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Reviews

Materials Needs for Catalysts To Improve our Environment

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Catalysts are part of a group of advanced materials which are designated among the USA's critical technologies. Among their broad applications in the chemical, automotive, and power industries, catalysts are vital components in many commercial processes for removing environmental pollutants. This review begins with current examples for the use of catalysts applied to improving our environment and then seeks to look at some specific opportunities which may merit more fundamental materials research in this topical area. These include opportunities in monolith technology; heat resistant, high surface area materials; nonprecious metal catalysts; nonvolatile, strong, solid acids; inorganic membranes; low-temperature O_2 transport materials; new catalysts for HCFC production, polyurethane foams, NO_x decomposition, and catalytic combustion; and a number of desirable, direct one-step chemical processes.

Introduction

Catalysis plays a vital part in all our lives and is of critical importance to our present-day standard of living and quality of life because of the many products and energy-related activities derived from its applications. "Catalysis" is a term that describes the process of accelerating a chemical reaction while the agent of change (the enabling material) is the "catalyst". The total value of fuels and chemicals derived through catalysis in the US in 1989 is estimated at \$891 billion, or ~17% of the US GNP.[1] As part of its contribution to society, catalysis serves a major, worldwide role in improving our atmosphere and reducing pollution. Commercial, everyday examples of environmental catalysis are the catalysts used for controlling automobile emissions, for removing volatile organic compounds (VOCs), and for reducing power plant emissions[2] (see Table 1). As one of our critical technologies, catalysts represent one aspect of materials research, and many new catalyst compositions will be needed to meet our advanced material needs. Through the next decade, catalysis will continue to provide attractive means to remove undesirable pollutants.

The EPA has declared its current priority (Table 2) is primary pollution control: don't make waste products at all or minimize the production of any waste.[3] By avoiding the production of waste materials, one needs to treat less. Recycling and separation are secondary alternatives. Waste treatment and disposal are among the least desirable alternatives. Catalysis or catalysts can be used to eliminate or minimize environmental pollutants. Catalytic technology can improve the yields of products in a chemical process, minimize the production of undesirable products, provide new process routes, and/or treat undesirable emissions.

Table 1. Some Examples of Environmental Catalysis in Action

- automotive emission control catalysts
  use of three-way catalyst mounted under the car
  controls emission on NOx, CO, and hydrocarbons
  precious metal catalyst supported on ceramic monolith
- selective catalytic reduction [SCR]
  treats NOx emission from power plants
  uses NH_3 injection to reduce NOx
  typically a vanadia on titania or zeolite catalyst
  supported on a honeycomb
- removal of VOCs (volatile organic compounds)
  used in dry cleaning establishments for odor removal
- ozone removal in high altitude aircraft
- wood and coal stove exhaust catalysts
- production of CFC substitutes
- decomposition of N_2O

Table 2. EPA Priorities

1. reduce waste at the source
   don't make waste
   minimize waste
   at source vs after production
2. recycling
3. waste separation
4. waste treatment/incineration
5. disposal at landfill, etc.

This review will describe the author's prospectives for opportunities for some new materials needed in the catalysis area to continue to improve our environment. Instead of focusing on the past, older approaches will be used to develop suggestions for new opportunities. Specific topics will include the area of monolith technology [preparation, engineering, and coating], new catalytic materials, and specific processes needing improved catalysts. Throughout this review, key suggestions for future research efforts will be highlighted in italics.

[●] Abstract published in *Advance ACS Abstracts,* May 1, 1994.

