh monolithic catalyst within microseconds. The partial oxidation reaction could also operate under a much milder condition than that required for steam reforming to produce syngas from natural gas.

Ways of directly utilizing natural gas in fine chemical synthesis would also be extremely attractive. Oxidative coupling of methane has been extensively studied for the production of hydrocarbons with longer chains. The conversion of this process has been limited to 30%. Recently, 97% methane conversion, 85% ethylene selectivity, and 88% yield of total C_2 hydrocarbons have been achieved by a gas recycle electrocatalytic reactor-separator [97]. The separator is the key factor for the success of this process, selectively trapping the ethylene produced by adsorbents so that the unreacted methane can be recycled through the catalytic reactor. The idea of non-equilibrium reaction in combination with effective catalyst and adsorbent can offer other breakthroughs in the utilization of natural gas for fine chemical manufacturing.

6.1.3. Catalysts for carbon dioxide utilization.
There is substantial interest in developing processes that would recycle the large amount of carbon dioxide exhaust from petrochemical plants to minimize its contribution to the greenhouse effect. Using carbon dioxide in methane reforming to produce useful syngas represents one such example,

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$
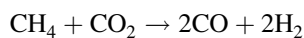
By improving upon the Cu/ZnO catalyst used for syngas production of methanol, CO_2 can also be used with H_2 to produce methanol [98]. Nanocomposite materials may provide higher dispersion of active phases to further increase the reactivity for this catalytic reaction. Economic analysis has indicated a similar capital investment for this approach compared to that using syngas feedstocks. The advantage of this new process is its smaller units that will make use of the on-site CO_2 exhaust streams.

6.1.4. Catalysts for redox reactions.
New redox catalysts need to be developed with higher activity and selectivity for fine chemical synthesis. The

processes involved typically require a redox catalytic center to facilitate the electron or charge transfer for bond breaking and formation. Nanocrystalline and nanoporous mixed metal oxides offer significant potential as new redox catalysts. Transition metal doped nanoporous materials for the synthesis of oxygenated hydrocarbons should be prepared in a fashion that prevents the catalytically active sites from aggregating. Direct incorporation of the transition metal cations into the framework structure will greatly benefit the stability of the catalysts. Currently, a very limited amount of these redox centers can be introduced. The successful synthesis of transition metal oxide molecular sieves, such as OMS-1 and TMS1, opens new possibilities for the selective catalytic production of fine chemicals. The extension of the TMS1 family of mesoporous oxides beyond the early transition metals to other metals with versatile oxidation states would be of interest. Microporous transition metal oxides would be of great benefit towards regio-selective catalyzed reaction of short chain hydrocarbons since the creation of smaller cavities and channels should impose a very different chemical effect on catalytically active sites and on reactant molecules, and lead to unique activation of bond breakage and product selectivity.

The mobility of oxygen vacancies in nonstoichiometric nanocrystalline catalyst enables the transport of quasi-free electrons to surface adsorption sites for high activities in a variety of redox reactions [38,40]. However, the vacancies are unstable in the presence of oxygen at high temperatures. Chemical modification and dopant introduction may be used to sustain the nonstoichiometry of nanocrystalline oxides. These materials await to be tailored in surface chemistry towards partial oxidation catalysis. In particular, an appropriate system that can activate C-H bond in methane to generate oxygenated species would be very exciting.

6.1.5. Asymmetric catalysts for selective production of chiral compounds.
Asymmetric catalysis attracts a great deal of attention with the increasing demand for specific enantiomers in the pharmaceutical industry [99,100]. Nanoporous materials with surface modification may be tailored to yield active sites which preferentially adsorb one side of a steric drug molecule to selectively catalyze one part of the molecule to generate a chiral product. Creation of

steric barriers within the pore structure could also play a similar role as the selective adsorption sites.

