

Catalysis Research of Relevance to Carbon Management: Progress, Challenges, and Opportunities

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I. Introduction

There is increased recognition by the world's scientific, industrial, and political communities that the concentrations of greenhouse gases in the earth's atmosphere, particularly CO₂, are increasing.¹ For example, recent studies of Antarctic ice cores to depths of over 3600 m, spanning over 420 000 years, indicate an 80 ppm increase in atmospheric CO₂ in the past 200 years (with most of this increase occurring in the past 50 years) compared to the previous 80 ppm increase that required 10 000 years.² The 160 nation Framework Convention for Climate Change (FCCC) in Kyoto focused world attention on possible links between CO₂ and future climate change and active discussion of these issues continues.³ In the United States, the PCAST report⁴ "Federal Energy Research and Development for the Challenges of the Twenty First Century" focused attention

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Table 1. Sources of World Carbon Emissions by Industrial Sector^a

	1990 (MMTC)	projected 2008–2012 (MMTC)
transportation	432	628
industrial	454	563
buildings	460	612
electrical	477	663
total	1823	2466

^a MMTC = millions of metric tons of carbon.

on the growing worldwide demand for energy and the need to move away from current fossil fuel utilization. According to the U.S. DOE Energy Information Administration,⁵ carbon emission from the transportation (air, ground, sea), industrial (heavy manufacturing, agriculture, construction, mining, chemicals, petroleum), buildings (internal heating, cooling, lighting), and electrical (power generation) sectors of the World economy amounted to ca. 1823 million metric tons (MMT) in 1990, with an estimated increase to 2466 MMT in 2008–2012 (Table 1).

A recent analysis of the Kyoto Protocol by the American Society of Mechanical Engineers (ASME)⁵ examined the impact of reducing annual U.S. CO₂

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Modeling A Carbon Technology System : The Results

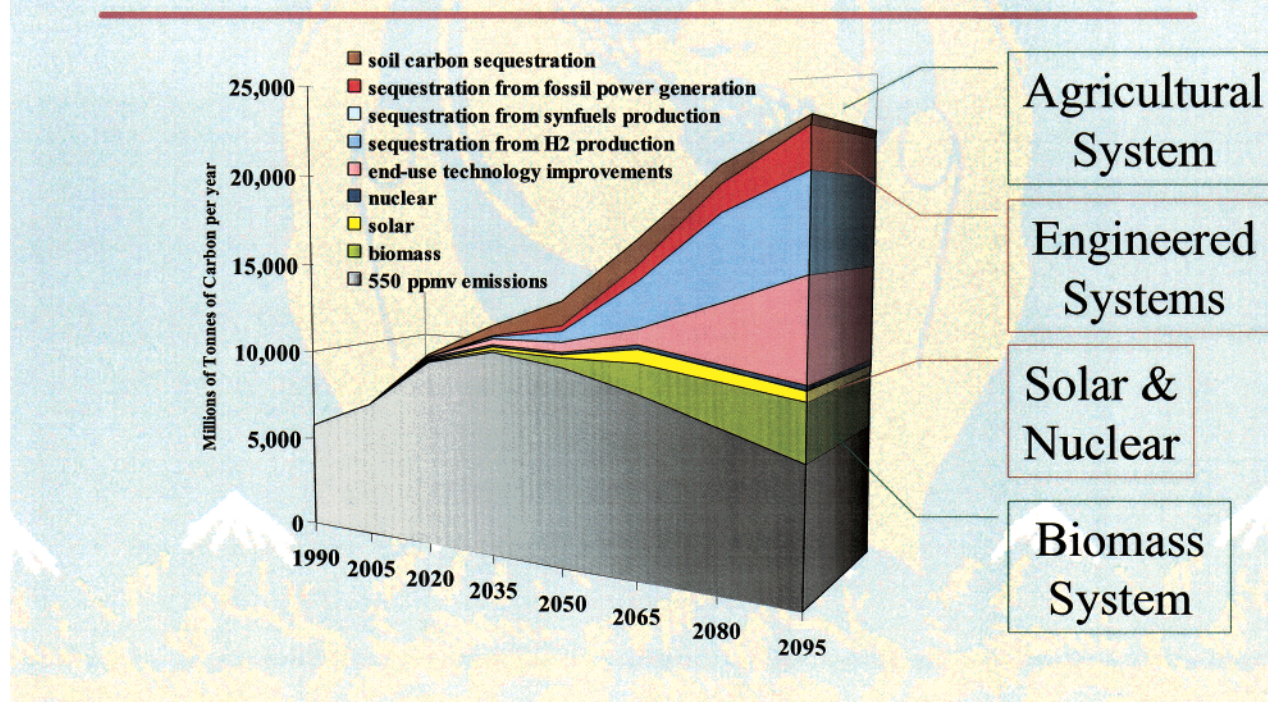


Figure 1. Timeline for projected world CO₂ emission and the potential impact of various carbon management technologies in a typical scenario.

emissions to 7% below 1990 levels on the above four sectors of the U.S. economy (transportation, industry, buildings, electric power). This 7% reduction represents a diminution of 551 MMT in annual CO₂ emission below 1998 levels, as compared to estimated CO₂ emissions from U.S. electric utilities alone of 663 MMT in 2008. The ASME report further estimates that improvements based on today's technologies can realistically reduce emissions by only 164 MMT (the most optimistic estimate) for the aforementioned four economic sectors in the 2008–2012 time frame. The ASME report also recognized that a vigorous R&D program is required to have any hope of achieving the additional 387 MMT of CO₂ emissions reductions needed to meet the Kyoto protocols in just the United States alone. The magnitude of the problem is even greater viewed on a worldwide scale. The Intergovernmental Panel on Climate Change⁶ predicts that emissions of CO₂ to the atmosphere will increase from 7400 MMT atmospheric carbon per year in 1997 to approximately 26 000 MMT/year in 2100.

Since 1997 there have been a number of published analyses dealing with carbon management issues. These include "Technology Opportunities to Reduce U.S. Greenhouse Gas Emissions",⁷ "Scenarios of U.S. Carbon Reduction: Potential Impacts of Energy-Efficient and Low Carbon Technologies by 2010 and Beyond",⁸ and "State of the Science and Technology of Carbon Sequestration"⁹ and address various aspects of the growing international interest in, and

concern regarding, carbon management with a focus on lowering the emissions of CO₂. An analysis of the reports mentioned above leads to the following conclusions if the unpredictable climatic outcome of increased atmospheric CO₂ concentrations is to be avoided: (1) the efficiency of our energy production and consumption processes must be significantly increased, (2) the carbon intensity of our economy must be significantly decreased, and (3) our ability to capture and sequester atmospheric CO₂ must be significantly improved.

Moreover, the above tasks must be accomplished while maintaining acceptable worldwide economic growth and quality of life, especially as less developed nations undergo energy-intensive industrialization. There is growing recognition that reducing concentrations of atmospheric CO₂ will be a long-term task. Figure 1 illustrates a reasonable scenario for the projected CO₂ concentration by the end of the next century and suggests areas over the long term where reductions of CO₂ emission/sequestration may be possible. U.S. Secretary of Energy William Richardson has stated "We (DOE) are starting with a bold vision of what might be possible by 2025—a safe, predictable, and affordable way to prevent CO₂ build up in the atmosphere and research could provide new options for the world to respond to climate-change concerns".¹⁰

In considering various approaches to addressing the global atmospheric CO₂ problem, it becomes

evident that enhanced capabilities in the area of chemical catalysis could play a significant role. This role could in principle range from more efficient production of low/non-carbon fuels (e.g., water-splitting, electrolysis), to more efficient fuel and electrolytic cells, more effective catalytic converters allowing leaner burning, more carbon-efficient vehicular engines, more efficient conversion of renewable resources (e.g., biomass) to fuels, and to more effective technologies for the sequestration, utilization, and/or permanent disposal of CO₂. Taking the United States as an example, catalysis currently plays a major role in ~90% of the current chemical manufacturing processes. These consume large quantities of energy and, in the United States, currently lead to emissions of over 10 MMT of CO₂/year (a significant but relatively small component of Table 1). Improved catalytic processes could lead to more atom-efficient and energy-efficient use of fossil fuels such as hydrocarbons, to higher yield conversions of other carbon-containing feedstocks to desired products, and to new industrial uses for CO₂. This becomes especially critical if CO₂ emissions taxes are imposed in the future. Indeed, many of these issues are also raised in the recent Council on Chemical Research "Vision 2020 Catalysis" report,¹¹ and research programs focused on identifying promising carbon management approaches are active in a number of industrialized countries.

The multifaceted and worldwide scientific and technological challenges posed by carbon management raise the need for a research-oriented and cross-disciplinary assessment of contributions that catalytic research has and could make in addressing these challenges. To this end, a four-day international workshop was organized under the auspices of the U.S. Department of Energy Council on Chemical Sciences and took place in Santa Fe, NM, from April 30 to May 4, 1999. The goal was to bring together internationally recognized experts from academic, industrial, and national laboratories working in fields related to catalytic research of current and potential impact on carbon management. The backgrounds of the participants were necessarily diverse, including organic, organometallic, theoretical, coordination, solid state, and bioinorganic chemistry, surface science and spectroscopy, homogeneous and heterogeneous catalysis, catalytic reactor design and process chemical engineering, materials science, and condensed matter physics. The participants came from Europe, Japan, and the United States.

The primary goals of the workshop were to review in depth the current state of knowledge, barriers to further scientific and technological progress, and promising scientific research in five important, interconnected areas relating to greenhouse gases and carbon management: (1) hydrogen generation and utilization; (2) light hydrocarbon activation and utilization; (3) carbon dioxide activation, utilization, and sequestration; (4) emerging physicochemical techniques and directions in catalysis research; (5) catalysis for more efficient transportation engines. The choice of topics was necessarily focused. However, these areas share many common themes and

represent cases where a greater knowledge base could arguably lead to improved (in terms of rate, selectivity, environmental acceptability, and economy of operation) catalytic processes, thus having a significant positive impact. The product of the workshop was to be a scholarly review designed to reach a large segment of the international chemical research community and to be suitable for publication in a respected, peer-reviewed scientific journal.

The workshop format consisted of lectures and panel discussions. The program began with presentations outlining the motivations for a global research effort concerning greenhouse gases and carbon management, as well as the important role that catalysis could potentially play in addressing these problems. This was followed by a presentation of the workshop goals, agenda, and writing assignments. Then, for each topical area, specialists reviewed research achievements in their field of expertise, illustrating with results from their own research and from that of others. Each speaker then presented his/her views of what the significant barriers to further progress are and an assessment of what the high pay-off basic research needs/opportunities are. These presentations were moderated by a discussion leader, and in most instances, vigorous exchanges of opinions ensued. For each area presentations were followed by a panel discussion in which important points were further explored and consensus regarding barriers, needs, and opportunities were refined. Each topical group then met and, led by a writing team, drafted input for the review. Input from the entire workshop group was then sought as the draft was polished. Further additions of figures, tables, and references then took place either during the workshop or electronically from home. In a number of cases, opinions of experts not able to be present at the workshop were also solicited. This review article presents the results of this effort.

II. Hydrogen Generation and Carbon Management

A. Introduction

Hydrogen is forecast to become a major source of energy in the future, thus offering a potentially nonpolluting, inexhaustible, efficient, and cost-attractive energy carrier. In the last 10 years, the defining issues with respect to H₂ economics have changed dramatically. Before the 1990s, H₂ was in plentiful supply with refineries being major H₂ producers. However, refineries now have become large net consumers of H₂ in an effort to reduce pollution and meet environmental regulations. The use of H₂ as an energy carrier or fuel offers significant reduction in the emissions of nitrogen oxides (NO_x), hydrocarbons (HC's), CO, and CO₂, that is, assuming H₂ can be produced by environmentally benign means (i.e., nonfossil fuels or reformed from fossil fuels with CO₂ sequestration) and that air is not used as the source of O₂. Molecular hydrogen is a clean burning fuel. It can be stored as a solid (in the form of hydrides), liquid, or gas; it can be distributed via pipelines and tanker trucks, and potentially it could be a long-term replacement for natural gas.¹² For this

to occur, vast quantities of inexpensive H_2 are required. However, significant quantities of hydrogen are typically highly localized at present, e.g., in refineries, although efforts are underway to improve the large-scale distribution of H_2 .

Currently, steam reforming of hydrocarbons (SR), in particular steam methane reforming (SMR; $CH_4 + H_2O \rightarrow CO + 3H_2$), is the largest and generally the most economical way to produce H_2 . SMR consists of many different catalytic operations, including desulfurization, pre-reforming, reforming, high- and low-temperature water-gas shift, methanation, and NO_x removal. As long as natural gas- and petroleum-based hydrocarbons remain relatively inexpensive, SMR will continue to be the preferred method for hydrogen synthesis. Steam reforming is a mature technology. However, this area remains a fertile ground for technological improvements. One recent, popular approach in the literature on H_2 production involves CO_2 reforming of methane ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$). Nevertheless, widespread implementation of this approach faces significant hurdles¹³ and is really a means to produce more CO rather than H_2 . Future methods for producing H_2 could emerge based on the selective oxidation of natural gas exclusively to CO and H_2 . Research continues on photolysis, electrolysis, and thermal processes for H_2 production (vide infra). Alternative noncatalytic approaches include partial oxidation of heavy oil or coal¹⁴ coupled with CO_2 sequestration. With the availability of inexpensive electricity, electrolysis of water offers an alternative, commercial approach to hydrogen production. While there are secondary issues of storage, separation, and systems integration, catalysis will play an important role in photolytic and electrolytic H_2 generation technologies.

Excellent, in-depth background references for topics within this review include Twigg's book¹⁵ on major processes using or producing H_2 , an encyclopedic review,¹⁶ and Gunardson's recent book¹⁷ on the production of industrial gases.

B. CO_2 Management

Beyond 2010, the availability of hydrocarbons and/or environmental issues may eventually force adoption of alternative H_2 technologies since steam reforming is an endothermic process, where CO_2 is a coproduct and H_2 purification is usually necessary. H_2 production is linked to CO_2 as a coproduct when fossil fuels are reformed. The wider use of H_2 as a fuel could reduce worldwide CO_2 emissions if we begin to shift to even greater use of CH_4 as a SR feedstock. Use of nonfossil fuel sources for H_2 production would avoid the problem of CO_2 coproduction. Highly efficient end use devices (i.e., optimized conventional technologies—internal combustion engines, turbines, etc.) and fuel cells offer a sensible means for using H_2 as a fuel for both stationary and mobile power needs. Over the next 10 years, installation of a hydrogen infrastructure, using mainly nonrenewable hydrogen coupled with sequestration of CO_2 or some other intelligent carbon management scheme, is one near-term approach. Longer term H_2 production based on renewable fuels or nonfossil fuels

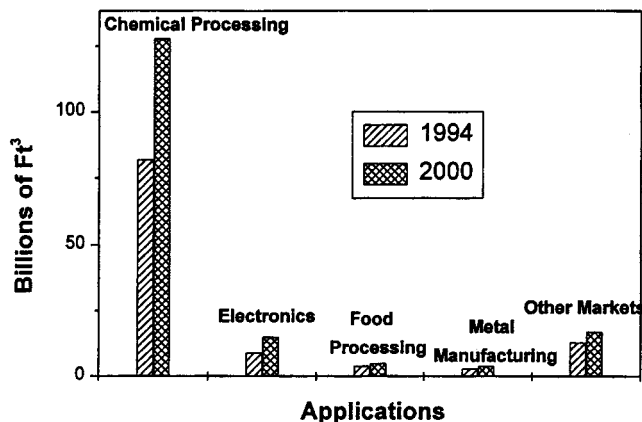


Figure 2. Nonrefinery U.S. Demand for H_2 .

should be a target. To implement the technologies that are suitable for the future, we need to focus on developing reforming technologies on much smaller scales suitable for industrial site applications, refueling stations, small businesses, and individual dwellings. For example, a small reformer could be used to process part of the hydrocarbon fuel to produce H_2 and CO_2 where the H_2 is then blended back into the fuel stream producing hydrogen-enriched fuel for use in stationary turbines for NO_x reduction. This does nothing for CO_2 management today, but it does put into place some of the end-use technologies for tomorrow. In the future we can replace these small reformers with H_2 generated in a CO_2 neutral fashion. We can also accelerate increasing the H/C ratio used in these systems.

C. H_2 Supply

Courty and Chauvel¹⁸ described the dramatic shift in the supply and demand for H_2 which has evolved in the last 20 years. In the 1980s, demand for H_2 was low and less than the production of H_2 , then a byproduct within most refineries. In fact, refineries often managed to supply their own H_2 needs by careful balance of reaction chemistries. With the advent of more stringent emission controls for automobiles (demanding less benzene and sulfur compounds in the gasoline) and more stringent nitrogen oxide emissions requirements, refineries have responded by using the proven technologies of hydrodesulfurization and hydrodenitrogenation. In the past, production of large volumes of benzene as a refinery product often resulted in byproduct H_2 . The mandated drop in the levels of aromatics in gasoline resulted in less H_2 production in the refineries coupled with an increase in the demand for H_2 for hydrogenation reactions. Refineries were once viewed as net producers of H_2 ; however, they are now major consumers of H_2 with the establishment of many independent H_2 production plants (using steam methane reforming or partial oxidation) on the perimeter of many of the world's major refineries. The long-term forecast is for the overall demand to increase into the next century with some dramatic deficiencies forecast between supply and demand.^{13,19,20} These demand increases apply both to refinery and nonrefinery uses (see Figure 2). Cromarty also draws this conclusion in a recent market review on H_2 .²¹

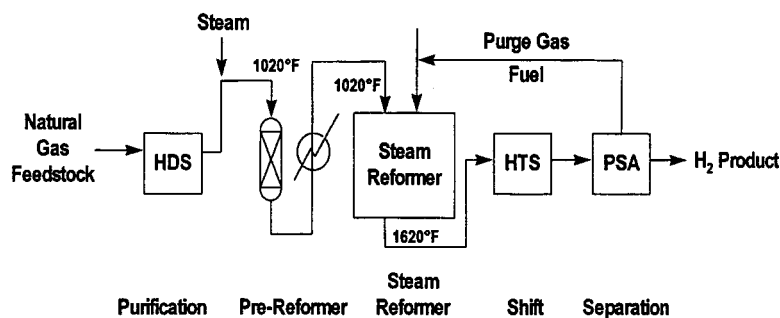


Figure 3. Simplified process flow diagram for steam reforming of methane.

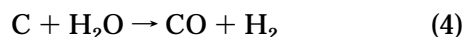
D. Carbon Formation

In H_2 production, there are always concerns with regard to carbon formation²² which can build rapidly and poison the process. Carbon leads to “fouling” (clogging) of the reactor and blocks active sites on the catalyst, and thus it is important to inhibit carbon formation. For these reasons, coproduction of carbon presents a serious processing hurdle. There must be acceptable, energy-efficient means to remove any accumulating carbon coproduct.

There are two major pathways for carbon formation:



The tendency to form carbon on the catalyst surface depends on reaction kinetics, process conditions (temperature, pressure flow rates), and reformer design.²³ These carbon-forming reactions are delicately balanced by carbon-consuming reactions such as in eqs 3 and 4, which are also dependent upon reaction kinetics, process conditions, and reactor design.



In fact it has been proposed that the working commercial SMR-reduced Ni catalyst is coated with a working layer of carbon. Laboratory operations over periods of days are not sufficient to test for carbon formation; instead, new catalysts must be evaluated for months under simulated process conditions and reactor configurations. Carbon deposit types²⁴ and their formation^{25,26} have been characterized. Commercial approaches to minimize potential carbon formation include high ratios of steam to hydrocarbon, the continual addition of ppm levels of sulfur compounds to the feed stream,²⁷ the addition of alkali promoters,²⁸ and added support phases such as Mg–Al spinel.

E. Steam Reforming of Hydrocarbons to Produce H_2 : Where the Field Stands

Currently, steam methane reforming [SMR] is the most commonly utilized process for H_2 production with feedstocks ranging from methane to light hydrocarbons (see Figure 3). This is a mature technol-

ogy, but there is certainly room for improvements. Current Ni or Ru catalysts are adequate to produce H_2 , which is currently thermodynamically limited for this very endothermic process. Formation of carbon (coke) during the process is a critical issue that impacts performance and lifetime of commercial catalysts. Current technology can remove and minimize coke formation. However, the goal of current research must be to do so more effectively, to extend catalyst life, to reduce the operating temperatures (admittedly at the expense of lower conversions), and to reduce the steam-to-hydrocarbon ratio. Typically, excess steam-to-hydrocarbon (3/1) is used to minimize coke formation on commercial catalysts. By sulfur catalyst passivation (continual addition of trace levels of sulfur compounds to the feed) or by the incorporation of noble metals, it is also possible to minimize carbon formation. This latter approach is predominantly considered only when CO-rich syngas is required, not as a preferred approach to making H_2 .

In research on improvements to SMR, catalysts must be studied at high pressures [> 10 atm] because pressure can impact carbon deposition profoundly. Catalysts can also fail because of Ni sintering or carbon deposition in cold spots within the reactor tubes. In this respect it is noteworthy that commercial processes operate with a significant temperature gradient along the catalyst bed with the outlet temperature of some reformers approaching 930 °C.²⁹ Therefore, thermal reactions occur after the products emerge from the catalyst bed. Furthermore, the catalyst is very sensitive to poisons, and the high reaction temperature limits the operating lifetime of the Ni alloy reactor tubes. Finally, a poorly prepared catalyst can lead to migration of the alkali from the catalyst, resulting in downstream corrosion.¹⁵ Any research on catalyst improvement should consider all pertinent issues that impact the optimization of the catalyst in a SMR reactor.

F. Barriers to Further Progress

Issues of thermodynamics and heat transfer restrict operating temperatures. Membrane reactors have been considered as alternatives. However, these are not easily scaled-up and are currently unreliable. Furthermore, they are too expensive to operate because H_2 must be utilized in these reactors at elevated pressure and the cost of the required compression is prohibitive.¹² There is considerable interest in producing H_2 as a fuel for fuel cells. However, no current fuel cell can operate within the temperature limits of commercial reformers.

A significant part of the catalyst loaded into tubular reformers is unused or poorly utilized because heat transfer is often the limiting factor. Engineering design advances are needed and are being pursued, such as heat exchange reformers or alteration of the catalyst geometry. Operation of steam reformers for CO production is also limited by metal dusting arising from the production of CO and its reaction with the nickel alloys of the reactor tubes at ~ 650 °C. Operating outside the regimes for metal dust formation offers advantages of safer operation, lower costs, and corrosion avoidance.

The use of ex-situ surface science methods to better understand the working catalysts is hampered by the extreme temperatures (850 °C) and pressures (400 psig) needed for operation of current commercial catalysts. The implementation of in-situ surface science techniques to monitor catalyst performance should be explored (see Section V). For example, ultraviolet Raman,³⁰ sum frequency generation,³¹ and synchrotron-based methods such as X-ray scattering³² could be applied toward these kinds of systems at extreme process conditions.

G. Promising Areas for Research

At the fundamental research level, there is a need for in-situ catalyst characterization at >20 atm, the actual process pressure. In the United States, with the exception of several industrial laboratories, there are few facilities that have capabilities for studying and testing reforming catalysts under actual process conditions. The lifetime of the catalyst is an important criterion in evaluating new catalysts with respect to current commercial SMR technologies; claims of superior catalytic performance must be verified by operation at the high pressures and temperatures of conventional processes for extended periods, i.e., thousands of hours. Of particular value would be a simple, accelerated aging test that allows assessment of catalyst life in hours or days rather than the usual period of months.

Other promising research areas include understanding catalyst sintering, sulfur poisoning, and metal dust formation. Only 50% of the fuel used to heat SMR reactors is actually used to make H₂; the balance of the heat energy is recovered in steam, which is then sold to other customers but is not typically useful for making additional H₂. Research to discover a more efficient way to utilize the energy in SMR operations (e.g., heat exchange reformers) is needed to reduce costs and CO₂ production. Sintering of active Ni metal particles limits current catalyst performance; thus, a better understanding of the factors that impact this aspect of catalyst behavior would be highly desirable. Since sulfur is present in many of the feedstocks, additional research efforts should address sulfur removal as well as the development of more sulfur-tolerant catalysts. A further understanding of metal dust formation and corrosion of the reactor system is needed as well as an understanding of those factors that contribute to methane decomposition to elemental carbon.

Major improvements in the current technologies could be realized with new catalysts that optimize

CO₂ and/or H₂O adsorption, enhance surface reactions, or inhibit the formation of elemental carbon. Current reformers are heat-transfer-limited rather than catalyst-limited and are loaded with large excesses of catalyst because of the space velocities utilized. Better methods for the transfer of heat into the reactor, including novel catalyst shapes, are needed to impact overall yield and process performance.

In addition, there is a need to develop nonconventional approaches to H₂ generation. Plasma decomposition of methane to carbon has been explored.³³ However, the inherent energy-intensive nature of this approach makes its commercial viability questionable. Operating SMR in a cyclic mode, that is, separating the decomposition of methane to carbon and H₂ from the water/carbon reaction has been demonstrated in the laboratory to generate CO-free hydrogen.³⁴ However, large-scale development and lifetime tests have not been carried out. The advantage of this methodology is the possibility of coupling H₂ synthesis with fuel-cell power generation, which requires H₂ with CO levels typically below 20 ppm. In any case, in all approaches to the generation of H₂ from hydrocarbons, a very important issue is carbon formation and its transformation into an inactive form that leads to excessive carbon buildup.

There are a number of emerging and attractive approaches to H₂ production. However, the greatest opportunities with respect to CO₂ production are those nonfossil fuel-based H₂ technologies where major breakthroughs are needed. In considering new technologies for H₂ production, one must consider the integrated process, that is, the separation and purification steps, the net energy demands and balance, the quality of the feed, etc. Ultimately, the route chosen to produce H₂ will depend not only upon the technological advances, but also on the economics, the related environmental issues, and the market demands.