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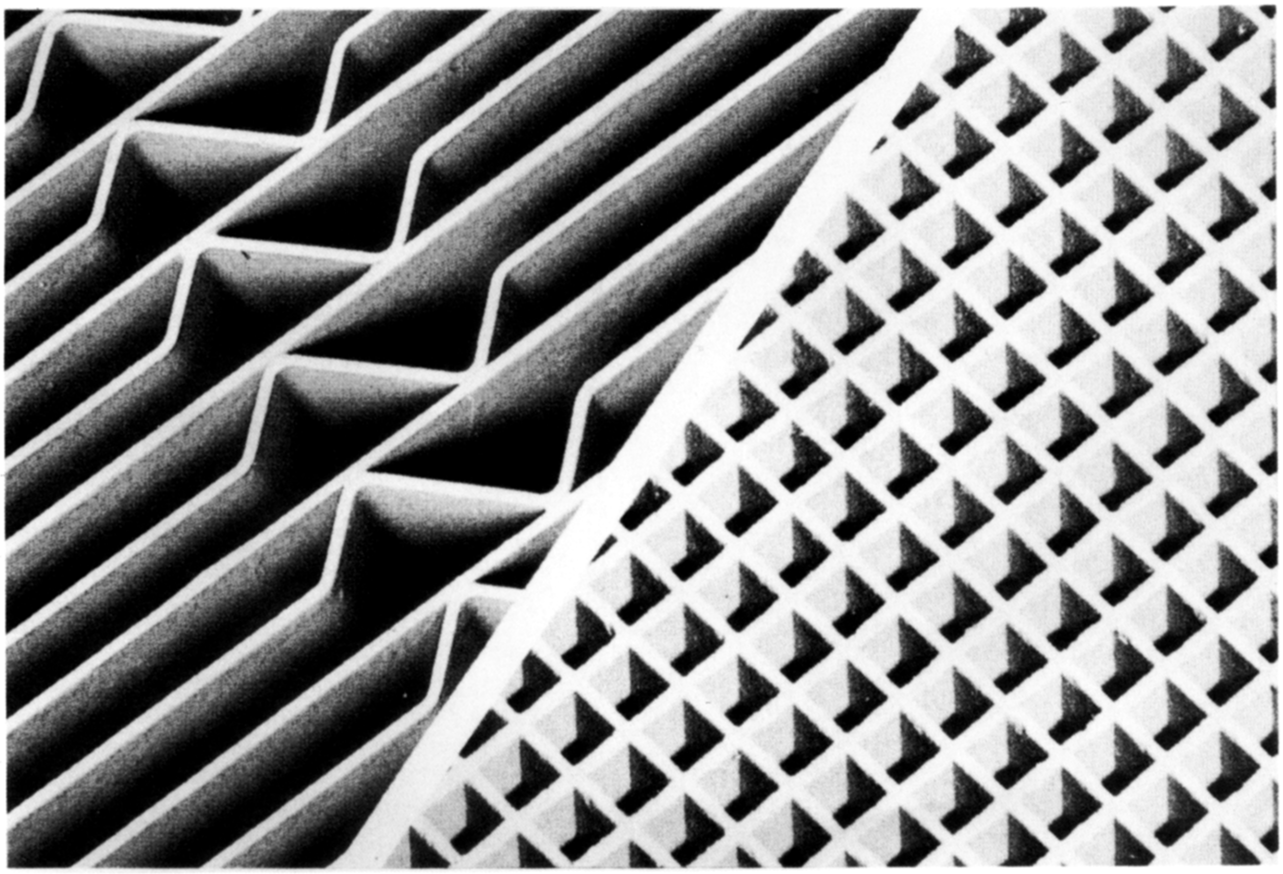

Figure 1. Typical ceramic honeycomb (right) and herringbone (left) monolith structures (from Siemens AG brochure).

Table 3. Processes Which Use Monoliths

- auto exhaust catalyst
- diesel exhaust catalyst
- VOC treatment systems
- ozone decomposition/jet aircraft
- selective catalytic reduction of NO_x
- creosote decomposition in wood-burning stoves

Monolith Supports for Emissions Control Catalysts

A majority of current emission catalysts rely upon a high surface area ceramic support that requires heat resistance, thermal stability, a coefficient of thermal expansion that matches the catalyst, mechanical strength, and chemical stability. Generally flue gas streams are at very high velocities [velocity of exhaust/volume catalyst $> 10^5\ h^{-1}$] which also demands a catalyst support with low-pressure drop. Currently most monolithic, ceramic honeycomb structures are made of cordierite [$2MgO \cdot 2Al_2O_3 \cdot 5\ SiO_2$].[4] Open-channel monolith structures composed of either a ceramic material in a honeycomb array or metal-based substrates in a herringbone array (Figure 1) are among the most widely used supports for distributing a catalyst within a catalytic device (see Table 3). Since emission exhausts often are quite dilute and large pressure drops in a stream need to be avoided, these high-temperature-resistant, open-channel structures are often the support of choice. There is very limited information regarding the preparation of catalysts on ceramic monoliths from a scientific point of view. Most of this commercial technology is described in patents or regarded as closely held trade secrets within several industrial corporations. There have, on occasion, been some published articles that try to define the art of preparing and coating these monolith structures, but any science to this art is still **not** fully described in the open literature.

Worldwide there are a number of commercial vendors of both ceramic (Cormetech, W. R. Grace & Company, Engelhard Corp., Norton Chemical Process Products Corporation, Steuler Gmbh, Siemens AG, and Mitsubishi Heavy Industries) and metal monoliths [Johnson Matthey, Siemens AG, and Camet (a division of W. R. Grace & Company)]. A recent review[5] on engineering monoliths for auto and power plant emissions summarizes the leading work of Corning in this area. One can often purchase a monolith structure from these companies but the composition available is quite limited; cordierite from Corning or Cormetech, $VO_x/TiO_2/SiO_2$ from W. R. Grace, and cordierite or α-alumina from Norton. Companies will either sell the uncoated monolith or, in some cases, a coated monolith. Zeolite-based monoliths are available from Engelhard[6] and Steuler.[7] The procedures for extruding and coating the monolith structures are spread throughout the patent literature and depend on the type of support and the active material to be coated. Given the continuing growth of monolith structures as preferred supports and their critical function in emission control systems, new compositions of monolith supports or technology for providing uniform coatings are continually being pursued and developed.

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Early automotive emission controls catalyst comprised either the ceramic monolith structures or spherical beads to support a precious metal catalyst. Currently almost all automobile emission control catalysts use monolith configurations. As laws become more demanding, more effective catalysts need to be discovered which further stretch the limitations of the current monolith structures. Some of these limitations will be described below with regard to the current state of the art and where opportunities may exist.

