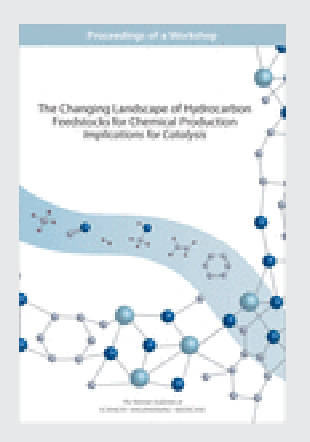

The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop

DETAILS

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Proceedings of a Workshop

Joe Alper, Rapporteur

Board on Chemical Sciences and Technology

Division on Earth and Life Studies

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Acknowledgments

This Proceedings of a Workshop has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published Proceedings of a Workshop as sound as possible and to ensure that the Proceedings of a Workshop meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the process.

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Although the reviewers listed above have provided many constructive comments and suggestions, they did not see the final draft of the Proceedings of a Workshop before its release. The review of this Proceedings of a Workshop was overseen by **Levi Thompson,** University of Michigan, who was responsible for making certain that an independent examination of this Proceedings of a Workshop was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this Proceedings of a Workshop rests entirely with the rapporteur and the institution.

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Acronyms and Abbreviations

ACC	American Chemistry Council
ARPA-E	Advanced Research Projects Agency-Energy
ASU	air separation unit
BTU	British thermal unit
DOE	U.S. Department of Energy
EIA	U.S. Energy Information Agency
LLDPE	linear low-density polyethylene
ME	Middle East
MIT	Massachusetts Institute of Technology
MTO	methane-to-olefin
NSF	National Science Foundation
PDH	propane dehydrogenation
PET	polyethylene terephthalate
USGC	United States Gulf Coast

1

Introduction and Overview[1]

A decade ago, the U.S. chemical industry was in decline. Of the more than 40 chemical manufacturing plants being built worldwide in the mid-2000s with more than $1 billion in capitalization, none were under construction in the United States. Today, as a result of abundant domestic supplies of affordable natural gas and natural gas liquids[2] resulting from the dramatic rise in shale gas production, the U.S. chemical industry has gone from the world's highest-cost producer in 2005 to among the lowest-cost producers today (see Figure 1-1). According to the American Chemistry Council (ACC) estimates, as of September 2015 companies from around the world have announced 246 projects and $153 billion in potential capital investments in U.S. chemical-processing facilities (American Chemistry Council, 2016), up from 97 projects and $72 billion as of March 2013 (American Chemistry Council, 2013). Largely as a result of the shale gas boom, U.S. jobs related to plastics manufacturing alone are expected to grow by 462,000, or more than 20 percent over the next decade (American Chemistry Council, 2015a).

The U.S. Energy Information Administration (EIA) estimated proven U.S. reserves of natural gas and natural gas liquids as of December 31, 2014, to be 388.8 trillion cubic feet, an increase of 8.8 percent over the prior year's estimate and nearly double that of 10 years earlier (see Figure 1-2). This increase is primarily the result of the ability to extract hydrocarbons from shale deposits using a combination of horizontal drilling and hydraulic fracturing. Production of natural gas and natural gas liquids from these reserves has also soared over the past decade and is forecast to continue to rise (U.S. Energy Information Agency, 2016). As a result, the U.S. chemical industry is in the process of switching from naphtha, derived from crude oil, as its major feedstock to natural gas and natural gas liquids. In order to maximize the benefits and take advantage of today's inexpensive source of natural gas and natural gas liquids to create investments and jobs in the United States, it is important to develop new and more efficient processes related to catalytic conversion of natural gas to higher value materials.

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[1] The report summarized the views expressed by individual workshop participants. While the committee is responsible for the overall quality and accuracy of the report as a record of what transpired at the workshop, the views contained in the report are not necessarily those of all workshop participants, the committee, or the National Academies of Sciences, Engineering, and Medicine.

[2] Natural gas liquids consist primarily of ethane, propane, and butanes.

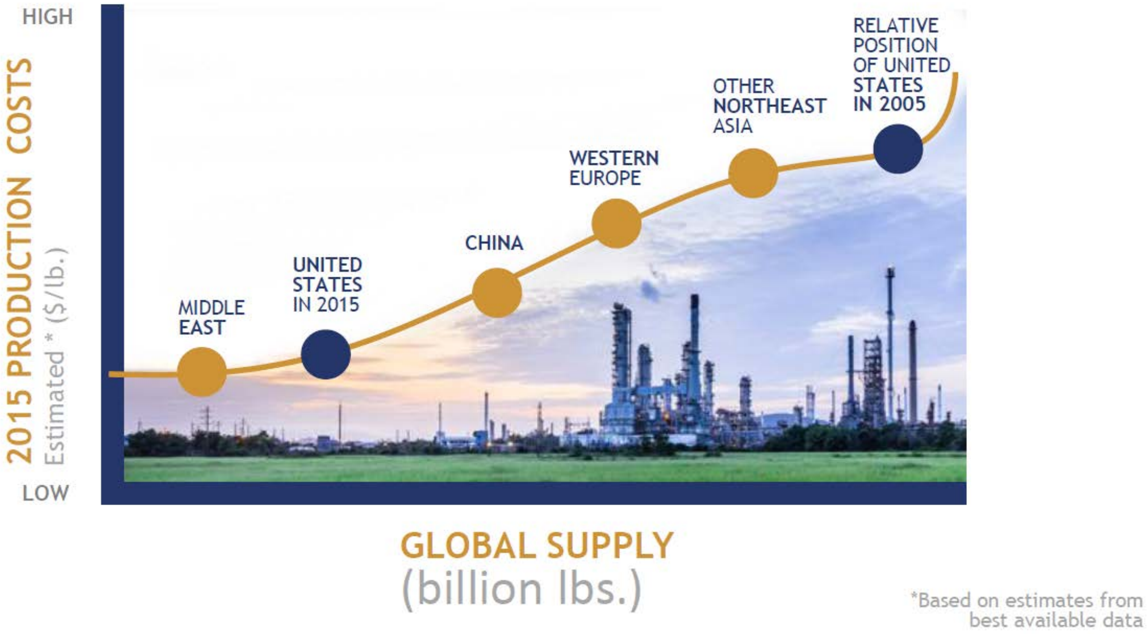

FIGURE 1-1 Relative position of the U.S. petrochemical production costs.
SOURCE: American Chemistry Council, 2016.

OPPORTUNITIES FOR CATALYSIS

The low cost and increased supply of natural gas and natural gas liquids in the United States provides an opportunity to discover and develop new catalysts and processes to enable the direct conversion of natural gas and natural gas liquids into value-added chemicals with a lower carbon footprint. The economic implications of developing advanced technologies to utilize and process natural gas and natural gas liquids for chemical production could be significant, as commodity, intermediate, and fine chemicals represent a higher-economic-value use of shale gas compared with its use as a fuel.[3] The shift from heavier petroleum-based feedstocks to lighter shale gas sources has created opportunities for the U.S. petrochemical industry, but it has also changed the relative availability and cost of certain chemicals. For example, while the cost of ethylene has dropped, the prices of butadiene and aromatic chemicals such as benzene and toluene—all byproducts of naphtha/oil cracking to produce ethylene—have increased as supplies have become constrained with the shift from naphtha to natural gas feedstocks (DeRosa and Allen, 2015). While the prices of butadiene and BTX swing with time and demand, the trend is toward lower production of these chemicals as more ethane and natural gas liquids are used to produce olefins. As a result, there is an increasing demand for on-purpose, catalytically driven routes to convert natural gas liquids into these industrially important chemical intermediates. In order to maximize the benefits and take advantage of today’s inexpensive source of natural gas and natural gas liquids to create investments and jobs in the United States, it is important to

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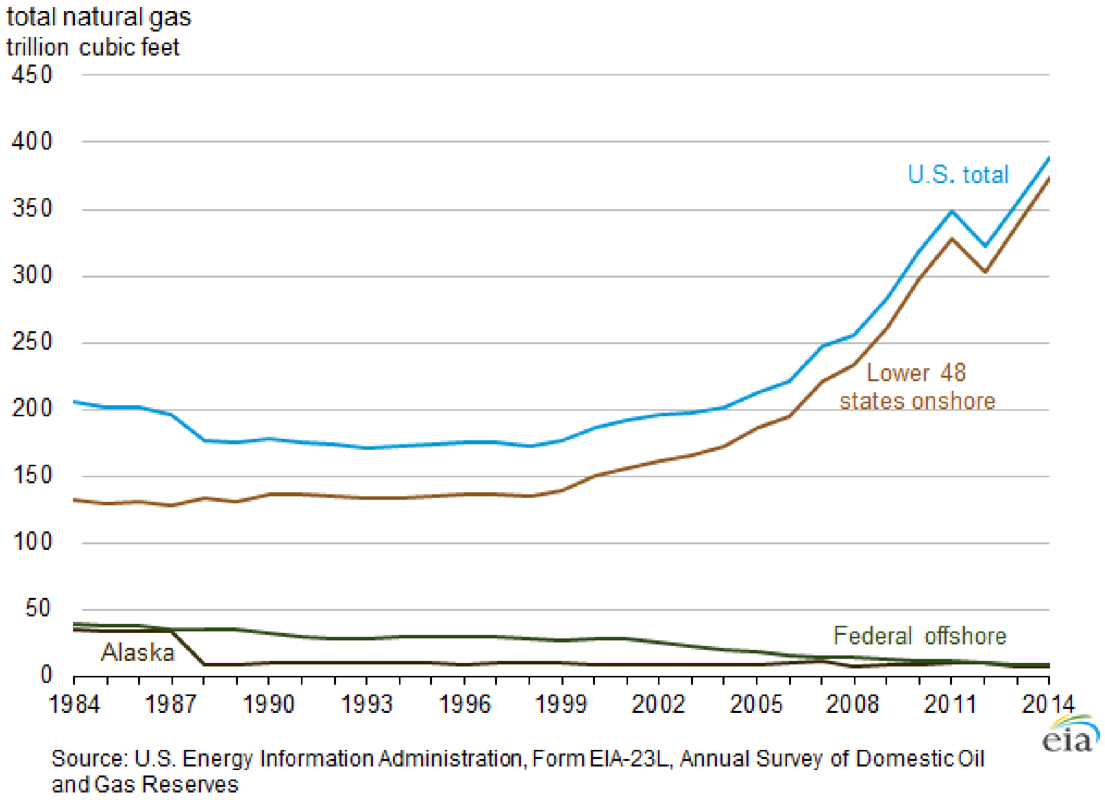
[3] Economic return from various uses of shale gas should trend similarly to returns from use of oil. While less than 4 percent of oil consumed in the United States is used for production of petrochemical products that use generates close to half of the pre-tax revenue derived from each barrel of oil utilized in the United States (Duff, 2012).

develop new and more efficient processes related to catalytic conversion of natural gas to higher value materials. Because natural gas and natural gas liquids are abundant and lower in cost than equivalent oil-based feedstocks, along with the almost unique situation with large reserves and existing pipelines and other infrastructure, new catalytic processes would give advantage to U.S. producers of chemicals and plastics, and allow for the retention of the value of the carbon in natural gas, rather than burning the gas for its caloric value, which typically is the lowest value use.



Source: U.S. Energy Information Administration, Form EIA-23L, Annual Survey of Domestic Oil and Gas Reserves

FIGURE 1-2 U.S. proven reserves of natural gas and natural gas liquids, 1984-2014.
SOURCE: U.S. Energy Information Agency, 2015.

CHARGE TO THE COMMITTEE

To better understand the opportunities for catalysis research in an era of shifting feedstocks for chemical production and to identify the gaps in the current research portfolio, the National Academies of Sciences, Engineering, and Medicine's Board on Chemical Sciences and Technology conducted an interactive, multidisciplinary public 2-day workshop on March 7-8, 2016, in Washington, DC, and focused on identifying gaps and opportunities in catalysis research in an era of shifting feedstocks for chemical production (see Box 1-1).

BOX 1-1
Statement of Task

An ad hoc committee will develop and conduct an interactive, multidisciplinary public workshop that focuses on how chemical feedstocks and processing are changing in the United States and what the implications of those changes are for research in the area of catalysis. The 2-day workshop will:

1. Describe the changes that are occurring or are expected to occur in the chemical industry with the shifts to lighter feedstocks (particularly, shale gas) and how these changes in the pathways to chemicals affect catalysis needs.
2. Provide an overview of the current state-of-the-art in catalysis with respect to the relevant feedstocks and chemicals.
3. Review and discuss gaps and opportunities in catalysis research.

Workshop participants will include representatives from academia, the chemical and energy industries, the U.S. government, national laboratories, and professional organizations, such as the American Chemical Society. A workshop report will be prepared and published.

The goal of this workshop was to identify advances in catalysis that can enable the United States to fully realize the potential of the shale gas revolution for the U.S. chemical industry and, as a result, to help target the efforts of U.S. researchers and funding agencies on those areas of science and technology development that are most critical to achieving these advances. It is the hope of the committee that this workshop will provide a basis for designing research that will lead to the development of new catalysts for converting methane, ethane, and other natural gas liquids into higher-value chemical intermediates under moderate conditions or that enable new routes to chemicals traditionally produced as byproducts of crude oil refining.

STRUCTURE OF THE REPORT

While the committee is responsible for the overall quality and accuracy of the report as a record of what transpired at the workshop, the views contained in the report are not necessarily those of all workshop participants, the committee, or the National Academies of Sciences, Engineering, and Medicine. In accordance with the policies of the Academies, the workshop did not attempt to establish any consensus conclusions or recommendations about needs and future directions, focusing instead on challenges and opportunities identified by the speakers and workshop participants.

Chapter 2 provides an overview of the shale gas boom and its implications for the U.S. chemical industry and catalysis, while Chapter 3 discusses the key messages of two presentations on potential opportunities for chemical and biological catalysis to enable the more efficient use of shale gas components as feedstocks for value-added chemical production. Chapter 3 also recounts the reports from four working groups that discussed the challenges and opportunities for converting methane to useful feedstocks and value-added products. Chapter 4 reviews key advances in catalytic conversion of ethane and propane and summarizes the reports from four working groups that discussed the challenges and opportunities in this area, as well as some of the emerging opportunities for novel approaches to natural gas conversion, including the use of nontraditional oxidants. Chapter 5 provides a review of a panel session on environmental issues related to shale gas conversion into value-added products, and Chapter 6 summarizes the key lessons learned from the 2 days of presentations and discussions.