H. Alternative Means of Producing H₂

Besides improvements to the existing technologies for producing H₂, there are a number of other potential pathways^{12,35} to produce H₂. These include the following: (1) methane decomposition, (2) use of membrane reactors, (3) solar energy for electrolysis of water, (4) solar-assisted SMR or CH₄ decomposition, (5) photocatalysis, (6) selective oxidation of methane, (7) oxidative dehydrogenation, (8) electrolysis of water using fuel cells, (9) biomass conversion, and (10) biological H₂ production. Only the use of solar energy for decomposition of water offers a direct, non-carbon approach, although, in principle, biomass may offer a CO₂ neutral approach.

I. Use of Methane

Methane is used via SMR as an indirect source of H₂. However, it could be used directly as a source of hydrogen for other catalytic transformations. There are reports in the literature in which CH₄ is decomposed to H₂ and carbon, which is then converted in a separate step to CO or CO₂³⁶ or used in an elemental

carbon product. In addition to using methane as a source of hydrogen, one can also envision pyrolysis of methane to H_2 and C_2 hydrocarbons as in eq 5.

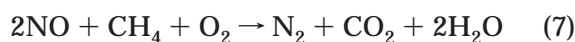


The difficult step in both reactions is the formation of carbon from the decomposition of methane, according to eqs 5 and 6



Parmon³³ discussed this concept and the use of microwave or plasma energy to carry out reaction 6; however, consideration of the overall energy balance likely makes this approach economically impractical. The use of fluidized beds of nickel catalysts operating at 650 °C and 1 atm to produce H_2 is also possible. Obviously, in either of these processes the incorporation of a separation step to recover the H_2 from the carbon coproducts as well as a market for the carbon coproducts would be required.

With regard to the potential of using the hydrogen value within methane, without having to produce H_2 , methane has also been used as a chemical reducing agent to convert nitrobenzene to aniline over a copper chromite catalyst.³⁷ Methane can also be used to reduce NO_x as can H_2 ,^{38,39} however, H_2 is simply too expensive to be used for destroying NO_x in large, global quantities. Methane [in the presence of O_2] can also be used to reduce NO_x to N_2



and is an example of using the hydrogen value of methane as a H_2 substitute for NO_x reduction.^{40,41} In a nonoxidizing stream, CH_4 can be used to reduce NO_x but with a large excess of CH_4 . There is currently a coal-fired power plant in New Mexico which uses local supplies of natural gas from wells to reduce SO_2 to H_2S , which is then converted to sulfur using Claus technology (10% of the electricity generated is used for SO_2 scrubbing!). This H_2S product as well as other natural H_2S supplies are potential sources of H_2 ; however, their utilization presents another set of very challenging problems.

J. Use of Membrane Reactors

There continues to be interest in using H_2 permselective⁴² metal alloy membranes to produce ultrapure H_2 , typically used concurrently in chemical processing. Some examples of Pd alloys for enhancing dehydrogenation⁴³ or SMR⁴⁴ reactions have been reported. Economic evaluations of these processes suggest some positive aspects. However, the application of membrane reactors for H_2 production has been questioned.⁴⁵⁻⁴⁷ The use of membranes in enhancing H_2 production is limited by the quality of the reactant streams available. Reactants containing CO, H_2S , or aromatics are unacceptable because of their tendency to poison Pd surfaces; therefore, these reactors will be limited by mass transport and suffer from low working surface area. Membrane fouling is unacceptable with these systems. Today's Pd-based alloy membranes produce very pure H_2 , but almost always

at low pressure. Currently, when scaled-up, large Pd membranes have a history of catastrophic failure⁴⁸ and require a thickness which reduces the flux of H_2 to unacceptable levels. Typical industrial uses require H_2 at high pressures [>20 bar] with the associated cost of compression prohibitive. Thus, the current limitation of membranes to the production of low-pressure H_2 is a serious barrier to commercialization. Polymer-based membranes, although capable of producing up to 98% purity H_2 , are sensitive to high temperatures and to the presence of organic amines in the reactant stream (often present from prior CO_2 removal operations). There is a brief description⁴⁹ regarding the recovery of H_2 at high pressure from an NH_3 purge gas stream. However, these results have not been verified or confirmed. In an alternative approach, Sircar et al. demonstrated the use of carbon-coated supports for the recovery of H_2 from targeted refinery streams.^{50,51} In these selective surface flow membranes, H_2 is rejected from the membrane allowing recovery of high-pressure H_2 (with some other rejected components from the membrane) in an enriched retentate stream.

K. Solar Energy for Photoelectrolysis and Photocatalysis of Water Reactions

Water is the ultimate feedstock for H_2 production. Using visible light to photocatalytically decompose water into H_2 and O_2 in an efficient manner would have an enormous impact on the future production of H_2 . This is a formidable research problem that has been under study for decades by many groups around the world with very limited success. Early research used ultraviolet light to decompose water, albeit inefficiently, over titania and other oxides.⁵² However, for practical reasons visible light rather than UV radiation must be used for any commercial application of photocatalysis. There are limited materials that can utilize a significant portion of the visible spectrum, and progress is being made in this direction.⁵³ Extensive research toward the development of photocatalytic and photoelectrochemical materials that efficiently absorb visible light are being conducted.^{54,55} For example, Arakawa's group split water to H_2 and O_2 stoichiometrically using mixtures of sodium carbonate with NiO_x/TiO_2 and solar radiation.⁵⁶⁻⁵⁸ Arakawa and Linkous proposed a dual-bed photocatalytic water splitting system for utilizing visible light and for the separate production of H_2 and O_2 using narrow band gap semiconductor photocatalysts such as WO_3 . Domen and co-workers demonstrated the production of H_2 using mixed-metal oxides, albeit with UV light.^{59,60} Technological barriers include raising the current quantum yields substantially from a fraction of a percent to at least 10% while utilizing light out to 600 nm. New materials with suitable band structures to utilize the theoretically applicable solar spectrum are crucial to the success of this effort. An alternative approach is a hybrid system that combines organic and inorganic materials, e.g., a low cost and efficient, dye-sensitized oxide semiconductor solar cell.^{61,62} Along these lines, Grätzel^{61,62} and co-workers demonstrated a tandem cell composed of a photocatalyst and a dye-sensitized

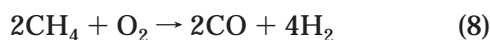
oxide semiconductor solar cell which promises improved efficiencies. The overall, primary goal must be the development of a very efficient catalyst that operates at or near ambient temperature and pressure with high activity and selectivity. The long-term goal is the efficient utilization of the entire solar spectrum with photocatalysts and/or solid-state devices having long lifetimes and exceptional reliability. Laboratory photovoltaic devices already operate at 30% efficiency which, when coupled with the 80–90% efficiency of electrolysis, provide a 24–27% total conversion efficiency. As in electrocatalysis, the production of H₂ and O₂ must be separated spatially. Devices which decompose water into H₂ + O₂ mixtures are less attractive in view of explosion hazards and problems of secondary separations, for which Pd membranes are principally unsuitable. Homogeneously catalyzed photodecomposition also has been pursued. Efficiencies and routes to H₂ formation are more advanced than those for generation of O₂. Progress hinges on increasing the thermodynamic and mechanistic understanding of metal hydrides, metal–oxo complexes, and related systems.

A potential alternative approach to H₂ generation is to employ an external power source or photovoltaic device (solar driven) to electrolytically decompose water. Turner⁶³ reported that water decomposition can be carried out with an overall efficiency of 12% using a monolithic photovoltaic/photoelectrochemical device (GaAs/GaInP_x). However, several technical problems must be resolved before commercialization of this approach is feasible. It should also be noted when considering the implementation of this and related technologies that the current hydroelectric capacity is completely subscribed; thus, additional electrical power generation capability would be required to implement extensive electrolytic hydrogen generation.

For a solar-based process to be practical, it must be highly efficient, having both a high overall quantum yield with minimum formation of any coproduct and using as much of the incident light as possible. Furthermore, the photocatalyst must be long-lived, low-cost, and capable of operation in hostile environments (sand storms, salt spray, etc). Ultimately, the H₂ and O₂ must be separated, requiring additional processing and cost. Therefore, the prospects for the development of successful technologies for the efficient generation of H₂ using solar radiation are certainly long term (>5 years out). Nonetheless, photocatalytic and photoelectrolytic processes are attractive nonfossil fuel approaches to H₂ production.

L. Catalytic Selective Oxidation of Methane to Synthesis Gas

The oxidative decomposition of methane into CO and H₂ is favorable; however, it is extremely difficult to avoid further oxidation of methane to CO₂ and water. Ideally, it is desirable to perform a gentle, selective oxidation of methane with O₂ (eq 8)



and to avoid detonation of CH₄/O₂ by use of catalytic

thermal partial oxidation (POX = partial oxidation). This is particularly acute for large systems. However, this approach (POX and a variant known as auto-thermal reformation) is being aggressively pursued by scaling to small- and medium-sized applications. This is the reformation technology of choice being considered by the transportation sector for on-board vehicular reformation; however, this approach still requires carrying out the water–gas shift to convert CO to H₂ (CO + H₂O ⇌ CO₂ + H₂). Many industries considering hydrogen as fuel endorse this and other reformation technologies carried out at a central site with the hydrogen, stored on-board, used to fuel the vehicle. This central facility for hydrogen generation could utilize the same technology as that proposed for on-board vehicular applications. However, it would also provide a point source for CO₂ generation and management.

Schmidt and co-workers⁶⁴ made substantial progress in understanding mechanistically the very difficult partial oxidation of methane using noble-metal-coated monoliths with very short reaction contact times (see also Section III.C on hydrocarbon oxidation). There are two recent U.S. patents^{65,66} which report interesting results suggesting that some of the difficulties can be circumvented or minimized. A Shell patent⁶⁵ claims that reaction 8 can be carried out using a 0.5% Rh/ZrO₂ monolith operating at 1155 °C and 3 atm pressure with 97% CH₄ conversion and 92% selectivity to CO and 90% selectivity to H₂. Another recent report⁶⁷ has shown that the addition of Gd to a cobalt oxide catalyst with a CH₄/O₂/helium ratio of 2/1/4 at 830 °C yields 73% conversion with 80% selectivity to CO/H₂. Any practical extension of this latter work will depend on the intended application and may require the avoidance of helium or any diluent (because of the need for separation and purification of the H₂ product), the demonstration of sustained catalyst lifetime over months of operation, and process function in a commercially acceptable safe operating regime. The current lab-bench experiments require the use of CH₄/O₂ mixtures in the detonation regime and are unacceptable for large-scale commercial units. However, there may be opportunities with respect to developing this technology on a smaller scale, e.g., sizes on the order of 50–100 kW, where the processes can be more easily controlled. A recent review by Peña²³ provides other useful commentary and insight regarding new developments in this technology.

M. Other Methods for H₂ Generation

Other noncatalytic approaches include the thermochemical splitting of water using a solar furnace or nuclear energy. The heat from a nuclear reactor or a solar furnace can be used to drive a series of chemical reactions with net production of H₂ and O₂.⁶⁸ These are not catalytic and require large amounts of heat at temperatures in excess of 700 °C. Alternatively, the solar furnace can be used to increase the temperature of the water supplied to an electrolysis unit, which, in turn, reduces the amount of energy required to split water into H₂ and O₂. However, separation of the H₂ from the O₂ must still be incorporated into these alternative approaches.

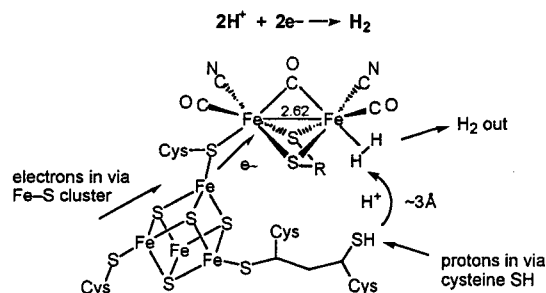


Figure 4. Structure of the active site of hydrogenase from *C. Pasteurianum*, determined by Peters,^{71a} showing proposed H₂ activation at the site occupied by a displaceable water ligand in the crystal structure. Electrons presumably flow in from the protein via an Fe–S cubane cluster and into the Fe–Fe unit, which is reduced and then protonated by a nearby cysteine SH group. A labile molecular hydrogen (η^2 -H₂) ligand can form, which dissociates to releases H₂ gas. Adapted with permission from ref 73e.

There has also been a good deal of interest in using biomass⁶⁹ as a means for generating H₂. While this allows potential recycling of CO₂, it demands large acreages for growth of the trees and plants that consume CO₂. Power plants, in turn, burn these to produce energy and CO₂. However, use of prime agricultural resources in such a manner does not appear viable. On the other hand, the use of wet biomass and organic wastes is a viable alternative, offering the same CO₂ benefit without the need to use prime agricultural resources solely for the production of an energy crop. Wet biomass and organic wastes could be efficiently gasified under hydrothermal conditions to produce a hydrogen-rich fuel gas. One approach is the hydrothermal conversion of organic material with the addition of alkali metals at high pressures in water,⁷⁰ such as the gasification of glucose in hot water at 600 °C and 300 bar. This provides a much higher thermal efficiency, an H₂-rich (60%) gas with low CO yield in one step, suppressed tar formation, without the need for extensive N or S removal. Technical hurdles that remain include: (1) the need for pilot-plant studies and reliable high-pressure feeding systems; (2) the avoidance of fouling problems of the heat exchanger, the preheater, and the reactor; (3) the use of metallic process equipment resistant to H₂-induced structural embrittlement, and (4) a waste treatment plant to handle the exhaust.

Another H₂ production approach uses biologically based systems such as the hydrogenase enzymes in anaerobic microorganisms to catalyze production of H₂ from proton sources such as water. The active sites in these enzymes surprisingly have been found to have dinuclear iron or Fe–Ni centers with organometallic ligands such as CO and CN (Figure 4).⁷¹ Molecular hydrogen coordination (η^2 -H₂) to the active site is presumably important here and in all homogeneous reactions of hydrogen, and such σ complexes are intermediates in C–H bond activation as well (see Section III on functionalization of hydrocarbons).⁷² It should be possible to design organometallic mimics⁷³ for these sites, although a key hurdle is the electron-donor source needed to reduce protons to H₂. While the enzymatic approach is highly efficient (10⁶ turnovers/s!) and operates at 1 atm and room tem-

perature, it requires an energy source such as a sugar or other electron donors. Incorporating a means to provide reasonable energy input is a critical issue that should be addressed as part of such alternative approaches. Indirectly, since a major fraction of the hydrogen produced globally is used to synthesize NH₃, one can also envision mimicking nitrogenase, a related metalloenzyme which fixes N₂ and H₂ equivalents to produce NH₃ without formally producing H₂. Efforts in this direction have been significant for the past 30 years. Recent structural data for the Fe–Mo active site offers fresh insight for designing an inorganic catalyst.⁷⁴ It is quite clear from studies of biosystems that compounds of the least expensive transition metal, iron, are remarkably efficient catalysts for a wide range of small molecule conversions. Thus, any new research in this area should first consider Fe-based catalysts with polymetallic sites, such as that discussed above and the dinuclear Fe site in methane monooxygenase (see Section III.E).

N. Fuel Cells

There is considerable recent interest^{75,76} in using H₂-based fuel cells as a future source of energy. A number of fuel cell devices are under consideration, most of which use H₂ at 1.0 atm pressure or less. These are discussed in detail in Section VI.D. We note here that for transportation to remote customers, H₂ compression and distribution will be required. Often methanol is the fuel of choice for H₂-based fuel cells; however, it should be noted that costs to transport the methanol from the production site to the fuel cells will be significant, since a suitable methanol distribution system and infrastructure does not exist.

O. Needs/Challenges/Opportunities

In summary, the key points with respect to research needs, challenges, and opportunities emphasized in this section are as follows: (1) more catalyst evaluation and in situ characterization studies at > 10 atm under in-situ conditions; (2) need for accelerated aging studies to quickly assess catalyst performance under real operating conditions; (3) better mechanistic understanding of factors which cause catalyst sintering; (4) more efficient means of energy input into SMR operations; (5) overcome heat transfer limitations in SMR operations; (6) improved control of metal dust formation and corrosion; (7) pursuit of nonfossil fuel-based H₂ production technologies; (8) use of CH₄ as a substitute for H₂ in chemicals production; (9) development of safe operating processes for direct CH₄ oxidation to CO/H₂; (10) development of efficient photocatalytic processes for H₂O splitting that operate at or near ambient temperature and pressure with high activity and selectivity; (11) utilization of the entire solar spectrum for photocatalytic/photoelectrolytic processes for H₂O splitting; and (12) better mechanistic understanding and implementation of what is learned from biomimetic H₂ formation processes.

P. Summary

This section summarizes the status of various H₂ production science and technology. There is consider-

Table 2. Processes under Study or Development for the Oxyfunctionalization of Light Paraffins (C₁–C₆) in the Petrochemical Industry^a

raw material	product	phase	development stage
methane	chloromethanes	gas, heterog.	industrial
methane	methanol	gas, het./hom.	pilot plant
methane	syngas	gas, het./hom.	research
methane	ethylene	gas, het./hom.	pilot plant
	1,2-dichloroethane, vinyl chloride	gas, heterog.	pilot plant
ethane	acetic acid	gas, heterog.	research
ethane	ethylene	gas, het./hom.	research
propane	acrylic acid	gas or liquid	research
propane	propyl alcohol	liquid, homog.	research
propane	acrylonitrile	gas, heterog.	demonstrative plant
propane	propylene	gas, heterog.	research
<i>n</i> -butane	acetic acid	liquid, homog.	industrial
<i>n</i> -butane	maleic anhydride	gas, heterog.	industrial
<i>n</i> -butane	butadiene	gas, heterog.	industrial abandoned
isobutane	methacrylic acid	gas, heterog.	pilot plant
isobutane	isobutene	gas, heterog.	research
isobutane	<i>t</i> -butyl alcohol	liquid, het. or hom.	research
<i>n</i> -pentane	phthalic anhydride	gas, heterog.	research
cyclohexane	cyclohexanol, one	liquid, homog.	industrial
cyclohexane	cyclohexanone	liquid, het. or hom.	research

^a Het./hom. indicates the likely presence of a mechanism initiated on the catalyst surface and transferred to the gas phase.

able room for improvement in the most widely used commercial approach, steam methane reforming, especially at higher pressures. However, more research is critical with respect to alternative technologies, especially those that do not utilize fossil fuels. In the near term, methane (natural gas) is an attractive source of H₂. However, more direct and less energy intensive approaches are needed for H₂ production from CH₄. Combined with intelligent carbon management, reformation of our hydrocarbon resources can provide a near term environmentally sensitive source of H₂. In the long term, photocatalysis with sunlight or photoelectrolysis offer nonfossil fuel routes to H₂, some of which would produce O₂-free H₂ without the necessity of H₂/O₂ separation.

III. Selective Functionalization of Hydrocarbons

A. Introduction

Olefins and aromatics are used by the chemical industry as primary building blocks to produce chemical intermediates and polymers. These chemical precursors are made by high-temperature, endothermic processes, such as cracking, dehydrogenation, and reforming, starting from petroleum and natural gas. CO₂ is generated by the combustion of fuel to supply the energy required to produce olefins and aromatics, and additional CO₂ is generated during the partial oxidation of these products to oxygen-containing compounds (e.g., aldehydes, alcohols, carboxylic acids), since these latter processes typically have selectivities of 50–80%.

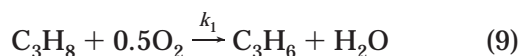
A significant reduction of these CO₂ emissions could be achieved by developing selective oxidation processes for converting methane and C₂–C₄ alkanes to olefins and oxygenates directly. There are also economic incentives for this approach, since low molecular weight alkanes, particularly methane, are readily available and are less expensive than olefins and aromatics. As a consequence, one can envision the replacement of highly endothermic processes

needed to generate unsaturated precursors with exothermic, single-step alkane-oxidation processes that, if properly operated, would generate energy as well as chemical products. If catalysts could be devised to do this selectively, a green chemical process technology with enormous economic benefits would result. The development of more selective catalysts for the oxidation of olefins and aromatics should also be pursued, since success will contribute to additional reductions in CO₂ emissions.

Several illustrations of the processes currently under study or development for the oxyfunctionalization of light alkanes are presented in Table 2. While only four of the processes listed have been commercialized, a much larger number are being actively investigated in academic and industrial laboratories. The implementation of novel processes for the conversion of alkanes to olefins and oxygenated compounds requires the discovery, understanding, and development of homogeneous and heterogeneous catalysts exhibiting high activity, selectivity, and stability as well as the development of novel concepts of catalytic reactor design and operation. Progress made toward these ends and the research challenges that must be met in order to develop catalysts exhibiting high activity and selectivity are discussed in the following sections.

B. Oxidative Dehydrogenation of Alkanes to Alkenes

The oxidative dehydrogenation (ODH) of alkanes offers a potentially attractive means for the production of alkenes. As illustrated below for the case of propane conversion to propene, the central issue is how to achieve a high yield of propene while avoiding the combustion of propane or propene to CO₂ (eqs 9–11).



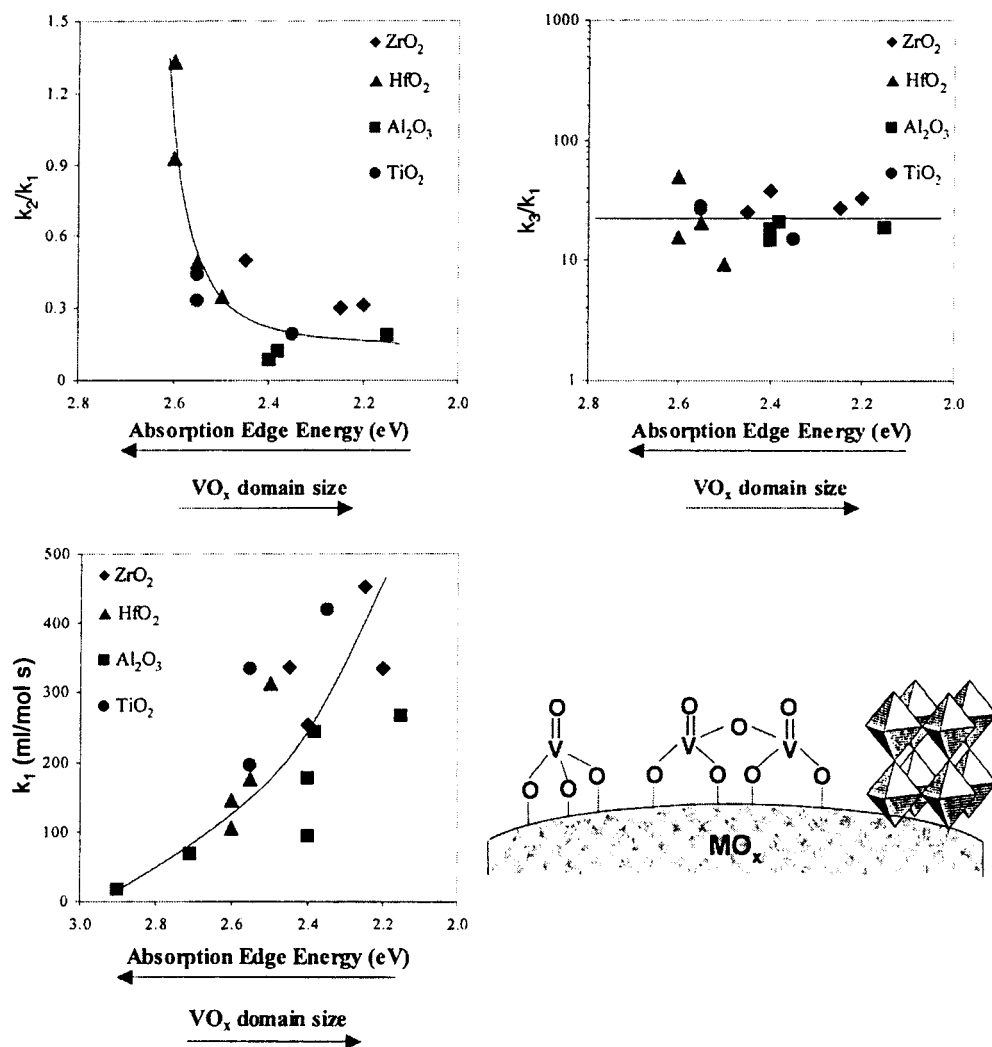
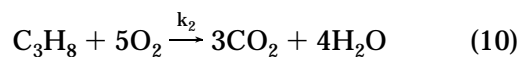


Figure 5. Dependence of the rate constant ratios for the oxidative dehydrogenation processes of eqs 9–11 on the VO_x domain sizes and optical absorption band edge for vanadia supported on various metal oxides.



While many oxide catalysts exhibit high alkene selectivity (e.g., >80%) at very low alkane conversion levels, all show a decrease in alkene selectivity with increasing alkane conversion. For supported metal oxides, it has been observed empirically that the decline in olefin selectivity with increasing alkane conversion decreases with increasing basicity of the support.⁷⁷ While a large body of literature exists on the ODH of alkanes, current understanding of the elementary processes involved in both the formation of alkenes and their subsequent combustion is limited. In particular, there is a lack of understanding concerning the relationships of catalyst composition and structure to catalyst activity and selectivity. Knowledge of these relationships would be very useful for guiding the modification of existing catalysts and for the synthesis of totally new classes of catalysts.