6.2. Opportunities for Catalytic Production of Fuels

The development of economically competitive and environmentally benign processes is the driving force behind fuel refining and production. The chief goals in petrochemical catalysis research are to improve the utilization of light hydrocarbons and heavy residuals, and to reformulate fuels to eliminate/minimize pollution in the manufacturing or combustion processes.

6.2.1. Catalysts for high octane fuels.
Maintaining a high octane number while lowering the aromatic content in fuels represents a major challenge in fuel reformulation. Alkylation is a process which holds potential for catalytically converting mixed butenes and isobutanes to branched iso-octanes to improve the octane number of gasoline without aromatic introduction [101]. The current catalysts are corrosive and environmentally hazardous hydrofluoric and sulfuric acids. Replacement of these homogeneous catalysts with solid acid catalysts is an urgent call. Substantial studies have been devoted to zeolitic and sulfated zirconia superacid catalysts. Coking and loss of active sites represent the common problems encountered in these systems, requiring frequent catalyst regeneration. The recently developed mesoporous Zr-TMS1 materials [102] may be useful for this application with its high surface area and mesoporosity. By allowing faster diffusion through the porous structure, the coking experienced in zeolitic catalysts may be avoided. The mesoporous zirconium oxide could be phosphated or sulfated as an acid catalyst through retention of phosphate or sulfate surfactant. The resulting material might have substantially different surface chemistry from conventional sulfated zirconia such that loss of the active acidic sites could be minimized during reaction. Synthesis of TMS1 and MCM-41 materials also offers flexibility for dopant introduction and mixed oxide compositions to enhance catalytic activity and stability.

6.2.2. Residual cracking and hydrotreating catalysts.
Over the years, the available petroleum feedstocks have become ''heavier'' with more residual components, and ''dirtier'' with more heavy

metals and nitrogen-/sulfur-containing compounds. To maintain the high yield of quality gasoline, fluidized catalytic cracking (FCC) of residual has been widely adopted. The success of this process depends heavily on catalysts with a tailored pore size and tolerance against heavy metal poisoning. The active component in FCC catalysts is zeolite Y which has a pore opening of 7.4 Å. The micropores hinder the processing of polyaromatic compounds in the residual. The development of nanoporous structures with larger well-defined pore sizes, such as the MCM family of materials, may facilitate the processing of heavier petroleum feedstocks.

Hydrocracking is the best approach for converting heavy residual to high-quality fuels, without the catalyst coking problem. However, the high operating expense (high pressure and temperature) and the lack of hydrogen supply limit the wide application of this process. New hydrocracking catalysts need to be developed to enable operations under milder conditions. Since it is mandatory to remove sulfur and nitrogen from the fuel, the synthesis of hydrotreating catalysts with high activities for hydrocracking, hydrodesulfurization and hydrodenitrogenation will be extremely useful. The conventional hydrotreating catalysts do not satisfy the new regulation on the content of sulfur, nitrogen and aromatics in fuels. Some studies have shown that metal sulfides have attractive activity, but are limited by their low surface areas. Nanocrystalline metal sulfides may be developed as novel hydrotreating catalysts with high surface activity. It would be of particular interest to prepare such compounds by sulfiding nanostructured mixed metal oxides in a tailored layered morphology to maximize the active site concentration from an ultrahigh edge-to-basal plane ratio.

6.2.3. Hydrogen production catalysts. The demand on hydrogen in petrochemical processes is expected to increase since polyaromatics in heavy residual are hydrogen-lean, and need to be converted to saturated, high-octane hydrocarbon fuels. The removal of nitrogen and sulfur compounds from fuels in hydrotreating processes consumes large amounts of hydrogen too. High usage of hydrogen may also come from the production of coal-liquefied synthetic fuel, if the latter is developed commercially as an alternative fuel. Current hydrogen production uses light hydrocarbons as a feedstock. Catalysts that improve this process efficiency would be very useful.