It is important to get the cell density (number of channels per square inch) as high as possible without in fact generating so much back pressure that the device becomes unacceptable. Current ceramic monolith structures are made by grinding a fine powder material with appropriate binders and dispersants and generating a thick dough-like material that is then pressed through a heated die to generate a perfectly regular channel like structure (see Figure 1). Depending on the composition of the material being extruded there are current limitations with regard to the cell densities that one can achieve. For some of the newer formulations such as $VO_x/TiO_2/SiO_2$[8] or zeolites,[6] it certainly would be desirable *to be able to generate a more densely channeled (e.g., 200 cells/in*^{2}*) material than is currently available.* The limitations depend on a number of factors, many of which are not fully understood. Corning has recently announced a new, thinner alumina wall designs and mullite alumina–titanate compositions that can handle higher exhaust temperatures.[5]

In some cases coating the raw monolith with a suspension of high surface area materials such as alumina is often desirable in order to hold and distribute the catalyst particles. This may be done by washcoating a fine particle alumina slip onto the channel structure with or without the catalyst present. The method for coating honeycombed structures is quite an art. If the catalyst is absent, then sometimes just dipping this washcoated monolith structure into a solution of the catalyst material is enough to get sufficient adherence of catalyst to the walls of the monolith. The article is then fired in order to set the catalyst in place and produce a product whereby the catalyst is not blown or eroded off the channels at the high space velocities often encountered in emission controls systems. Alternatively, one may pour the ceramic slip onto the monolith structure. In either technique, wicking occurs so that one gets an uneven distribution of slip over the channel structure. A recent thesis by Kolb[9] describes the coating of monolith structures with regard to the analysis of the flow patterns, bubble formation, and processing. To achieve an optimal coating, a high-pressure stream of air (often applied with an "air knife") is passed over the wetly coated channel structure in order to spread the slip more uniformly across the channellike structure.[10,11] Obvious limitations occur when one is coating longer monolith structures (about 4 in.) versus 1-in. structures. A recent article summarizes critical issues in producing honeycombs with regard to pressure drops and the design of the substrate.[12] *Certainly monolith coating would be easier if we could define enough science in the technique to control the process.*

Procedures for wash-coating monolith structures are described in a number of articles.[13–17] The viscosity of the slip medium is critical to the coating of the channellike structure. The thickness of the coating is dependent upon the porosity and dimensions of the monolith. *A better understanding of the coating process in terms of fundamentals needed to scale-up the process may lead to improved coating capabilities.*[18]

The procedure for coating a Pd/Pt solution onto an alumina wash-coated monolith is described in a number of articles.[19,20] A recent paper by Philippopoulos[21] describes the impregnation of ceramic monolith structures with alumina dispersions while varying the particle size distribution, acid concentration and viscosity. By carefully controlling the pH to 3.5–3.8, slurries with high solid contents and minimum viscosities can be prepared. Impregnation of monoliths with materials having different particle size distribution affects the pore structure of the aluminum coating.[22] Also, the reactivity of monolithic catalysts can be dramatically affected by the particle size distribution of the alumina slurry.[23] All this information still is not together in any one place. One needs to assess issues of the pH of the slip, particle size, composition, viscosity, and chemistry from one system to another and to understand the complex interaction of all these variables. This will depend on the composition of the washcoat (alumina versus titania versus zeolite). One even encounters support effects and some of these are documented in an article dealing with rhodium-washcoat interactions in the preparation of automotive exhaust catalysts.[24] *A more careful study and scientific understanding of washcoating a monolith is necessary in order better optimize or more quickly achieve the end product.*

There has been an intense amount of recent interest in using zeolite-based catalysts for NO_x emission control, and an effort has been made to coat these zeolites onto monolith supports. Even for those familiar with this area, it is not easy to transition from the older technology with precious metals on alumina supports to provide coatings of zeolite on the same types of monoliths. New techniques and variables crucial to obtaining uniform and adherent coatings are emerging. Some of this work is described in

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(11) Shimrock, T.; Taylor, D.; Collins, Jr., J. M. U.S. Patent 4,550,034, 1985.

(12) Montierth, M. R.; Day, J. P. *Ceramics Today—Tomorrow's Ceramics*; Vincenzini, P., Ed.; Elsevier Publishers BV: Amsterdam, 1991; p 2497.