2

The Shale Gas Boom and Its Impact on the American Chemical Industry

The modern, capital-intensive U.S. chemical industry converts fractions of fossil fuels—naphtha from oil and natural gas liquids from natural gas—into two major chemicals, ethylene and propylene, which it then uses to produce polyethylene, polypropylene, and a limited number of other bulk chemicals (see Figure 2-1). The chemical industry and its customers then use these bulk chemicals to produce a wide range of higher-value products. The technology for converting naphtha and natural gas liquids is based on the steam cracker, which dates to the 1920s and relies on heat, not catalysis, to convert ethane and propane into the corresponding olefins. While this technology is well established, with superior production economics, it is energy- and capital-intensive and emits a substantial amount of carbon dioxide as a by-product. As such, an economically competitive catalytic process that reduces energy use, capital demands, and carbon emissions could offer significant benefits for the chemical industry.

While olefin production has been growing steadily at more than a 4 percent compound annual growth rate since the 1990s, the U.S. chemical industry has gone through upheavals over that same period. These upheavals resulted from the combined effects of two recessions and several periods when the cost of energy from natural gas exceeded that of oil. Until the first of these cost inversions, oil and natural gas prices had been relatively stable and the U.S. industry had an economic advantage because of two factors: the availability of natural gas liquids that traded below the price of petroleum-derived naphtha and the industry's reliance on light steam crackers optimized to use natural gas liquids as the feedstock.

One reality of the global chemical industry, explained Mark Jones, Executive External Strategy and Communications fellow at The Dow Chemical Company, is that feedstocks are not fungible. European and Asian chemical industries primarily use naphtha because they have almost no natural gas resources of their own and it is less expensive to import oil than natural gas liquids. Saudi Arabia and other oil-producing nations in the Middle East primarily use natural gas liquids because of the ready supplies of low-value natural gas that would otherwise mostly be flared. Jones noted that around 2004, proven U.S. reserves of natural gas were falling, and chemical plants were being disassembled and moved to production sites outside of the United States. Chemical industry researchers even began looking at other feedstocks such as syngas—a mixture consisting primarily of hydrogen, carbon monoxide, and carbon dioxide—produced from coal, biomass, and methane.

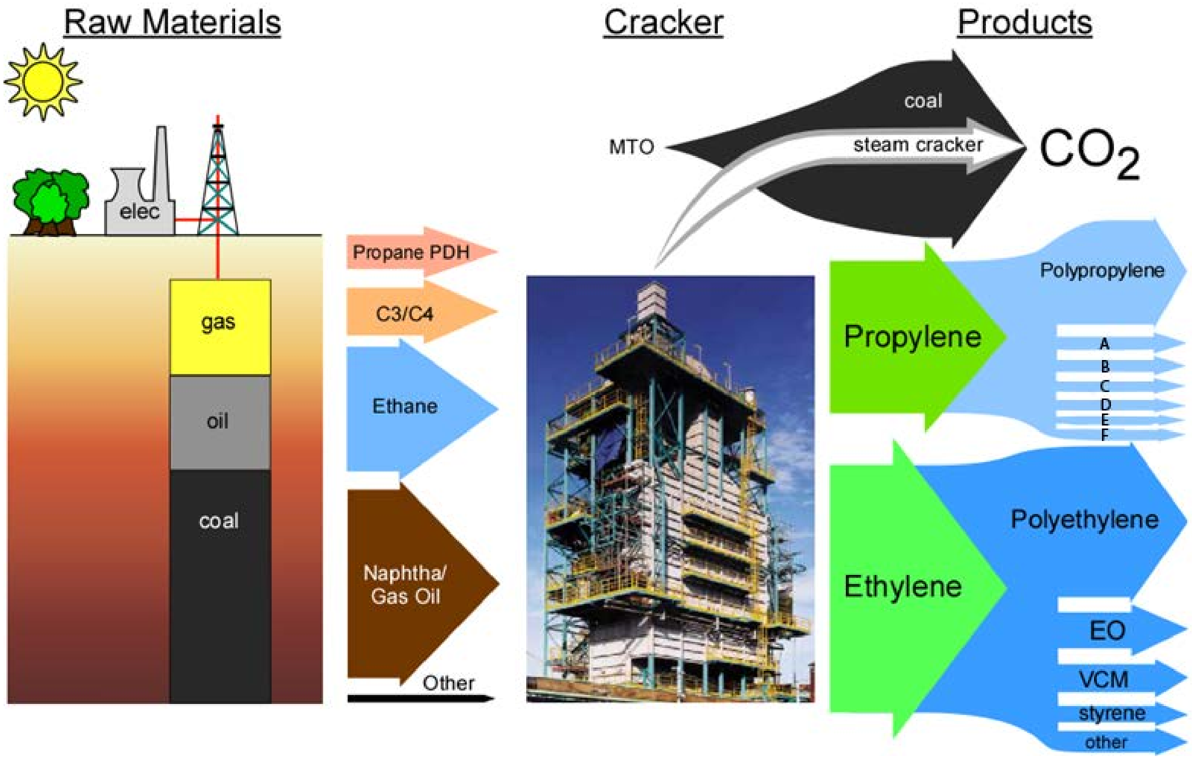


FIGURE 2-1 A snapshot of the chemical industry and its major products. (A. Propylene Oxide; B. Oxo Alcohols; C. Acrylonitrile; D. Cumene/Phenol; E. Acrylic Acid; F. Other).
SOURCE: Jones, 2016.

That bleak scenario, which dominated the chemical industry's outlook from 2000 to 2006, vanished with the successful demonstration that oil and gas from the huge shale deposits in the United States could be recovered economically. By 2010, shale gas production was rising dramatically. More importantly for the U.S. chemical industry, natural gas from shale is "wetter" than from other sources, meaning it has a higher percentage of the natural gas liquids that the chemical industry desires. As a result, the shale gas boom has led to a concomitant increase in the supply of natural gas liquids (see Figure 2-2), and the U.S. chemical industry moved from being disadvantaged from a cost perspective to highly advantaged relative to all but some Middle Eastern countries.

Of even greater importance to the rebirth of the U.S. chemical industry is the fact that proven reserves of shale gas have also risen. As Jones explained, the shale gas boom is not a revolution of geology but of technology. That is, the locations of shale deposits had been known for years, but it took technological development to tap those deposits economically. He also noted that because the locations of shale are well mapped, the risks involved with extraction of oil and natural gas from those deposits is greatly reduced compared with traditional exploration and drilling ventures. The end result for the U.S. chemical industry is that it should have ready access to lower-cost feedstocks, relative to most other countries, for the foreseeable future, which bodes well for the U.S. economy, given what has already transpired over the past decade. Between 2004 and 2014, the value of chemical shipments increased by 48 percent, chemical exports doubled, capital expenditures in the United States rose by 77 percent, and chemical industry research funding jumped 50 percent (see Figure 2-3).

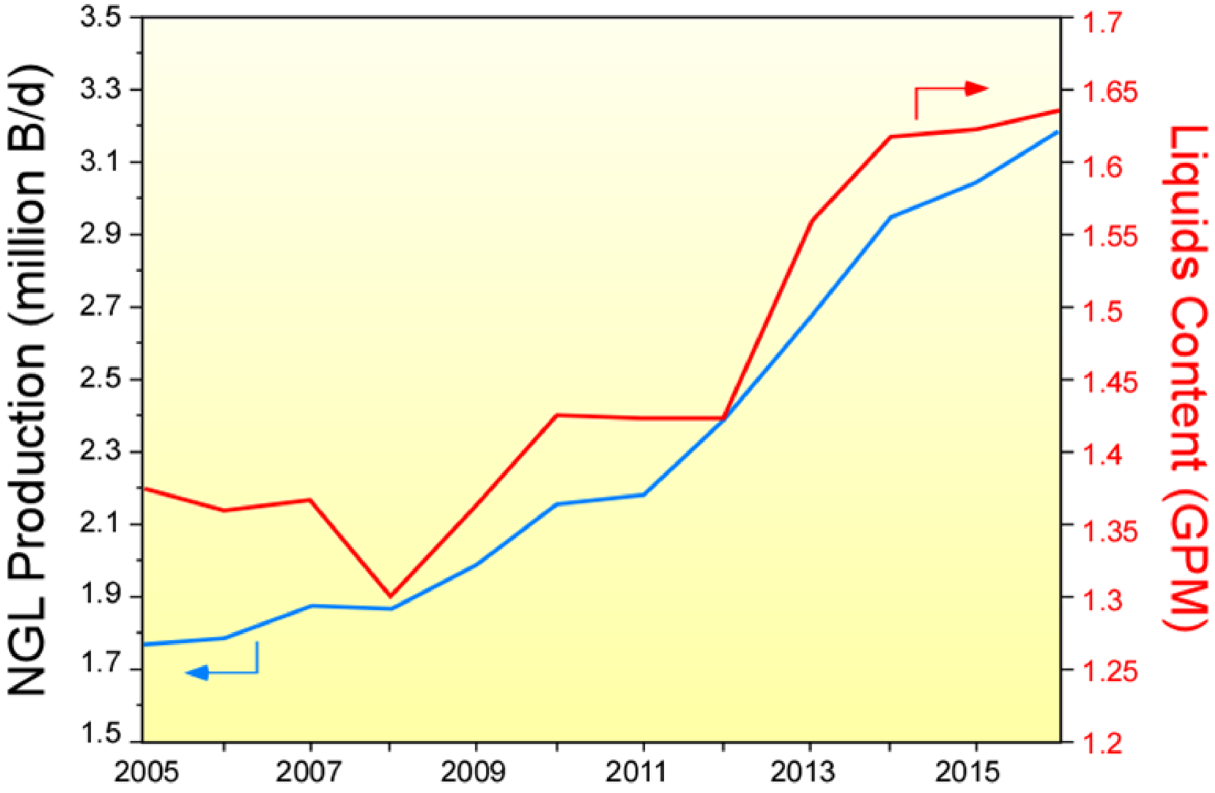


FIGURE 2-2 Growth in production of natural gas liquids.
NOTE: B/d = barrels per day; GPM = gallons per thousand cubic feet; NGL = natural gas liquids.
SOURCE: Jones, 2016.

Jones noted that even with the recent fall in oil prices, natural gas liquids still maintain a significant cost advantage over oil-derived naphtha. In addition, natural gas crackers are less expensive to build and operate than naphtha crackers, and ethane cracking is more efficient than naphtha cracking. Approximately 30 percent of the naphtha fed into a steam cracker is converted to ethylene, while approximately 80 percent of the ethane is converted to ethylene (see Figure 2-4). The tradeoff is that naphtha cracking produces chemicals such as propylene, butadiene, benzene, and toluene that the chemical industry had found uses for when naphtha cracking was more prevalent. In addition, some chemicals, such as cyclopentadiene, are only produced economically via naphtha cracking. Jones said that the rapid growth in propylene-based products and the move to lighter feedstocks that reduced the supply of propylene has resulted in ethylene and propylene being nearly at price parity, while butadiene and benzene prices have risen substantially. Many of these molecules are now the subjects of development efforts as chemists search for catalytic processes that can convert methane, ethane, and other lighter hydrocarbons into these in-demand chemical intermediates. He also noted the low cost of natural gas liquids and the high demand for ethylene and propylene has created an optimal scenario for the chemical industry, one in which the price spread between raw material and product makes chemical production highly profitable.

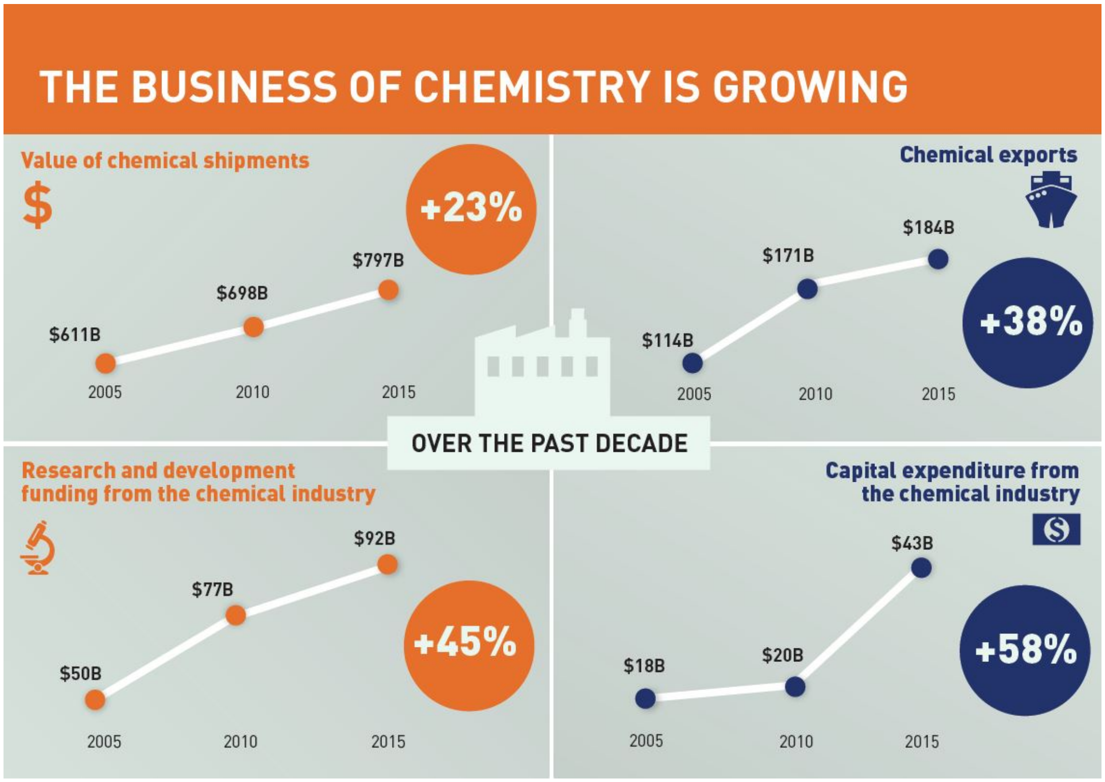


FIGURE 2-3 Growth of the U.S. chemical industry since the start of the shale gas boom.
NOTE: B = billions.
SOURCE: American Chemical Council, 2014. Reproduced with permission by Ryan Baldwin.

Natural gas liquids contain a significant amount of propane, with the result that propane prices have fallen far enough that it has become economical to produce high-demand propylene directly from propane via catalytic propane dehydrogenation. As many as seven new propane dehydrogenation plants have been announced in the United States, and up to 17 are slated for construction in China, which is importing propane from the United States. Jones noted that the United States is also exporting smaller amounts of ethane and butane relative to propane.