Some progress in understanding the relationships between catalyst structure and performance has been reported recently for metal oxide-supported vana-

dia.^{78,79} A series of catalysts ranging in V₂O₅ weight loading from 1% to 15% were prepared and then characterized by X-ray absorption, Raman spectroscopy, UV–visible absorption spectroscopy, and EXAFS. Since calcination at 773 K caused changes in the BET surface area of the samples, which depended on the weight loading of vanadia, the loading of vanadia is expressed in V atoms/nm². Selective adsorption of CO₂ on the zirconia support reveals that up to 1.2 V/nm², corresponding to 60% coverage of the support, is deposited primarily as monomeric vanadate species. At higher vanadia surface densities, polyvanadates appear, and the surface of the zirconia becomes fully covered by a monolayer of vanadia at a surface density of 7.5 V/nm². Raman spectroscopy and UV–visible absorption edge energy measurements confirm the progressive growth in the nuclearity of the supported vanadia species with increasing vanadia surface loading. Values of the rate coefficients for eqs 9–11 were determined and examined as a function of vanadia domain size, which correlates with the UV–visible absorption band edge energy. As seen in Figure 5, while the value of k_1 increases with increasing domain size, the ratio of k_2/k_1 decreases and the ratio of k_3/k_1 is independent of domain size. These results indicate that ODH

Table 3. Active Vanadium Oxide Species and Catalytic Properties of Vanadium-Based Catalysts

Catalyst	Vanadium species (d)	Selective reaction (e)	H-abstraction selectivity	Oxygen insertion power
Mg ₃ V ₂ O ₈	Isolated VO ₄	C ₃ H ₈ to C ₃ H ₆	↑	undetected
VO _x /SiO ₂ (a)		C ₄ H ₁₀ to C ₄ H ₆		
VAPO-5				
V-silicalite				
MgV ₂ O ₆	Isolated VO ₆	C ₃ H ₈ to C ₃ H ₆ (f)		
Mg ₂ V ₂ O ₇		C ₃ H ₈ to C ₃ H ₆ (g)		
VO _x /TiO ₂ (b)	Incomplete	<i>n</i> -butane to AA		
V ₂ O ₅		<i>o</i> -xylene to PA		
VO _x /Al ₂ O ₃ (c)	Incomplete	butadiene to MA		
VO _x /SiO ₂ (c)				
(VO) ₂ P ₂ O ₇	Incomplete	<i>n</i> -butane to MA		

^a At low vanadium content. ^b Monolayer catalysts. ^c At high vanadium content ^d V, and va = vanadium with tetrahedral octahedral coordination respectively. ^e AA = acetic acid, PA = phthalic anhydride, MA = maleic anhydride. ^f Ethanal is also observed. ^g Acrolein is also observed.

requires large vanadia domains. Propene combustion also occurs preferentially on large polyvanadate domains, but propane combustion occurs preferentially on smaller domains.

C. Selective Oxidation of Hydrocarbons to Oxygenated Products: Approaches Involving Heterogeneous Catalysts

The selective oxidation of hydrocarbons to oxygenates represents a significant challenge, since often more than one oxygenated product can be produced from a given starting material, and all products are susceptible to complete combustion to CO₂. Examples of the reactions one would like to carry out include the conversion of methane to methanol or formaldehyde; ethane to ethylene glycol, acetic acid, or acetaldehyde; propane to acrolein, acrylic acid, or 1,3-propane diol; butane to 1,4-butane diol or maleic anhydride; and isobutane to methacrylic acid. While considerable research has been carried out on each of these reactions, only two have been commercialized: the conversion of butane to acetic acid and the conversion of butane to maleic anhydride.

Mixed-metal oxide catalysts, often containing V as one of the elements, have been examined as candidates for the selective oxidation of alkanes. However, as seen in Table 3, such catalysts produce only small to moderate yields of the desired product. An exception is the work reported by Mitsubishi in which propane is oxidized to acrylic acid in yields exceeding 52% over a catalyst formulated as MoV_{0.3}Ti_{0.23}Nb_{0.12}O_x.⁸⁰ This catalyst is even more effective in catalyzing the conversion of propane directly to acrylonitrile when the vapor-phase oxidation is run in the presence of ammonia.⁸¹ Another example is the announcement by BP of a process to carry out the conversion of propane to acrylonitrile over a VSbO₄ catalyst.⁸² These results suggest that the catalytic properties of oxygen associated with vanadium can be tailored by altering the environment in the im-

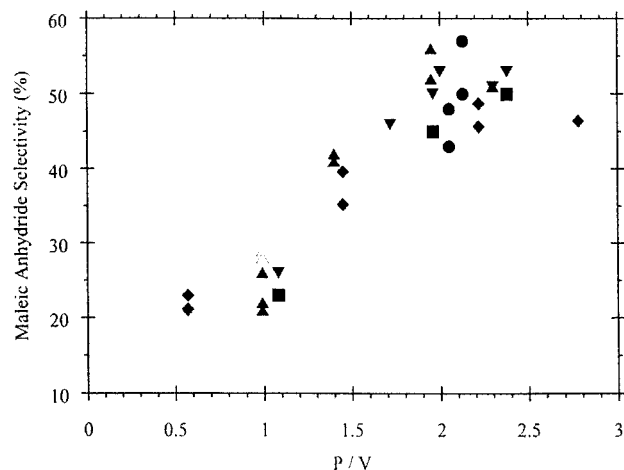


Figure 6. Effect of phosphorus/vanadium ratio on the selectivity of maleic anhydride formulation via oxidation over vanadium phosphate catalysts.

mediate vicinity of the V atoms. This idea is supported by recent investigations of butane and pentane oxidation over supported vanadia catalysts.⁸³

Figure 6 shows that the effects of the phosphorus/vanadium ratio on the selectivity of maleic anhydride formation via butane oxidation over supported vanadium phosphate catalysts.⁸⁴ The selectivity to maleic anhydride increases monotonically with increasing P/V (phosphorus/vanadium) ratio. Near-edge analysis of X-ray absorption spectra taken during butane oxidation suggest that the high selectivity to maleic anhydride observed when P/V = 2 is associated with the stabilization of a high proportion of the V in the 4+ oxidation state.⁸⁵ A similar conclusion was reached in studies of pentane oxidation to maleic anhydride over alumina-supported vanadia.⁸⁶

Polyoxometalates (POMs) have recently emerged as a potentially interesting class of catalysts for the selective oxidation of alkanes and other hydrocarbons.^{87–91} Figure 7 shows representative examples of such polyoxometalate anions. The properties of POMs can be varied dramatically by substitution of different metal ions into the anion framework. For example, starting with H₃PMo₁₂O₄₀, one can exchange other cations for the protons which serve as counteranions, one can substitute other metals such as W, V, and Cu into the framework of the heteropolyanion, and one can use heteroatoms such as Si in place of P. Thus, both the acidity of these materials and the redox properties of the heteropolyanion framework can be varied.

The considerable flexibility of POMs within a well-defined structure has led to the application of these materials as homogeneous and/or heterogeneous catalysts for a wide range of acid-catalyzed and oxidative conversions of organic molecules. Examples of the applicability of POMs for alkane oxidation include isobutane to methacrolein and methacrylic acid using H₃PMo₁₂O₄₀ and vanadium-substituted derivatives,^{92–94} oxidative dehydrogenation of alkanes using iron-substituted heteropolytungstates and heteropolymolybdates,^{92,93} propane oxidation to acrylic acid,⁹⁵ and methane oxidation to formic acid using Pd–Cs salts of PVMo₁₁O₄₀.^{94–96} There is also evidence

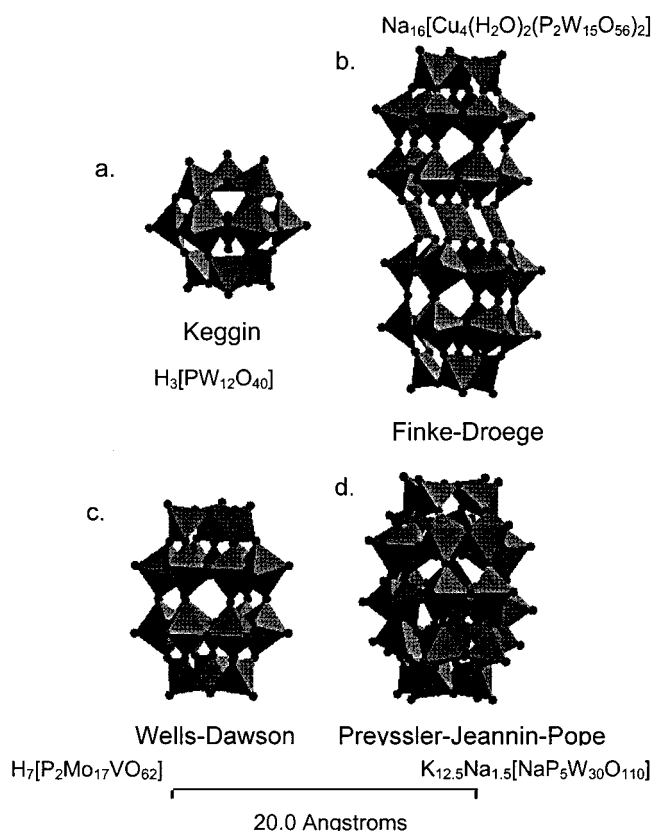


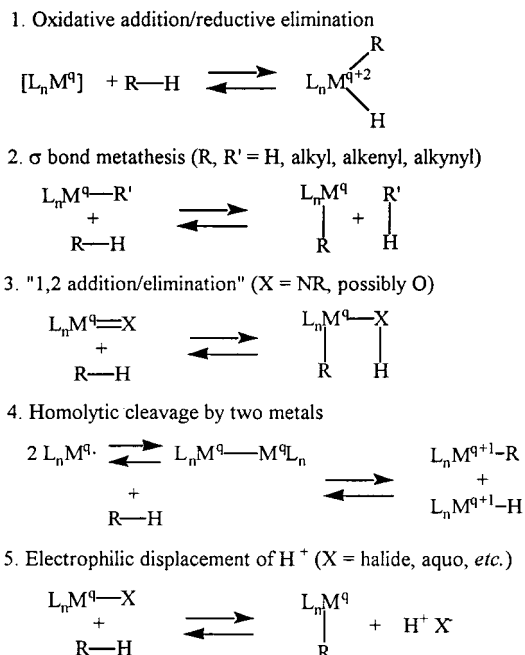
Figure 7. Schematic of heteropolyanion structures.

suggesting that improved activity and selectivity for various metal-catalyzed oxidation processes can be achieved by coupling redox-active metal centers with redox-active POMs. Ordered surface structures consisting of both pure and mixed arrays of polyanions can be produced for catalysis and surface science experiments. The attractiveness of this approach is not only the chemical flexibility that it provides, but also the ability to interrogate the system by scanning tunneling microscopy (STM) in order to identify the changes occurring in individual POM units upon reaction.

D. Approaches Involving Homogeneous Catalysts

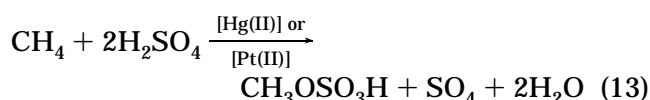
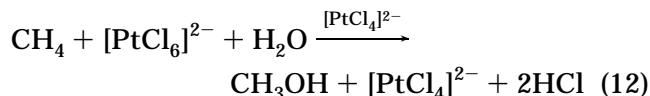
Although alkanes are generally unreactive toward soluble transition-metal complexes, organometallic chemists have identified several classes of compounds that react readily with the carbon–hydrogen bonds of hydrocarbons, including alkanes, under mild conditions. Five general mechanisms have been identified for the activation of C–H bonds of alkanes under mild conditions (Scheme 1):⁹⁷ (1) oxidative addition of the C–H bond to a low-valent, electron-rich transition-metal center, yielding an alkyl hydride product, (2) σ -bond metathesis of the C–H bond with high-valent electrophilic metal hydrides or hydrocarbyls to exchange the alkyl fragments between metal and hydrogen, (3) 1,2-addition of the C–H bond across the metal–nitrogen double bond for metal imido complexes, yielding the corresponding metal amido alkyl product, (4) homolytic cleavage of the C–H bond (especially for methane) by two metal-centered radicals to afford a metal alkyl and a metal hydride product, and (5) electrophilic activation.

Scheme 1. Five Mechanisms for Homogeneous C–H Bond Activation with Organotransition-Metal Compounds



Although the first four processes represent highly significant developments and the elucidation of their mechanisms major achievements in organotransition-metal chemistry, none of these systems appears suited for the catalytic oxidative functionalization of hydrocarbons, e.g., the oxidation of methane by O₂ to methanol. Organometallic reagents capable of effecting the first and fourth pathways are oxidatively unstable, and those capable of effecting the second and third pathways are protolytically unsuited, since they form prohibitively strong metal–OR bonds.

Electrophilic activation by late transition-metal ions such as Pt(II),⁹⁸ Pd(II),⁹⁹ Rh,¹⁰⁰ and Hg(II)¹⁰¹ stands in marked contrast (eqs 12 and 13).



Such systems have been shown to effect both stoichiometric and catalytic oxidations of alkanes, including methane. Although none of the present systems is practical (since none display acceptable rates or do not use dioxygen as the oxidant), there have been some recent developments (discussed below) that are encouraging for eventual development of a workable catalytic alkane oxidative functionalization system.

The most attractive feature of these electrophilic systems is their *selectivity*: the reactivity of the methyl group is substantially greater than that of an already functionalized position such as H–CH₂OH or H–CH₂SO₄H (by as much as 100 times). It is

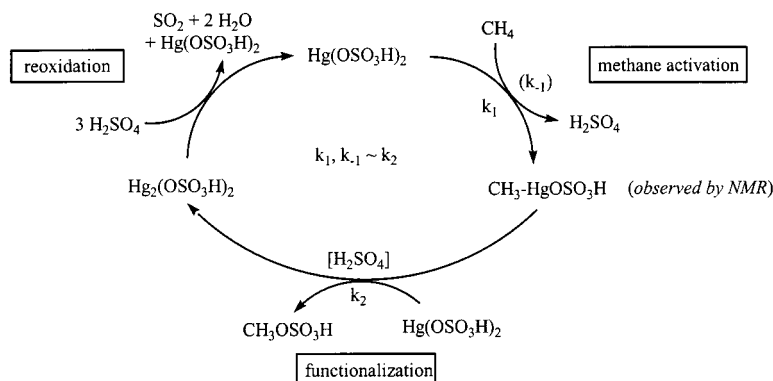
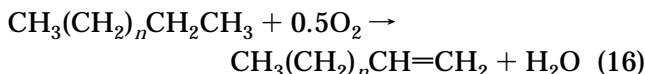
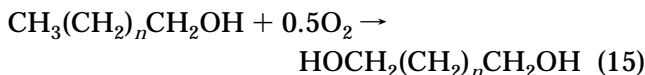
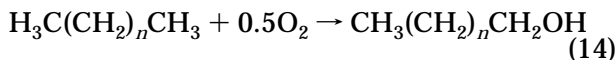


Figure 8. Reaction mechanism of the Hg(II) methane activation catalyst system.

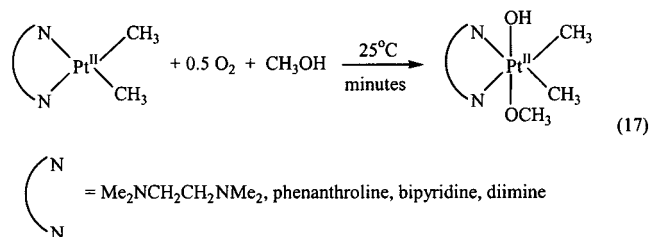
possible by using the Shilov system to effect the remote oxidation of highly flexible linear and branched alkyl chains. The order of reactivity is $\alpha\text{-C-H} \ll \beta\text{-C-H} < \gamma\text{-C-H} < \delta\text{-C-H}$ for alcohols and $\alpha\text{-C-H} \ll \beta\text{-C-H} < \gamma\text{-C-H} \approx \delta\text{-C-H}$ for carboxylic acids, sulfonic acids, and phosphonic acids.¹⁰² As a consequence of these properties, it is possible to achieve precise control with respect to the extent of oxidation (eq 14). These selectivity patterns suggest that higher alkanes might be sequentially oxidized to α,ω -diols (eq 15) and when coupled to primary alcohol dehydration alkanes to α -olefins (eq 16).



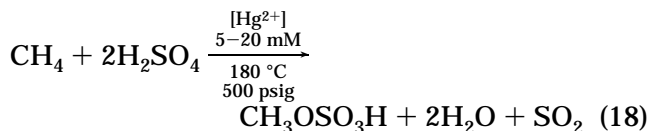
The mechanisms of the “Shilov” system,¹⁰³ representing one class of such electrophilic hydroxylation systems, have now been studied extensively, and many of the mechanistic features have been established.¹⁰⁴ The reaction takes place in three stages: (i) electrophilic activation of R–H by Pt(II) via a σ complex and a Pt(IV) alkyl hydride that undergoes deprotonations to a Pt(II) alkyl; (ii) oxidation by Pt(IV) to give a Pt(IV) alkyl; (iii) nucleophilic, $\text{S}_{\text{N}}2$ attack of water at the α carbon of the latter with loss of H^+ to give alcohol with Pt(II) as the leaving group. A key feature of the system is that the first step involves electrophilic attack by Pt(II) at the alkane C–H bond, generating a platinum(II) alkyl-polarized $\text{Pt}^{\delta+}\text{-C}^{\delta-}$; following oxidation to platinum (IV) in second step, the bond reverses polarity to $\text{Pt}^{\delta-}\text{-C}^{\delta+}$, becoming susceptible to nucleophilic attack at carbon in step iii. A complication with the original “Shilov” chemistry involving only water and chloride ancillary ligation for platinum arises from the fact that the Pt(IV)/Pt(II) couple and the Pt(II)/Pt(0) couple have virtually the same redox potentials. Hence, Pt(II) may compete with Pt(IV) in the oxidation step (ii) and Pt(0) deposits from solution. Platinum metal particles appear to catalyze unwanted over-oxidation reactions.

Using this mechanistic model as a guide, cationic Pt(II) systems have been developed that effectively

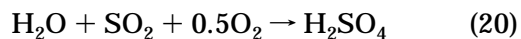
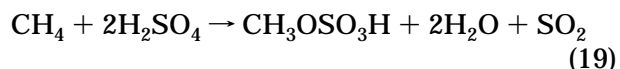
activate alkanes, e.g., $[(\text{tmeda})\text{Pt}(\text{CH}_3)(\text{sol})]^+$ and most recently $[(\text{diimine})\text{Pt}(\text{CH}_3)(\text{sol})]^+$, with solv = pentafluoropyridine, nitromethane, and $\text{CF}_3\text{CH}_2\text{-OH}$.¹⁰⁴ Significantly, step i is most likely endothermic, and the success of the alkane functionalization with these highly electrophilic metal complexes results from oxidation of the intermediate Pt(II)–alkyl, competitive with reprotonation to alkane via the reverse sequence. Obviously, replacing $[\text{PtCl}_6]^{2-}$ with more practical alternative oxidants, most preferably O_2 , is required for developing a practical oxidative functionalization system. A very promising finding in this regard is that certain types of Pt(II) dialkyls undergo clean reactions with O_2 in alcohols to generate Pt(IV) alkoxy–hydroxides¹⁰⁵ (eq 17). Coupling this reaction as a replacement for step iii, although clearly nontrivial, would demonstrate the electrophilic approach to alkane oxidative functionalization, offering exciting possibilities for further development.

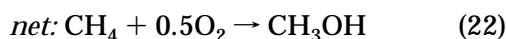
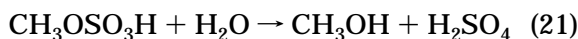


Catalytica developed some strategies for the selective oxidation of methane to methyl hydrogensulfate utilizing electrophilic metal complexes in sulfuric acid. One of the first systems developed utilizes Hg^{2+} in sulfuric acid.^{101,106} Maximum one-pass yields of approximately 40% at $\geq 90\%$ selectivity are obtained (eq 18, Figure 8).

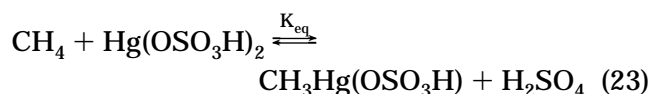


A potentially practical scheme based on the known oxidation of SO_2 and hydrolysis of methyl esters can be envisioned (eqs 19–22).

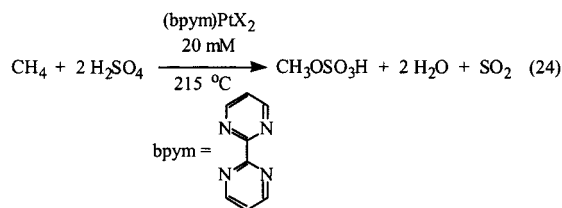




The key features of the reaction mechanism appear to involve three stages: (i) dissociative substitution of methane for a ligand (likely hydrogensulfate) at Hg^{2+} to generate a methane σ complex, which subsequently undergoes deprotonation to a methylmercury intermediate, (ii) functionalization by $\text{S}_{\text{N}}2$ displacement of methyl hydrogensulfate with reduction of mercury and net formation of mercurous hydrogensulfate, and (iii) oxidation of mercurous to mercuric by sulfuric acid with release of SO_2 and water. Interestingly, the first stage, methane activation, is reversible and the equilibrium constant for methylmercury formation is approximately 1.0 under reaction conditions (eq 23).



Other electrophilic cations have been investigated in an effort to find a substitute for $\text{Hg}(\text{II})$. Recently, the Catalytica group established that $\text{Pt}(\text{II})$ with the chelate bipyrimidine provides a superior catalyst system as compared to the mercury system.¹⁰⁷ Moreover, this catalyst is thermodynamically robust and may be generated not only by addition of bipyrimidine to $[\text{PtCl}_2]_n$ in sulfuric acid, but also via oxidation of platinum black by bipyrimidine/ H_2SO_4 mixtures at 220 °C (eq 24). Maximum one-pass yields of methyl

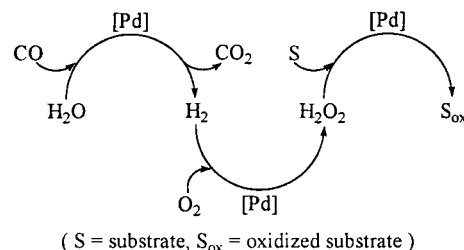


hydrogensulfate with this system are approximately 73%. Not surprisingly, there are many mechanistic similarities of this system with the original Shilov platinum system that operates in aqueous solution with $\text{Pt}(\text{IV})$, rather than with sulfuric acid as oxidant.

While the yields of this catalytic system are among the highest ever reported for the direct oxidation of methane to an oxygenate, there are several disadvantages that have prevented commercialization of the process. The most important factors in decreasing order of disadvantage are as follows: (a) turnover frequencies are still at least 2 orders of magnitude too low, (b) methanol recovery from concentrated sulfuric acid is too costly, and (c) SO_2 reoxidation to sulfuric acid is impractical. As an indication of the commercial possibilities of such systems, several companies have worked on various approaches to overcoming the key disadvantages with, however, no success to date.

Recently, two catalytic systems have been reported which *simultaneously* activate both dioxygen and alkane C–H and C–C bonds, resulting in the direct oxidations of alkanes.^{108,109} Although the mechanisms of these reactions have not yet been established, their

Scheme 2. Palladium-Catalyzed Oxidation of Alkanes with CO and O_2



general features, especially the chemoselectivities (higher reactivity of alkanes compared to alcohols; preference for methyl groups in functional organics), suggest that alkane activation likely occurs by an electrophilic pathway as discussed above. In the first system, a combination of metallic Pd and Cu chloride was found to catalyze the oxidation of methane and ethane by dioxygen at 70–110 °C in the presence of carbon monoxide.¹⁰⁹ No alkane oxidation is observed in the absence of added carbon monoxide. Studies indicated that the overall transformation encompasses three catalytic steps in tandem (Scheme 2). The first step is the water–gas shift reaction involving the oxidation of carbon monoxide to carbon dioxide with the simultaneous formation of dihydrogen. It is possible to bypass this step by replacing carbon monoxide with dihydrogen. The second catalytic step involves the combination of dihydrogen with dioxygen to yield hydrogen peroxide (or its equivalent). The final step involves the metal-catalyzed oxidation of the substrate by hydrogen peroxide (or its equivalent).

In the second (slower) system, RhCl_3 in the presence of several equivalents of chloride and iodide is found to catalyze the direct functionalization of methane in the presence of carbon monoxide and dioxygen at 80–85 °C.¹⁰⁸ The reaction proceeds in water to yield acetic acid as the principal product. It is possible to selectively form either methanol or acetic acid by a simple change in the solvent system.

The Pd/Cu- and the Rh-based systems exhibit similar selectivity patterns that are, for the most part, without precedent. For example, in both cases, methane is significantly more reactive (>5 times) than methanol. For the Rh-based system, even methyl iodide is found to be less reactive than methane. A more interesting reactivity pattern exhibited by these two systems is their preference for C–C cleavage over C–H cleavage in the case of higher alkanes. For example, the Rh-based system converted ethane to a mixture of methanol, ethanol, and acetic, with the ratio of products formed through C–H versus C–C cleavage of ~0.6 on a per bond basis. A curious aspect of the Pd/Cu- and Rh-based systems is that, apart from their ability to simultaneously activate both dioxygen and alkane, both require a coreductant (carbon monoxide). Thus, there is a striking resemblance to monooxygenases, which require a coreductant to deliver one oxygen per O_2 reactant.