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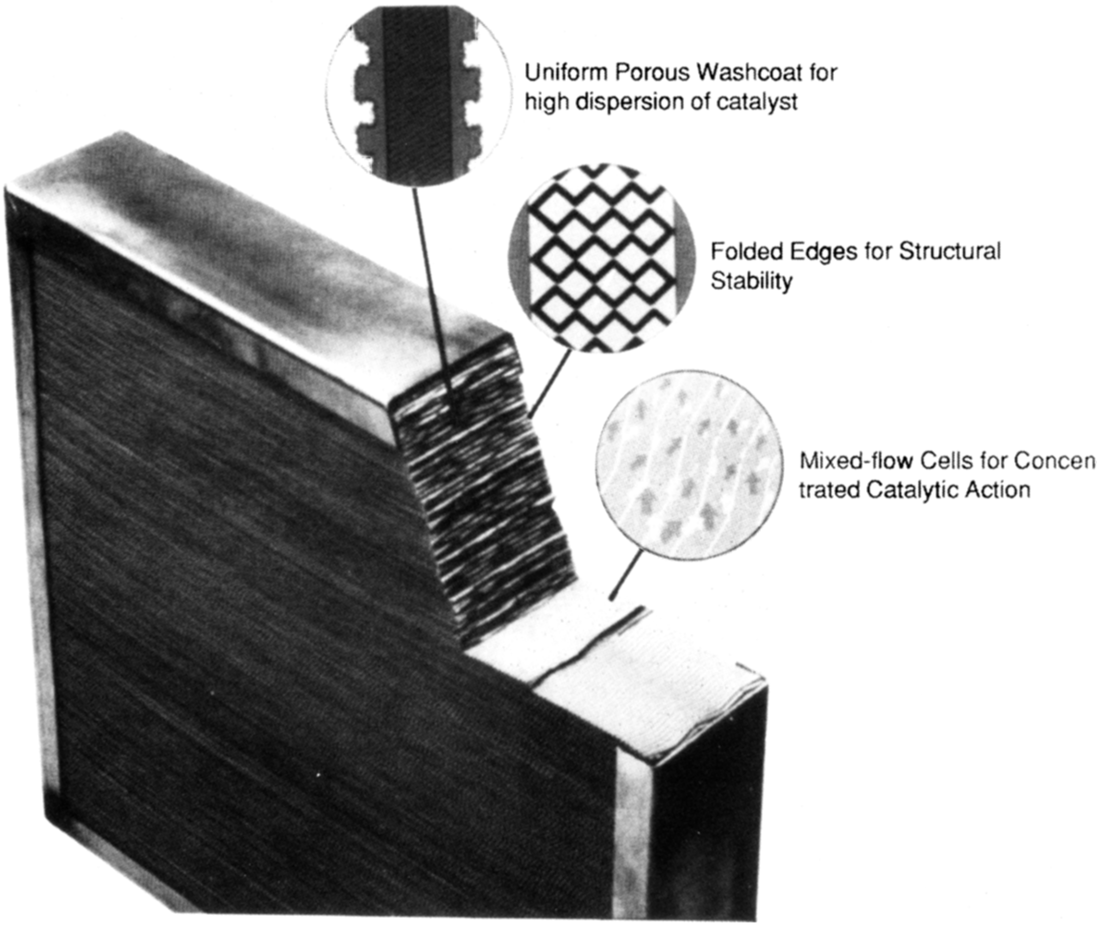

Figure 2. Metal monolith structure (from W. R. Grace & Co. brochure).

recent patents to Corning Glass and Tosoh Corp.[23],[25,26] Many of these zeolites of interest often contain a transition-metal cation which may need to be postexchanged onto the coated zeolite (because of the harsh conditions required for coating the zeolite onto the monolith). What is often not discussed is a great deal of the chemistry involved in the process of coating a monolith structure. What results is not simply a physical interaction between the catalyst and the structure but also a chemical interaction. If one is to use a post impregnation or exchange procedure, then one has to be confident that the cations are going into the zeolite and not just onto the monolith support. *A better understanding of how to coat different zeolite formulations onto ceramic or metal monoliths is desirable.*

Metal, herringbone structures (Figure 2) are also often used for supporting a ceramic-based washcoat. A comparison of the features of metal versus ceramic substrates is given by Day and Thompson.[27] Properties of metal monolith catalysts with regard to controlling exhaust emissions are described in an article by Pereira and Plumlee.[28] Unlike ceramic materials, the metal structures are pressed and shaped, stacked together, and finally surrounded within a "can".[29-31] Because a metal substrate is being used, different technology is required to adhere a washcoat to the metal substrate. This often depends on pretreating or activating the metal substrate in order to improve the adherence between washcoat and metal substrate. Switching to a zeolite catalyst for the washcoat requires different technology, and some of this is described in a recent article by Li et al.[32] *More research on washcoating a variety of catalyst compositions onto useful non-cordierite substrates that operate at high temperatures would be beneficial.*

Cordierite structures are often preferred because of their low coefficient of thermal expansion and the good match to an alumina washcoat. This minimizes the possibilities of delamination and thus maximizes adhesion between the washcoat and the monolith structure. For this reason other monolith compositions have not received as much attention. Unfortunately washcoating sometimes does not provide enough of a catalytically active surface in order to sufficiently treat the exhaust stream. Gas can diffuse readily through the washcoat into the meso and macroporous support structure where there is little benefit of the support itself with regard to removing the pollutant. As a result there has been new activity with regard to extruding the catalyst into a monolith form.[33] For

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example, one can prepare extruded titania monoliths (Corning[34]) or $VO_x/TiO_2/SiO_2$ (W. R. Grace[35]). There are now carbon monolith supports available from Corning (referred to as Celcore).[36] (Unfortunately for exhaust streams which contain oxygen at high temperatures, carbon based monolith structures certainly will be inappropriate.) However it is clear that newer compositions of monolith structures will become available as demand warrants. Nonetheless, the technology resides within a handful of suppliers and the knowledge for the *fabrication of novel catalyst compositions into monolith structures is simply not widely available.*