The abundant supplies of cheap ethane, and to a lesser extent propane, from shale gas are fueling a rebirth of the U.S. chemical industry (see Figure 2-5), but the predominant component of shale gas is still methane and it, too, has uses as a chemical feedstock. For the most part, methane is first converted to syngas, which is then turned directly or indirectly via catalytic processes into ammonia, methanol, acetic acid, and formaldehyde. During the natural gas price spike, ammonia and methanol production also moved off shore, but as with ethylene and propylene production, methanol and ammonia production is now returning to the United States with the ongoing renaissance in the U.S. chemical industry. This resurgence bodes well for the U.S. balance of trade, as the chemical industry has historically contributed positively to the balance of trade. In fact, from a low of $18.1 billion in 2005, the balance of trade surplus generated by the U.S. chemical industry as a whole, excluding pharmaceutical production, increased to $36.7 billion in 2014 (American Chemistry Council, 2015b). It has also led to a growth in employment: Since 2010, the number of chemical industry jobs has grown from 786,500 to 805,600, with a concomitant increase in the average hourly wage from $21.07 to $22.75.

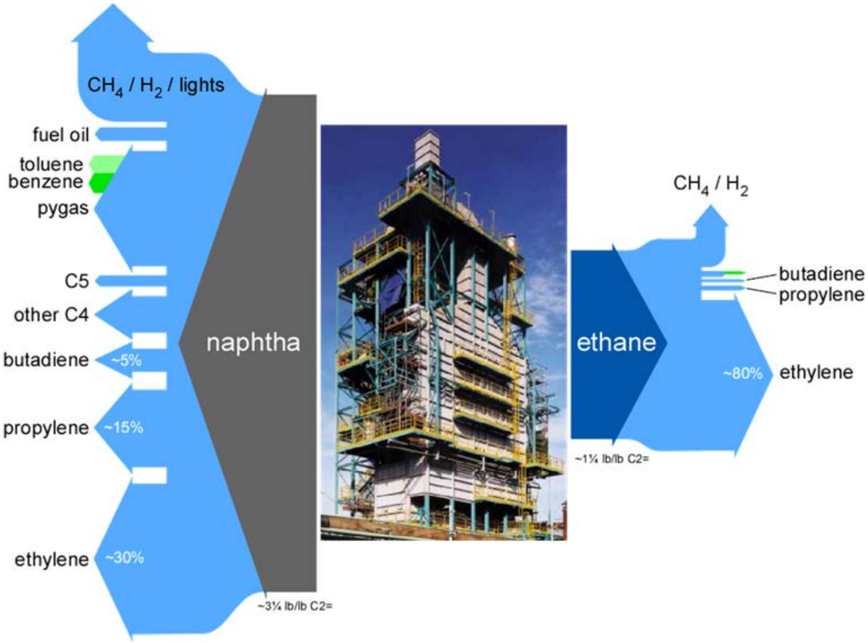


FIGURE 2-4 A comparison of naphtha and ethane cracking.
NOTE: CH_4 = methane; H_2 = hydrogen.
SOURCE: Jones, 2016.

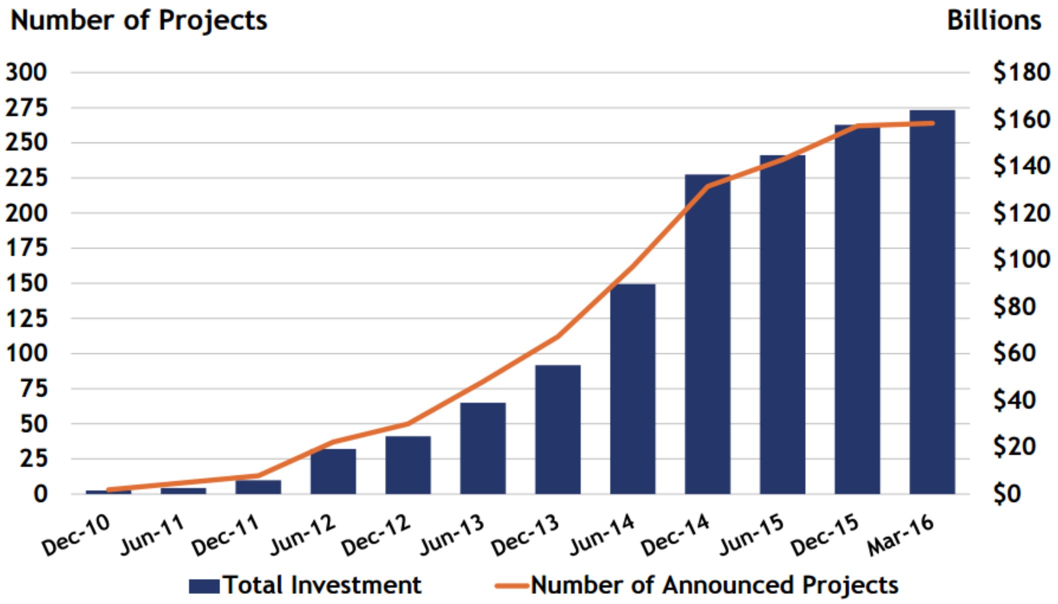


FIGURE 2-5 Cumulative announced chemical industry investments from shale gas from December 2010 to March 2016.
SOURCE: American Chemistry Council, 2016.

IMPLICATIONS FOR CATALYSIS

Today, the availability of low-cost methane and natural gas liquids offers a transitional opportunity to lower the carbon footprint of the chemical industry if new catalytic approaches (see Figure 2-6) can be developed, said Johannes Lercher, professor of chemistry at the Technical University of Munich and Director of the Institute for Integrated Catalysis at the Pacific Northwest National Laboratory. He noted that one of the bigger challenges facing chemists is to link what is known about catalysis with insights from materials science research to create industrial-scale catalysts that will be stable and resist sintering under the sometimes harsh conditions required for many conversion processes involving light alkanes (e.g., reforming to synthesis gas (syngas), dehydrogenation, and aromatization). Other major drivers for new research in catalysis are related to the economic demand to convert small amounts of stranded or associated gases to condensable energy carriers to curtail well-head methane flaring with regulations aimed at reducing greenhouse gas emissions, said Lercher.

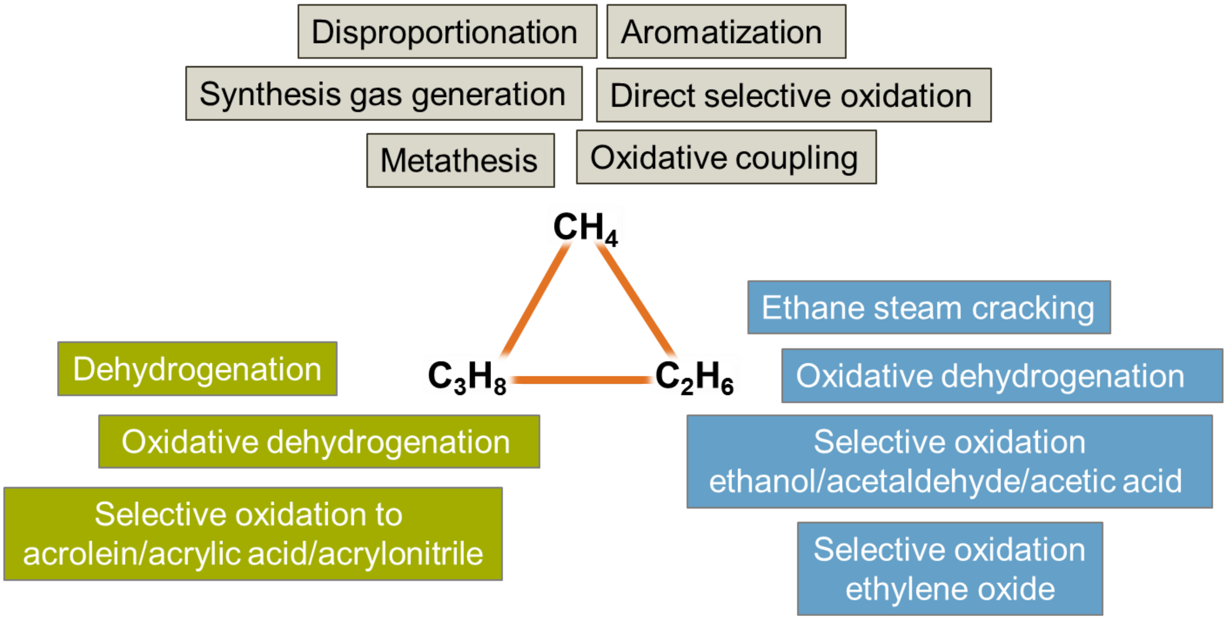


FIGURE 2-6 Potential approaches to converting methane and light alkanes, the major component of natural gas, into other valuable products.
NOTE: C_2H_6 = ethane; C_3H_8 = propane; CH_4 = methane.
SOURCE: Lercher, 2016.

Catalytic Conversion of Methane

The idea of converting methane into higher-value chemicals is not a new one, and chemists have developed a number of catalytic systems for doing so. One approach converts methane to methanol, which is then converted to ethylene. Another approach uses catalysts to achieve oxidative coupling of two methane molecules to produce ethylene. Given that ethane today costs less than methane on the U.S. Gulf Coast, neither of these approaches makes sense economically at today's prices. However, new regulations with the goal of restricting the wasteful practice of natural gas flaring could change the economics rapidly.

There are several routes by which methane could be converted catalytically into higher-value chemicals, including production of synthesis gas (syngas) via processes known as reforming, oxidative coupling, conversion into aromatic compounds, coupling it, e.g., with propane via a reaction known as metathesis, and direct selective partial oxidation of methane into methanol (see Figure 2-6). Note that the use of methane metathesis has been introduced by Basset et al. 2010 for the reaction of methane with an alkane. In the case of propane, the result is two molecules of ethane. The reaction is, thus, the reverse of the ethane metathesis. Production of syngas is widely commercialized at large scale and is a usual process component in the production of ammonia, Fischer–Tropsch synthesis of hydrocarbons and methanol synthesis. There are well-established laboratory and in some cases even pilot plant-scale catalytic processes for the other routes, but all require further research to turn them into economically viable commercial processes. Methane steam reforming, in which methane reacts with water to a mixture of carbon monoxide and hydrogen in the presence of a catalyst is a mature technology, but the challenge, said Lercher, is to understand the process by which carbon deposits on the catalyst and renders parts of the catalyst inactive. The probability and rate of the carbon deposition increases as the C-O-H ratio in the reacting mixture changes, for example, by replacing water with carbon dioxide in the reacting mixture. If thermodynamically feasible, carbon will form under many operating conditions, though it is more severe at higher pressures.

The kinetically relevant step in reforming, regardless of the reactants, is breaking the carbon–hydrogen bond in methane (Wei and Iglesia, 2004), and the rate of carbon removal depends on the oxygen coverage at the catalyst surface (Chin et al., 2013). A high concentration of active oxygen at the catalyst surface reduces the carbon concentration and helps the surface remain active even under harsh conditions. However, if activity only depends on surface oxygen level and the amount of carbon present, the support should not influence the rates of reactions. Under severe conditions strong impact of the support on the stability of the catalyst is observed, suggesting that the support or the interface between the support and the metal provides alternative routes to remove carbon formed in the reforming pathway. This observation, said Lercher, points to better understand how to design catalysts so that they maintain their activity under industrially relevant conditions.

For oxidative coupling of methane to produce ethylene, besides the challenge of selectivity, the main challenges are to reduce the temperature needed to activate the carbon–hydrogen bond and to generate reactive oxygen at the catalyst surface, given that the catalysts currently available are not stable under high-temperature conditions (Salehi et al., 2016; Schwach et al., 2015). Aromatization, which involves methane dehydrogenation to produce reactive carbene and carbyne species and subsequent reactions of these species in combination with acid-catalyzed ring closure to generate aromatic molecules, faces the challenge that excessive dehydrogenation as well as reactions among aromatic molecules will cause the formation of carbon that will block the active catalyst and deactivate the catalyst. Several molybdenum-containing zeolites have been reported to catalyze this reaction slightly below 1,000 kelvin (K), though carbon deposition requires the catalyst to be regenerated regularly (Liu et al., 1999). Lercher pointed also to a recent report of an iron–silica catalyst operating at 1,360 K that remains stable (Guo et al., 2014).

Incorporating methane into larger alkanes via the relatively low-temperature dehydrogenation of propane and metathesis of the resulting olefin or the parent alkane in the presence of methane can be achieved using tantalum-based catalysts supported on a silica surface (Soulivong et al., 2004). Problems to be solved with this reaction include the tight specifications for operating the catalyst, the extremely low rates achieved with the current catalysts, and thermodynamic limitations that require the resulting alkanes to be separated from the hydrogen produced.

Direct partial oxidation of methane to methanol using electrophilic late metal catalysts has, at times, generated excitement from chemists (Periana et al., 1993, 1998, 2003), but these reactions require concentrated sulfuric acid and/or sulfur trioxide or dissolved as oxidant. The process requirement to regenerate the diluted sulfuric acid to reform concentrated sulfuric acid/sulfur trioxide in this catalytic cycle is the major reason this technology has not been developed toward commercialization. While the sulfate provides a stable product, which can be hydrolyzed to methanol, continuous-direct methane-to-methanol processes have poor selectivity that leads easily to over-oxidation. Enzymes, however, have routes to convert methane and oxygen into methanol under mild conditions and at low temperatures. Two types of enzymes are known, one is a membrane-bound enzyme known as Cu-methane monooxygenase, while one enzyme in the cell itself is based on iron. The active site of this enzyme contains 2–3 copper atoms (Chan and Yu, 2008; Lieberman and Rosenzweig, 2005), and chemists are trying to recreate the active site to enable this reaction without the need for the enzyme. Zeolite based catalysts have been found to be the best models so far both with iron (Wood et al., 2004) as well as with copper (Groothaert et al., 2005; Grundner et al., 2015; Woertink et al., 2009). These materials work only stoichiometrically and methanol has to be purged out (or hydrolyzed), which requires the regeneration of the zeolite after each cycle producing methanol. Lercher explained that the challenge here is not so much to find a more active catalyst, but to identify a material that maintains the copper atoms in the right configuration regardless of the environment in which the reaction was conducted. There is also the economic reality that methanol currently has a 30 percent price premium compared with methane, which is produced via methane steam reforming followed by methanol synthesis. This makes it very challenging for direct processes to be successful, Lercher estimated. “We should focus on this type of chemistry, but not be under the illusion that it will lead to quick results,” he said. “What it should do is to lead us to new chemistry that will teach novel pathways to functionalize methane as well as other light alkanes.”