E. Enzymatic and Biomimetic Systems

Nature has evolved a number of iron-requiring enzymes that activate dioxygen and catalyze the

oxidation of aliphatic C–H bonds.^{110a} Prominent among these are the heme-containing cytochrome P450 and the nonheme enzymes methane monooxygenase and fatty acid desaturases. Since these hydrocarbon oxidation reactions in biology are carried out at ambient temperature and pressure, catalysts designed based on this chemistry may have the advantage of requiring significantly less energy input than present technology based on heterogeneous catalysts. In the 1980s, much of the effort in biomimetic oxidations focused on the use of iron porphyrin catalysts, paralleling the development in our understanding of the mechanism of cytochrome P450. However, porphyrin ligands are susceptible to oxidative destruction, so more robust alternative ligand systems are desired.

Stimulated by early work on cytochrome P-450 mimics,^{110b} metalloporphyrin complexes have been employed either as catalysts for the oxidation of alkanes using single oxygen atom transfer agents such as iodosyl benzene or for direct reaction of the alkane with molecular oxygen.^{110c} When oxygen is used as the oxidant, elevated temperatures are required for alkane conversions, radical reactions predominate, and the metalloporphyrin catalysts suffer rapid oxidative degradation. Total replacement of the 28 hydrogens of metallotetraphenylporphyrin complexes with halogens (F, Cl, Br) enhances the stability of the complexes to oxidative degradation, causes large increases in the $M(n+1)/M(n)$ reduction potential, and greatly increases catalytic activity toward oxidation of secondary and tertiary C–H bonds in alkanes by accelerating selective homolytic decomposition of intermediate hydroperoxides to alcohols via alkoxy radicals.^{110c}

Transition-metal complexes, such as cobalt carboxylates and acetylacetonates, have long been used in the industrial production of oxygenates from alkanes such as cyclohexane, butane, and others. These promoters of alkane autoxidation exhibit low activity toward alkanes. The unreactive primary C–H bonds are inaccessible, and elevated temperatures are necessary for activating secondary and tertiary C–H bonds in alkanes. Since high temperatures accelerate C–C bond cleavage reactions in alkoxy radical intermediates, many undesirable byproducts can result and selectivity to the desired oxygenate can be poor. Some of the problems encountered with application of traditional metal complexes can be illustrated by oxidations of isobutane to *tert*-butyl alcohol, TBA, in the presence of cobalt salts.^{110d} When isobutane is oxidized in the presence of cobalt(II) acetylacetonate at 100 °C, *tert*-butyl hydroperoxide, TBHP, is a major product together with TBA. When the temperature is raised to 150 °C, TBHP is substantially decomposed but major byproducts of C–C cleavage including acetone and CO₂ are formed. At intermediate temperatures one observes the worst of both worlds in which both unwanted hydroperoxide and C–C bond cleavage products are formed. In all cases, TBA selectivity is low, never exceeding 77%.

By comparison, the autoxidation of isobutane to TBA can be carried out in the presence of [*meso*-tetrakis(pentafluorophenyl)- β -octachloroporphyrin]-

iron(III) hydroxide at room temperature, giving TBA in 95% selectivity with very little C–C bond cleavage.^{110c} Industrially acceptable rates can be achieved at 80 °C while maintaining 90% selectivity at a 50% conversion level. No hydroperoxide build up can be detected. The reason for not observing TBHP in crude reaction products and for accelerated reaction rates using these electron-deficient metalloporphyrin complexes is their extremely high activity for decomposing hydroperoxides, acting as living initiators that continuously provide high radical flux at low reaction temperatures.

The unusually high reactivity of electron-deficient metalloporphyrin complexes toward hydroperoxidic intermediates has stimulated several additional applications of these versatile catalysts. Direct, selective decomposition of hydroperoxides to alcohols gives near quantitative yields of cyclohexanol or TBA when electron-deficient iron perhaloporphyrin catalysts are used. Electron-deficient ruthenium complexes are able to catalyze the direct oxidation of alkanes using hydroperoxides as oxidants. This reaction has potential application in the generation of nylon intermediates from cyclohexane. Co-oxidations of alkanes in the presence of easily activated C–H bonds can bring more difficult secondary C–H bonds into reaction. For instance, co-oxidation of cyclohexane with acetaldehyde gives KA oil (a ~9:1 mixture of cyclohexanol:cyclohexanone used in Nylon manufacture) in good yield with tens of thousands of turnovers using electron-deficient ruthenium or manganese fluoroporphyrin complexes.^{110e} Acetaldehyde is oxidized to the peracid, which in turn is the oxidant for cyclohexane. A process has been envisioned^{110e} for the co-oxidation of acetaldehyde and cyclohexane to produce KA oil and acetic acid as coproducts.

Despite being highly efficient, alkane autoxidation catalysts which afford high turnover rates for alkanes having tertiary C–H bonds, electron-deficient metalloporphyrin complexes are not yet active enough to give the rapid rates of unactivated secondary C–H bonds at the low temperatures needed for commercial applications. Although they are more stable under oxidation conditions than unsubstituted metalloporphyrins that have many C–H bonds, they are still not robust enough to be used in most industrial applications. Finally, even though improved synthetic procedures have been developed, they are still too expensive to be used for catalysts in commodity chemical oxidations. If longer lived, more active, and less expensive analogues could be designed and synthesized, the selectivity of a number of important catalytic chemical process technologies could be vastly improved. These might include the direct oxidations of cyclohexane to KA oil, isobutane to TBA, propane to IPA/acetone, butane to MEK/*s*-butyl alcohol and others. Catalysts of this type would complement the electrophilic complexes which preferentially attack primary C–H bonds, affording catalysts which attack secondary and tertiary C–H bonds in preference to primary bonds, and do so in a selective manner without forming CO₂ and other unwanted byproducts. Such a battery of new complexes, if they could be developed, would provide the ability to

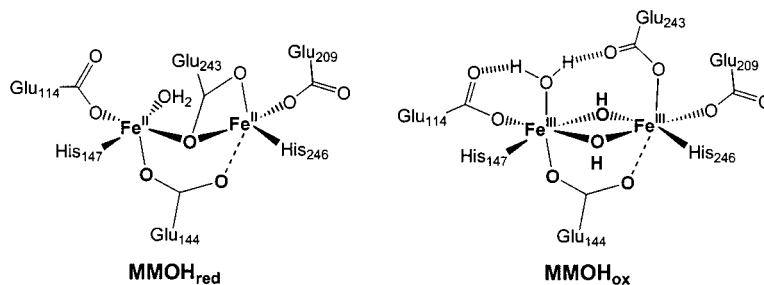


Figure 9. Structures of the reduced and oxidized forms for the methane monooxygenase hydroxylase component (MMOH).

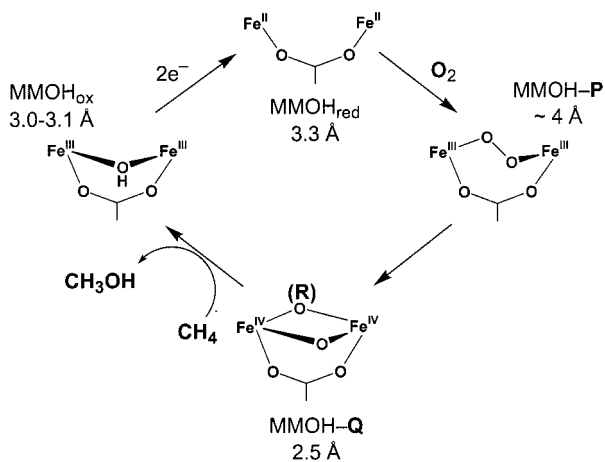


Figure 10. Proposed oxygen activation mechanism for methane monooxygenase.

selectively activate primary, secondary, and tertiary C–H bonds in alkanes to give valuable oxygenates at will.

In the past 10 years, research efforts on methane monooxygenase and related enzymes have substantially increased our understanding of oxygen activation at nonheme diiron active sites.¹¹⁰ Figure 9 shows the active site of the hydroxylase component of methane monooxygenase (MMOH) in its reduced and oxidized forms as deduced from X-ray diffraction.¹¹¹ The nonheme diiron center is coordinated to six amino acid ligands, namely, two histidines and four carboxylates. Two of the carboxylates act as bridging ligands to the diiron center in MMOH_{red} , with available sites for dioxygen binding. Upon exposure to O_2 , MMOH_{red} is converted to MMOH_{ox} and the monodentate carboxylate bridge becomes a terminal ligand with two solvent-derived ligands taking its place as bridges. Oxygen activation proceeds via two key intermediates, MMOH-P and MMOH-Q , identified in the rapid kinetic studies of Lipscomb and Lippard. Figure 10 illustrates a proposed mechanism for MMO, with oxidation state assignments derived from Mössbauer measurements. The proposed mechanism follows the paradigm for oxygen activation by metalloenzymes where dioxygen first binds to a reduced metal center to form a metal–peroxo species, which is then converted to high-valent metal–oxo species that serve as the actual oxidizing agent of the reaction. Two electrons from an electron donor such as NADH are required to close the catalytic cycle. The core structures associated with MMOH-P and MMOH-Q are proposed on the basis of comparisons with available model complexes.^{112a} MMOH-P is deduced to be a (μ -1,2-peroxo)diiron(III) species on

the basis of the similarity of its optical and Mössbauer properties^{112b} to those of $[\text{Fe}_2(\mu\text{-O}_2)(\mu\text{-C}_6\text{H}_5\text{-CH}_2\text{CO}_2)_2(\text{Tp}^i\text{Pr}_2)_2]$ (Tp^iPr_2 = hydridotris(3,5-diisopropylpyrazolyl)borate anion), a model complex first synthesized by Kitajima and more recently structurally characterized by Kim and Lippard.^{112c} Similarly, MMOH-Q is proposed to have an $\text{Fe}_2(\mu\text{-O})_2$ diamond core structure.^{112d} EXAFS studies show that MMOH-Q has an Fe–Fe distance of 2.5 Å, a short distance which requires the presence of two or three single-atom bridges. To date, the only synthetic high-valent complex with a comparably short Fe–Fe distance is $[\text{Fe}^{\text{III}}\text{Fe}^{\text{IV}}(\mu\text{-O})_2(5\text{-Et}_3\text{-TPA})_2](\text{ClO}_4)_3$ (5-Et₃-TPA = tris(5-ethyl-2-pyridylmethyl)amine), which has an $\text{Fe}_2(\mu\text{-O})_2$ diamond core with a 2.68 Å Fe–Fe distance.^{112e} One or two additional carboxylate bridges may be required in the enzyme to shrink this distance to 2.5 Å. The catalytic cycle as presented in Figure 10 thus requires the active site to accommodate a change of Fe–Fe distance from 2.5 to 4.0 Å.

Reactivity studies show that $[\text{Fe}^{\text{III}}\text{Fe}^{\text{IV}}(\mu\text{-O})_2(\text{TPA})_2]^{3+}$ (TPA = tris(2-pyridylmethyl)amine) can oxidize cumene to cumyl alcohol and α -methylstyrene, transformations analogous to the hydroxylation and dehydrogenation reactions catalyzed by methane monooxygenase and fatty acid desaturases.^{113a} Thus, a high-valent $\text{Fe}_2(\mu\text{-O})_2$ diamond core is a viable candidate to carry out the oxidation chemistry of these enzymes. However, the synthetic complex is incapable of attacking C–H bonds stronger than benzylic C–H bonds. This less than desirable oxidative reactivity may derive from the fact that the synthetic complex is in the $\text{Fe}^{\text{III}}\text{Fe}^{\text{IV}}$ oxidation state, rather than the $\text{Fe}^{\text{IV}}\text{Fe}^{\text{IV}}$ state associated with MMOH-Q . Since the synthetic complex is obtained from the reaction of a diiron(III) precursor with H_2O_2 , intermediates analogous to MMOH-P and MMOH-Q may be involved en route to the formation of the $\text{Fe}^{\text{III}}\text{Fe}^{\text{IV}}$ complex. Thus, when 10 equiv of H_2O_2 is added to the precursor complex in the presence of cyclohexane, cyclohexanol and cyclohexanone are obtained in a 4:1 ratio with 40% of the oxidant converted to oxidized hydrocarbon products.^{113b} Subsequent addition of more aliquots of H_2O_2 affords more products in the same ratio at the same peroxide conversion efficiency. These results demonstrate that the $\text{Fe}(\text{TPA})/\text{H}_2\text{O}_2$ combination produces an oxidant capable of attacking the C–H bonds of cyclohexane.

There have been many reports of alkane oxidation by combinations of iron complexes and peroxide oxidants.^{113c} Often such combinations give rise to Haber–Weiss chemistry and the aliphatic C–H bond is cleaved by an alkoxy or hydroxy radical. Subse-

quent trapping of the incipient alkyl radical by O_2 leads to approximately equimolar amounts of alcohol and ketone products. However, by careful control of the concentration of peroxide, the involvement of Haber–Weiss chemistry can be minimized and oxidation by a metal-based oxidant can be manifested. To illustrate, the addition of 10 equiv of H_2O_2 to a 1 mM CH_3CN solution of $[Fe_2O(TPA)_2(H_2O)_2]^{4+}$ results in an immediate evolution of O_2 due to the formation of hydroxyl radicals and attendant decomposition of H_2O_2 . If the oxidant is instead syringe-pumped into the solution in the presence of cyclohexane over a 15 min period, 40% of the peroxide is converted to cyclohexanol and cyclohexanone in a 4:1 ratio.^{113b} The high alcohol/ketone (A/K) ratio suggests that a radical chain mechanism is not involved, a notion further supported by the fact that the A/K ratio is unaffected by carrying the reaction out under Ar. More convincingly, the oxidation reactions are stereospecific (e.g., in the case of *cis*-1,2-dimethylcyclohexane).^{113c} Indeed, this system represents the first example of stereospecific oxidation by a synthetic nonheme iron catalyst. These observations exclude the significant participation of hydroxy radicals in the mechanism. Furthermore, reactions carried out in the presence of $H_2^{18}O$ yield alcohol products that incorporate label from the solvent.^{113d} This result provides strong evidence for the involvement of a high-valent iron–oxo species that can undergo oxygen-atom exchange with water in the solvent prior to the formation of the product C–O bond. The demonstration that a simple nonheme iron complex can catalyze stereospecific alkane hydroxylation via a nonradical mechanism akin to that proposed for methane monooxygenase brightens prospects for developing inexpensive biomimetic iron catalysts that can hydroxylate alkanes.

F. Novel Reactor Concepts

The successful development of new processes for the oxidative conversion of alkanes to olefins and oxygenates will likely require novel types of reactors as well as novel catalysts. Such reactors may utilize ultrashort contact times, cycling catalyst beds, catalyst recirculation between oxidizing and reducing conditions, and the integration of chemical reaction and separations. The potential for ultrashort contact time (~ 1 ms) reactors has recently been demonstrated for the oxidative conversion of methane to synthesis gas (CO and H_2) and for the oxidative dehydrogenation of ethane to ethene. For example, methane + O_2 can be converted to synthesis gas with greater than 95% selectivity at 1273 K over Rh/Al_2O_3 ¹¹⁴ and ethane + O_2 can be converted to ethene with over 85% selectivity at 1123 K over Pt/Al_2O_3 .¹¹⁵

Oxidation of alkanes and olefins under anaerobic conditions utilizing only the oxygen derived from the catalyst itself has been demonstrated to result in higher selectivities to oxygenated products than can be achieved when hydrocarbon and oxygen are cofed. For example, DuPont commercialized a process for converting butane to maleic anhydride using a recirculating fluidized bed (see Figure 11).¹¹⁶ The catalyst, a specially formulated vanadium pyrophos-

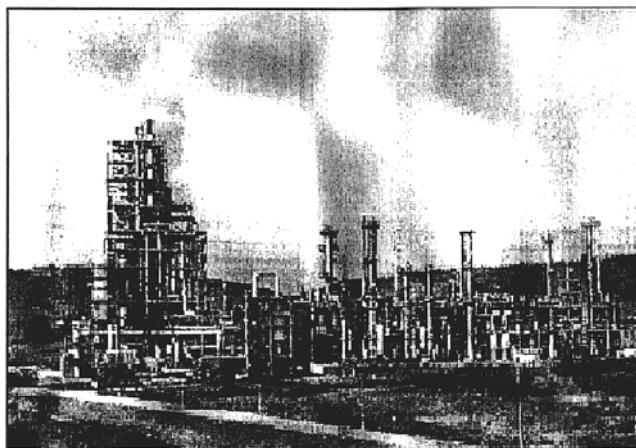
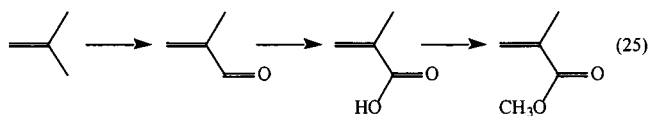


Figure 11. Recirculating fluidized-bed process for butane oxidation to maleic anhydride commercialized by DuPont.

phate, is circulated from a riser reactor where it is contacted with butane to a fluidized regeneration reactor where it is then reoxidized. By this means, a maleic anhydride selectivity improvement of 10–15% is achieved in an anaerobic environment versus operation in a conventional fixed bed using air. In addition, since no oxygen is present with the hydrocarbon, much higher concentrations of maleic anhydride can be obtained, resulting in significantly lower downstream investments. The advantages of anaerobic oxidation have also been demonstrated on the pilot-plant scale for butane oxidation to butadiene and in the laboratory for isobutene dimerization to 2,5-dimethyl-1,5-hexadiene.¹¹⁷

G. Alternative Processes

Creative thinking is required to develop new routes to large-scale commodity chemicals that reduce investment and give higher yields. An example is the production of methyl methacrylate (MMA). MMA is currently prepared from isobutylene via two high-temperature gas-phase oxidations followed by esterification (eq 25). These high-temperature conditions



result in low yield and carbon dioxide production. Asahi Chemical is in the process of building a new plant¹¹⁸ based on the oxidative esterification of methacrolein directly to MMA. This new process operates in a slurry phase, under mild conditions, and eliminates one process step.¹¹⁹ Overall yield is much higher and investment is lower.

H. Alternative Oxidants

Although air is the cheapest source of oxygen, it provides the lowest selectivity in many reactions. Over the past 10 years, new catalysts have been developed for the use of oxidants such as hydrogen peroxide, alkylhydroperoxides, and nitrous oxide. Panov¹²⁰ discovered that an Fe-doped ZSM-5 catalyst is very selective for the oxidation of benzene to phenol with N_2O . At temperatures of 300–500 °C, selectivity

to phenol is reportedly >99%. The process has been developed by Monsanto (Solutia)¹²¹ to take byproduct N₂O from adipic acid manufacture and use it to hydroxylate benzene. The phenol is then hydrogenated to cyclohexanone and oxidized to adipic acid. This discovery represents a significant improvement in the economics for Nylon intermediates production. Chemists at Enichem found that a titanosilicalite catalyst is very effective for mediating the reaction between hydrogen peroxide and olefins, aromatics, and ketones.¹²² This catalysis has been extended to macroporous silicates and other metals.¹²³ While the use of these oxidants provides cleaner processes and produces less carbon dioxide, the cost of N₂O and H₂O₂ relative to air prevent wider applications beyond those used at present. Either environmental regulations or unique situations will be required to see these oxidants applied to large-volume chemical synthesis. Needless to say, the mechanisms of these processes are not well understood.

I. Research Challenges and Needs

A number of significant challenges must be overcome in order to develop catalysts for the selective, energy-efficient oxidation of alkanes to valuable chemical products without large quantities of unwanted byproducts such as CO₂. These include the following: (1) identification of the reaction pathways leading to primary and secondary products and determination of the rate coefficients for each path; (2) in situ identification of reactive intermediates; (3) determination of the reactivity of different forms of oxygen present at the catalyst surface and their role in catalyzing desired and undesired oxidation processes; (4) identification of the elementary processes involved in hydrogen abstraction, carbon-carbon bond cleavage, and oxygen insertion and the role of redox properties of metal cations in these processes; (5) establishment of the relative reactivities of carbon-hydrogen bonds (1°, 2°, 3°, H-CH₂X (X = OH, halide, etc.) toward soluble transition-metal complexes capable of electrophilic C-H bond activation; (6) identification of the mechanisms and requirements for oxidation of Pt(II) alkyls; (7) developing approaches for rapid screening of potential electrophilic transition-metal complexes for selective, *catalytic* hydrocarbon oxidations under dioxygen; and (8) for new biomimetic catalysts, the development of robust ligands that can withstand oxidizing conditions of the reaction, the design of reaction conditions that maintain low oxidant concentrations to minimize undesirable side reactions such as hydroxy radical formation, and the development of catalysts that utilize O₂ as oxidant.

To meet these objectives will require the following: (1) synthesis of model catalytic systems containing well-defined sites; (2) in situ studies involving a variety of spectroscopic techniques, designed to determine the nature of the active sites, active phases, and reaction; (3) utilization of computational formalisms to determine the relationships between catalyst site composition and structure and the manner by which oxygen atoms associated with the site interact with hydrocarbons; (4) exploration of novel reactor

concepts (e.g., ultrashort contact times, recirculating beds) to achieve higher product selectivities than those that can be obtained with conventional fixed-bed reactors; (5) while the desire is *not* to operate in an explosive regime and to control the possibility of any explosion, those working in the explosive regimes needed for rapid screening for selective, catalytic hydrocarbon oxidations under dioxygen will require special safety requirements, including high-pressure, blast-proof reactors. Collaborations between academic, industrial, and national laboratories would allow such studies, since most academic laboratories do not have experience working with these explosive mixtures and do not have the specialized equipment required.

IV. Utilization of Carbon Dioxide

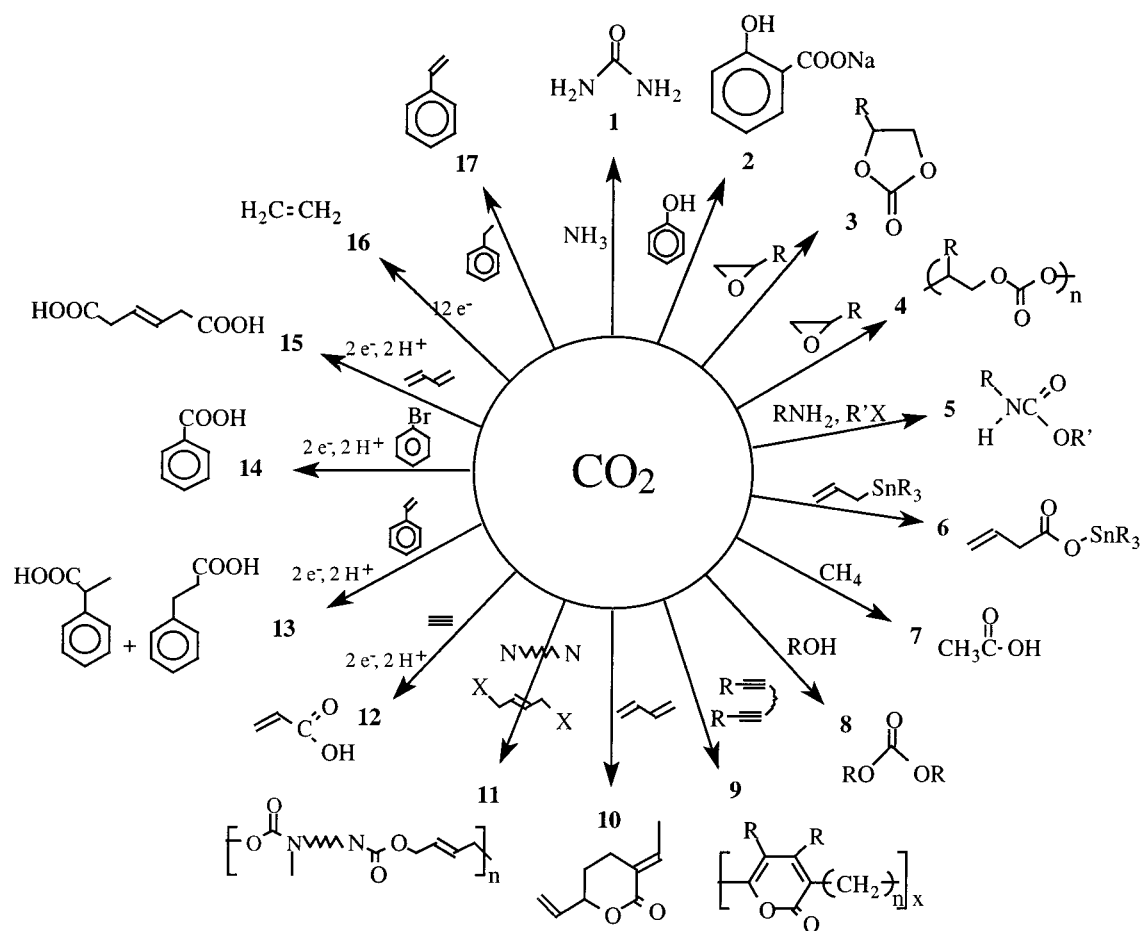
A. Introduction

Carbon dioxide recovered from flue stacks or the atmosphere can be sequestered in oceans or spent gas and oil wells in an effort to mitigate atmospheric CO₂ increases. Alternatively, recovered CO₂ can be used for producing chemicals, fuels, and other useful products. There are a number of recent reviews and books on various aspects of CO₂ utilization.¹²⁴ The objective here is to provide a brief review of research progress in the field, to identify barriers to further progress, and to suggest possible avenues for future research.

There are several motivations for producing chemicals from CO₂ whenever possible. (1) CO₂ is a cheap, nontoxic feedstock that can frequently replace toxic chemicals such as phosgene or isocyanates. (2) CO₂ is a totally renewable feedstock compared to oil or coal. (3) The production of chemicals from CO₂ can lead to totally new materials such as polymers described below. (4) New routes to existing chemical intermediates and products could be more efficient and economical than current methods. (5) The production of chemicals from CO₂ could have a small but significant positive impact on the global carbon balance.