With the above background on the state of the art and its limitations, one sees that there exist a number of opportunities with regard to enhancing our understanding of monolith-based catalysts for cleaning up exhaust streams. There is reliance upon a handful of suppliers for obtaining a monolith structure, and many of these structures are only available in large sizes. Experimental laboratory reactors require smaller structures without the tolerances often required by the commercial structures. This limits the development of these materials. Further a good deal of art with regard to fabricating these monoliths into dense channel structures exists among a handful of companies. The washcoating procedure varies depending on the composition of the monolith and the washcoat composition as well. There is a completely different process for coating metal monolith vs ceramic-based monoliths which results in a number of engineering considerations. *In addition, there is probably an opportunity to use computer-aided design to improve the type, selection, configuration, light-off, and composition* of monolith catalysts.[37,38] Looking at this entire area, it seems that there is room for *a greater scientific understanding of how all these components (engineering, preparation, coating, and composition of the monolith) interact in producing attractive catalyst structures in various monolith forms.* All these features simply have not been carefully defined in the open literature, and the application of these materials will be limited as a result.

Alternatives to Ceramic Honeycombs. Creative approaches may be needed to discover and develop new monolith configurations for supporting future environmental catalysts. Channel monolith structures provide high surface area with minimal pressure drop. Beyond the regular honeycomb or herringbone arrays, alternative configurations may be possible. Recently ceramic foam materials have become available. One application for these was described in a recent US Patent by Campbell.[39] Here a foamed ceramic is used to support cobalt and noble-metal compounds for the oxidation of ammonia to nitric acid. In the patent they refer to problems associated with the current Pt-based metal gauze catalysts (Pt volatilization, dimensional stability, and fragility). Their invention describes a foamed ceramic structure (High-Tech Ceramics, Alfred, N.Y.) coated with an even layer of cobalt and noble metal salts resulting in a catalyst with higher heat capacity per unit surface area. In a comparative pilot plant trial, 16 8-in. diameter Pt gauzes were compared with a 10.5% Pt on ceramic foam (8-in. diameter, 0.08 in. thick) using less than one-fifth the amount of Pt in the gauze. The foam catalyst gave about the same level of conversion with a slightly higher level of HNO_3 produced upon adsorption. No detectable loss in activity or Pt assay was apparent after 60 days of operation. *Perhaps other compositions, designs, or configurations are possible.*

New Catalytic Materials

Heat-Resistant, High Surface Area Materials. A number of catalytic processes, combustion in particular, operate at very high temperatures, 800–1200 °C. While gas-phase reactions dominate, the catalyst still plays a very important role.[40] Such processes require catalysts with high heat resistance and often the desire still exists to maximize surface area in order to raise productivity or efficiency. One must continually fight to suppress sintering which visibility occurs for most oxides at such high temperatures. The surface area is dependent on melting point, phase transformation, water vapor pressure, O_2 partial pressure, and impurities. For example, dramatic losses of surface area are exhibited by alumina (γ to α at $\sim$1100 °C) or titania (anatase to rutile at $\sim$700 °C). For alumina the addition of oxides such as BaO, La_2O, SiO_2, K_2O, Li_2O, or MgO serves to retain some surface area by preventing atomic diffusion which leads to phase transformation.[41] Additives of alkali, alkaline earth, and rare earth oxides to alumina result in the formation of hexaluminate phases which also provide resistance to sintering to $\sim$1200 °C. Such stability can be a function also of time at temperature. *New additives or preparative techniques which provide even higher or longer term phase stability* not only to Al_2O_3 but also to other traditional oxide supports such as TiO_2, MgO, or SiO_2 would be desirable.[42]

Nonprecious Metal Auto Exhaust Catalysts. For decades the cost and volatility (of some) of the precious metals used in catalysts have driven interests in developing base-metal[43] oxide catalysts to displace Pt, Rh, and/or Pd. A recent announcement by the Japanese[44] and Allied Signal[45] suggests that acceptable all-Pd-based automotive exhaust catalysts are now possible. While Pd is much cheaper than Pt/Rh, *a nonprecious metal catalyst would be certainly more attractive.* This approach was actively pursued from 1950 to 1970. Base meals are often quite susceptible to sulfur poisoning. Perhaps with the discovery of the Cu[46] or Co[47] zeolite formulations (base metal catalysts), new, more active base metal catalysts will be discovered.