Catalytic Conversion of Ethane

Turning to the possibilities of developing catalysts for converting ethane into higher-value chemicals, Lercher said that the economics of ethane steam cracking make this a particularly challenging problem. Researchers have been investigating catalytic approaches aimed at wringing costs out of today’s steam-cracking ethylene plants, largely by reducing the costs of separating ethylene from unreacted ethane, which accounts for 80 to 90 percent of the capital costs of an ethylene plant. “It only makes sense to go from steam cracking to oxidative dehydrogenation if we can operate with 95-plus percent selectivity and a 60 percent conversion operating in a pressure range that works for industry,” said Lercher. The main challenge to achieving those parameters is that ethane, when activated by a catalyst in the presence of oxygen at the desired operating pressures, not only from ethene, but will be further functionalized with oxygen. One successful approach, for example, coats a redox active oxide carrier with a layer of molten chloride salt (Gärtner et al., 2013, 2014). Another approach uses complex oxides of molybdenum, vanadium, tellurium, and niobium as catalysts, in which the catalytic activity subtly depends on the exact atomic arrangement within the crystal (Melzer et al., 2016). Ethane has also been directly oxidized with hydrogen peroxide, using an iron/copper/zeolite, to produce acetic acid, ethanol, and ethylene (Forde et al., 2013), and efforts to convert ethane into aromatic compounds using gallium-based catalysts have demonstrated some promise, said Lercher, as have catalytic processes for converting propane to acrylic acid and catalytic propane dehydrogenation.

Catalytic Conversion of Propane

Propane is a significant component of natural gas liquids and is readily available. As a result, propane prices have fallen far enough that it has become economical to produce high-demand propylene directly from propane via catalytic propane dehydrogenation (PDH). Thermal (no catalyst) cracking of propane yields predominantly ethylene, not propylene. A catalyst is required to convert propane to a high yield of propylene. Thermolysis of propane predominantly breaks the CH3-CH2 bond, giving a methyl radical and an ethyl radical, which ultimately give ethylene and methane as products. Of all of the technologies that have been developed that produce propylene, PDH provides the highest yield, and because of the price differential between propane and propylene, PDH economics are quite favorable and continued investment in plant construction are being supported.

Several challenging characteristics of PDH technology include temperatures that exceed 600°C and low-pressure conditions. Another challenge of PDH technology is that coke formation is unavoidable, leading to a catalyst life of days and the need for frequent regeneration. As in all catalytic–process technology, the process and catalyst are intertwined and cannot be separated.

Possibilities for Catalysis

Summarizing the possibilities for catalysis, Lercher said that conversion of light alkanes may be challenging, but it also holds significant untapped potential. In his opinion, a concerted research effort combining kinetics, spectroscopy, and theory should be used to understand the catalytic process on an atomistic and molecular level and to translate that knowledge into the development of catalysts with precisely tailored properties that will retain their integrity under industrial operating conditions. He also suggested that chemical engineers and chemists work together with the goal of creating optimal reactor designs for specific catalytic processes. Achieving this vision for catalyst development, said Lercher, transformative developments in analytical capabilities that will enable characterizing catalysts structurally and chemically in a timely and spatially resolved manner is important. It will also require collaborations between materials science and chemistry aimed at synthesizing robust, single-site catalysts and between reactor engineering and chemistry to create processes that allow development at variable scales.

3

Catalytic Conversion of Methane

While the plentiful supplies of inexpensive ethane, propane, and butane from shale gas have revitalized the U.S. chemical industry, those components make up less than 25 percent gallons per thousand cubic feet (Mcf) of a typical shale gas stream (Keller, 2012), with the major component being methane. At some point, it may be desirable to have economically viable processes for converting methane into ethylene and other value-added hydrocarbons, as well as processes that are more efficient than the current industrial methods for converting methane into syngas. Such a circumstance could arise, for example, if the demand for ethane outstrips the supply, if a new process made it economical to convert methane into transportable liquids for stranded gas (i.e., methane reserves that are too small and too far from current pipelines that are often flared or burned unproductively), or if emissions policies change to prevent or penalize the current practice of flaring methane at the wellhead or that tax carbon dioxide emissions as stated by Reinhard Schomäcker, professor of technical chemistry at the Technical University of Berlin.

What would make methane conversion to ethane economically viable? Schomäcker said that any process would have to achieve a suitable added value, not waste much of the methane as byproducts, utilize low-energy separation technologies, and not have unreasonable capital costs for the process equipment. Meeting those requirements, he said, boils down to the issue of selectivity in terms of how much methane is converted to the desired product, such as ethylene, and how much byproduct has to be separated from the desired product.

METHANE TO ETHYLENE VIA OXIDATIVE COUPLING

To illustrate some of the approaches that have been or are being developed for the catalytic conversion of methane, Schomäcker discussed oxidative coupling of methane to produce ethylene. The pioneering work in this area, he noted, occurred in the 1980s (Hinsen and Baerns, 1983; Jones et al., 1984; Keller and Bhasin, 1982), and despite a great deal of effort that resulted in more than 100 publications, chemists were unable to achieve ethylene yields of much greater than 25 percent (see Figure 3-1). Throughout the 1990s, researchers developed a number of novel catalysts, including a lithium–magnesium oxide catalyst that deactivated over time (Lunsford, 1995) and a manganese-tungsten catalyst (Fang et al., 1992) that maintained stable activity for more than 100 hours without the need for regeneration. Schomäcker and his colleagues, along with dozens of other research teams worldwide, have since been able to reproduce the latter results (Simon et al., 2011).

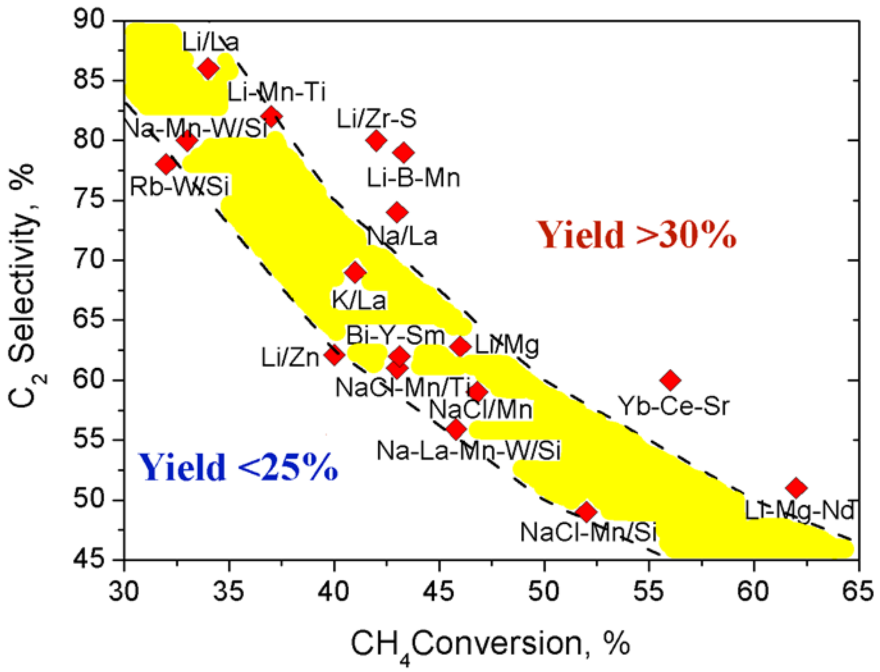


FIGURE 3-1 Conversion efficiency and selectivity of oxidative coupling catalysts.
SOURCE: Zavyalova et al. 2011, Reproduced with permission by Wiley-VCH Verlag GmbH & Co. KGaA.

Another milestone in the field was the development of the first detailed kinetic model for oxidative coupling of methane, in this case for a lanthanum-based catalyst (Stansch et al., 1997). This model proposed that important steps in the reaction occur both at the catalyst surface and in the gas phase, though it did not explain how these steps (listed as 1-8; see Figure 3-2) fit together to yield the desired product.

Step 1: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
Step 2: $2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O$
Step 3: $CH_4 + O_2 \rightarrow CO + H_2O + H_2$
Step 4: $CO + 0.5O_2 \rightarrow CO_2$
Step 5: $C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O$
Step 6: $C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$
Step 7: $C_2H_6 \rightarrow C_2H_4 + H_2$
Step 8: $C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2$
Step 9: $CO + H_2O \rightarrow CO_2 + H_2$
Step 10: $CO_2 + H_2 \rightarrow CO + H_2O$

Lanthanum oxide catalysts, which numerous groups have studied, using a variety of analytical methods (Au et al., 1997; Dubois et al., 1990; Ferreira et al., 2013; Levan et al., 1993; Lin et al., 1986; Louis et al., 1993; Palmer et al., 2002; Sekine et al., 2009), have the highest activity known. Schomäcker noted that it has been easy to improve the performance of lanthanum oxide by forming lanthanum oxycarbonate or by doping it with iron or ceria, each of which increases the selectivity of the reaction substantially, though not enough for industrial use.

Researchers have even tried some unconventional approaches to boost selectivity, including going to very high temperatures in the absence of oxygen (Guo et al., 2014) or by using sulfur as a “soft” oxidant (Zhu et al., 2013).

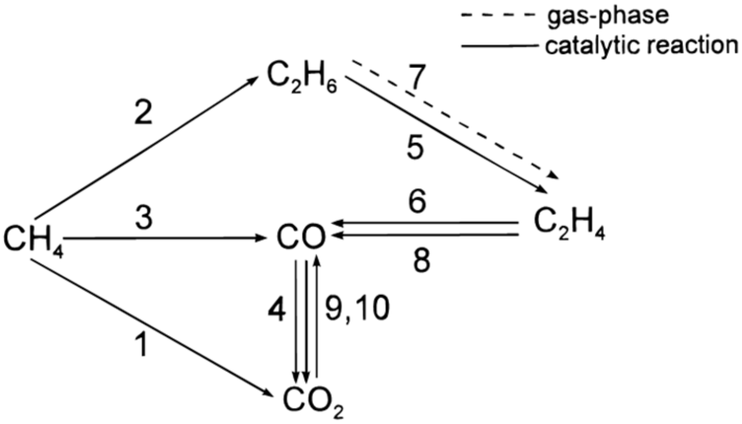


FIGURE 3-2 Reaction scheme of a kinetic model for oxidative coupling of methane (CH_4) as well as for the consecutive reactions of ethane (C_2H_6), ethylene (C_2H_4) and carbon oxides.
SOURCE: Stansch et al., 1997.

When Schomäcker started his studies on methane oxidative coupling, he decided that rather than try to create yet another catalyst, he and his colleagues would study two existing catalysts—lithium/magnesium oxide and a sodium tungstate compound—for more detailed analysis using a variety of approaches. These studies produced a wealth of information, each piece of which provided some insight into a possible mechanism for oxidative coupling (Beck et al., 2014; Cui et al., 2013; Kwapien et al., 2014). One key finding was that the atomic structure of the catalyst had a profound effect on the outcome of the reaction and led to predictions that adding a trace metal to the magnesium oxide catalyst would improve performance. Indeed, adding a trace amount of iron to the catalyst boosted activity and selectivity and increased ethylene yield by a factor of five (Schwach et al., 2013). These studies, he explained, also revealed that the way in which the catalyst activates oxygen is the most important aspect of determining the reaction selectivity. Applying the knowledge gained from these studies, Schomäcker and his colleagues created a series of bimetallic catalysts using sodium tungstate and manganese oxide on a variety of silica support materials, the best of which proved to be a mesoporous silica material known as SBA-15 (Yildiz et al., 2014a, 2014b). He and his collaborators then tested this catalyst in a number of different reactor designs and used the data from these experiments to conduct an economic analysis estimating that, at a 15 percent rate of return, the payback period for a commercial methane to ethylene plant would be between 4 and 7 years.

HYDROCARBONS TO CHEMICALS AND FUELS VIA ENGINEERED MICROBES

In addition to the opportunities for chemical catalysis to contribute to the efficient use of the nation's shale gas reserves, researchers are making progress harnessing the power of biological systems to convert methane and natural gas liquids to value-added products. As Lercher noted, biological approaches have the potential to lower the energy costs associated with the high temperature regimes required for methane, ethane, and propane conversion using chemical catalysis. Realizing that potential, said Greg Stephanopoulos, professor of chemical engineering at the Massachusetts Institute of Technology (MIT), would support biological systems to serve as the basic enabling technology for the 21st-century chemical industry.

Stephanopoulos outlined the currently envisioned routes for biological methane activation and conversion to chemical products and biofuels. An overall pathway of methane activation to an active intermediate CH_3X and a possible assimilation route leading to the synthesis of some product like 3-hydroxybutyrate or butanol was shown. Assimilation can proceed via methanol, which is dehydrogenated to formaldehyde, and processing the latter to an intermediate metabolite of the pentose phosphate pathway. Methane activation is presently possible via anaerobic methanotrophic consortia and aerobic methanotrophs that utilize the activity of a methane monooxygenase enzyme. A challenge with the biological production of certain chemicals like methanol or butanol is the low titers in which the products are made, leading to high energy requirements for recycling huge amounts of water. However, other products like lactic acid, succinic acid, polyhydroxybutyrate (PHB), and lipids may be produced at high concentrations without issues of toxicity to the microorganisms.

Anaerobic consortia have the potential of methane activation at high efficiency, but they exhibit low rates and operate as a mixed culture whereby methane oxidation is coupled with sulfate reduction catalyzed by sulfur-reducing bacteria. No single culture of anaerobic methanotrophs has been isolated yet. Aerobic methanotrophs exhibit a higher rate of methane oxidation albeit at lower energetic efficiency. Various products have been detected to be naturally synthesized in aerobic methanotrophs, such as lipids (potential for biodiesel production) and the polymer PHB, but their concentrations are low (below 1g/l) (Kalyuzhnaya, et al., 2015; Shah et al., 1996; Strong et al., 2015). There is potential in engineering natural aerobic methanotrophs to either increase the figures of merit of naturally produced compounds such as the above, or to endow the host organisms with the pathways required for the synthesis of other products of interest. However, the biological toolkit required for the genetic modulation of these organisms remains underdeveloped, said Stephanopoulos.

On the other hand, Stephanopoulos noted, model organisms like *E. coli* have been engineered for the production of numerous products from carbohydrates and other substrates. These organisms could be further engineered to allow them to utilize methane, which would enable a seamless system whereby methane is activated by these model organisms, converted to an intermediate such as methanol, and the latter converted to the product of choice. Although many of the concepts for such a scheme have been worked out for other systems, formidable challenges remain in achieving the same for the activation and conversion of methane to target products. Stephanopoulos stressed that more research in this area will help develop the basic biological tools and platform strains required to realize this vision.

WORKING GROUP SESSIONS

Following Schomäcker's presentation, the workshop participants broke into four predefined working groups, each of which explored one aspect of catalytic conversion of methane: methane to syngas, methane to ethylene, methane to aromatics, or methane to methanol. Each group, after hearing a short introductory presentation by an expert in the session topic, was asked to answer a set of questions over the course of their deliberations (see Box 3-1). Following the 2-hour discussion period, each group's designated rapporteur summarized the group's work to the reassembled workshop participants. An open discussion followed the four reports.