As fossil fuels are depleted and/or global warming becomes severe, renewable energy (solar electric, wind, hydroelectric, geothermal, solar thermal, and biomass) and nuclear energy will become our primary energy sources. Of these future energy sources, only biomass produces fuels directly. Although biomass-derived fuels will doubtless contribute to meeting future fuel requirements, they will not be able to meet a large fraction of future fuel needs. The reduction of CO₂ to methanol, methane, and other carbon-based fuels using renewable energy sources or nuclear energy would provide a future energy distribution system based on high-energy density liquid and gaseous fuels and without any net increase in atmospheric CO₂. This could have a significant impact on future CO₂ emissions, especially from the transportation sector.

Carbon dioxide is generally considered to be a green, or environmentally benign, solvent in that it is relatively nontoxic, is nonflammable, and is naturally abundant. As such, CO₂ has been suggested as

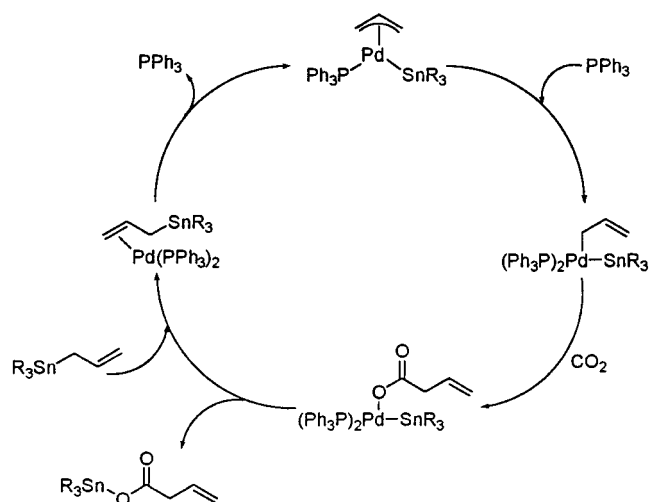
Scheme 3. Chemical Transformations of CO₂

a sustainable replacement for organic solvents in a number of chemical processes.¹²⁵ While CO₂ is certainly not a panacea, it possesses a number of characteristics that suggest the use of CO₂ could provide both environmental and economic benefit.

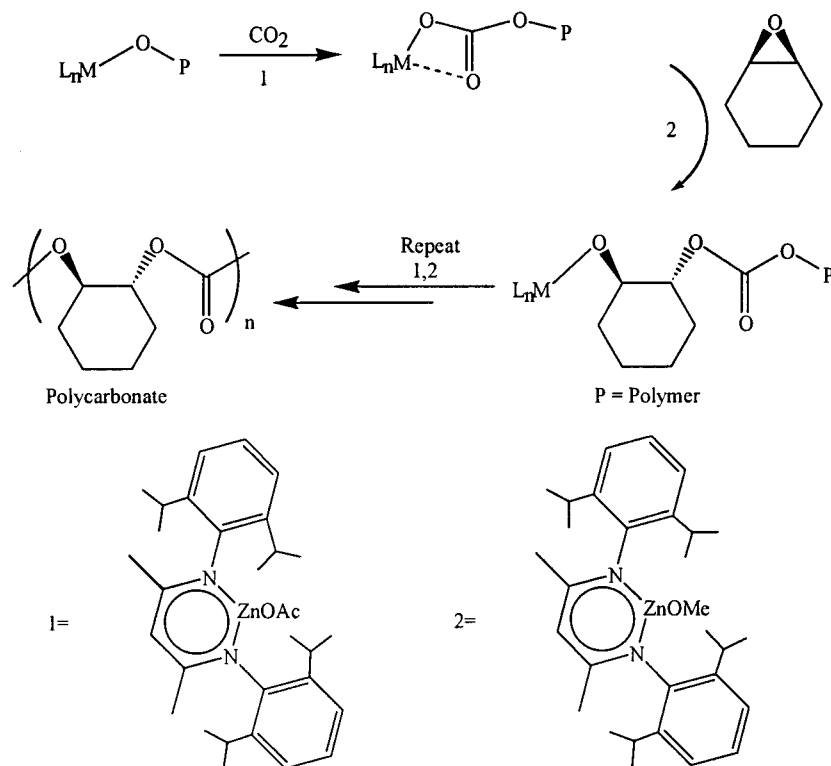
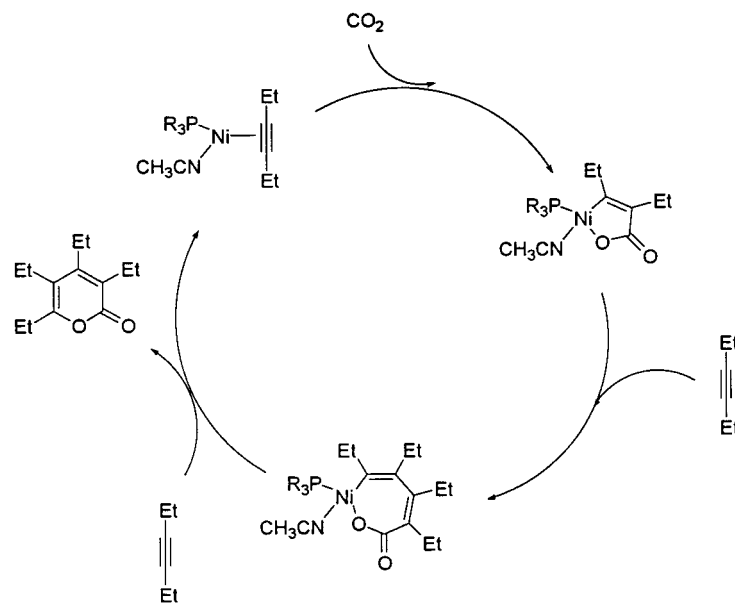
B. Current Status*1. Chemicals*

Approximately 110 MT (megatons) of CO₂ are currently used for chemical synthesis annually.^{126a} The chemicals synthesized include urea (**1**), salicylic acid (**2**), cyclic carbonates (**3**), and polycarbonates (**4**). The largest of these uses is urea production, which reached approximately 90 million metric tons per year in 1997.^{126b} In addition to these commercial processes using CO₂ (compounds **1–4** in Scheme 3), there are a number of reactions currently under study in various laboratories that hold promise (remaining reactions in Scheme 3). These reactions differ in the extent to which CO₂ is reduced during the chemical transformation.^{126c}

The simplest reactions of CO₂ are those in which it is simply inserted into an X–H bond. Examples are the insertion of CO₂ into organic amines to afford carbamic acids which may be converted into organic carbamates.^{127,128} More recent examples include the insertion of CO₂ in P–N bonds of P(NR₂)₃ compounds to form P(NR₂)(CONR₂)₂ compounds and the reaction of ammonium carbamates (derived from CO₂)

Scheme 4. Proposed Mechanism for the Pd-Catalyzed Coupling of CO₂ and Allyl Tin Compounds

with alkyl halides in the presence of crown ethers to form useful urethane intermediates (**5**).¹²⁸ This is an example of using CO₂ to replace phosgene, a highly toxic intermediate in chemical synthesis.¹²⁹ Reactions are known in which CO₂ undergoes insertion into Sn–C bonds of allyl tin compounds to form carboxylated allyl derivatives (**6**)¹³⁰ and which are catalyzed by Pd complexes; these are shown in Scheme 4. Another interesting reaction is the insertion of CO₂ into alkanes such as methane to form acetic acid

Scheme 5. Zinc-Catalyzed Copolymerization of CO₂ with Oxiranes**Scheme 6. Proposed Mechanism for the Nickel-Catalyzed Coupling of CO₂ and Acetylenes**

(7).¹³¹ Although the turnover numbers for this catalytic process are low, the simultaneous activation of a C–H bond and CO₂ insertion is intriguing. The thermodynamics of this reaction are marginal; however, adjusting the reaction conditions and coupling this reaction with energetically favorable product processes could improve conversion efficiencies. Carbonates, (RO)₂CO (**8**), can also be prepared by inserting CO₂ into O–H bonds followed by dehydration or by oxidative carboxylation of olefins.¹³² This synthetic approach has the possibility of providing a new route to compounds that have very large potential markets.

Related reactions in which CO₂ is incorporated into product molecules without reduction have been used

in the synthesis of polymers. Initial work in this area was performed by the groups of Inoue¹³³ and Kuran.¹³⁴ In recent years, a number of new catalysts have been developed for copolymerization of CO₂ and oxiranes to form polycarbonates (**4**),¹³⁵ an example is shown in Scheme 5. These studies have increased the productivity of this reaction by ~10² times and have also expanded the range of applicable monomers (oxiranes). Another potentially interesting new class of polymers, polypyrones (**9**, Scheme 3), has been prepared from diacetylenes and CO₂ in the presence of Ni catalysts; the suggested pathway is shown in Scheme 6.¹³⁶ A related reaction is the telomerization of butadiene and CO₂ to produce lactones (**10**), which

can be important chemical intermediates.¹³⁷ Polyurethanes (**11**) have also been prepared by the reactions of dicarbamate ions formed by insertion of CO₂ into diamines, followed by Pd-catalyzed coupling to 1,4-dichloro-2-butene.¹³⁸

Reductive carboxylations in which the CO₂ unit is incorporated into the product are also known. In the case of alkynes and olefins, electrochemical reductive carboxylations result in effective addition of the formic acid C–H bond to C–C double or triple bonds. For example, building on the earlier stoichiometric results of Hoberg,¹³⁹ Dunach and co-workers¹⁴⁰ used Ni bipyridine complexes and sacrificial Mg anodes to reductively couple acetylene and CO₂ to form propenic acid (**12**). Similarly, Sylvestri reported that the reductive coupling of CO₂ with styrene (**13**) is catalyzed by benzonitrile.¹⁴¹ Bromoarenes can also be reductively carboxylated to form the corresponding carboxylic acid (**14**) using Ni diphosphine catalysts.¹⁴² More recently, the sequential reductive coupling of two molecules of CO₂ to butadiene to form 3-hexen-1,6-dioic acid has been reported (**15**).¹⁴³ This approach provides a new route to a Nylon precursor. Another important monomer, ethylene (**16**), can be prepared by electrochemical reduction of CO₂ in aqueous solutions with current efficiencies as high as 48%.¹⁴⁴ The production of this monomer by this remarkable 12-electron reduction offers a potential route to polyethylene from CO₂. The preceding results clearly indicate that it may be possible to produce a large variety of polymers in the future using materials derived from CO₂. Under oxidative conditions, CO₂ may react with olefins to afford cyclic carbonates that find wide industrial applications.^{132,145} Heterogeneous catalysts are currently more promising than homogeneous ones in these transformations. Another potentially useful reaction of CO₂ is the dehydrogenation of hydrocarbons. Examples are the dehydrogenation of ethylbenzene and propane over metal oxides to form styrene (**17**) and propene, respectively.^{146,147} In these reactions, no part of the CO₂ molecule is incorporated into the organic product, rather the oxygen of CO₂ serves to remove two H atoms of the hydrocarbon. This reaction is at the opposite extreme of the simple insertion reactions discussed above.

C. Fuels

Unlike chemicals that derive value from their intrinsic chemical and physical properties, the value of fuels is in their energy content and the ease with which they are stored and transported. Currently no fuels are currently made by the reduction of CO₂. This is because the electricity and hydrogen produced today are largely derived from fossil fuels which produce large amounts of CO₂. Renewable energy sources and nuclear energy do not produce CO₂, and therefore, production of fuels from these sources would provide fuels but not contribute to net CO₂ emissions. Equations 27–34 show CO₂ reduction reactions in which energy in the form of electricity or hydrogen, derived from nuclear or renewable resources, is stored as either liquid or gaseous carbon-based fuels (ΔE° and ΔG° values are for 298 K). The

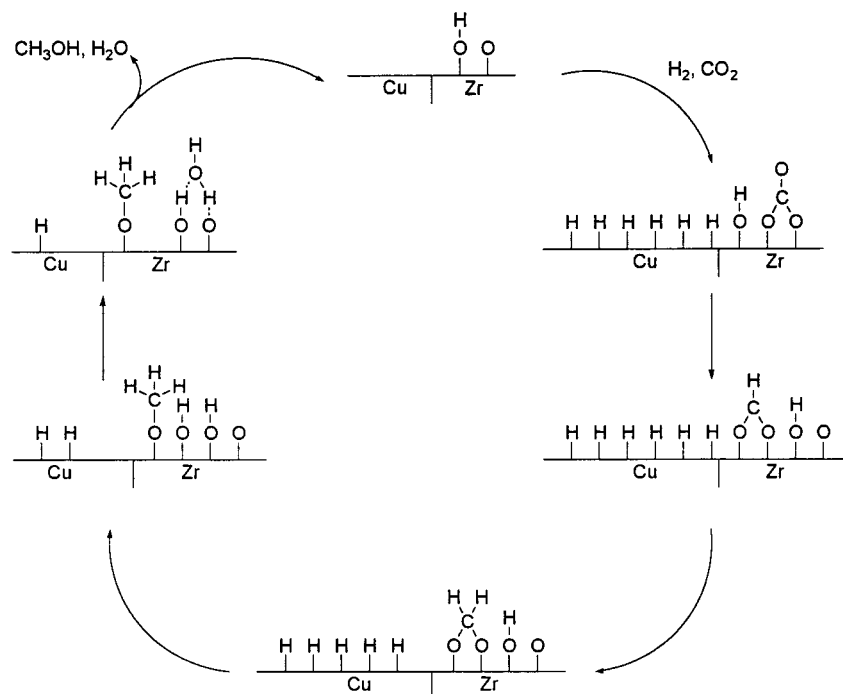
high energy density of these fuels and their transportability makes them desirable; however, the energy required to produce these fuels must be minimized to ensure efficient use of renewable and nuclear energy sources. In general, entropy considerations suggest that these energy storage reactions are best carried out at low temperatures to reduce the free energy required. Both hydrogenation reactions and corresponding electrochemical reactions are shown in eqs 27–34. In the electrochemical reactions, CO₂ is reduced at the cathode and O₂ is produced at the anode. These electrochemical reactions may be considered as the sum of the corresponding hydrogenation reactions and the water splitting reaction shown in eq 26.

	ΔE° (V)	ΔG° (kcal/mol)	
H ₂ O → H ₂ + 0.5O ₂	1.23	56.7	(26)
CO ₂ + H ₂ → HCOOH		5.1	(27)
CO ₂ + H ₂ O → HCOOH + 0.5O ₂	1.34	61.8	(28)
CO ₂ + H ₂ → CO + H ₂ O		4.6	(29)
CO ₂ → CO + 0.5O ₂	1.33	61.3	(30)
CO ₂ + 3H ₂ → CH ₃ OH + H ₂ O		-4.1	(31)
CO ₂ + 2H ₂ O → CH ₃ OH + 1.5O ₂	1.20	166	(32)
CO ₂ + 4H ₂ → CH ₄ + 2H ₂ O		-31.3	(33)
CO ₂ + 2H ₂ O → CH ₄ + 2O ₂	1.06	195	(34)

D. Hydrogenation Reactions

CO₂ is currently used as an additive in the synthesis of methanol from CO and H₂,¹⁴⁸ and it is believed that reduced forms of CO₂ are kinetically important intermediates in this process.¹⁴⁹ Recently, efficient heterogeneous catalysts have been developed for CO₂ hydrogenation to methanol, and pilot-scale plants based on this technology have been demonstrated.¹⁵⁰ However, the thermodynamics for methanol production from H₂ and CO₂ are not as favorable as that for production of methanol from H₂ and CO. For example, at 200 °C the equilibrium yield of methanol from CO₂ is slightly less than 40% while the yield from CO is greater than 80%.¹⁵¹ The reduction of CO₂ can be rendered more favorable by the use of hybrid catalysts that dehydrate methanol to form dimethyl ether.¹⁵² Other copper-based catalysts have also been used for methanol synthesis. Fisher and Bell¹⁵³ studied Cu/ZrO₂/SiO₂ catalysts by in-situ infrared spectroscopy and suggested the pathway shown in Scheme 7 for the route to methanol. Ethanol has also been produced by the hydrogenation of CO₂.¹⁵⁴ This fuel is attractive because it has a somewhat higher energy density than methanol and it is not as toxic. However, the selectivity for ethanol production is generally low (<40%). The hydrogenation of CO₂ to methane and higher hydrocarbons is also known.¹⁵⁵ For C₂ and higher hydrocarbons, hybrid catalysts such as Cu–ZnO–Cr₂O₃ and H–Y zeolite are generally used.

Pioneering work has been carried out by Noyori et al.^{124,156} on the catalytic synthesis of formic acid derivatives by CO₂ hydrogenation, together with other substrates, in supercritical CO₂. In part because of the high solubility of H₂ in scCO₂, an economical synthesis of dimethylformamide is achieved. The

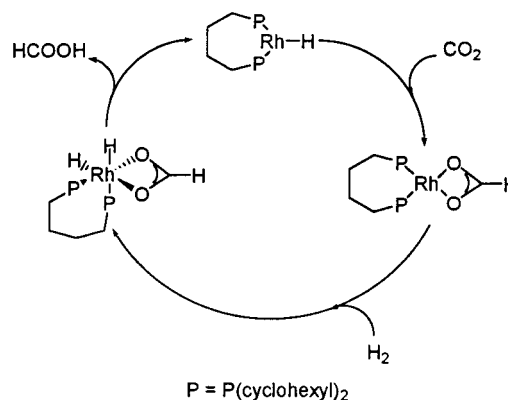
Scheme 7. Proposed Mechanism for the Heterogeneous Catalytic Hydrogenation of CO₂ to Methanol

process is superior to conventional methods because of its high efficiency ($\text{TON} = 4.2 \times 10^5$, where $\text{TON} = \text{moles of product per mole of catalyst}$) and high selectivity; the catalyst precursor is $(\text{Me}_3\text{P})_4\text{RuCl}_2$, and the operating temperature is 100 °C.

Homogeneous catalysts are also known that mediate the rapid hydrogenation of CO₂ to formate.¹⁵⁷ Because this reaction is not thermodynamically favored, amines and supercritical CO₂ have been used to drive this reaction. Under the appropriate conditions, very high turnover numbers and rates can be achieved. For example, Leitner et al. examined complexes of the general type $[\text{R}_2\text{P}-(\text{X})-\text{PR}_2]\text{Rh}(\text{hfacac})$ ($\text{X} = \text{bridging group}$; $\text{hfacac} = 1,3\text{-bis}(\text{trifluoromethyl})\text{-acetylacetonate}$).¹⁵⁸ All of the compounds are active catalysts for formic acid production from H₂ and CO₂, but the most effective has $\text{X} = (\text{CH}_2)_4$ and $\text{R} = \text{cyclohexyl}$ and exhibits a turnover frequency of 1335 h⁻¹ at 25 °C and 40 atm of 1:1 H₂:CO₂. The selectivity to formic acid is nearly 100%; the suggested pathway is indicated in Scheme 8.

E. Electrochemical Reduction of CO₂

Carbon dioxide reduction at a number of metal electrodes has been investigated,¹⁵⁹ and Cu electrodes have been found to catalyze CO₂ reduction to methane in bicarbonate solutions with current efficiencies as high as 65%.¹⁶⁰ Although overpotentials are large (1.5 V), this is a remarkable transformation in which eight electrons are transferred to CO₂ with cleavage of two C–O bonds and formation of four C–H bonds. Cu electrodes have been studied extensively to gain insight into the mechanism, which is thought to involve coordinated CO as an intermediate, and to overcome poisoning of the electrode under catalytic conditions.¹⁶¹ Under slightly different conditions, CO₂ can also be reduced to ethylene at Cu electrodes as discussed above. Copper oxides on gas diffusion

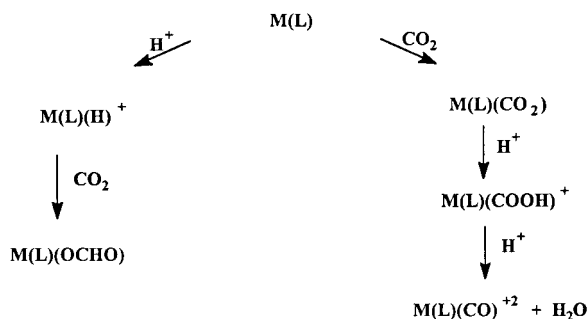
Scheme 8. Proposed Mechanism for the Rhodium-Catalyzed Hydrogenation of CO₂ to Formic Acid

electrodes at large negative potentials have also been reported to reduce CO₂ to ethanol.¹⁶²

Homogeneous electrocatalysts typically catalyze CO₂ reduction by two electrons to either formate or CO together with H₂ formation. However, for some catalysts, CO₂ reduction occurs with current efficiencies close to 100%, even in acidic solutions. This indicates high selectivity for CO₂ reduction over the more thermodynamically favored reduction of protons to H₂. For example, the reduction of CO₂ to CO by nickel cyclam catalysts occurs with nearly 100% current efficiency in water at pH 4.1,¹⁶³ and CO₂ is reduced to CO in 0.02 M HBF₄ in dimethylformamide solutions with current efficiencies greater than 95%.¹⁶⁴ In addition, some of these catalysts operate at low overpotentials so that the conversion of electrical to chemical energy is highly efficient. The selectivity in these cases appears to arise from the preferential reaction of 17-electron intermediates with CO₂ rather than protons.

This selectivity of reduced forms of the catalyst for H⁺ versus CO₂ also appears to determine the nature

Scheme 9. Possible Pathways for the Competing Interaction of Low-Valent Catalysts with Protons or CO₂

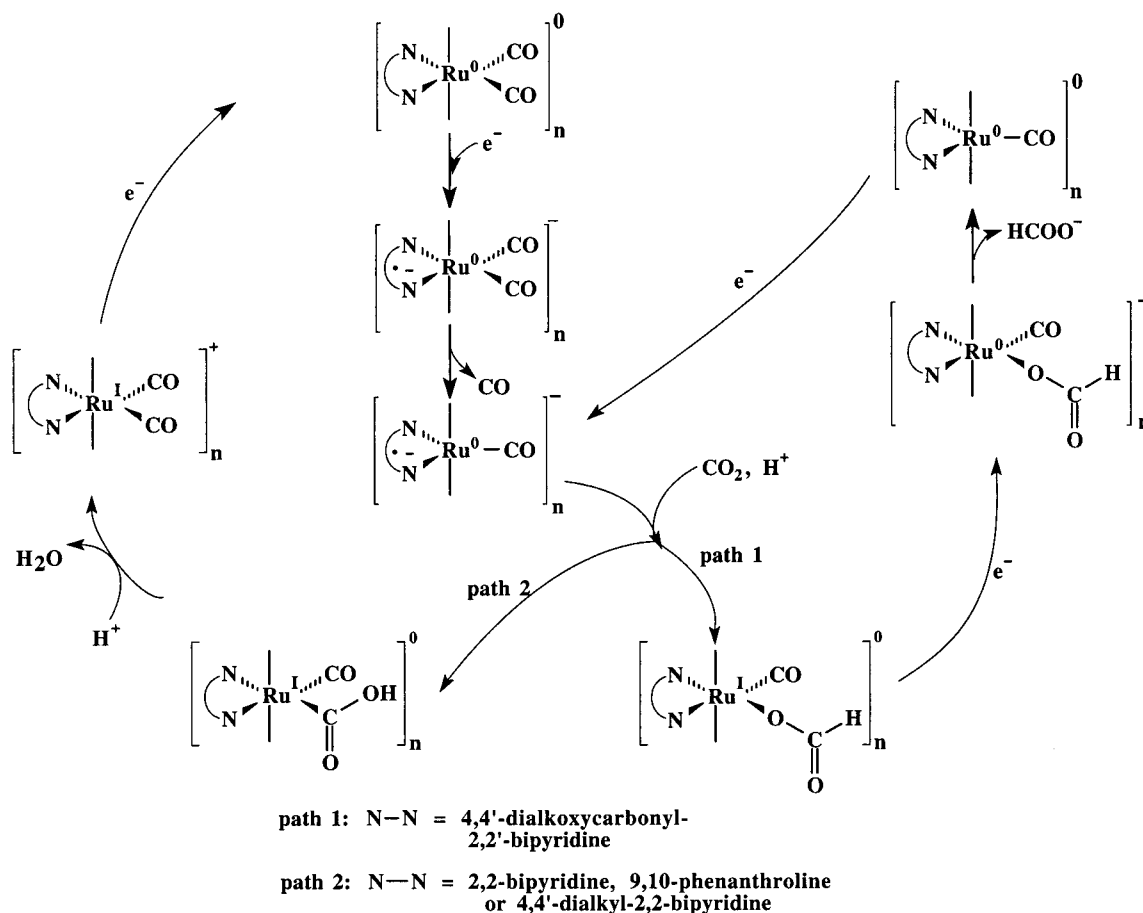


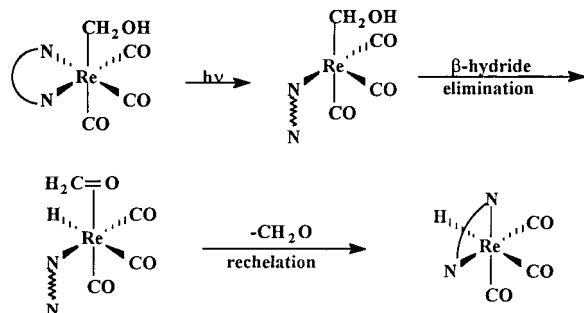
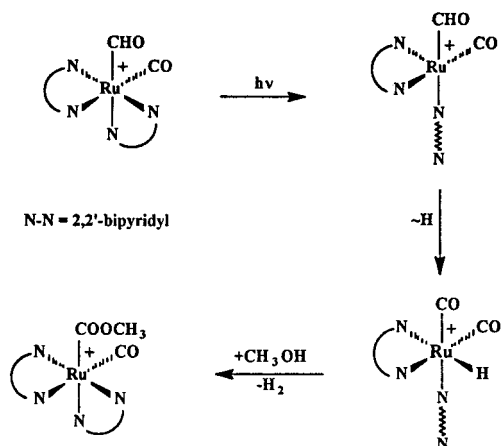
of the CO₂ reduction product observed. If the reduced form of the catalysts reacts with CO₂ to form a M-CO₂ complex, protonation yields a metalcarboxylic acid; further reaction can then produce CO by C-O bond cleavage to form hydroxide or water. Thus, reaction of a reduced form of the catalyst with CO₂, as opposed to protons, leads to CO formation. If the reduced form of the catalyst reacts with protons to form a hydride complex, subsequent reaction of the hydride with CO₂ leads to formate production; these two possibilities are illustrated in Scheme 9. An interesting example of such selectivity is CO₂ electrochemical reduction catalyzed by polymeric films based on [Ru(N-N)(CO)₂]_n (N-N = polypyridine ligand) in aqueous media. Deronzier and Ziessel et al. found that bipyridyl ligands with electron-withdrawing groups in the 4,4' positions gave cata-

lysts which are highly selective for formate at pH > 5 while those derived from the unsubstituted 2,2'-bipyridine or the 4,4'-dimethyl analogue primarily give CO at pH > 7.¹⁶⁵ Formate was thought to arise from an intermediate metal hydride, whereas CO was thought to arise from a metalcarboxylic acid generated by carbonation of an intermediate anion followed by protonation; the suggested pathway is shown in Scheme 10.