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Nonvolatile, Strong Acid Catalysts. There is a pressing need to replace corrosive, liquid acids such as HF or H_2SO_4 with solid acids. Large quantities of HF or H_2SO_4 are used for aromatic or paraffin alkylation or the nitration of aromatics. In 1991 the U.S. refinery industry consumed 4.6 million pounds of H_2SO_4 and 9 million pounds of HF with a combined market value of $257,000,000 in one year.[48] Smaller quantities are used in many process operations for the synthesis of fine and specialty chemicals. Solid acids such as zeolites have not been useful for alkylation catalysis because of their loss of life. There are recent attempts to use fluorinated solids such as HF or BF_3 supported on Al_2O_3. However, such modified catalysts will eventually suffer leakage of the acid agent and require regeneration. In addition, any solid acid needs to be able to withstand the rigors of regeneration. To date no single solid, strong acid has been discovered which meets all these requirements. There is an enormous need with a huge market for a *nonleachable, regeneration-stable, inexpensive strong solid acid catalyst to replace HF or H_2SO_4.*

Inorganic Membranes. Today there is a drive to produce cleaner chemical products. Traditional approaches of distillation or precipitation are often not satisfactory and the use of size selective, chemically resistant inorganic membranes have emerged as one exciting alternative. These have been used for the isotopic separation of UF_6 during the 1950's and more recently as filters for several industries (wine, etc.).[49] They offer advantages over organic membranes by being more durable, longer lived, and chemically resistant. Microporous alumina membranes down to 40 Å represent the current level of commercial inorganic membranes which are available in a large number of sizes and shapes. Research by a number of groups[50,51] suggests the possibility of preparing sub-10-Å membranes. These are still laboratory curiosities which often exist as small (~1 in.) disks. Materials technology needs to be developed *to produce asymmetric (<0.1-μm-thick working layer) size selective membranes in a variety of shapes and sizes that can be fitted to existing commercial vessels.* There are issues of the seals between the ceramic membrane and the steel containers that may need to withstand high temperatures. *Flawless membranes (crack free) must be prepared which are size selective at the molecular level and stable to repeated cycles of heating and cooling.*[52]

Zeolites [crystalline aluminosilicates] are one type of molecular sieve. These crystalline structures possess an ordered, cage-like array with pore entrances of molecular dimensions [~3–8 Å]. The field of zeolites and molecular sieves is under intense investigation with over 30 articles in the past 5 years for the preparation of these materials in the form of membranes. Zeolites were embedded into polymers,[53] grown onto mesoporous supports,[54,55] and covered with glazes[56] in efforts to prepare dense, permselective membranes. One patent by Haag and Tsikoyiannis[57] describes the direct synthesis of small platelike arrays of ZSM-5 crystals grown from a gel and deposited onto Teflon. The field of molecular sieve membranes continues to grow, but a key technical hurdle continues to be the development of very thin molecular sieve membranes. *Very thin structures (<0.1 μm) are needed to enhance the permeability of any such membrane material.* Beyond this critical hurdle still lies the issues already cited above (dense, crack free, large sheetlike structures of 1 m² or continuous coatings of tube structures several feet long, sealed to a device, and ultimately at a competitive cost relative to other separation materials).

Another membrane area in need of materials development is O_2 or H_2 permselective metal membranes. Thin metal membranes selective to either O_2 or H_2 permeability would be valuable for selective oxidation or hydrogenation/hydrogen separation needs within refineries. For years Pd and Pd alloy membranes[58] have been studied for permselective H_2 separation to drive chemical reactions.[59] One recent approach is the use of Pd alloy compositions[52,60] to prolong membrane life without seriously impacting permeability. Alternatively, niobium, tantalum, or zirconium membranes[61] may offer promise, but all these materials suffer from limited life and durability. Thin Pd coatings on a ceramic membrane are another approach, but *preparing durable, coated alloy compositions is still a challenge.* Limitations of Pd membranes were recently summarized[52] and include fabrication into thin shapes, suitable high temperature seals to membranes, commercial availability, new alloy compositions, impact of impurities (such as sulfur and CO) upon permeability of H_2, unpredictable fracture, regeneration, suitable life, and cost. Alternatively, silver metal membranes[62] offer a possibility of permselective O_2 transport for catalyzing selective oxidation reactions without the fear of using combustible feed compositions. These silver membranes are still at an early experimental level. *More research is necessary to develop O_2 permselective membranes from metals.*

Any new inorganic membrane technology must be scalable to large tube structures which can be produced commercially without enormous cost. Answers may be found in alternative compositions, new coating technologies, and imaginative "canning" procedures. Once such materials are engineered to meet these tough performance demands, applications will emerge in catalytic processes[59] and energy intensive separations.[63]

Low-Temperature O_2 Transport Materials. A lot of work has appeared for many years on inorganic oxide structures capable of transporting O_2. Such materials are potentially useful as catalysts for sensors (for example, see refs 64–66), for carrying out selective oxidation

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Table 4. Catalysts Opportunities

- replacement of precious metal catalysts with base metals
- highly selective catalysts
- alternative products (and catalysts to prepare them) to CFCs and HCFCs
- greater attrition resistant catalysts (via design or composition)
- replacement catalysts for those comprised of heavy metals or promoters such as Hg, Sn, or Pb. (e.g., Hg-free chloralkali process)
- truly nonleachable solid acids
- a catalyst that removes both SO_x and NO_x in one step
- an improved diesel exhaust catalyst
- a catalyst for lean engine exhausts
- an effective catalyst for NO decomposition into its elements

reactions or for transporting O_2 through a membrane. The latter can be envisioned for the production of O_2 from air through a dense membrane or for carrying out selective oxidations at a membrane surface. Perovskites are one large family of materials that offer the potential for such O_2 transport or activation.[64] Acceptable O_2 transport materials have yet to be discovered. Beyond fabrication and economic concerns which any such material faces, there is still a huge technical hurdle. These materials often do not transport O_2 rapidly enough until temperatures exceed 700 °C. Such high temperatures are inappropriate for most processes and too demanding on equipment, seals, etc. *New stable materials are needed to rapidly transport O_2 at <500 °C, reversibly.*