BOX 3-1
Methane Working Group Questions

1. What, if any, are the impediments to commercial viability of methane to useful feedstocks or value-added products?
2. What are the top two to three well-established research approaches to making methane-conversion processes viable and what are the challenges associated with them?
3. What are some promising but higher-risk novel approaches being undertaken?
4. What are the research opportunities that exist?
5. What should researchers be aware of in terms of industrial requirements and environmental constraints for new approaches to the utilization of natural gas?

Methane to Syngas

In his introductory remarks, Jan Lerou, principal of Jan Lerou Consulting, briefly reviewed the major commercial technologies now used to convert methane into syngas, which then serves as a feedstock for ammonia, methanol, and hydrogen production. The three main technologies are:

1. steam reforming,
2. partial oxidation via non-catalytic and catalytic processes, and
3. catalytic auto-thermal reforming.

In addition, he listed two technologies that are nearing industrial use: (A) short contact time catalytic partial oxidation and (B) oxygen transfer membranes as well as two emerging technologies for converting methane into syngas: (C) chemical looping and (D) dry reforming.[1] Each of these technologies has its own unique limitations and challenges, which if addressed satisfactorily would improve the economics of the processes using these technologies.

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[1] A method of producing synthesis gas from the reaction of carbon dioxide and methane.

Discussion

Following the presentation, this group spent much of its time identifying four key objectives for research aimed at improvement of the available commercial processes, said Maria Flytzani-Stephanopoulos, distinguished professor and the Robert and Marcy Haber Endowed Professor in Energy Sustainability at Tufts University. These research objectives included:

1. Identifying alternatives for the currently used air-separation unit, which adds to capital and operating costs;
2. Improving the carbon or thermal efficiency of these processes, which at present burn a great deal of methane to generate the necessary process heat;
3. Understanding how multifunctional catalyst support materials interact at the interface among materials to enable the design of better catalysts and integrate catalysts and advanced separation membranes; and
4. Employing process intensification, which focuses on molecular-level kinetics, thermodynamics, and heat and mass transfer, to optimize process performance, something that is happening more in Europe than in the United States at the present time.

From these objectives, this group developed a list of research opportunities for the methane-to-syngas process.

- Develop oxygen ion- and proton-conducting ceramic membranes as dual-function materials that would replace the current energy-intensive methods used to separate oxygen from air and also serve as a catalyst support matrix.
- Determine if additive manufacturing using three-dimensional printing could enable co-printing copper or tin catalysts with reactor internals to improve heat transfer, a crucial parameter for methane-to-syngas processes.
- Develop advanced heat-exchange systems and catalyst supports with novel structures.

Flytzani-Stephanopoulos also reported that the breakout group discussed chemical looping reforming, a process in which a reduced metal oxide is oxidized in one reactor and then used to partially oxidize methane to yield carbon monoxide and hydrogen while recovering the initial metal oxide form, is a relatively new technology that shows significant promise as a more efficient means of producing syngas. Flytzani-Stephanopoulos reported, research is required, however, to improve the process itself, to develop novel materials for the reactors, and to characterize the kinetics of the process and the catalytic surface parameters that contribute to coke formation in the reactors. In particular, developing and applying methods for in situ characterization of catalyst active sites under very high temperatures typical in a chemical looping process will enable better understanding of the loss of active sites under those conditions.

Computational chemistry and experimental procedures used together have the potential, Flytzani-Stephanopoulos reported, to drive the discovery of new catalytic materials from first principles. Finally, this group felt that short-contact-time reactors have shown some promise, but there is still much to be done to achieve the level of process reliability required for an industrial process.

Methane to Ethylene

As Schomäcker had noted, oxidative coupling of methane to ethylene is technically feasible, but there are a number of features that at present make direct methane-to-ethylene processes uncompetitive commercially, a message reiterated in the introductory presentation by Bob Maughon, vice president for performance plastics and hydrocarbons research and development at The Dow Chemical Company. Maughon did note that several companies are developing novel catalytic systems for converting methane to ethylene, and one company, Siluria Technologies, is operating a demonstration plant using the catalyst it has developed.

Discussion

Following that presentation, the working group identified three specific issues that act as impediments to commercial viability, as reported by Anne Gaffney, director of process science and technology at the Idaho National Laboratory.

1. The first impediment is the lack of substantial capital investment to build an industrial-scale facility for oxidative coupling compared with building an ethane cracker, even when using the first commercially available system developed by Siluria Technologies (see Figure 3-3).
2. Selectivity for producing ethylene, which Schomäcker discussed, is another obstacle, particularly because poor selectivity increases the expense of separating ethylene from the reaction byproducts.
3. The working group, said Gaffney, noted that the development of cost-effective and robust membrane separation technologies could significantly improve the economic competitiveness of methane oxidative coupling to produce ethylene, though the relative low cost of ethane compared to methane today makes the economics of methane-to-ethylene conversion challenging even with technological improvements.

One way in which the direct conversion of methane to ethylene could be cost-effective would be for converting geographically isolated sources of methane into a transportable liquid. Such sources include smaller deposits of “dry” natural gas, stranded natural gas and gas associated with oil production, all of which are currently flared, and biologically-derived methane. The challenge here would be to develop a processing technology that is economical at small scale and perhaps even transportable between these different sources.

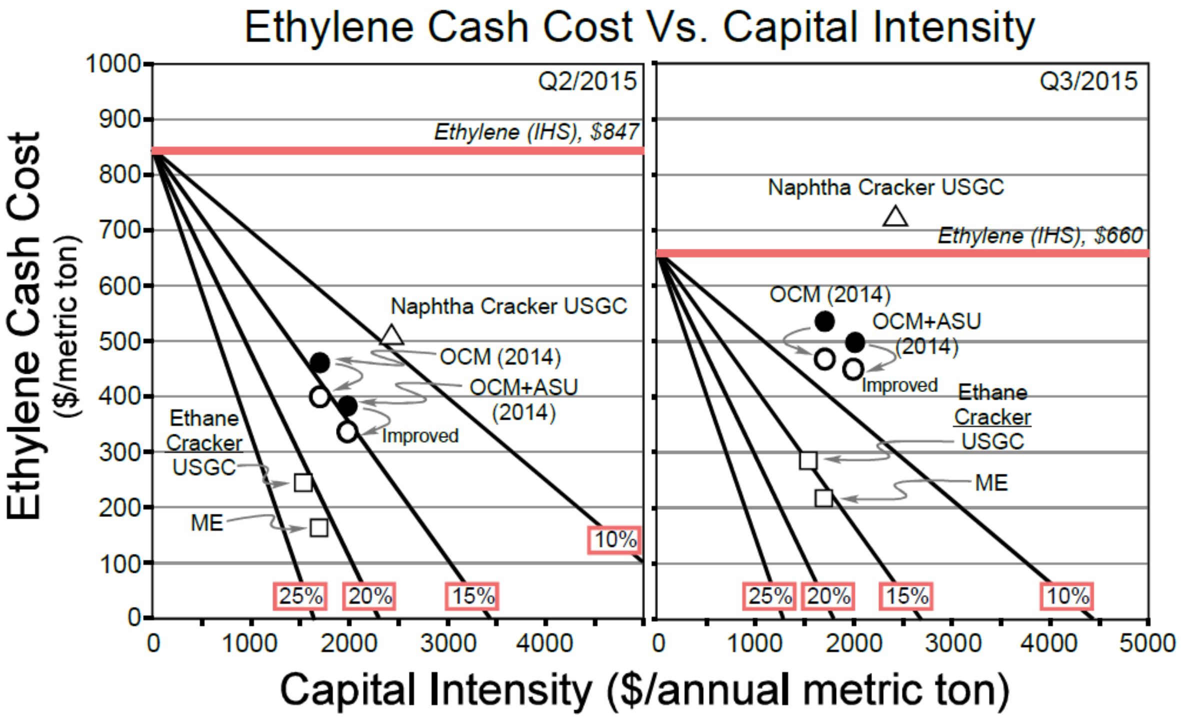

FIGURE 3-3 Comparison of ethylene cash cost for Q2 (left) and Q3 (right) 2015 as a function of total capital with lines showing return on investment for feedstock prices reported.
NOTE: Ethane cracking (open squares) shows the highest return on investment for both the Middle East (ME) and the U.S. Gulf Coast (USGC). Naphtha cracking (open triangle) carries a higher raw material cost and capital burden, combining to make it uneconomical relative to reported ethylene price in Q3, but not in Q2. Oxidative coupling of methane (OCM) points (circles) are intermediate, advantaged to naphtha but disadvantaged to ethane. OCM data are taken from IHS report PERP 2014-07 is shown as filled circles. Return is largely unchanged by inclusion of an air separation unit (ASU) in the capital. Open circles reflect data from Linde American Institute of Chemical Engineers (AIChE) paper 207a, AIChE 2015 Spring National Meeting (Austin, Texas), April 2015. OCM points reflect public analysis of the Siluria process.
SOURCE: Maughon, 2016.

Among the top well-established research approaches for making methane-to-ethylene conversion viable, the group listed oxidative coupling, other oxidative routes, and non-oxidative coupling that would stop at ethylene rather than proceed to produce aromatic compounds, as well as routes based on first creating syngas from methane and using that as a feedstock for ethylene production.

One of the promising but high-risk approaches being studied involves taking ethylene produced at a remote site and oligomerizing it to produce 1-hexene or 1-octene, value-added chemicals that could be readily transported. This group discussed the possibility of developing Fischer–Tropsch catalysts and processes that would favor ethylene production rather than longer-chain hydrocarbon production. Researchers are working on developing solid oxide oxygen- or proton-conducting membranes, but stability has been a problem. These membranes, Gaffney explained, can become fouled with carbonates that form from the carbon dioxide in the effluent gas stream, reducing their lifetime and efficiency. Routes to acetylene, rather than ethylene, are being explored, but coking has been a major issue. Chemical looping, which Schomäcker mentioned, holds promise if the challenge of being able to carry enough oxygen in the chemical looping agent to make the process economically viable can be solved. The group also noted work on the development of biologically mediated conversions as having some potential.

With regard to research opportunities, the group identified metal-organic frameworks as ripe for study as agents for absorbing or separating ethylene from the production stream. Electrochemical approaches to catalysis were mentioned, though the yields achieved so far have been too low to attract much interest. Research could lead to carbon-based methods for dehydrogenation, new approaches for separating olefins from paraffin, and methods that would enable the separation of dilute ethylene from product streams for low-yield processes. The group also noted that there are many new tools available that could generate transformational results through studies of catalysts and catalytic processes. These included environmental transmission electron microscopy, atmospheric pressure X-ray photoelectron spectroscopy, and simulated moving bed chromatography, the latter which could be used to develop new separations technologies. The group discussed the potential of accelerated screening, characterization, and synthesis tools for developing improved catalysts, and of work in the area of intrinsically safe design to improve the safety and reliability of oxidation reactions. Gaffney stated that the national laboratories possess many of these tools and the expertise to use them, and there is a value with making these tools and the associated staff expertise available to the nation. Finally, this group noted that for the development and widespread use of standardized practices with regard to catalyst formation and use, reactor methodologies, and standard operating procedures are not yet the norm in this field.

Methane to Aromatics

In his introductory presentation to the third working group, Israel Wachs, the G. Whitney Snyder Professor Chemical Engineering and director of the Operando Molecular Spectroscopy and Catalysis Research Laboratory at Lehigh University, described the mechanistic work that his group has performed to better understand the factors influencing the catalytic activity of a promising ZSM-5-supported molybdenum catalyst that achieves the dehydro-aromatization of methane to liquid aromatics, primarily benzene, and hydrogen (Gao et al., 2014, 2015). This catalyst, he said, first converts methane into ethylene and further reactions at the catalyst produce a mixture of chemicals, of which 70 to 80 percent are aromatics. The catalyst is eventually deactivated by coke formation, though it can be completely regenerated by oxidation treatment in a second reactor.

Discussion

Following this presentation, the group’s discussion, as reported by Monty Alger, director of the Pennsylvania State University’s Institute for National Gas Research and professor of chemical engineering at Pennsylvania State University, started by identifying two reasons for why it would be desirable to develop industrial processes for converting methane to aromatics: the substantial price spread between methane and naphtha and the increasing demand for aromatics that is starting to outstrip capacity. Because of the low cost of ethane in the United States, more ethane than naphtha is being used to produce ethylene, which produces fewer aromatics as by-products. The group then discussed the barriers to commercialization of the process Wachs described, starting with the energy input required to drive this endothermic reaction and the lack of reactors designed to deliver and manage the high temperature at which this reaction occurs. Other barriers the group identified included:

- deactivation of the catalyst by coking,
- low methane conversion rates that result from the buildup of hydrogen,
- the capital costs associated with this process relative to that for aromatics production from petroleum, and
- the lack of cost-effective methods to remove hydrogen from the reactor and to separate benzene from naphthalene, the other major aromatic compounds produced by this reaction.

Alger added that the working group discussed the possibility that environmental regulations to limit carbon emissions could make this technology attractive compared with today's alternatives.

With regard to additional research that could improve this process and develop other routes for converting methane into aromatics, Alger said the group noted two major impediments: the lack of sustained research funding in the United States for this type of work and the shortage of good ideas in this area. Two promising routes have been described recently—one involves a non-oxidative conversion of methane to ethylene, aromatics, and hydrogen using a lattice-confined iron catalyst (Guo et al., 2014), the other utilizing copper-based catalysts (Grundner, et al., 2015) —and further research would help to characterize these systems and determine their suitability for industrial use. Additional research would also aid in verifying the results that Wachs and his colleagues obtained at high temperatures. In general, said Alger, there has been research published, but most of it has been descriptive with little mechanistic detail that could be used to develop a coherent, systematic view of the technology for converting methane to aromatics.

Much of the discussion this group had about promising but higher-risk approaches focused on combining catalysts, developing new materials, and building a mechanistic knowledge base. The group had some discussion about biocatalysis, which is not being explored currently for producing aromatics but which could have longer-term opportunities, said Alger. The group also noted the potential for the lattice-confined iron system developed in China and the possibility of designing a membrane-based reactor that could separate products from reactants and perhaps improve the yields of these processes.

The group had a long discussion on research opportunities, said Alger. These included

- Rigorous high-temperature characterization during reaction;
- Reproducing and understanding high-temperature results;
- High-temperature material stability and catalyst support;
- Fast reactions with short-residence/contact/surface interaction time;
- Catalyst/process modification to avoid coke formation;
- Exploring the possibilities for hybrid-solid-molten salt catalyst;
- Using predictive methods to create catalysts by design;
- Developing non-ZSM-5 catalyst systems;
- Identifying and studying non-oxidative chemistries; and
- Conceptualizing new reactor designs and technologies.