6.2.4. Catalysts for Alternative Fuel. The conversion of methane to liquid fuels may be achieved through (i) oxidative coupling of methane for the production of longer chain hydrocarbons; (ii) indirect two-stage conversion to synthesis gas, then to liquefied fuels; (iii) reforming with carbon dioxide to produce syngas; and (iv) homogeneous catalysis of methane to methanol via hydrolysis of CH_3OSO_3H intermediate or oxychlorination to CH_3Cl. Natural gas can be a valuable new feedstock for chemical production as discussed earlier. The key issue is the promotion of the energy-intensive catalytic conversion of methane to syngas, or the elimination of this intermediate step to directly convert to the final products. Catalytic fuel cells employing methane-based fuels present an environmentally benign process, but the efficiency of the current technology does not yet meet the commercial needs.

With the abundance of coal and the declining supply of petroleum, coal liquefaction deserves further research. In the last couple of decades, Fischer-Tröpsch catalysts have been dramatically improved, but the cost of gasification remains substantial. The post-processing of Fischer-Tröpsch products and the need for sulfur/nitrogen removal represent two areas of research needs. With the use of catalysts with smaller grain sizes, it may be possible to substitute environmentally benign compositions for the active but toxic or expensive materials currently used. An example is the successful development of nanocrystalline iron-based catalysts in place of Mo- or Co-based catalysts for coal liquefaction [26].

7. Opportunities for Nanostructured Catalysts in Environmental Protection

With the increasing concern on environmental issues, much emphasis has been placed on green technology in the development of new chemical processes [103]. Catalysis will play an even more important role in chemical processes as we search for means to replace conventional processes involving hazardous materials. Innovation is needed to phase out or minimize environmentally hazardous feedstocks, intermediates and by-products through utilization of novel catalysts and new feedstocks. Manufacturing processes which incorporate green catalytic technology in their development would be highly attractive. It is also

expected that remediation of certain unavoidable end-of-pipe polluting wastes will continue to involve catalytic post-treatment.

7.1. Catalysts for Emissions Control

Catalysis is widely used for emissions control of environmentally unfriendly exhausts. Removal of NO_x is an example of great interest since NO_x is not only a health hazard, but also reacts with volatile organic compounds (VOCs) to form smog that depletes the ozone layer. NO_x is commonly generated from combustion in air, and it is produced in larger quantities under the high temperatures needed for more complete combustion. The emissions problem may be minimized if pure oxygen can be used instead of air, but this is currently not possible for automobile applications and too expensive for power plants. Most efforts on NO_x control are therefore focused on post-combustion treatment via catalytic reduction or decomposition. Selective catalytic reduction is a commercially available technology for NO_x removal from stationary sources [104]. Using ammonia as reductant, supported V_2O_5 catalyst can selectively reduce NO_x to nitrogen in the presence of oxygen, and the only by-product is water. This process is widely used in fuel, coal and methane power plants. Its main disadvantage is the complication in storage and handling of large amounts of anhydrous ammonia.

Modified ZSM-5 zeolites have been found to be successful towards selective reduction of NO_x with hydrocarbons [105]. More recently, however, scientists in Switzerland detected hydrogen cyanide in the product streams of NO_x reduction with olefins, indicating that more thorough studies are needed to check the feasibility of these catalytic processes. It was shown in 1993 that NO_x reduction could also be achieved with methane, a reductant which has been widely believed to be nonselective [106]. Using methane as a reductant for NO_x is very attractive for emission control in gas turbines, since availability and handling of methane are not an issue as they are in the case of ammonia. For direct NO_x decomposition, currently the most active catalyst is Cu-ZSM-5 [62,63]. The typical drawback in employing zeolites in NO_x reduction or decomposition lies in the poor hydrothermal stability of these molecular sieves. A new catalyst with greater activity and stability for NO_x removal would be very attractive. Nonstoichiometric nanocrystalline metal oxides pre-sent interesting potential towards this application with its high surface area and the possibility of selective active sites tailoring via better compositional and stoichiometry control [107]. Development of new catalysts should focus on the fixation of active sites and on the tailoring of active sites more specific to the chemisorption of NO_x than O_2. For NO_x control from stationary sources, it would also be important to design the catalysts with resistance to sulfur poisoning.