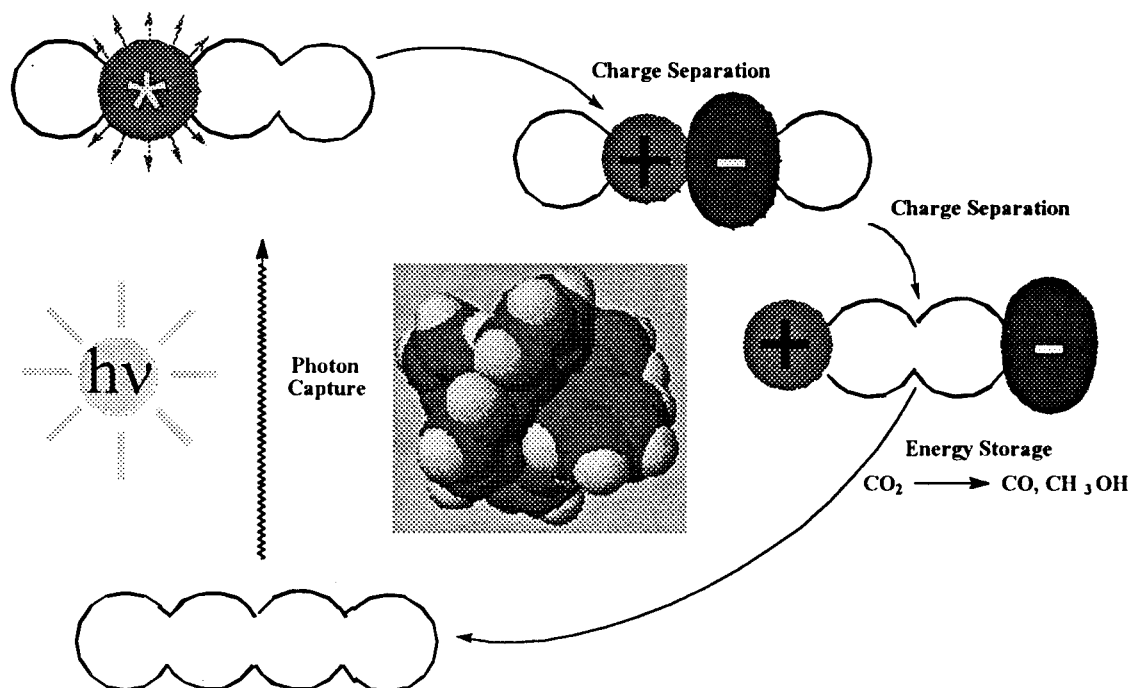
It is unusual for homogeneous catalysts to form reduction products that require more than two electrons. However, Tanaka and co-workers reported the formation of glycolate (HOCH₂CO⁻), glyoxylate (OCHCO⁻), formic acid, formaldehyde, and methanol as CO₂ reduction products using [Ru(tpy)(bpy)(CO)]²⁺ complexes as electrocatalysts (bpy = 2,2'-bipyridine, and tpy = 2,2':6',2''-terpyridine).¹⁶⁶ Although turnover numbers were not given for these more highly reduced species, their formation raises the exciting possibility that a single-site catalyst can result in multielectron reductions of CO₂ and even C-C bond formation. Tanaka¹⁶⁷ and Gibson¹⁶⁸ recently succeeded in isolating key Ru C₁ compounds with polypyridine ligands that are models for catalytic intermediates. Gibson et al.¹⁶⁹ also isolated Re C₁ complexes with polypyridine ligands. The importance of photochemistry in reactions of some of the Re and Ru complexes has been demonstrated,^{168,169} as illustrated in Schemes 11 and 12. The formation of formaldehyde has also been reported in electrochemical CO₂ reduction using transition-metal ter-

Scheme 10. Ligand-Dependent Pathways for the Catalytic Reduction of CO₂



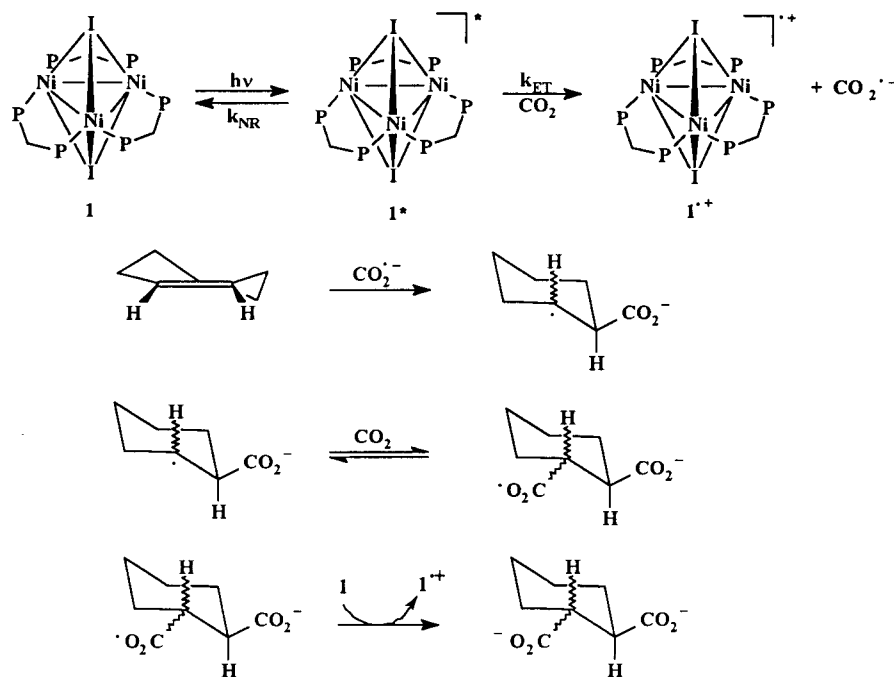
Scheme 11. Photochemical Transformations of Re-Bound C₁ Fragments

Scheme 12. Photochemical Transformations of Ru-Bound C₁ Fragments


pyridine complexes polymerized on glassy carbon electrodes.¹⁷⁰ The relatively mild conditions and low overpotentials required for some of the homogeneous catalysts make them attractive for future studies; however, a number of barriers must be overcome before useful catalysts are available for fuel production.

Scheme 13. Artificial Photosynthesis for CO₂ Reduction with Ru(bpy)₃²⁺

F. Photochemical Reduction of CO₂.

Many of the reactions described above rely on energy input either in the form of reactive bonds (alkenes, alkynes, etc.), hydrogen, or electricity. Photochemical systems, the main features of which are depicted in Scheme 13, have been studied in an effort to develop systems capable of directly reducing CO₂ to fuels or chemicals using solar energy. Transition-metal complexes have been used as both catalysts and solar energy converters, since they can absorb a significant portion of the solar spectrum, have long-lived excited states, are able to promote the activation of small molecules, and are robust. Carbon dioxide utilization by artificial photoconversion presents a challenging alternative to thermal hydrogenation reactions which require H₂.

The systems studied for photochemical CO₂ reduction studies can be divided into several groups: Ru(bpy)₃²⁺ both as a photosensitizer and a catalyst;¹⁷¹ Ru(bpy)₃²⁺ as a photosensitizer and another metal complex as a catalyst;¹⁷² ReX(CO)₃(bpy) or a similar complex as a photosensitizer;^{172a,173} Ru(bpy)₃²⁺ and Ru(bpy)₃²⁺-type complexes as photosensitizers in microheterogeneous systems;¹⁷⁴ metalloporphyrins both as a photosensitizers and catalysts;¹⁷⁵ and organic photosensitizers and transition-metal complexes as catalysts.¹⁷ Photochemical CO₂ reduction is normally carried out under 1.0 atm CO₂ at room temperature. Therefore, the concentration of dissolved CO₂ in the solution is low (e.g., 0.28 M in CH₃CN, 0.03 M in water). These systems produce formate and CO as products. In the most efficient systems, the total quantum yield for all reduced products reaches 40%.¹⁷⁷ In some cases with Ru or Os colloids, CH₄ is produced with a low quantum yield.¹⁶⁴ Under photochemical conditions, the turnover number and the turnover frequency are dependent on irradiation wavelength, light intensity, irradiation time, and

Scheme 14. Proposed Mechanism for Ni-Mediated Photoinduced Coupling of CO₂ and Cyclohexane

catalyst concentration, and they have not been optimized in most of the photochemical experiments described. Typical turnover frequencies for CO or HCOO⁻ are between 1 and 10 h⁻¹, and turnover numbers are generally 100 or less.

The aforementioned molecular sensitizers can be replaced with semiconductor electrodes or particles to achieve light harvesting. These systems may use enzymes or catalysts to promote electron transfer from the semiconductor–solution interface to CO₂ or reduce CO₂ directly.^{178,179} Typically these reductions require a potential bias in addition to solar energy input to achieve CO₂ reduction and electrode corrosion is a major concern. This corrosion can sometimes be overcome using high CO₂ pressures.¹⁸⁰

Interesting examples of stoichiometric photochemical reactions of CO₂ promoted by metal complexes have also been reported. Thus, Aresta et al.¹⁸¹ found that CO₂ can be incorporated into cyclopropane to afford butyrolactone. Kubiak et al.¹⁸² demonstrated the reduction of CO₂ to the radical anion and subsequent coupling to cyclohexene via a Ni complex as proposed in Scheme 14.

G. Chemistry in Supercritical CO₂ as a Reaction Medium and 'Green' CO₂ Chemistry

As noted above, CO₂ is generally considered to be a green or environmentally benign solvent and is naturally abundant. CO₂ has been suggested as a sustainable replacement for organic solvents in a number of chemical processes and is currently used in the extraction of caffeine, in dry cleaning, and in parts degreasing.¹²⁵ While CO₂ is certainly not a panacea, there are a number of characteristics which suggest that CO₂ could provide environmental and economic benefits.

The nontoxic nature of CO₂ has a number of advantages. For example, in food and pharmaceutical applications, CO₂ use greatly reduces future liability

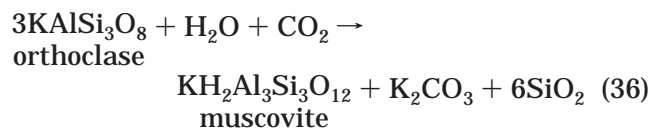
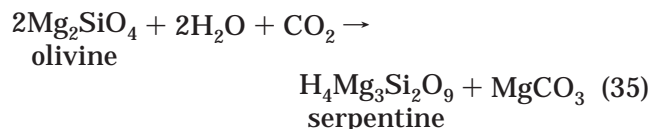
costs and can also facilitate regulatory approval of certain processes. An example is the conversion of pharmaceuticals into nanometer-size particles for injectable uses.¹⁸³ Another instance in which supercritical carbon dioxide could be advantageous is in situations involving contact between hydrophilic and hydrophobic solvents. In this case, the mutual solubility of the two phases is designed to be small. However, some cross-contamination is inevitable, typically leading to a costly remediation. The use of CO₂ as the hydrophobic phase produces contamination that is both benign and readily reversible. Examples include liquid–liquid extraction between organic and aqueous phases as well as emulsion polymerization of water-soluble monomers. In applications where emissions are unavoidable, CO₂ is relatively benign to the environment. Examples range from use of CO₂ in enhanced oil recovery to use as a foaming agent or as the solvent in dry cleaning.

Using supercritical CO₂ as a solvent also has advantages that arise from chemical and/or physical properties. In reactions involving gaseous reactants in liquid phases, the use of supercritical CO₂ with its ability to dissolve large amounts of most gases could allow kinetic control of reactions as opposed to limiting of reaction rates by the transport of the gaseous reactant across the gas–liquid interface. In reactions where CO₂ is a reagent, its use as a solvent would also favor the reaction. Carbon dioxide may also offer advantages in reactions such as free-radical polymerizations and oxidations where a chemically inert solvent is required.

H. Carbon Dioxide Fixation by Inorganic Materials

The reaction of CaCO₃ and CO₂ in water to form Ca(HCO₃)₂ is responsible for the fixation of large quantities of CO₂ in the oceans. However, it is kinetically slow. Similarly, CO₂ can also be fixed by

naturally occurring minerals as shown in eqs 35 and 36.¹⁸⁶



Although the reactions are thermodynamically favorable, they are slow and would need to be enhanced kinetically before they could contribute significantly to adjusting the carbon balance. Furthermore, this would generally require mining and processing large amounts of materials to store relatively little CO₂. Currently, large quantities of CaCO₃ are converted into CaO and CO₂ (which is released into the atmosphere) in cement manufacture. If a natural ore could be substituted for CaO, a significant release of CO₂ into the atmosphere could, in principle, be avoided.

I. Barriers to Further Progress

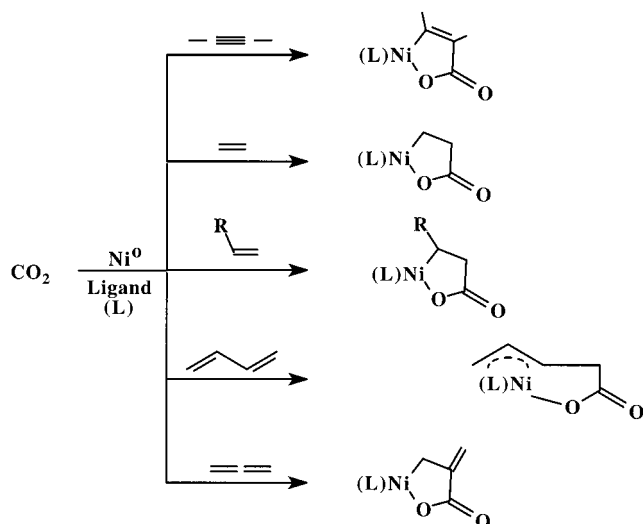
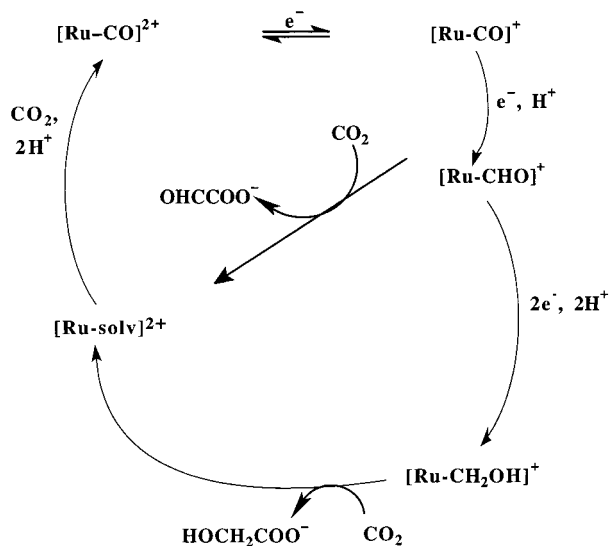
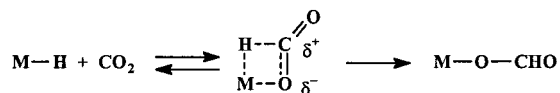
Social, economic, and technical barriers all exist to utilizing CO₂ as a feedstock to produce fuels and chemicals. To make decisions on potential ways to address this issue, information is needed concerning (1) the magnitude of environmental consequences, (2) the economic costs of these consequences, (3) options available that could help avoid or diminish the damage to our environment and the economy, (4) the environmental and economic consequences for each of these options, (5) an estimate of cost for developing the technology to implement these options, and (6) a complete energy balance which accounts for energy-demanding steps and their costs.

Economic barriers to CO₂ utilization can be associated with introduction of new products, the properties of which are unknown, introduction of new processes for existing products, and lack of complete life-cycle analyses for production of many chemicals. Polycarbonate polymers produced by copolymerization of epoxides and CO₂ are examples of new products. As catalysts for these reactions improve, focus is shifting from the technical obstacles associated with production to potential markets for these new materials. The situation is not unlike that encountered with the first production of polymers that are currently used on large scales. Similarly, if alternative processes to produce existing products are found, introduction may be slow due to the large capital investments already made in current processes. For example, direct hydrocarboxylation of butadiene to adipic acid or production of polyurethanes from carbamates (both derived from CO₂) could be economically and environmentally attractive. However, these processes may not be commercialized because of competition with existing processes which have incurred large capital investments. Finally, methods must be developed that allow complete life-cycle analyses of competing synthetic strategies.¹⁸⁵ Analyses must

include economic and environmental costs as well as the conservation of materials. It is possible that a process using CO₂ as a feedstock could actually produce more CO₂ than one not using CO₂. Full life-cycle analyses should permit quantitative evaluation of how much CO₂ is avoided by one process versus another. These analyses must also include the possibility of replacing fossil energy sources with non-fossil sources.

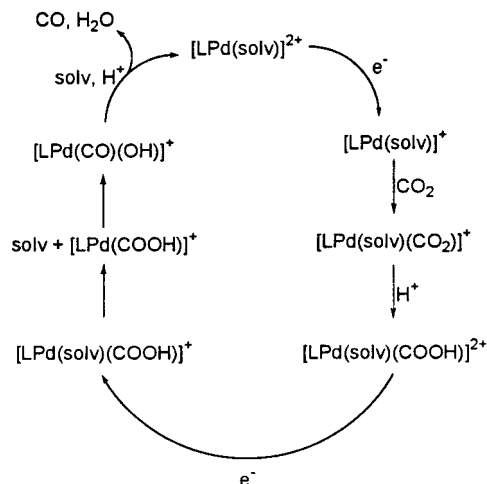
For fuels production, the availability of electrical energy or a source of H₂ is critical. Electricity can be produced from either nuclear or renewable energy sources, and the electrolysis of water using this electrical energy could produce H₂ from a nonfossil source. Nuclear energy currently accounts for approximately 20% of the U.S. electrical production. For the purpose of illustrating the potential of renewable energy sources, it is estimated that a 10% conversion efficiency of solar energy to methanol could produce one gigaton of methanol using 1% of the area of the United States.¹⁸⁶ The theoretical efficiency of a single band-gap solar cell is 33%, and higher efficiencies are possible with stacked cells having different band gaps.¹⁸⁷ For example, solar energy conversion efficiencies of 30% have been obtained with dual band-gap cells,¹⁸⁸ and single band-gap devices have been reported with 25% conversion efficiencies.¹⁸⁹ If CO₂ could be reduced to fuels such as methanol and methane with a 75% energy conversion efficiency, ultimate solar energy conversion efficiencies in the 15–25% range are not unrealistic. The crucial question lies in identifying materials, catalysts, and processing conditions that will afford these high conversion efficiencies economically since there are no fundamental thermodynamic barriers. However, there are significant issues involving how to account for the cost of H₂, the energy required to produce H₂, and the acceptance of nuclear energy.

Significant barriers exist in every area of CO₂ utilization. For the synthesis of fuels and chemicals, many barriers are common and progress will require a better understanding of reaction mechanisms, thermodynamics of reaction intermediates, and structure–reactivity relationships. Reactions of CO₂ that must be better understood include C–C, C–H, and C–X bond formation and C–O bond cleavage reactions. For example, formation of C–C bonds between olefins + CO₂ and alkynes + CO₂ appears to involve initial alkene or alkyne coordination followed by CO₂ attack at an activated carbon atom.¹⁹⁰ These reactions are effective for a variety of applications as shown in Scheme 15. However, for HOCH₂COOH formation, CO₂ coordination and reduction to a hydroxymethyl ligand (CH₂OH) is proposed to precede C–C bond formation (Scheme 16).¹⁶⁶ The coordination site requirements in various CO₂ transformations are also poorly understood, and systematic studies of this important mechanistic aspect are needed. Insertion of CO₂ into M–H bonds occurs via an associative pathway in which hydride directly attacks the CO₂ carbon atom as an M–O bond forms and the M–H bond is cleaved (Scheme 17).¹⁹¹ This reaction may be accelerated by a vacant coordination site as in olefin insertion reactions; however, data are

Scheme 15. Oxidative Coupling Reactions Involving CO₂**Scheme 16. Proposed Pathway for Reduction of CO₂ to HOCH₂CO₂H****Scheme 17. Mechanism for the Insertion of CO₂ into a Metal-Hydrogen Bond**

not available on this point. During many catalytic cycles, M-H or M-C bonds are formed; however, thermodynamic data for their homolytic or heterolytic cleavage are generally not available. Such data would be useful in designing new catalytic processes.

The cleavage of C-O bonds as CO₂ is reduced is also not well understood. During CO₂ electrochemical reduction to CO mediated by Pd catalysts, a vacant coordination site facilitates the C-O bond cleavage.¹⁹² This cleavage occurs via migration of a water molecule or hydroxide ion from a metal carboxylate carbon atom to a vacant coordination site on the metal (Scheme 18). In other C-O bond cleavage reactions, formation of MC(O)OM' linkages or one-electron M-COOH reduction appears to facilitate C-O bond cleavage.¹⁹³ The energetic differences

Scheme 18. Proposed Mechanism for the Pd-Mediated Electrochemical Reduction of CO₂ to CO

between possible pathways are not understood and could be clarified by theoretical calculations. In many instances, CO₂ binding occurs via bonds to both the CO₂ carbon and oxygen atoms. The role of such cooperative interactions is not well understood, and systematic studies should be informative.

Factors controlling regio- and stereoselectivity of metal-centered CO₂ transformations are also ill-defined. These may be important in polymer synthesis using propylene oxide and related monomers in analogy to propene polymerization. Likewise, chain transfer reagents to control polymer molecular weights are also needed. Catalysts with higher turnover frequencies than currently available are needed. Finally, extension of successes in polycarbonate synthesis to polyesters from olefins and CO₂ is an attractive goal.

Regarding heterogeneous CO₂ hydrogenation catalysis, the principal barriers are poor product selectivity and unacceptably high reaction temperatures. Thus, in ethanol production by CO₂ hydrogenation, ethanol is generally one component of a mixture of alcohols and hydrocarbons, and more selective catalysts are needed. Catalysts capable of operating at lower reaction temperatures for hydrogenating CO₂ to methanol are also needed. Current catalysts operate at ~250 °C and the thermodynamics for CO₂ to methanol conversion are entropically unfavorable (and enthalpically favorable). At lower temperatures, the equilibrium concentration of methanol is higher, which would lead to higher conversion per pass and more efficient operation. Homogeneous hydrogenation catalysts typically catalyze the reduction of CO₂ to formate-based products. Catalysts capable of reductions beyond the formate level are desirable for more useful products.

Electrocatalysts for CO₂ reduction would permit the conversion of electrical energy to fuels in a single step, but many barriers exist. Heterogeneous electrocatalysts are needed that operate at lower overpotentials with higher selectivity. Although Cu electrodes catalyze CO₂ reduction to methane, comparable catalysts for producing methanol are unknown. Methanol production has been reported at Mo electrodes but selectivity and current densities are very low,

typically less than 40% and 1 ma/cm², respectively.¹⁹⁴ Similarly, homogeneous catalysts possessing all of the desired properties for CO₂ reduction are not known. Fast, selective, and energy-efficient homogeneous electrocatalysts are known for reducing CO₂ to CO but are unstable. Other catalysts operate at unacceptably large overpotentials, require Hg electrodes, or have low catalytic rates. Additionally, rapid and efficient homogeneous catalysts for catalyzing CO₂ reduction by more than two electrons are unknown. Better understanding is needed of the requirements for reducing CO₂ beyond formate and CO in either a single or sequential steps.

Photochemical processes offer an attractive approach to CO₂ reduction using sunlight. However, significant obstacles exist such as the requirement of expensive sacrificial reagents, rather than water, to quench the sensitizer and to provide the thermodynamic driving force for CO₂ reduction. Also, sensitizers more completely using the solar spectrum are desired. Direct photochemical reactions of CO₂ complexes are rare and offer the possibility of coupling CO₂ reduction to O atom transfer; such reactions have yet to be demonstrated.

Regarding supercritical CO₂ utilization, understanding the binary and ternary phase behavior of CO₂-substrate-reactant systems is needed to conduct reactions under the most favorable temperature and pressure conditions (i.e., to generate the number of phases and phase compositions desired). Most catalytic reactions studied to date have not utilized catalysts specifically designed to operate in supercritical CO₂. This led to solubility problems and use of catalysts not capitalizing on the properties of supercritical CO₂.