Processes Needing Improved Catalysts. The concern about our environment is forcing Industry and Society to seek high yield, zero waste processes. Several past examples are given in a recent review.[2] Concern has recently been demonstrated at a worldwide level with the replacement of current chlorofluorocarbons (CFC) products by hydrochlorofluorocarbons (HCFC).[65] Some opportunities are summarized in Table 4 and will be discussed below.

High Yield–Low Waste Processes. Beyond efforts to seek direct routes to important chemicals, there is a widespread need to develop more highly selective processes. Selectivity will naturally improve yield and minimize waste. One example of such an improvement was recently described by Manzer.[69] The synthesis of HCFC-141b is a key alternative to ozone depleting CFCs used as solvent blends, azeotropes, and blowing foams. DuPont has discovered a specially prepared AlF_3[70] produces HCFC-141b in ~100% yield! Previously reaction 1 produced not only 141b but higher fluorinated products

$$CH_2{=}CCl_2 + HF \rightarrow \underset{141b}{CH_3CFCl_2} + \underset{142b}{CH_3CF_2Cl} + \underset{143a}{CH_3CF_3} \qquad (1)$$

(142b and 143a). Using a two-stage reactor, they obtain 99.5% of 141b with <500 ppm $CH{=}CCl_2$ remaining in the product. This allows DuPont to avoid additional refining and recycle.

Similar unlimited opportunities for process improvement via selectivity enhancement with new catalyst compositions exist throughout the chemical process industry. For example, *more selective catalysts are needed to improve para selectivity in aromatic nitration.*[71] *A better understanding of material properties of key supports* (alumina, titania, silica, MgO, ZrO_2, etc.) and key active phases (transition-metal oxides, alkali ions, mixed oxides, etc.) *will lead to selectivity improvements.* In addition, *new supports or active phases need to be identified as replacements for precious metal based catalysts, heavy metal catalysts, or catalyst containing undesirable, leachable promoters, such as chloride. Additional studies in nitrides*[72] *or sulfides*[73] *may offer attractive catalyst substitutes.*

New Fluorination Catalysts. Current catalysts to HCFCs were developed over a very short time. Hence, *there is probably room for improvement for more active fluorination catalysts.* In addition, even HCFCs do not represent a permanent solution. They are more difficult to synthesize than CFCs, hence more costly, and there is no single replacement that perfectly matches any current CFC. They still contribute to depletion of the ozone layer,[74] and some are more toxic than originally anticipated.[75] HCFC 134a is one desirable replacement for CFC-12 [CF_2Cl_2], a refrigerant. A current one step process via

$$\underset{TCE}{CHCl{=}CCl_2} + HF \rightarrow \underset{133a}{CF_3CH_2Cl} + \underset{134a}{CF_3CH_2F} \qquad (2)$$

TCE (eq 2) always produces 133a coproduct. *A single step route to 134a, a major HCFC alternative would be highly desirable.* In addition, Manzer points out that "many opportunities exist for innovation, improved catalysts, and fundamental understanding.[68]

Alternatives to High Nickel Catalysts. Nickel is a very popular selective hydrogenation catalyst used throughout the chemical industry. To achieve high productivity, large amounts of nickel are usually deposited on catalyst supports. Invariably this leads to a number of issues. Catalyst attrition, reuse, and stability result in nickel salts being carried with the products. Because nickel is regarded as toxic in large levels, soluble nickel needs to be recovered from products as an extra process step. In addition the spent catalyst must be returned to the supplier for recovery, recyle, or disposal. Alternative metals such as ruthenium, cobalt, or palladium are often considered as substitutes for the nickel center.[76] Alternatively *more active nickel catalysts with much lower levels of nickel or more firmly adhered nickel would be another solution.* The added environmental costs for handling nickel can change the economic attractiveness of a process. In addition, a few commercial processes still use mercury, lead, or tin salts as catalysts or promoters. *Replacement of those heavy metals with alternative compositions with comparable activity and performance would be highly desirable.*

Catalysts for Polyurethane Foams. The entire polyurethane foam business is on the verge of a major processing change as foam makers switch to water or CO_2 foam-based processes to replace CFC sources of foam

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Table 5. Direct Processes Needing a Catalyst

- $CH_4 + {}^1/_2O_2$ to methanol
- NO to $N_2 + O_2$
- benzene + O_2 to phenol
- propylene + O_2 to propylene oxide
- $NH_3 + O_2$ to hydroxylamine