For NO_x emission control in mobile sources, three-way Pt-Rh catalyst supported on an alumina-ceria washcoat on honeycomb monoliths represents the most developed technology [108–110]. However, Pd/Al_2O_3 will soon become competitive as a less expensive system for catalytic converters. Mitsubishi Motor Company has also patented an even cheaper base metal catalysts, Cu/zeolite, for lean combustion engines. Relatively little attention has been paid to NO_x removal from diesel engine exhaust. The lower combustion temperature in diesel engine produces less NO_x, but the existing three-way catalyst technology cannot be used in the lean combustion conditions of the diesel engines. Additional complications are encountered in diesel engine exhaust due to the high level of sulfur content in diesel fuel.

It would be of significant interest to include nanostructured catalysts directly in the combustion processes to simultaneously improve fuel efficiency and minimize toxic emissions. Currently studied combustion catalysts typically involve a noble metal (e.g., Pd and Pt) and/or an active oxide (e.g., doped MgO and hexaaluminate). Noble metals are active at low temperatures, preventing the formation of thermal NO_x, but they suffer from sintering and vaporization at high combustion temperatures. The oxide materials serve to promote a homogeneous flame front at the lowest temperature possible to minimize prompt NO_x emission. However, at the typical temperature range of operation ($\sim$1300°C), conventionally processed oxides can only retain $\sim$10 m^2/g of surface area. Nanocrystalline processing has recently established a remarkable surface area in excess of 90 m^2/g at 1300°C for barium hexaaluminate [111]. It would be of interest to examine if a nanocomposite of a noble metal supported on a complex oxide could be utilized to provide high catalytic activities over a wide range of combustion temperatures to minimize NO_x emissions while attaining more complete combustion at fuel-lean conditions.

SO_x represents another major air pollutant from fossil fuel combustion, and is a leading cause for acid rain. It also leads to catalyst poisoning in many processes. Most of organic sulfur compounds are removed from liquid fossil fuels by hydrotreating. However, much higher organic sulfur contents are present in diesel fuel than in gasoline, and in the coal-generated liquefied fuel for power plants. Post-treatment of SO_2 currently involves a lime scrubber that produces a large amount of gypsum that has to be disposed of by landfilling. An attractive alternative is catalytic reduction of SO_2 by CO. A nanocomposite Cu-CeO$_{2-x}$ catalyst has been found to be an excellent catalyst for this reaction [38,40]. SO_2 could be selectively reduced to useful elemental sulfur by this novel material at a low temperature of 420°C. The nanocrystalline material was synthesized with a high degree of nonstoichiometry that attracted highly active surface adsorbed superoxides for redox reactions. The reservoir of oxygen vacancies associated with the nanocrystalline CeO$_{2-x}$ further provided greater poisoning resistance. The ultrahigh dispersion of Cu on CeO$_{2-x}$ offered by nanocrystalline processing also greatly enhanced chemical spillover effects with an exceptional thermal stability.

7.2. Catalysts for Treatment of Volatile Organic Compounds

Volatile organic compounds in the waste stream of chemical plants can cause air and water pollution if they are not properly treated. They pose a particular threat to ozone depletion, and a 90% reduction of about 120 toxic VOCs was mandated in the Clean Air Act of 1990. The most efficient approach may be catalytic oxidation or combustion of VOC's to carbon dioxide and water. Precious metal on alumina, for example, has been developed as effective catalysts by Allied Signal for this application [112]. The key to developing successful technology is to lower the reaction temperature, thereby reducing the energy costs of heating the VOC stream. A TiO_2 catalyst coated on a monolith has been found to be very active for treating chlorinated compounds, but not benzene. Multicomponent catalysts, such as Pt/TiO_2-V_2O_5-WO_3-SnO_2, would be needed for the removal of mixed VOCs. Nanostructured catalysts would offer significant advantages in achieving ultrahigh phase dispersion and uniformity in complex catalyst compositions. This would greatly enhance the chemical synergism between the components, increasing the number and stability of active sites.