J. Promising Research Directions

Future research objectives should be to overcome the knowledge barriers identified above and to provide a better understanding of CO₂ chemistry and fundamental reaction processes. The production of chemicals and fuels from CO₂ would be significantly enhanced by fundamental studies of the kinetics and thermodynamics of catalytically relevant C-H, C-X, M-H, M-X, and M-C bond-forming and -cleavage reactions. Increased use of CO₂ as a replacement for phosgene is another attractive goal. Catalysts that facilitate carboxylation of saturated and unsaturated hydrocarbons are another important objective. Biomimetic studies of CO and formate dehydrogenase and methanogenic enzymes are relatively unexplored areas. New catalysts for epoxide and olefin + CO₂ copolymerization are needed that are less sensitive to water and oxygen, more active, and more stereoselective. Chain transfer reagents for such reactions are also needed. Catalysts for formation of polyurethanes and polyesters using CO₂ as a monomer would also be desirable. Heterogeneous catalysts that are more selective and active must be developed. In situ techniques that lead to better structural characterization of catalytic intermediates are also needed (see Section V). Specifically modified surfaces to improve selectivity and surfaces modified with single-site catalysts are important areas for future development.

In photochemical and electrochemical CO₂ reduction, protons are the ultimate source of product H atoms. A better understanding of features promoting selective reactions with either CO₂ or protons is needed. Similarly, a better understanding of factors controlling formate versus CO production is needed as well as how they relate to ultimate methanol or methane production. New approaches to reduce CO₂ by six or eight electrons with high selectivity and low overpotentials are required. Better understanding of C-C bond-forming reactions is necessary to design catalysts that selectively produce ethanol or ethylene. First-row transition-metal catalysts and water-soluble catalysts will be important in reducing costs and in lowering resistive losses, respectively. Flash photolysis and pulsed radiolysis experiments coupled with time-resolved spectroscopy offers fundamental information on transient intermediates. CO₂ complex photoactivation represents a possible route to C-O bond cleavage coupled with O-atom transfer.

Supercritical CO₂ is a relatively inert solvent for hydrogenations, oxidations, carbonylations, polymerizations, electrophilic reactions, and activation of small molecules. The study of catalysts designed specifically for use in supercritical CO₂ is important for understanding reactions in this medium and factors influencing regio- and enantioselectivity. The ability to predict ternary and quaternary phase behavior would also significantly enhance development of this field. Heterogeneous catalysis in supercritical CO₂ has received relatively little attention, although initial results using surfactants, micelles, and emulsions are promising.

V. Emerging Physicochemical Techniques and Research Directions

A. Introduction

Carbon management research and development will benefit greatly from the new techniques and directions of research that have emerged in recent years. Several techniques have been developed that permit molecular level characterization of surfaces in situ, under conditions employed in actual catalytic technology. These will be reviewed in the first part of this section. To achieve 100% reaction selectivity, catalyst particles with identical size, structure, and composition must be fabricated and their spatial arrangement should also be controlled. Such high technology catalysts can now be prepared by several techniques, among which electron beam lithography is perhaps the best developed. The new catalyst fabrication techniques are discussed in the second part of this subsection. Computer simulation and modeling is developing rapidly and promises to provide guidance and help to experimentalists working with problems of surface science ranging from structures of transition states to kinetic parameters of surface reaction dynamics. The state of computer modeling for surface processes is discussed in the third part of this section. Finally, combinatorial techniques for rapid screening of surface catalytic properties are reviewed in the final part.

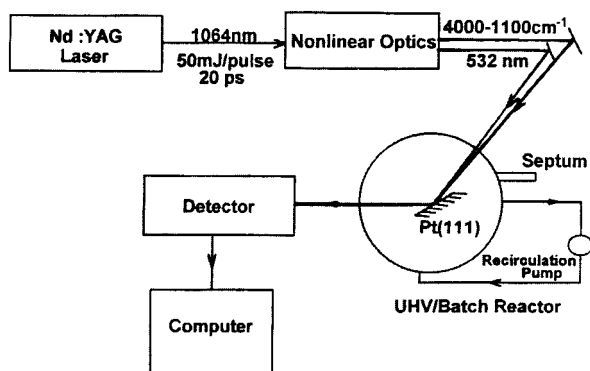


Figure 12. Instrumentation for the study of surface science and catalysis by sum frequency generation spectroscopy.

B. In Situ Molecular Characterization Techniques

During the past 10 years, new techniques have emerged that permit molecular level studies of surfaces under actual reaction conditions.^{195–206} Table 4 lists the principal characterization techniques that can be used at high pressures and temperatures at the solid–gas interface and also at solid–liquid interfaces with references to key review papers. Among these, sum frequency generation (SFG)–surface vibrational spectroscopy¹⁹⁹ (e.g., Figure 12) and the scanning probe microscopies (scanning tunneling microscopy [STM] (e.g., Figure 13) and atomic force microscopy [AFM])²⁰² have the sensitivities to be applicable for studies on small area ($\sim 1 \text{ cm}^2$) catalysts. Adsorption–reflection infrared spectroscopy¹⁹⁷ and synchrotron-based techniques (grazing angle X-ray diffraction and X-ray absorption)²⁰⁴ can also be used for external surfaces with small areas. All the other techniques including visible and UV–Raman spectroscopy¹⁹⁸ and positron emission²⁰⁰ are

Table 4. Molecular Surface Characterization Techniques Operating under High-Pressure Reaction Conditions

	technique
1	isotope exchange ¹⁹⁵
2	in situ NMR ¹⁹⁶
3	Fourier transform infrared spectroscopy ¹⁹⁷
4	in situ Raman spectroscopy (visible, UV, surface-enhanced) ¹⁹⁸
5	sum frequency generation-surface vibrational spectroscopy ¹⁹⁹
6	positron emission ¹¹ C, ¹³ N, ¹⁵ O ²⁰⁰
7	in situ Mössbauer spectroscopy ²⁰¹
8	in situ scanning tunneling microscopy ²⁰²
9	in situ electron microscopy ²⁰³
10	in situ X-ray absorption spectroscopy ²⁰⁴
11	neutron scattering ^{205,206}

more applicable to higher surface area ($>1 \text{ cm}^2$) microporous catalysts.

Neutron scattering methods^{205,206} are emerging as a potentially powerful, microscopic probe for in-situ characterization of catalytic materials. The reasons are as follows: (1) neutrons have very low absorption cross-sections for most elements and can therefore easily penetrate most types of reaction vessels to probe ‘real’ bulk catalysts; (2) thermal neutron wavelengths and energies are well matched to typical interatomic distances and excitation energies, respectively, so that neutron scattering can be used both for structural (diffraction) as well as dynamic studies (inelastic neutron scattering, INS) over time scales from molecular translational diffusion through catalysts to molecular vibrations; (3) neutron scattering may also differ substantially between different isotopes of the same element so that isotopic substitution can produce scattering contrast, e.g., between a guest and the host material; and (4) neutron scattering occurs from atomic nuclei (a simple point

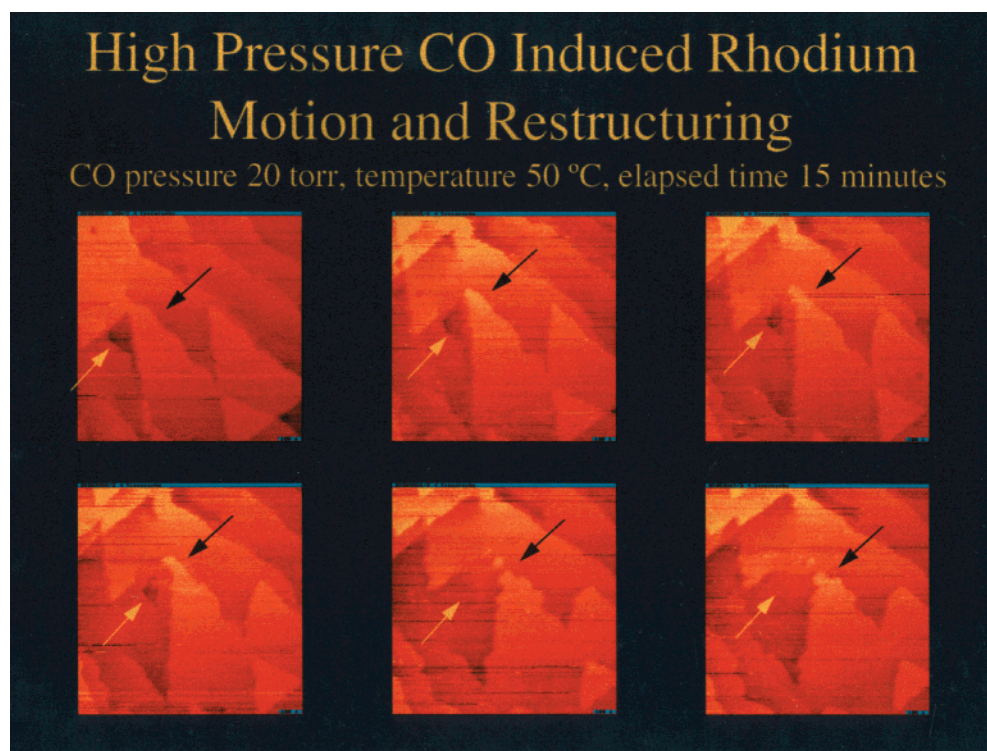


Figure 13. Scanning tunneling microscope images of Rh surface restructuring upon CO chemisorption.

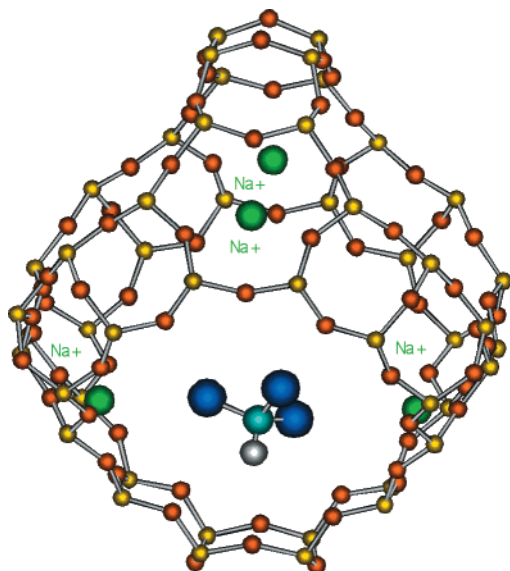


Figure 14. Result of Monte Carlo docking calculations combined with Raman and inelastic neutron scattering studies of chloroform adsorbed in zeolite Y.²⁰⁹

interaction) so that cross-sections can be readily calculated. Recent advances²⁰⁶ in calculating (molecular mechanics, *ab initio*, scaled *ab initio*) molecular vibrational frequencies and associated vibrational amplitudes coupled with improved INS instrumentation have enormously increased the utility of this technique for studies of adsorbate vibrations and guest–host interactions.

There are several areas related to heterogeneous catalysis where neutron scattering techniques provide unique results. Virtually all such experiments can be applied *in-situ*, as recently demonstrated for zeolite crystallization.²⁰⁷ A recent example of neutron scattering methods used in conjunction with theoretical simulations and optical spectroscopy are studies of adsorption complexes in zeolites, such as water²⁰⁸ and halocarbons.²⁰⁹ The geometry of chloroform in faujasite derived from computer simulations is shown in Figure 14. These predict that binding is dominated by a hydrogen bond between the C–H group and framework O atoms. This prediction was verified by Raman and INS spectroscopies, which reveal, respectively, weakening of C–H stretching and strengthening of C–H bending modes upon H-bond formation. However, adsorption of single CHCl₃ molecules does not result in a long-range ordered structure, so the molecule could not be located by conventional analysis of diffraction data. Instead, a differential pair distribution function (PDF)²¹⁰ was obtained from diffraction data for HCCl₃ and DCCl₃.²¹¹ The differential PDF (analogous to an XAFS experiment on H) provides the first direct evidence for this guest–host H-bonding with a H···O distance of 2.2 Å.

The reviews referenced above also discuss the principles, instrumentation, and operating conditions of the various surface techniques. Experimental challenges include the continuous push for improving time and spatial resolution toward picosecond time response and nanoscale spatial sensitivity. The dream of catalyst scientists is to monitor the reaction of a single molecule on a sufficiently short time scale to

identify the transition state including change of active site configuration as the product molecule forms. Developments in surface instrumentation are aimed at achieving this goal.

C. Rational Design of Catalysts To Achieve 100% Selectivity in Catalytic Reactions

Carbon management would greatly benefit from catalytic processes that can produce desired products with 100% selectivity. In this way, waste disposal or recycling of undesirable byproducts can be minimized. Rational catalyst design is at the heart of attaining this goal. Experiments indicate that selectivity can be influenced by the following variables: (1) changing the surface structure of catalysts, for example, by increasing the concentration of high coordination sites, defects (steps, kinks, vacancies); (2) blocking high coordination sites or blocking defect sites that strongly bind sulfur or other impurities; (3) controlling diffusion paths of reaction intermediates by changing distances between active reaction sites or by constructing pore sizes in the molecular diameter regime; and (4) producing oxide–metal interface sites where both metal catalysis (H₂, O₂ dissociation, etc.) and acid catalysis (charge transfer at strong Lewis acid or Brønsted acid sites) can occur. There is evidence from surface science studies under reaction conditions that (1) there is large surface atom mobility that is essential during the catalytic process; (2) there are strongly adsorbed stagnant reaction intermediates that restructure the metal surface, thereby producing reaction sites; however, these intermediates do not turn over; (3) weakly adsorbed molecules or molecules that are present only under high pressure reaction conditions are frequently the reaction intermediates. All these features, the control of active structural sites, as well as the mobility of surface metal atoms and adsorbates must be part of the ultimate catalyst system that would be fabricated on the nanoscale by rational design.

One way to achieve the above goals is by use of electron beam lithography to produce ordered nanocluster arrays of transition-metal catalyst particles on oxide supports. This lithographic technique which is widely used in the microelectronic industry is shown schematically in Figure 15. The Pt nanoparticle arrays that are fabricated this way are shown in Figure 16 as imaged by electron microscopy and in Figure 17 as scanned by atomic force microscopy. A minimum metal particle size of 25 Å can be obtained in this manner. The supports SiO_x, Al₂O₃, and TiO_x have been employed. Silver nanoparticles for application in ethylene partial oxidation to ethylene oxide must be deposited on α -Al₂O₃ because they form silver silicate via reaction with the silica support under reaction conditions. These nanoparticles exhibit remarkable thermal and chemical stability. They can be cleaned by low-energy (~200 eV) Ne⁺ bombardment to remove surface carbon. The controllable variables in their fabrication include the diameter and height of the metal particles, the distances between particles, and the oxide–metal periphery area. Multimetallic arrays can be fabricated as well as alloy clusters, as desired.

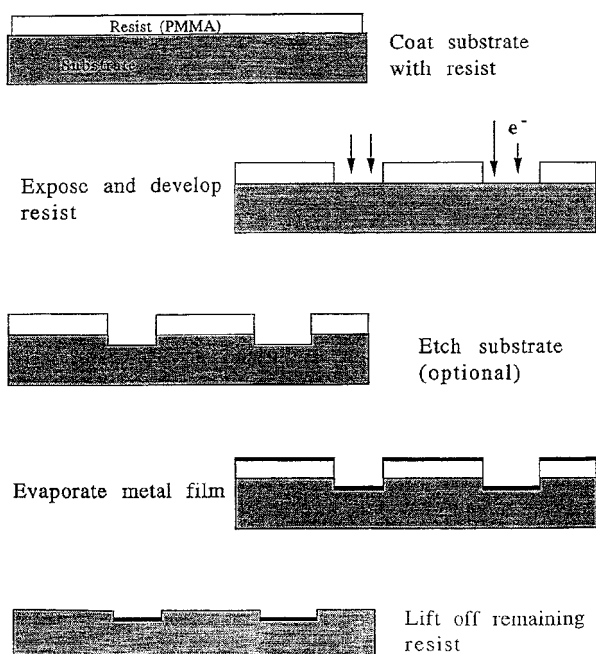


Figure 15. Scheme for fabricating arrays of metal nano-clusters by electron beam lithography.

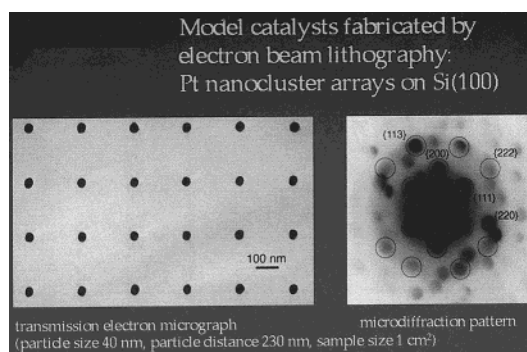


Figure 16. Transmission electron microscopy and electron diffraction. Characterization of metal nanoparticle arrays fabricated by electron beam lithography.

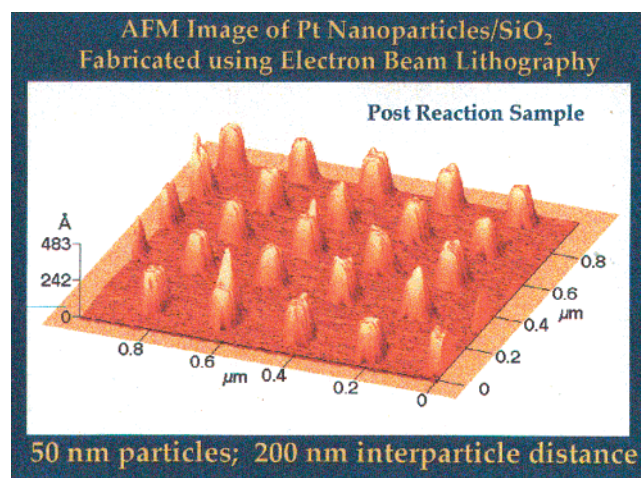


Figure 17. Atomic force microscopy. Characterization of metal nanoparticle arrays fabricated by electron beam lithography.

To mass produce the nanocluster arrays, imprint lithography can be employed by pressing the cluster array into a viscoelastic polymer. The indentation can

then be ion etched to reproduce the structure of the original array. To increase the surface area of the nano-fabricated catalyst, the metal arrays must be produced in three dimensions. In this way, by fabricating nanosize channels, catalysts with surface areas $100 \text{ m}^2/\text{cm}^3$ can be produced.

Other techniques aimed at producing unique new catalysts with nano-controlled structure include (1) deposition of transition-metal clusters in zeolite cages, (2) spin-coating of metal clusters onto flat supports by nucleation and growth from solution, and (3) uniform nanocluster fabrication in surfactant solutions by colloid preparation techniques. In this circumstance, the nanoclusters are capped with an organic coating that must be removed to produce the active catalyst surface. Importantly, 100% selectivity in catalytic reactions can only be achieved if there is a concerted research program initiated to produce catalysts by rational design with nanoscale control of the fabrication process.

D. Computer Simulation-Modeling

To address the complex issues of carbon management research, all available tools at our disposal must be employed. The chemical research enterprise is undergoing a revolution as it exploits advances in computer hardware and software and in new mathematical and theoretical approaches. There have been important advances in the area of electronic structure methods²¹² so that computation now rivals experiment in terms of accuracy for predicting small molecule thermochemistry. In addition, it is now possible to make predictions about the behavior of molecular ensembles using the techniques of molecular simulation. The exploding number of scientific papers citing computational chemistry results and the recent Nobel Prizes awarded to Professors John A. Pople and Walter Kohn²¹³ for pioneering work in this area are clear indications that chemical process modeling has reached a significant development point.

Modeling, theory, and simulation can enhance our understanding of known systems. They can provide qualitative/quantitative insights into experimental results and guide the choice of which experimental system to study and/or enable design of new systems. This is most useful if the simulation approach has been benchmarked on well-established systems. Furthermore, simulation allows exploration of temporal and/or spatial domains not accessible by present experimental methods. A critical aspect for quantitative simulations is the need for high accuracy. For example, a factor of 2–4 in catalyst efficiency may determine whether a process is economically viable. A factor of 4 in a rate constant at 25°C corresponds to a change in activation energy of $\sim 1 \text{ kcal/mol}$, while for a 50:50 starting mixture of two components, a ΔG change of less than 1.5 kcal/mol changes the equilibrium constant by a factor of 10, leading to a 90:10 mixture at 25°C . These accuracy requirements in turn require the ability to predict thermodynamic quantities such as bond dissociation energies (D_e or D_0°) and heats of formation (ΔH_f) to better than 1 kcal/mol and activation energies to within a few tenths of a kcal/mol —a daunting task.

Table 5. Theoretical and Experimental Heats of Formation at 0 K (all energies in kcal/mol)^a

molecule	$\Delta H_f^0(\text{CCSD(T)})^b$	$\Delta H_f^0(\text{expt})^c$	ZPE ^d	spin-orbit ^e	core/val ^f	scalar rel ^g	ΣD_e^h
CH	141.7 ± 0.3	141.2 ± 4.2	4.04	-0.04	0.2	0.0	83.8
CH ₂	93.9 ± 0.4	92.2 ± 1.1	10.55	-0.08	0.8	-0.2	189.4
CH ₃	35.9 ± 0.6	35.6 ± 0.2	18.6	-0.08	1.0	0.0	306.7
CH ₄	-15.9 ± 0.7	-16.0 ± 0.1	27.71	-0.08	1.3	-0.2	419.1
CH ₂ O	-25.1 ± 0.3	-25.0 ± 0.1	16.53	-0.30	0.9	-0.4	373.6
		-26.8 ± 1.5					
HCO	9.8 ± 0.3	10.3 ± 1.9	7.7	-0.30	1.2	-0.3	277.9
CO	-27.4 ± 0.2	-27.2 ± 0.04	3.1	-0.30	1.3	-0.2	258.7
C ₂ H ₄	14.6 ± 0.6	14.58 ± 0.07	31.5	-0.16	2.3	-0.3	561.6

^a See Dixon, D. A.; Feller, D. F. *Chem. Eng. Sci.* **1999**, *54*, 1929 for most of these results. ^b Calculated heat of formation. ^c Experimental heat of formation. ^d Zero-point energy correction. ^e Spin-orbit correction. ^f Core/valence correction. ^g Scalar relativistic correction. ^h Total dissociation energy at the CCSD(T) level extrapolated to the complete basis set limit.

Dramatic improvements in computers have occurred over the past 20 years with the development of vector and vector/parallel computers, RISC architectures, powerful desktop computing, and, more recently, massively parallel computing systems based on lower cost RISC processors. With the availability of high-performance computers, new algorithms, and new theoretical methods have been developed to take advantage of increased computational power. Furthermore, the development of moderate cost, high-performance workstations has made it easier to generate input data and to analyze and view results of large calculations as well as to perform reasonably complex calculations. By combining workstation processors into massively parallel computing (MPP) systems with distributed memory, it is now possible to attain >250 Gflops of peak performance for reasonable cost, and the cost of teraflop computing will soon be within reach of many laboratories. Furthermore, with the advent of easier-to-use software coupled with user-friendly graphical interfaces, access to high-performance computing is becoming available to a broad user community.²¹⁴

Along with hardware advances have come dramatic advances in software and algorithm development. To make optimal use of massively parallel computers, software must be created which is scaleable in terms of the number of nodes, in terms of problem size, and is portable to different computer architectures for broad applicability with minimal cost for porting. Finally, software must be high performance and take full advantage of modern theoretical and algorithmic advances. Such software, together with the tools developed to operate and utilize massively parallel computer systems as well as the software needed to handle and interpret the large amounts of data generated, represent as important a part of the revolution as the computers. A key component of any successful scientific software development program is the use of teams of computer scientists, applied mathematicians, application developers, and users to design and implement software. This synergy facilitates development of the highest performing software with the best algorithms and the longest in-use lifetime. These advances and their implications for catalysis research have been reviewed²¹⁵ and noted in the U.S. chemical industry Technology Vision 2020¹¹ report.

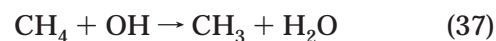
E. Computational Thermochemistry

Thermodynamic properties play a critical role in the design of most industrial chemical processes and are critical to understanding a wide range of chemical behavior. Extensive tabulations of thermodynamic data are available, but there are often significant "holes" due to the lack of experimental information and/or to difficulties in interpreting measurements.²¹⁶ There is less reliable thermodynamic information available for radicals or highly reactive intermediates because of difficulties associated with synthesis, isolation, and properties measurements. Scientists have therefore successfully resorted to computational methods to obtain molecular thermodynamic properties with high accuracy.

During the past five years, there has been a revolution in computing molecular thermodynamic properties from first principles. This reflects a combination of factors: development of efficient computational implementations of the coupled cluster methods CCSD(T) for treating the correlation energy or the *n*-particle problem,²¹⁷ development of a family of efficient, increasingly accurate basis sets (correlation consistent) for treating the 1-particle problem;²¹⁸ and continuing advancements in hardware and software technology, as noted above.^{214,219} With current technology, it is possible to predict bond energies and heats of formation for molecules with six or fewer first-row atoms, including radicals and ions, to an accuracy of better than 1 kcal/mol as shown in Table 5.²²⁰ The range of accessible molecules will grow dramatically over the next several years.

F. Computational Reaction Kinetics

Besides the ability to predict thermodynamic properties, it is now possible to predict certain reaction rates with some reliability based on ab initio calculations. If one can predict such rates, then one can employ them in kinetic models such as transition-state theory or variational transition state theory,²²¹ to describe a chemical process in a large plant, or to describe the impact of a compound released into the environment, or to design a catalyst. Such a calculation has been carried out for an important reaction in the combustion of CH₄ (eq 37).



The rate constant for eq 37 has been calculated at quite high levels, and the result is within a factor of 2 of the experimental value over a range of more than 2000 °C.²²²

Continued developments in computational chemistry will doubtless result in a major increase in the ability to compute molecular thermochemical and kinetic properties. Such information is critical to process design and design of new catalytic systems. With the expected advances in computational chemistry and computers, it will be possible to calculate such data with known reliability.