The group also discussed commercial opportunities in the context of capital and operating costs. "The view of the group was that we are not creating new materials and products but are replacing existing materials, and therefore there are standards and upper bounds we need to be mindful of when thinking about benchmarking ideas versus existing alternatives," Alger reported. In particular, he noted, it is important for researchers and funding agencies to recognize that the opportunity for new technologies will be bounded by other options to produce the same products and that any new technology is required to fit within an economic operating window. It will also be likely that in a zero-carbon world that there may be environmental and regulatory advantages for one technology relative to others and these advantages must be understood and quantified.

Methane to Methanol

In his introductory remarks to the fourth working group, Tobin Marks, the Vladimir N. Ipatieff Professor of Catalytic Chemistry and professor of materials science and engineering at Northwestern University, pointed out that creative catalytic chemistry must be paired with excellent engineering to develop an industrially useful process capable of supplanting the current indirect process that first converts methane to syngas and then on to methanol at a price of approximately $0.75 per gallon using Earth-abundant catalysts. The main drawback to this process, which is practiced at a huge scale, is that it requires a significant amount of heat to produce syngas and the overall process capital cost intensity. In contrast, said Marks, the dream process of directly converting methane and oxygen to methanol is exothermic, that is, it generates heat, but realizing that dream will require addressing a number of challenges, including

- Managing heat and mass transfer;
- Catalytic selectivity;
- Product separation and purification;
- Catalyst cost and supply security; and
- Catalyst lifetime and regeneration.

Marks said that there have been many attempts using a variety of conditions and heterogeneous catalysts to achieve the direct conversion of methane to methanol (Alvarez-Galvan et al., 2011; Brown and Parkyns, 1991; Gesser et al., 1985; Holmen, 2009; Lunsford, 2000; Tabata et al., 2002), but any selectivity in the process was achieved at the expense of conversion and typical yields are 1 to 3 percent. Researchers at the Gas Technology Institute are reported to be developing a room-temperature, high-efficiency process to convert methane into methanol and hydrogen using metal oxide catalysts that are continuously regenerated. According to information from the Advanced Research Projects Agency-Energy (ARPA-E), this process has the potential to produce methanol at $0.24 per gallon from stranded methane or methane currently flared at the wellhead (ARPA-E, 2012).

Other approaches for direct conversion of methane to methanol have used homogeneous catalysts (Labinger and Bercaw, 2002, 2015), including functionalization of methanol using mercury-, thallium-, and platinum-based catalysts in concentrated sulfuric acid followed by reaction with water to produce methanol (Hashiguchi et al., 2012; Labinger and Bercaw, 2002, 2015; Palkovits et al., 2009; Periana et al., 1998; Soorholtz et al., 2013), and using zeolite-supported iron or copper catalysts and hydrogen peroxide as the oxidant (Hammond et al., 2012, 2013). Researchers have also explored enzymatic conversion of methane to methanol (Banerjee et al., 2015; Wang et al., 2015)

In concluding his introductory remarks, Marks said that there has been substantial progress in understanding key catalytic mechanisms and in developing new tools, including computational methods, for studying catalytic mechanisms and for predicting and screening catalysts. He also said that the materials science of heterogeneous catalysts is advancing rapidly.

Discussion

In the subsequent discussions, the working group enumerated several impediments to the commercial viability of direct methane-to-methanol conversion, including not having a direct route to offer substantial improvements over the current industrial processes based on syngas. As Karen Goldberg, the Nicole A. Boand Endowed Professor in Chemistry and director of the Center for Enabling New Technologies through Catalysis at the University of Washington, reported, the discussion raised the point that future environmental policies could serve as a driver for the development and commercialization of smaller plants for processing stranded and flared gas using some of the technologies Marks outlined in his presentation. Current methods of managing the oxidants required for direct conversion could be improved, the group noted, and it would help to some way reduce the cost of separating oxygen from air or to develop an air-recyclable oxidant such as the process used in one variant of the Wacker reaction that recycles copper (I) to copper (II). Improved methods for separating methanol from the water used in some schemes will be helpful, too, and despite advances in mechanistic understanding, there is still room for a better fundamental understanding of the catalytic activation of the carbon–hydrogen bond. The group also noted that electrocatalytic methane activation is a new approach that highlights ways to think about entirely new concepts for catalyzing conversion of methane to methanol, and, in this arena, opportunities exist for more efficient energy production using direct methane fuel cells, but new catalytic materials are seriously lacking.

The working group then discussed some of the challenges to making current approaches viable, starting with reducing the temperature of some of the reactions and improve their selectivity. For homogeneous systems, separations can be an issue. Two overarching challenges facing catalytic conversion of methane using either heterogeneous or homogeneous catalysts include avoiding coking, in which carbonaceous deposits form on heterogeneous catalysts and thereby limit catalytic activity, and developing new ligands for homogeneous catalysts that are stable under reaction conditions. Homogeneous organometallic catalysts that have enjoyed success in major catalytic processes such as hydrogenation, metathesis, and hydroformylation typically employ ligands such as phosphines that are unstable under the conditions required for methane oxidation, which generally involve strong oxidants, strongly acidic media, and water.

Other promising but higher-risk approaches being taken included the development of movable, small-scale plants for use with stranded and flared methane, and the development of oxidants that do not need separating from the product mix. The discussion raised the question of whether it would be a better idea to convert methane to dimethyl ether, whether it would be possible to develop an oxidant that did not need separate, and if routes to methanol through syngas in an integrated process could prove viable. Another promising avenue the group noted was to get experts in heterogeneous, homogenous, biocatalytic, and electrocatalytic processes and catalyst supports together in a forum such as this workshop to generate new ideas. Goldberg said there is currently not financial support available to convene such a forum.

She concluded her report on the group's discussions by noting some of the scientific and engineering advances that have come online and that will be useful in addressing the challenges the discussion raised. These included

- Operando and ex-situ spectroscopy to probe catalyst structure and dynamics;
- New chemical and analytical techniques to probe mechanism;
- High-throughput experimentation for optimization and discovery;
- Materials science of catalyst supports and plant construction materials;
- Ligand supply and design;
- Advances in synthesizing catalysts; and
- High-powered computational approaches for both understanding and prediction.

Additional areas of research that would benefit the field included development of new methods for synthesizing well-defined catalysts, stabilizing catalysts (especially homogeneous), and managing oxygen, both in terms of separations and for redox coupling, in a cost-efficient manner. Research that could better characterize the intermediates and transition states resulting from the interactions of methane with catalysts is another benefit.

DISCUSSION

In the ensuing open discussion, several workshop participants raised questions about the goal of eliminating the separation of oxygen from air before performing any of the catalytic oxidations identified by the working groups. Guido Pez, an independent consultant who retired from Air Products, noted that the U.S. Department of Energy funded a project that used a solid oxide-containing membrane as part of a methane oxidation scheme that did eliminate the importance for an air separation unit. Marks then asked if the methane-to-aromatics group discussed the possibility of making a specific aromatic compound or of avoiding the production of benzene. Wachs commented that there are other important issues that to address first and noted that there are many methods for taking benzene and further modifying it.

Eric Stangland from The Dow Chemical Company asked if industry needs another methane-to-methanol technology and wondered whether research funds should be spent on more pressing needs. José Santiesteban from ExxonMobil replied that industry's perspective is that any process has to make sense from an economic viewpoint, and also consider environmental issues and lifecycle analysis in decision making. He also said the same question could be asked for ethane-to-ethylene processes and noted that every time he hears that a particular area is mature, some development comes along that proves that idea wrong. In his opinion, research with the biggest potential for producing a breakthrough involves taking an entirely different approach to catalysis, such as the idea of combining different types of catalytic processes. Wachs added that the pulp and paper industry, the largest user of methanol as the feedstock for producing formaldehyde, strongly desires a one-step process for methane to formaldehyde or methane to methanol. Mark Barteau from the University of Michigan stressed the importance of considering the carbon budget of a process as well as the economic budget. "I think it would be a great tragedy if we had a scientific breakthrough that lowered the capital cost of a process and also lowered the carbon efficiency," he said.

Maughon commented that if the question is about prioritizing where to spend research dollars, the answer from Dow's perspective would be that methane-to-methanol conversion would not be a high priority, and he would guess that ExxonMobil would say the same thing. Stangland responded by saying that while it may not be Dow's priority, methane-to-methanol conversion might be a priority for the nation as it considers how best to use the nation's natural resources, though he agreed that methane-to-methanol conversion likely would not be a top priority given the potential for some of the other areas the working groups discussed to produce game-changing catalytic solutions for using methane to produce value-added chemicals. Santiesteban added that research prioritization should also consider what might be beneficial in the long–term. "The chemical industry goes through cycles, and so we need to be ready for different situations," said Santiesteban. "The technology we have now was not developed in 1 day. It was developed by people who had a vision and it is our responsibility to create a vision for tomorrow."

In that vein, Alexis Bell from the University of California, Berkeley, commented that industry may take a short-term view, but it depends on researchers at the national laboratories and universities to take a longer-term view and develop the science and basic engineering that would later enable industry to implement a technology if it made sense at that time. By the same token, added Goldberg, the basic science behind methane-to-methanol conversion is providing knowledge about how to selectively activate and functionalize the carbon-hydrogen bond and how to use oxygen effectively as an oxidant in a potential industrial process. Ultimately, that knowledge may not lead to a future process for making methanol, but it could lead to processes for using methane as a feedstock to make other valuable chemicals. Alger, agreeing with Goldberg, said that history has shown that most of the great inventions resulted from research not directly related to that invention. What is important, he said, is the cross-fertilization among fields that results in knowledge generated in one field being applied to problems in another technology area where the market is demanding a solution.

Shannon Stahl from the University of Wisconsin–Madison also commented on the importance of cross-fertilization and stressed the importance of including researchers from industry in any cross-disciplinary discussions and programs. He also suggested that the federal funding agencies consider funding a new type of program that would bring together small teams of researchers, including those from industry, to work on a focused problem as a complement to large center programs and individual investigator grants. In his opinion, this type of mid-sized team approach would provide a good return on investment and afford the opportunity to respond quickly to a research need. Alger seconded this idea and noted how little time professors have today to engage in the type of cross-disciplinary conversations this field is lacking.

4

Catalytic Conversion of Light Alkanes

The second day of the workshop began with a plenary session featuring three presentations designed to serve as background for subsequent breakout group discussions. Jeffery Bricker, Senior Director of Research at UOP, formerly known as Universal Oil Products, reviewed the history and state of the art of ethane and propane dehydrogenation catalysis. Alexis Bell, the Dow Professor of Sustainable Energy at the University of California, Berkeley, and Faculty Senior Scientist at the Lawrence Berkeley National Laboratory, described some of the lessons learned from theory and experiment about methane, ethane, and propane conversion over heterogeneous catalysts, and Shannon Stahl from the University of Wisconsin–Madison discussed the use of homogeneous catalysts to activate the carbon–hydrogen bond. Each presentation was followed by a brief discussion period.

HISTORY AND STATE OF THE ART OF ETHANE AND PROPANE DEHYDROGENATION CATALYSIS

There will be continued growth in worldwide demand for light olefins—ethylene and propylene—at a projected 4 percent compound annual growth rate, supporting investment in additional petrochemical facilities, said Jeffery Bricker. Driving this growth, he said, is demand from the expanding middle class in developing countries, particularly in China, India, and Southeast Asia. The majority of the demand for propylene, he added, will be filled by propane dehydrogenation (PDH) in North America and methane-to-olefin (MTO) plants in China, although China is also importing an increasing amount of propane from the United States.

Bricker explained that there is a growing gap in the supply-versus-demand curve for propylene (see Figure 4-1) as a result of two factors: steam crackers have been shifting to lighter feedstocks that produce less propylene, and flat demand for gasoline in some regions has limited the amount of propylene produced during the oil-refining process. His colleagues at UOP believe that so-called on-purpose propylene will supply one quarter of the world’s demand by 2021.

Of all of the technologies that have been developed that produce propylene, PDH provides the highest yield (see Figure 4-2), and because of the price differential between propane and propylene, propane dehydrogenation (PDH) economics are quite favorable and support continued investment in plant construction. Over the past few years, the price differential has been as high as $700 per ton, which Bricker said is “an unbelievable number in the petrochemical industry” and has led to the construction of plants capable of producing 1 million tons of propylene annually.

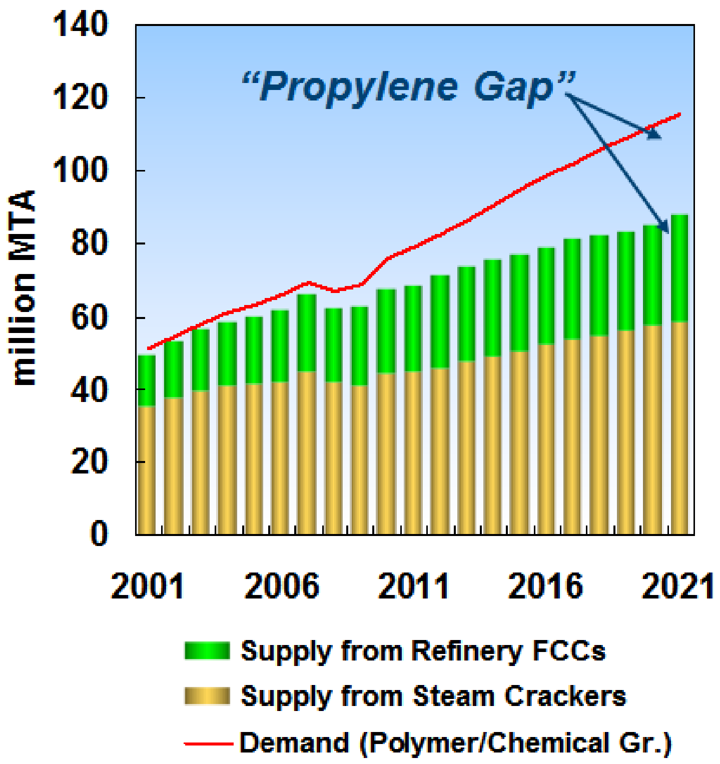

FIGURE 4-1 The growing gap between propylene supply and demand.
NOTE: FCC = fluid catalytic cracking; MTA = million tonnes per annum.
SOURCE: Bricker, 2016.