Due to the low concentration of VOC pollutants in typical waste streams, photocatalytic decomposition presents an attractive alternative for their complete destruction. TiO_2 is most widely used to generate electron-hole pairs for photocatalysis, and metals such as iron has been found effective at reducing chlorohydrocarbons. Photocatalytic technology is attractive for its low-energy requirements and wide applicability, but suffers from low quantum efficiency. Engineering of semiconductor nanocomposites, such as Pt/doped TiO_2, offers attractive improvements on photocatalytic processes by increasing surface reactivity while suppressing charge carrier recombination.

8. Recommendations

Nanostructure processing has shown a unique capacity for controlling surface area, cluster size, grain morphology, pore structure, component dispersion, phase distribution, and defect concentration to engineer advanced catalytic materials towards ultrahigh reactivity and selectivity. Substantial amounts of further research is needed to realize the full potential of novel nanocrystalline and nanoporous catalysts. To facilitate their development, the following short-term and long-term research goals are recommended.

8.1. Short-term Goals

1. Develop nanostructured transition metal oxide catalysts with redox ability for selective oxidation catalytic reactions and treatment of toxic flue gases.
2. Develop nanostructured solid acid catalysts with high concentration of stable, strong acid sites to replace liquid acid catalysts.
3. Develop active nanostructured catalysts for conversion of natural gas to chemicals and liquid fuels.
4. Develop highly active nanostructured gasification catalysts for coal liquefaction.
5. Develop nanostructured catalytic combustion materials to simultaneously increase fuel efficiency and decrease toxic emissions.
6. Develop asymmetric nanoporous catalysts for the production of chiral pharmaceuticals.
7. Integrate nanostructured materials synthesis with bench-scale and pilot-scale catalytic testing/

screening through close collaborations between academia and industry. Performance of experiments under realistic conditions along with economic analysis will be very useful towards identifying areas where nanostructured catalysts can really make an impact for industrial applications.

8.2. Long-term Goals

1. Develop novel methodologies and economical processes for nanocrystalline catalyst synthesis that will enable the tailoring of grain size, particle size and morphology, pore structure, dispersion of chemical components, crystal phase, and catalytically active sites.
2. Develop methodologies to encapsulate nanocrystalline catalysts in controlled matrices, and to graft clusters and fixate organometallic complexes in porous framework for effective isolation and stabilization of catalytically active sites.
3. Develop catalytic microreactors based on zeolitic cavities to simulate the function of enzyme catalysts.
4. Expand capability to synthesize mesoporous and microporous metal oxide catalysts with redox ability. Prepare highly dispersed transition metal-containing nanostructured mixed oxide catalysts with tailored oxidation states, coordination chemistry, and electronic structure.
5. Develop new characterization instrumentation with high resolution capabilities to examine the structure and chemistry of nanostructured catalysts. *In situ* surface characterization techniques will also be critical for establishing and isolating the reaction intermediates, and for achieving a better understanding of the catalytic mechanisms associated with nanostructured catalysts.
6. Develop sophisticated modeling that provides insights towards (i) templating-directed synthesis of novel molecular sieves, and (ii) nucleation and growth of clusters and nanocrystallites.
7. Investigate the relationships between the catalytic properties and the grain boundary and surface structure of nanocrystalline materials. Examine the effects of high defect concentration on the catalytic reactivity and mechanism of nanocrystalline materials.

8. Investigate the relationships between the catalytic properties and the composition, surface modification/functionalization, and pore size and structure of nanoporous materials.

Acknowledgments

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