-but need
  high yield
  good selectivity
  excellent catalyst life performance
  low capital

formation. This requires significant changes in the process, the additives, and the catalysts used to generate foam formation. *There are opportunities for new additives or catalysts compatible with a CO_2 or water-based process to meet the foam industry's current standards.*

Decomposition of NO_x. NO_x is a significant environmental problem, and a great deal of effort is underway to reduce NO_x emissions. Currently, the bulk of the published research is aimed at using hydrocarbons such as methane[77] or propane[78,79] as reductants. The use of a hydrocarbon in an oxidizing atmosphere often reduces process selectivity and generates additional CO_2 by product. The decomposition of NO into its elements (eq 3) represents a much more attractive approach to remove NO.

$$2NO \rightarrow N_2 + O_2 \tag{3}$$

Reaction 3 is thermodynamically allowed over a broad range of temperatures and does not require a reducing agent or produce an undesirable coproduct. A new family of catalysts was discovered by Iwamoto in the late 1980s for this reaction. Currently these CuZSM-5 catalysts are not active enough for commercial use. A further advance in catalyst performance and activity is necessary. Any new catalyst must be resilient and tolerant to true exhaust streams which contain either sulfur oxides, dust, and/or water vapor. The person(s) who achieves this will have a great impact on society, the chemical process industry, power plants, and mobile engines. *The applications and implementations for an effective catalyst for reaction 3 are enormous*!

Lower Temperature Combustion Catalysts. Catalytic combustion is one technology for generating power now and in the future. Methane (as natural gas) is often the fuel of choice in the USA. While there are mature systems to thermally combust methane, catalytic approaches are receiving renewed interest with the drive to improve efficiency and reduce emissions.[80] A catalytically enhanced combustor[81] operates at much lower temperatures than an open flame burner and the lower temperatures also mean reduced emissions of NO_x. Pd-based catalysts are generally the most active catalysts.[82] Recently Catalytica, Inc. and Tanaka Kikinzoku Kogyo working with General Electric have announced[83] a new, catalytic combustion technology for very low emissions from gas turbines. Previously, catalytic combustion of premixed fuel/air mixtures with low NO_x (<1 ppm) emissions has not been developed due to poor catalyst systems which do not meet engine manufacturers' demands. Catalytica claims an approach wherein combustion (flameless) is initiated by the catalyst and is completed by homogeneous combustion in the postcatalyst region. Avoiding high temperatures on the catalyst allows the use of commercially available monolithic supports and prolongs catalyst life. Their recent patent[84] describes the use of Pt group metals deposited on washcoated metal monoliths. With the metal monolith the heat of combustion is rapidly conducted into the gas stream. In general, Pd seems to be the most active catalyst for methane oxidation. Why? Are there other combinations of mixed oxides that will be equally effective. *A nonprecious metal catalyst contained by/within an acceptable support structure might offer further improvements in methane combustion.*

Synthesis Gas Formation via Direct Methane Oxidation. Recently Schmidt and co-workers[85] described the direct, highly selective oxidation of methane to CO/H_2 using Pt or Rh monoliths. This process might be highly attractive vs the current energy-intensive approach of steam methane reforming now practiced commercially. In the latter process, methane is combusted over a Ni/Al_2O_3 catalyst at ~900 °C to produce CO_2 and water which reacts with CH_4 to produce CO and H_2 (reaction 4). This

$$3CH_4 + 2O_2 \rightarrow CO_2 + H_2O + 2CH_4 \rightarrow 6H_2 + 2CO + CO_2 \tag{4}$$

is a slow reaction which requires some complete combustion to CO_2 to produce the stream needed for methane reforming. Here, replacement of Pt or Rh alternatives will be desirable. *Development of more active, lower temperature, nonprecious metal catalysts would be desirable.*

Alternatives to Phosgene. Phosgene, $COCl_2$, is an important reactant in some processes used to produce isocyanates, carbonates, and other speciality products. Not only is phosgene difficult to handle because its toxicity but also it produces a chloride-containing byproduct that must be separated and disposed. A number of alternative carbonylation catalysts have led to non-phosgene routes to toluene–diisocyanate (used widely for polyurethane foam formation) or methylene di-*p*-phenylene isocyanate. Currently, these alternative process routes are still not commercially attractive enough to replace phosgene based approaches. *More active, direct carbonylation catalysts are needed.*

Direct Processes To Replace Multiple Processes. Besides the improvements to the existing processes described above, direct processes are needed to replace complex chemical processes requiring many steps or producing needless by products. Some of these are summarized in Table 5. In all these cases thermodynamics permit a direct synthesis but yields or selectivities with

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current, known materials are unacceptable. *New catalytic materials need to be discovered and developed for these important processes.*

Conclusion

Beyond the current improvements being made in catalysts for environmental processes (such as auto exhaust, NO_x emissions, and VOC emissions), there are opportunities for new, step-out materials. Such materials need high-temperature performance, low-temperature operation, or unique fabrication and design of catalyst configurations which offer opportunities to break away from the traditional approaches. This article has tried to describe some of these opportunities and to provide some encouragement for additional research activities in support of these opportunities. Progress in these areas will require the creativity of the scientists and engineers, the wisdom of funding agencies, and patience from us all.