There are several challenging characteristics of PDH technology, Bricker noted, starting with the fact that the endothermic reaction is equilibrium limited, requiring temperatures that exceed 600°C and low-pressure conditions, making a reheat strategy critical. In his opinion, reheating is an area ripe for technological advancements going forward. Another feature of PDH technology is that coke formation is unavoidable, leading to a catalyst life of days and the need for frequent regeneration. As in all catalytic–process technology, he added, the process and catalyst are intertwined and cannot be separated. UOP's Oleflex process, he noted, can use mixed feedstocks—propane plus isobutylene or n-butane—and generate a product mix of propylene plus isobutylene or butenes, the latter of which can be converted to in-demand butadiene using other technology.

Bricker noted that World War II marked the first use of alkane dehydrogenation, and over the ensuing years several companies have steadily improved the catalysts and the processes using them. Today, two PDH technologies—UOP's Oleflex process and the Lummus Catofin process—dominate propylene production. In total, there are now 22 PDH units in operation worldwide, and unit capacities of the newest facilities have been increasing to as large as 1 million tons per year. Since 2011, 40 new PDH units have been ordered, and although UOP has won 34 of those contracts, the company continues to improve its technology in order to remain competitive.

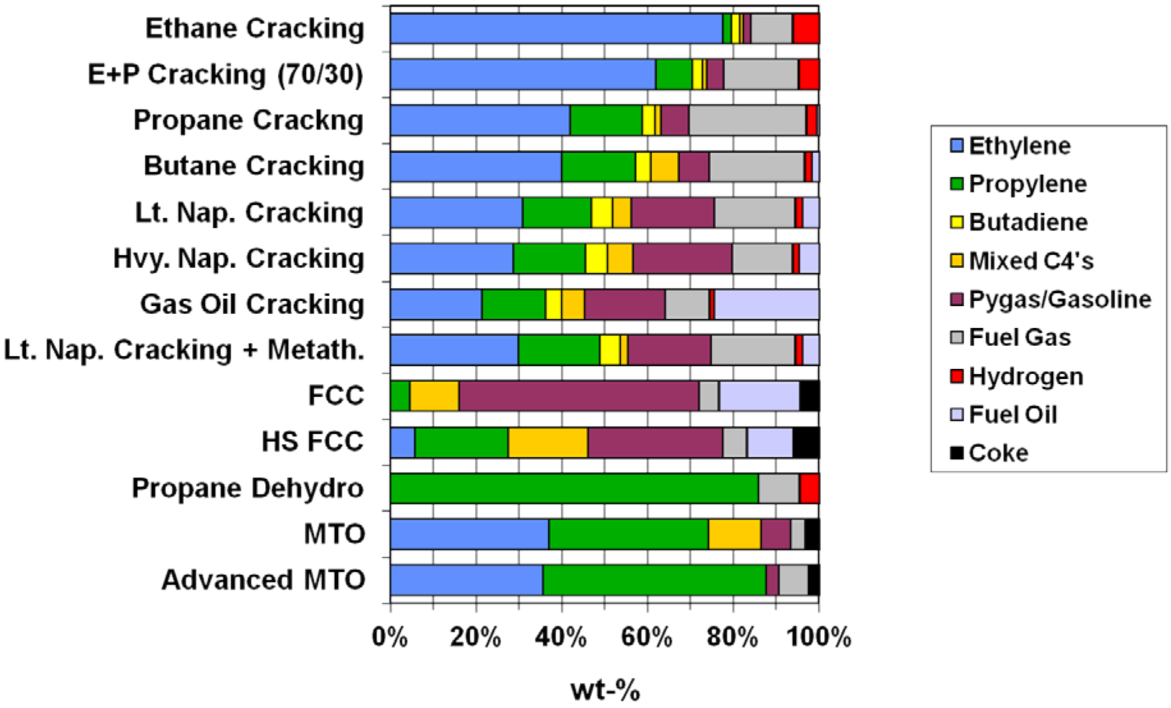

FIGURE 4-2 Propane dehydrogenation provides the highest yields of propylene.
NOTE: FCC = fluid catalytic cracking; MTO = methanol to olefin.
SOURCE: Bricker, 2016.

The Lummus Catofin technology, first developed in the 1940s, involves a cyclic reactor technology in which seven reactors go through a computer-controlled sequence of reaction, reheat, and regeneration using a catalyst developed by Clariant (see Figure 4-3). The UOP Oleflex technology uses a continuous moving bed process with a regenerator (see Figure 4-4). PDH units have four reactors, while mixed propane and butane units have three reactors. The spherical platinum-based catalyst travels several hundred meters through all of the reactors and is then regenerated to burn off the accumulated coke. Bricker explained that the catalyst coming out of the regenerator is indistinguishable from fresh catalyst and will last several years. He noted, too, that because the chemical reaction is endothermic, heat input is critical and any yield loss results from inefficient heat transfer, not from catalyst selectivity.

Going forward, UOP researchers are working on methods for improving heat transfer and on changes that will reduce propane consumption at a constant conversion. They have already developed process improvements that will increase the yield per pass and lower both utility and capital costs. Bricker said these improvements are on fast-track development and will be commercialized soon.

With regard to ethane utilization, Bricker said that ethane steam cracking is the only process used today to produce ethylene, and ethane steam crackers produce more than 100 million metric tons of ethylene annually. Important advances have been made with two other routes to ethylene—catalytic ethane dehydrogenation and ethane oxidative dehydrogenation—but there are no commercial units that he is aware of that either use or plan to use these technologies in the near future, largely because the economics of ethane stream cracking are hard to beat. Steam crackers, explained Bricker, not only have a low cost of production and capital cost, but the internal rate of return is projected to exceed 26 percent under both 2016 and 2019 pricing scenarios. The main downsides to ethane steam cracking are its high energy intensity (i.e., 16 gigajoules of energy are required to produce 1 ton of ethylene) and the more than 1 ton of carbon dioxide emitted per ton of ethylene produced (Gärtner et al., 2013). Oxidative dehydrogenation, he noted, could have a much lower energy and carbon dioxide footprint if done with high selectivity and at high ethane-conversion rates, and would likely enable a continuous production process.

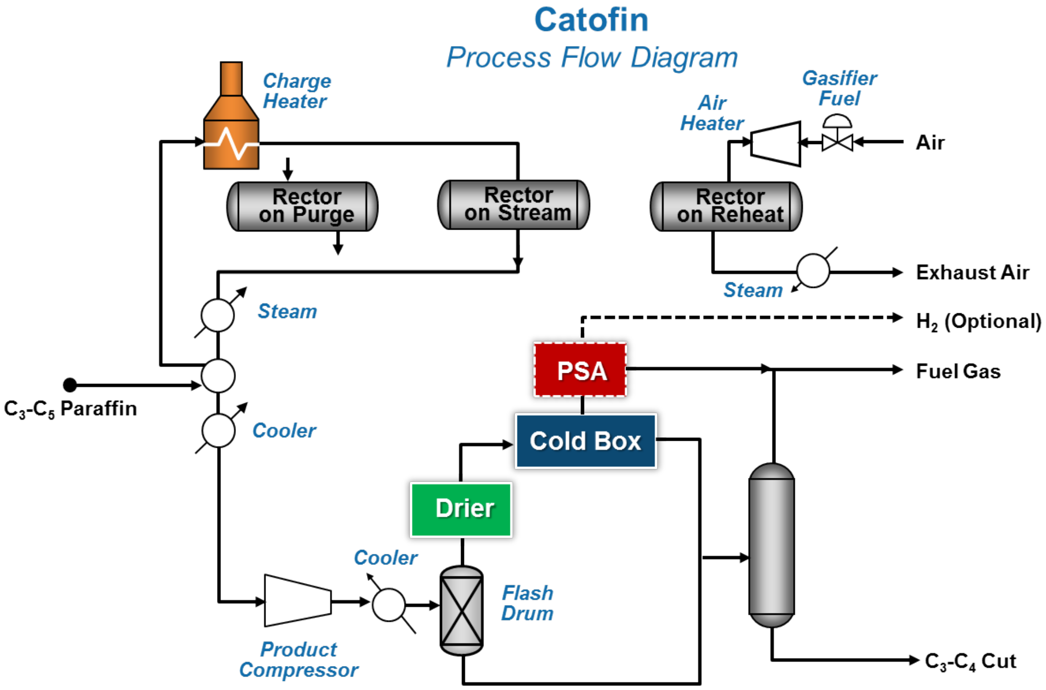

FIGURE 4-3 The Lummus Catofin process flow diagram.
NOTE: PSA = pressure swing adsorption.
SOURCE: Bricker, 2016.

Researchers have reported a number of different oxidative dehydrogenation catalysts that do achieve high selectivity for ethylene (see Figure 4-5). In the late 1980s, for example, Bricker adapted the Oleflex process to produce ethylene from ethane, but the heating strategy required to maintain the necessary temperature across six reactors made the process uneconomical, he explained. There has also been work on novel reactor designs using oxygen-permeable membranes (Czuprat et al., 2009; Ramos et al., 2000; Rebeilleau-Dassonneville et al., 2005), hydrogen-permeable membranes (Schäfer et al., 2003), microchannel reactors, and monolith-type reactors. Hydrogen-permeable membranes, for example, can shift the equilibrium of the dehydrogenation reaction to increase conversion, but the challenge then is to create a change in pressure across the membrane without resorting to a high-pressure regime or using a second gas to sweep hydrogen off of the membrane. The removed hydrogen could then be burned to provide some heating. Although an ionic oxygen-conducting membrane with palladium and vanadium–manganese oxide catalyst (Rebeilleau-Dassonneville et al., 2005) produced very high conversion rates and good selectivity, scaling such a system would likely be difficult, said Bricker. Also, it would probably not provide much benefit over steam cracking because of the need to run the reaction at high temperature. However, if someone could make an ion-conducting membrane that worked at 500°C rather than 777°C, such a process could prove workable at an industrial scale, he added.

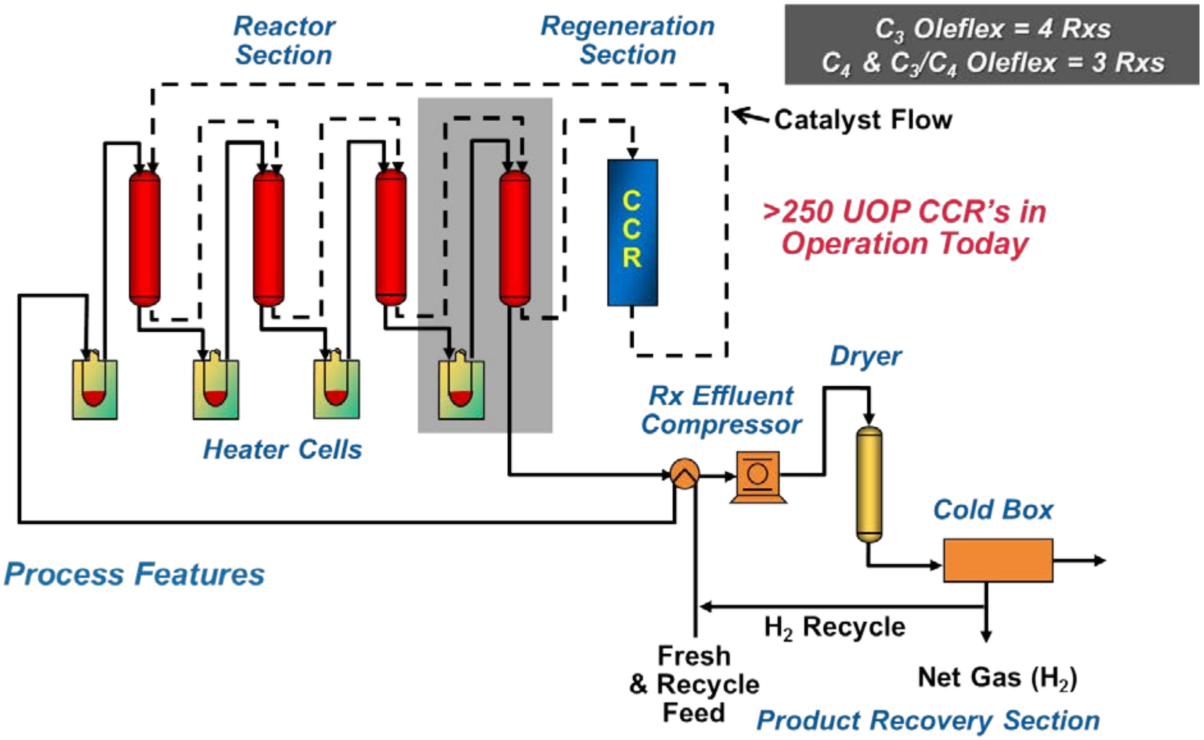

FIGURE 4-4 The UOP Oleflex process flow diagram.
NOTE: CCR = continuous catalyst regeneration.
SOURCE: Bricker, 2016.

A monolith reactor coated with a platinum and tin catalyst (Bodke et al., 1999; Silberova et al., 2004), similar in concept to the catalytic converter on a car, produced good results at high throughput rates. Feeding hydrogen into the reactor stream reduced carbon dioxide emissions substantially. Bricker said that at least one large chemical company tried to scale this process but without success. However, his group is now working with high-velocity reactor designs to see if it can figure out how to manage heat flow at an industrial scale.

Another interesting approach for oxidative dehydrogenation used sulfur as a mild oxidant in combination with a molten salt catalyst (Gaspar et al., 1974), which allows heat to dissipate rapidly and prevents hot-spot formation that would decrease selectivity. An advantage this system offers is that coke could be removed easily from the molten catalyst. While Bricker characterized this approach as being outstanding from the catalyst perspective, he suspects that scaling a system using molten salts and sulfur is likely to be difficult.