G. High-Throughput Screening (HTS)

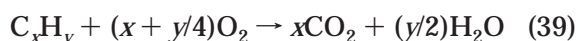
Combinatorial chemistry and high-throughput screening have revolutionized pharmaceutical discovery. These techniques are now being applied to development of other bioactive molecules, such as herbicides and pesticides. A goal of the biological work is to use a standard synthetic method, for example, solid-state peptide synthesis on a chip, to generate a diverse library of structures simply and efficiently. These compounds can then be used in high-throughput screening tests to quickly search for structure–activity relationships and efficacy for a specific process. Similar techniques are just beginning to be used in catalytic science, for example, the generation of transition-metal ligands for homogeneous catalysis.²²³ In addition to application of combinatorial approaches to catalyst design, these techniques have been used to design materials with improved magnetic,²²⁴ ferroelectric,²²⁵ and optical²²⁶ properties (e.g., phosphors for advanced display technologies). It has been possible to develop spatially addressable arrays of thin films offering artificial lattices, epitaxial overlayers, and unique patterning. With appropriate masks, one can generate spatially designed libraries of thin films for use in screening. The chemical composition, the effect of employing different underlayers, and the thickness can be varied. These can then all be used in a single screening system, for example, to assay for catalytic activity in the case of heterogeneous catalysts. Techniques for deposition include RF sputtering and pulsed laser ablation for thin film growth, solid-state synthesis and thermal annealing, and the use of inkjet printers to deposit precursor solutions. Although application of HTS techniques to both heterogeneous and homogeneous catalysis is in its infancy, we expect research in this area to accelerate greatly in the coming years.²²⁷ For heterogeneous catalysis, the principal limits are the spatial resolution of the masks, the resolution of the detectors and types of reactors that can be used, and the types of solid-state synthesis that can be carried out. For example, X-ray microbeam techniques based on synchrotron radiation including X-ray fluorescence, X-ray diffraction, and near-edge X-ray absorption spectroscopy have been used to determine chemical compositions, crystal structures, and metal valence states in combinatorial arrays.^{228,229}

VI. Catalysis Related to More Efficient Engines for Transportation

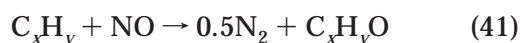
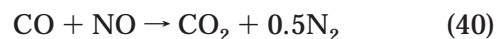
A. Exhaust Aftertreatment for Lean Burn Engines

1. Introduction and Current Status

Currently, approximately one-third of all CO₂ emissions are derived from mobile sources, particularly automobiles and trucks, by combustion of fossil fuels in gasoline or diesel engines. Compared with current-generation gasoline engines, the overall energy conversion efficiencies of *lean-burn* gasoline and diesel engines are up to 15% and 30% percent higher, respectively, with a corresponding reduction in CO₂ emission. These latter engines operate with much lower fuel/air ratios than the stoichiometric ratios in conventional gasoline engines.²³⁰ However, a crucial condition for large-scale transition to the use of lean-burn engines is availability of exhaust gas emission treatment systems that can lower the level of nitrogen oxides, NO and NO₂ (commonly called NO_x), to environmentally acceptable levels. The catalytic converters used in present day passenger cars, using “three-way” catalysts, are unable to remove NO_x from the emission of these lean-burn engines (Figure 18),²³¹ because these exhausts contain higher concentrations of oxygen than can be tolerated by these catalysts. Over the surfaces of these catalysts, the high concentration of oxygen in the emissions consumes the carbon monoxide and hydrocarbons by combustion (eqs 38 and 39).



These substances are also reductants which reduce NO_x in the exhaust (eqs 40 and 41).



Therefore, new types of catalysts are needed. For diesel engines, there is another important issue, which is control of particulate matter emission. Developing highly efficient, economical, and durable exhaust treatment systems for such engines is therefore crucial for large-scale application in transportation, especially for passenger cars.

An ideal exhaust treatment system should be similar to current-generation three-way catalytic converter systems, i.e., passive and with a minimal need for consumer maintenance. However, at present there are no catalytic systems that have the activity and durability to meet industrial targets. Depending on the type of engine, the nature of the exhaust gas differs, particularly in temperature as well as in concentration and type of hydrocarbons. For treatment of exhaust from lean-burn gasoline engines, the operating temperature window is 350–700 °C, with occasional excursions to higher temperatures. For heavy-duty diesel engines, the operating temperature window is approximately the same; however, the hydrocarbon concentration is substantially lower. For

light-duty diesel engines, the temperature window is 200–350 °C, with the possibility that the lower limit could be as low as 150 °C.

Currently, the technology to remove particulate matter from diesel engine exhaust makes use of soot combustion with a fuel burner or catalytic soot combustion, via either a fuel additive or a catalyzed soot filter.²³² In the latter case, because of the high soot ignition temperatures, excessive build-up of soot prior to ignition can result in damaging temperature runaways. Furthermore, the oxidation catalysts are sensitive to sulfur poisoning and fuel sulfur can be converted to sulfates over oxidation catalysts, which in turn contribute significantly to particulate emission. Thus, further development of more thermally stable filter materials and more active and sulfur-tolerant catalysts are needed.

The catalytic NO_x treatment technologies currently under consideration and their status can be summarized as follows. (1) Direct reduction of NO_x with hydrocarbon reductants present in the exhaust gas and/or derived from injected fuel over an active and selective catalyst. Although this is a highly desirable approach, there are no known catalysts that can meet the economic and performance targets. A practical catalyst must be selective in terms of both reduction of NO_x to N₂ and not to N₂O and reaction of hydrocarbon reductants with NO_x instead of O₂. Issues related to this technology are discussed below. (2) Direct reduction of NO_x with other injected reductants, such as urea, over an active and selective catalyst. This is a technology adapted from treatment of exhaust from stationary sources, such as power plants. Very high conversions (>90%) of NO_x can be achieved with known catalysts.²³³ One disadvantage to consumers is the inconvenience of maintaining a reductant supply on board a vehicle. Also, an “intelligent” urea injection system would be required to minimize/eliminate NH₃ slip and not to produce N₂O. (3) Use of a chemical trap.²³⁴ In this technology, the exhaust gas is passed over a bed that contains a catalyst that oxidizes NO_x to NO₂, which is then reacted with an oxide, for instance BaO, to form a nitrate. At regular intervals, the air-fuel intake of the engine is switched from fuel-lean to rich and the nitrate is decomposed. The released NO_x is reduced to N₂ by a catalytic component, also in the bed, that is similar to a conventional three-way catalyst. Performance degradation of the trap by SO_x in the exhaust is a serious problem. Implementation of regulations to lower sulfur levels in the fuel and/or methods to decompose the adsorbed sulfate to regenerate the trap would make this a viable technology. However, this technology is more complex than a passive catalytic device. (4) Catalytic decomposition of NO. Although this is the most desirable approach because of its simplicity, the activities of known catalysts are orders of magnitude lower than the industrial targets. (5) Nonthermal plasma-assisted catalytic reduction of NO_x.^{235,236} In this technology, the exhaust gas is first passed through a nonthermal plasma and then to an NO_x reduction catalyst. Alternatively, the exhaust contacts the plasma and catalyst simultaneously. This technology shows prom-

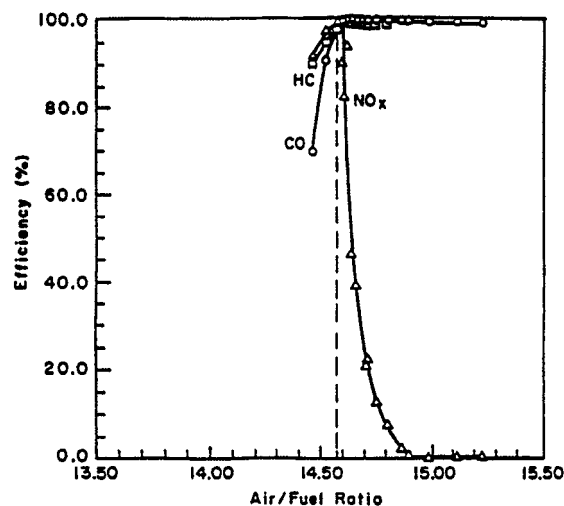


Figure 18. Conversion efficiencies of NO_x, CO, and hydrocarbon over three-way catalysts as functions of air/fuel ratio for a gasoline engine. Taken from: Shelef, M.; Graham, G. W. *Catal. Rev. Sci. Tech.* **1994**, *36*, 433.

ising results on a laboratory scale (up to ~60% NO_x conversion at low space velocities), but very little performance testing has been carried out with real engine exhaust and no accurate energy balance has been obtained.

B. Issues

The vast majority of research in this area in recent years has been devoted to catalytic NO_x reduction with hydrocarbons. Currently, three types of catalysts are being investigated: (1) zeolites containing transition-metal ions and their oxo complexes, (2) alumina-supported transition- and/or nontransition-metal oxides, and (3) supported noble metals.

Zeolite-based catalysts for NO_x reduction have been shown typically to exhibit high activity and selectivity over a temperature window of about 150 °C at temperatures above 350 °C. The most active catalyst in the class is Cu/ZSM-5,^{237,238} where ZSM-5 is a type of zeolite with an MFI structure. Its activity is suppressed significantly by water vapor, which is present at ~10% in engine exhaust. Fe/ZSM-5 is also very active and selective, and its activity remains high in the presence of water vapor (Figure 19).^{239,240} For these catalysts, heating above the normal operating temperature must be prevented by proper engineering because of the low zeolite hydrothermal stability at high temperatures. In addition, the operating temperature window of these catalysts is rather narrow, and their efficiency depends on the nature of the hydrocarbon reductant. They are also sensitive to sulfur poisoning.

There are M/ZSM-5 active site models formulated on the basis of spectroscopic information.^{241–244} For example, a dimeric Fe–O–Fe cluster has been proposed for Fe/ZSM-5 catalysts. However, most of the information has been acquired ex situ; there is very little information available under actual reaction conditions. It is known that hydrothermal degradation of catalysts is associated with dealumination of the zeolite and migration and agglomeration of the metal ions and oxo complexes.^{245,246} However, the

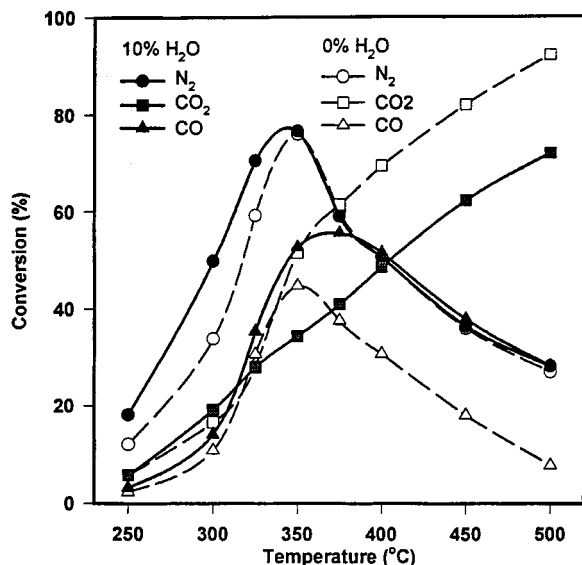


Figure 19. Conversion of NO_x to N_2 in reduction by isobutane over an Fe-ZSM-5 catalyst. Reaction conditions: NO 0.2%, isobutane 0.2%, O_2 3%, H_2O 0% (---) or H_2O 10% (—; GHSV 42 000 h^{-1}). Data taken from ref 240.

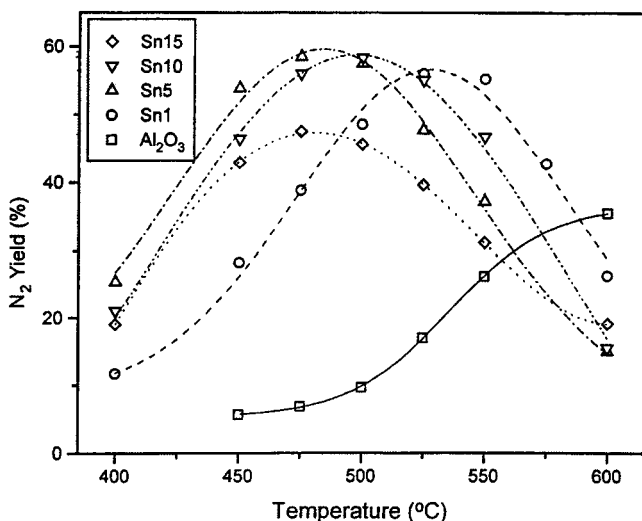


Figure 20. Conversion of NO_x to N_2 in reduction by propene over $\text{SnO}_2/\text{Al}_2\text{O}_3$ catalysts of various wt % Sn. Reaction conditions: 0.1% NO, 0.1% propene, 15% O_2 , 10% H_2O , SV = 30 000 h^{-1} . Taken from ref 253.

detailed mechanistic steps associated with deactivation, the kinetics of these steps, and their dependence on the metal ions as well as the zeolite structure and composition remain to be investigated. Likewise, information on the reaction mechanisms and energetics of the reaction steps is also incomplete.^{247–250} Alumina-based NO_x reduction catalysts have been shown to exhibit high activity and selectivity at temperatures above 425 °C. At high temperatures, their activities are higher than zeolite-based catalysts (e.g., Figure 20 for a $\text{SnO}_2/\text{Al}_2\text{O}_3$ catalyst);^{251–253} however, they also have a relatively narrow operating temperature window of about 150 °C. Their activities depend on the nature of the hydrocarbon and are suppressed by sulfur. They are potentially more durable than the zeolite-based catalysts, but there are insufficient data for definitive conclusions. More information is required on the reaction mechanism,

energetics of the reaction steps, and nature of the active sites.

Noble-metal catalysts are active for NO_x reduction in the low-temperature region, 200–300 °C. However, the selectivity is low—about 40% of the NO_x reduced is converted to N_2O instead of N_2 .^{254,255} These catalysts are also sensitive to sulfur poisoning, and their activity is hydrocarbon-dependent. The state of the noble-metal surfaces and the reaction mechanism are not known.

C. Promising Leads/Research Opportunities

(1) New catalytic systems should be explored, including multisite catalysts in which different active sites have optimal performance characteristics for different steps of the overall reaction pathway.

(2) The composition, structure, and location of the active sites on the support must be better understood. This information, as well as that obtained from computational and modeling studies, will be essential for understanding the dependence of catalytic activities on the structure of the zeolitic and alumina supports.

(3) Changes in the active sites due to deactivation must be understood. The chemical steps in the deactivation process and the kinetics of these steps should be determined. The dependence of these on the support structure (especially zeolitic) and the active site chemical nature should be identified.

(4) Detailed reaction mechanisms must be elucidated for the various catalytic systems, using appropriate experimental and computational approaches. Applications of in-situ techniques should be very useful. Characterization techniques, such as transient kinetic measurements, isotopic labeling, and spectroscopic techniques, as well as use of model compounds and model surfaces, should be used.

(5) The dependence of catalytic activity on the nature of the hydrocarbon and factors that determine the operating temperature window should be identified and understood, especially with respect to the energetics, nature of the bonding, and reactivity of the surface reaction intermediates.

(6) The mechanism of NO decomposition in the presence of O_2 should be elucidated to provide information for computational studies on the energetics of the reactions and search for much more active catalysts.

(7) Processes in nonthermal plasma-assisted catalytic reduction should be elucidated. The roles of the catalyst and plasma and the interplay between them should be identified. New and more active catalytic materials should be identified, and more efficient transfer of electrical power to the chemical reaction channels is desirable. Additionally, the cost and source of energy to produce the plasma must be better defined.

D. Fuel-Cell Powered Vehicles: Introduction and Current Status

Among the various technologies to convert fuel energy into useful power for transportation, fuel cells are considered by many to be the probable long-term

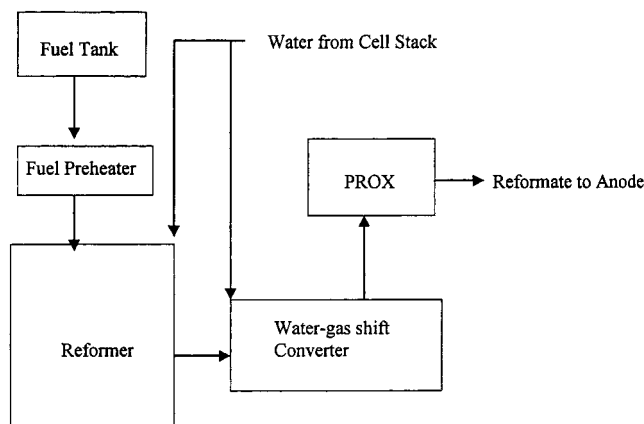


Figure 21. Simplified fuel processing flow diagram for an on-board vehicular fuel cell power plant.

replacement for internal combustion engines in automobiles and other transportation systems.²⁵⁶ The most advanced fuel cells in terms of development are hydrogen fuel cells. However, because of the difficulties in storing large quantities of H_2 on-board a vehicle compared to liquid hydrocarbon fuels and the lack of infrastructure to deliver H_2 , the current emphasis in the development of this technology is to combine the hydrogen fuel cell with an on-board catalytic reformer that converts a liquid fuel into H_2 . The leading candidates for liquid fuel are methanol and gasoline. Most of the major automobile manufacturers (Daimler Chrysler, GM, Ford, Toyota, etc.) have announced plans to introduce fuel cell powered vehicles by 2004, operating on H_2 .

The leading candidate under development as an on-board power plant consists of at least two units: a polymer electrolyte H_2 fuel cell stack (PEFC, also referred to as the PEM fuel cell for proton-exchanged membrane fuel cell) and a fuel reforming unit.^{257,258} Figure 21 shows a fuel processor flow diagram. A fuel processor consists of a fuel preheater/vaporizer for the liquid fuel and water. The vapor is fed to a catalytic reformer for conversion of the fuel mixture to a product rich in H_2 . There may be external supply of heat by burning the H_2 in the exhaust gas. The reformed gas is passed over a water-gas shift catalyst to lower the CO concentration and raise the hydrogen concentration. Finally, the gas is treated in a PROX reactor where CO is preferentially oxidized to CO_2 with minimal loss of H_2 . It is possible that after-treatment of exhaust emissions may be needed, especially during start up and other transient operation conditions. The PEFC operates at about $80\text{ }^\circ\text{C}$. It uses Pt or a Pt alloy as the electrocatalyst. These electrodes are easily poisoned by CO and sulfur. Therefore, the concentration of CO must be reduced to ppm level and even lower for sulfur. Research is underway to raise the PEFC operating temperature and the CO tolerance level to at least 100 ppm.²⁵⁹

Generating H_2 by reacting water with a hydrocarbon fuel over a catalyst, whether oxygenated or not, is a highly endothermic process. Currently, there are two approaches to supply heat:^{260–262} (1) introduction of air along with fuel and water to effect partial oxidation of the fuel and using the heat of oxidation

for the steam reforming reaction which occurs simultaneously and (2) burning some of the fuel directly or in the exhaust and transferring the heat via a heat exchanger to the reformer. Ideally, the reformed fuel (called reformato) would contain only CO_2 , H_2 , H_2O . In practice, depending on the operating conditions and the fuel, it also contains small amounts of CO, CH_4 , and other carbon-containing products. This requires treatment to lower the CO concentration to below 10 ppm. This can be accomplished by catalytic water-gas shift (which also increases the H_2 concentration) and either selective CO oxidation (oxidation of CO but not H_2) or selective CO methanation (conversion of CO but not CO_2 to CH_4). Membrane separation using Pd or a Pd alloy may also be used, which, however, is not likely to be economically competitive. The purified reformato is then used in the PEFC. The most promising selective CO oxidation catalysts are based on Pt-group metals.^{263–266}

Although an intense development effort is being put into automobile fuel cell technology, a unit constructed using current generation technologies in all components is still far from meeting industrial performance and cost targets. The size, weight, and cost of the unit must be reduced substantially, and durability must be enhanced to meet the 10 000 h lifetime goal, with operation that includes many cycles of start-up and shut-down. Since Pt-group metals are used in the various catalytic components, it is estimated that ~ 100 – 150 g of metal is required for a 50 kW fuel cell powered vehicle, versus about 2–5 g per vehicle used in the current catalytic converter for gasoline engines.²⁶⁷

A less developed technology is the methanol fuel cell, where methanol is used directly as fuel without conversion first into H_2 . The advantage of this technology is a potentially more compact system, since the on-board reformer and the associated reformato cleanup subsystems are no longer needed. However, the current electrocatalysts are much less active for this reaction. Thus, a much larger and more expensive fuel cell is needed.

E. Issues

(1) Although an ideal reformato should contain only CO_2 , H_2O , and H_2 , CO and other contaminants exist as undesirable byproducts. A comprehensive catalytic reaction network description is presently unavailable, especially for reforming with partial oxidation. There is little information on the mechanisms involved in these reactions, or the active phase and the active sites of the catalysts.

(2) Considering the cost and supply, the amount of Pt-group metals to be used per vehicle must be reduced by over 2 orders of magnitude. An alternative is to replace them with cheaper, nonnoble metals. In either case, the activities of these catalysts must be greatly enhanced.

(3) Pt-based electrocatalysts are sensitive to CO and sulfur poisoning. Developing electrocatalysts that are less sensitive to these contaminants will alleviate the need to purify the reformato.

(4) The large size and weight of the reformer is due to the low activities of the reforming and water-gas

shift catalysts. Additionally, some of these components are sensitive to sulfur poisoning. The active form of some of the traditional catalysts for these reactions, such as the Cu-based low-temperature water-gas shift catalyst and the Ni-based hydrocarbon steaming reforming catalyst, is the reduced metal. It is oxidized by exposure to air and must be activated by in-situ reduction, resulting in slow start up. Ni is also pyrolytic. Thermal sintering of the active components causes deactivation.

(5) The optimal operating temperatures are quite different for the different types of catalytic units and fuel cells, with the efficiency of a PEFC being higher at elevated pressures. These characteristics necessitate cooling of the gas between stages and use of a compressor, which represent loss in energy conversion efficiency. The efficiency is also lower at the higher current densities desirable for practical applications.

(6) Provision must be made for operating cells which produce H₂O in cold climates.

F. Promising Leads/Research Opportunities

(1) The reactions, their mechanisms and energetics, and the nature of the corresponding active sites involved in the reforming reactions should be elucidated, especially for the partial oxidation/reforming process. Owing to the complexity of such a process and the large number of reactions involved, it is likely that different catalytic phases and active sites are involved. Such information will be valuable in the search for more active and selective reforming catalysts that generate less CO and other contaminants.

(2) For selective CO oxidation in the reformat, it is important to minimize reverse water-gas shift (producing CO) and methanation (consuming H₂ fuel) reactions. Thus, elucidating the energetics and detailed atomic-level processes involved in selective CO oxidation under practical conditions is crucial. Better understanding the competitive interaction of CO, H₂, and O₂ with surfaces, especially in the presence of CO₂ and H₂O, may lead to higher selectivity by suitable modification of the catalytic components. Discovery of highly active, selective, nonnoble-metal catalysts for this reaction is also desirable.

(3) The interaction of CO with finely dispersed Pt-group metals and the modification by a neighboring second metal or metal oxide must be understood. The information would be valuable for developing more CO-resistant catalysts and electrocatalysts.

(4) New catalysts for low-temperature reforming and reformat treatment should be explored. Ideally, the reforming process can operate at the same temperature as the fuel cell to minimize loss in efficiency. Likewise, efficient electrocatalysts that operate at near ambient pressure would be desirable.

(5) The activity and durability of reforming and water-gas shift catalysts must be enhanced. New methods to stabilize the active phases against sintering or new catalysts must be developed.

(6) More active electrocatalysts are needed for direct conversion of methanol in methanol fuel cells. To support this effort, the energetics of the various

reaction steps in the direct conversion of methanol on electrocatalysts require elucidation.

VII. Summary

The goal of the "Opportunities for Catalysis Research in Carbon Management" workshop was to review within the context of greenhouse gas/carbon issues the current state of knowledge, barriers to further scientific and technological progress, and basic scientific research needs in the areas of H₂ generation and utilization, light hydrocarbon activation and utilization, carbon dioxide activation, utilization, and sequestration, emerging techniques and research directions in relevant catalysis research, and in catalysis for more efficient transportation engines.

Several overarching themes emerge from this review. First and foremost, there is a pressing need to better understand in detail the catalytic mechanisms involved in almost every process area mentioned above. This includes the structures, energetics, lifetimes, and reactivities of the species thought to be important in the key catalytic cycles. As much of this type of information as is possible to acquire would also greatly aid in better understanding perplexing, incomplete/inefficient catalytic cycles and in inventing new, efficient ones. The most productive way to attack such problems must include long-term, in-depth fundamental studies of both commercial and model processes, by conventional research techniques and, importantly, by applying various promising new physicochemical and computational approaches which would allow incisive, in situ elucidation of reaction pathways. There is also a consensus that more exploratory experiments, especially high-risk, unconventional catalytic and model studies, should be undertaken. Such an effort will likely require specialized equipment, instrumentation, and computational facilities. The most expeditious and cost-effective means to carry out this research would be by close coupling of academic, industrial, and national laboratory catalysis efforts worldwide. Completely new research approaches should be vigorously explored, ranging from novel compositions, fabrication techniques, reactors, and reaction conditions for heterogeneous catalysts, to novel ligands and ligation geometries (e.g., biomimetic), reaction media, and activation methods for homogeneous ones. The interplay between these two areas involving various hybrid and single-site supported catalyst systems should also be productive. Finally, new combinatorial and semicombinatorial means to rapidly create and screen catalyst systems are now available. As a complement to the approaches noted above, these techniques promise to greatly accelerate catalyst discovery, evaluation, and understanding. They should be incorporated in the vigorous international research effort needed in this field.

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