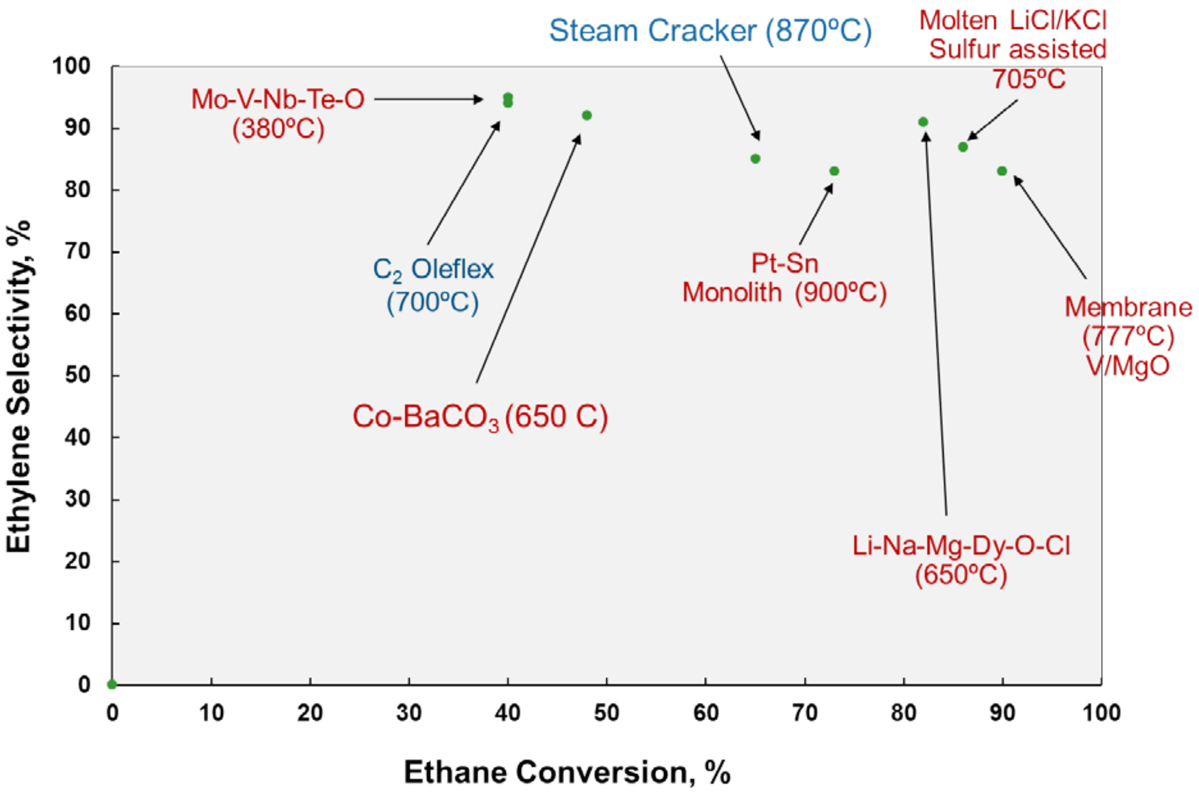

FIGURE 4-5 Examples of high-selectivity catalysts for oxidative dehydrogenation of ethane. SOURCE: Bricker, 2016.

With regard to catalytic oxidative dehydrogenation, researchers have developed upwards of 20 different systems, said Bricker. One approach he finds promising uses a molten alkali metal chloride supported on dysprosium oxide-magnesium oxide to achieve an 82 percent conversion and 91 percent selectivity to ethylene (Kumar et al., 2008). Another approach with potential uses a molybdenum-vanadium-niobium-tellurium oxide catalyst operating at the relatively low temperature of 400°C and dilution to achieve an 87 percent conversion and 84 percent selectivity (Botella et al., 2004).

Bricker concluded his presentation by noting that ethane cracking is still the most economical proven process for ethylene production, but that promising catalysts for ethane oxidative dehydrogenation are emerging. “If an overall economic process can be developed, there is a good chance that the future will include commercial ethane oxidative dehydrogenation plants,” said Bricker. For propane, PDH is now an economically attractive technology to fill the propylene gap. In closing, he added that “catalysis still provides a tremendous lever to provide value to society for environmental reasons and by providing high-value products.”

In the discussion period that followed, Alexis Bell asked Bricker, for the benefit of those in academia and at the national laboratories, in his opinion what longer-term research should be pursued that would enable companies such as his to be more effective. Bricker replied that there will always be value in people inventing new materials, noting that almost every advance in petrochemical processes came about because of the invention of a new material. Other areas in which academia and the national laboratories could help are in developing a better fundamental understanding of catalysis and new methods of modeling catalyst structures and reaction processes.

Eric Stangland from The Dow Chemical Company remarked that just as catalysts and processes are intimately linked, so too are the separations processes. Bricker agreed with this comment, adding that each catalyst–process combination produces a different mix of byproducts that have to be separated. He noted that his company has made a significant effort aimed at improving downstream separations.

HETEROGENEOUS CATALYSIS: LESSONS LEARNED FROM EXPERIMENT AND THEORY

Chemists have developed a number of different routes by which natural gas can be converted to chemicals using catalysis (see Figure 4-6), many of which form the technological foundation for the modern chemical industry. Yet despite their successful application at an industrial scale, there are still a number of central questions common to all of these chemistries that remain unanswered, said Alexis Bell. The four questions he listed, and that he addressed in his presentation, include

1. What is the rate-limiting step in the activation of methane and light alkanes?
2. What factors govern the formation of coke during the conversion of methane and light alkanes?
3. Can oxygenated compounds be formed directly from methane and light alkanes?
4. What is on the horizon and beyond?

With regard to the conversion of ethane or propane, respectively, to ethylene or propylene plus hydrogen, it is well-known that platinum is one of the better catalysts for this reaction but that it deactivates rapidly because of coke formation. Research has also shown that adding tin, gallium, indium, or other metals to create a bimetallic catalyst enhances alkene selectivity while also reducing coke formation (Feng et al., 2015; Galvita et al., 2010; Peng et al., 2012; Somodi et al., 2011, 2012; Sun et al., 2011; Wu et al., 2014a, 2014b, 2015). Several years ago, Bell and his colleagues began to look at the effect of platinum particle size and the concentration of tin on coke formation and to identify the mechanism of coke formation and its influence on platinum nanoparticles. After developing a process that enabled them to control the particle size and tin-to-platinum ratio, they were able to show that catalytic activity increased significantly when increasing the amount of tin relative to platinum while keeping the particle size constant. Activity also went up when holding the tin-to-platinum ratio constant while increasing the catalyst particle size. However, as the particle size increases, so too does the tendency to form coke.

Conversion of Methane

Pyrolysis:	$CH_{4(g)} \rightleftharpoons 1/6\, C_6H_{6(g)} + 1.5\, H_{2(g)}$
	$CH_{4(g)} \rightleftharpoons 1/2\, C_2H_{4(g)} + H_{2(g)}$
Steam Reforming:	$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3\, H_{2(g)}$
Dry Reforming:	$CH_{4(g)} + CO_{2(g)} \rightleftharpoons 2\, CO_{(g)} + 2\, H_{2(g)}$
Oxidative Coupling:	$CH_{4(g)} + ½\, O_{2(g)} \rightleftharpoons ½\, C_2H_{4(g)} + 2\, H_2O_{(g)}$
Partial Oxidation:	$CH_{4(g)} + ½\, O_{2(g)} \rightleftharpoons CH_3OH_{(g)}$

Conversion of Light Alkanes

Thermal Dehydrogenation:	$C_2H_{6(g)} \rightleftharpoons C_2H_{4(g)} + H_{2(g)}$
Oxidative dehydrogenation:	$C_2H_{6(g)} + ½\, O_{2(g)} \rightleftharpoons C_2H_{4(g)} + H_2O_{(g)}$
Partial Oxidation:	$C_3H_{8(g)} + O_{2(g)} \rightleftharpoons CH_3CH{=}CHO_{(g)} + H_2O_{(g)}$

FIGURE 4-6 Catalyzed conversion of natural gas to chemicals.
SOURCE: Bell, 2016.

To determine the source of the coke, Bell and his collaborators used ^{13}C-labeled ethylene to show that coke is formed by readsorption of ethylene onto the catalyst surface. Ethylene as the source of coke was confirmed, Bell explained, by high space velocity experiments, which showed there were lower levels of coke deposition at high space velocities. Theoretical calculations showed that one of the effects of adding tin is that it weakens the readsorption of ethylene or propylene onto platinum. High-resolution transmission electron microscopy studies showed that the amount and morphology of carbon changes with platinum particle size (Peng et al., 2012) (see Figure 4-7). These studies also confirmed theoretical predictions that carbon would grow at the steps of the catalyst particle (see Figure 4-8), and they demonstrated that carbon deposition induces step formation that then serves as additional nucleation sites for carbon formation.

Researchers have also studied oxidative dehydrogenation of ethane and propane by vanadium catalysts dispersed onto alumina. At low loading, most of the vanadium is present at isolated sites, and in that situation alkene selectivity is limited by deep oxidation of both the alkane and alkene (Zboray et al., 2009).

Summarizing what is known about the catalytic conversion of light alkanes, Bell said breaking the carbon–hydrogen bond is the rate-limiting step. Steam and dry reforming of methane follow identical kinetics, as do the thermal dehydrogenation of light alkanes and the dehydro-aromatization of methane. Graphene formation, he said, is nucleated at steps on the surface of metal particles and graphene growth can cause step formation. Graphene formation, he added, is suppressed by reducing metal particle size and increasing the lattice mismatch between the graphene and the metal, and soot formation is limited by very rapid thermal quenching. With regard to oxidation of methane to methanol, the rate of this reaction is limited by catalyst reactivation, and oxidative dehydrogenation of light alkanes is limited by both primary deep oxidation of the alkane and secondary oxidation of the alkene.

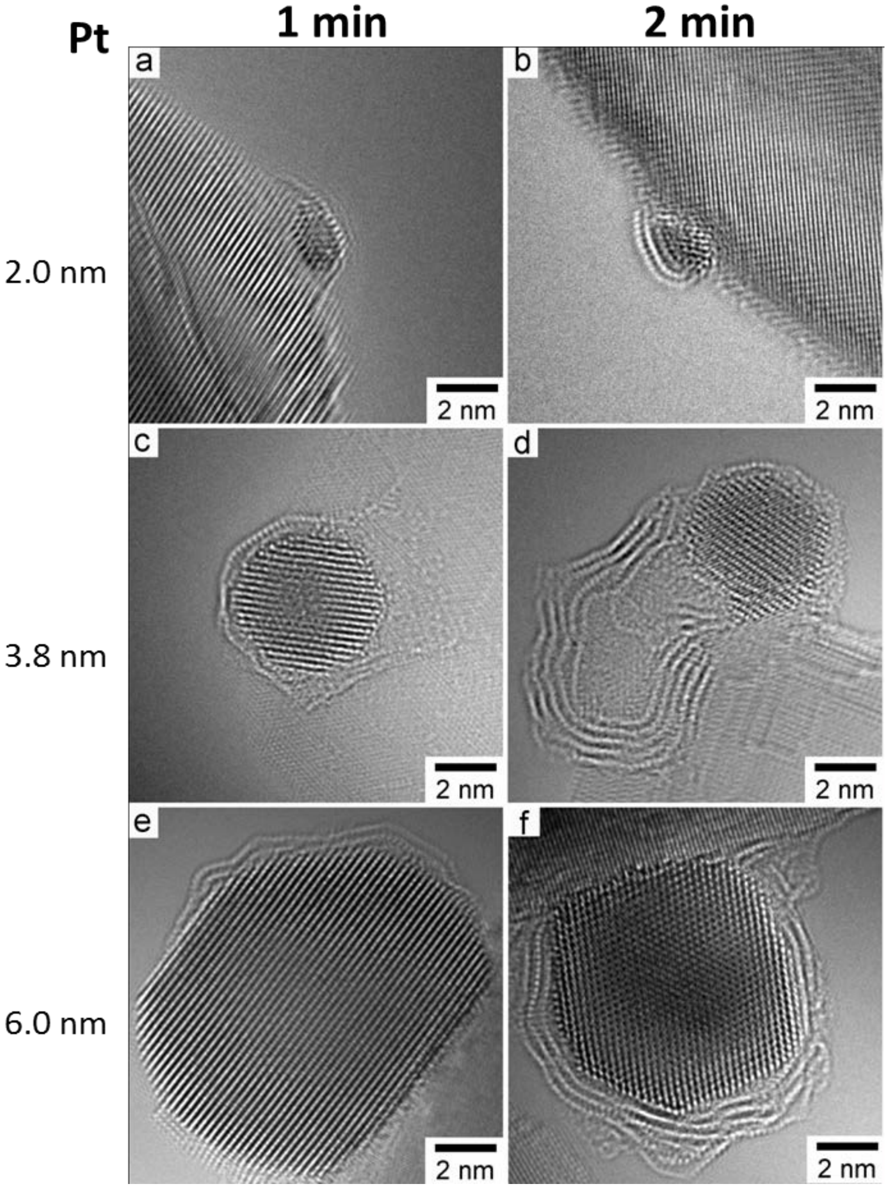

FIGURE 4-7 The effect of platinum particle size on carbon accumulation.
NOTE: nm = nanometer.
SOURCE: Peng et al., 2012.

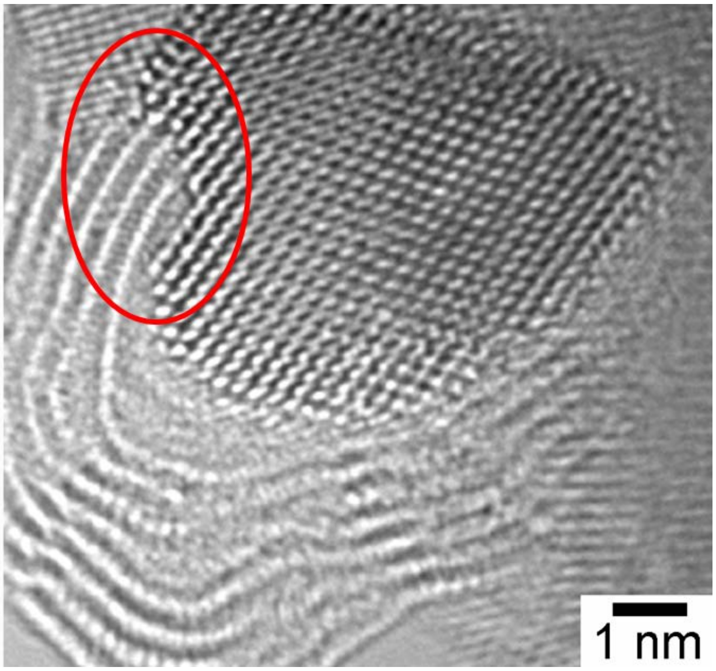

FIGURE 4-8 Graphene initiation occurring at the steps of large platinum particles.
NOTE: nm = nanometer.
SOURCE: Peng et al., 2012.

Two of the best catalysts for steam reforming of methane to produce syngas, said Bell, are ruthenium and rhodium, but their low abundance and high cost make them less attractive for use in large-scale, industrial process. As a result, nickel is the catalyst used in practice. Both experiment and theory show that the turnover rate for this reaction drops slightly from ruthenium to rhodium to nickel (Jones et al., 2008). For dry reforming, the results are nearly the same, with nickel predicted to be slightly less active than ruthenium and rhodium (German and Sheintuch, 2013; Wang et al., 2007). In both cases, the initial dissociation of methane to produce a methyl group and a hydrogen atom is the critical step that determines the reaction rate. In fact, one of Bell's colleagues demonstrated that steam reforming and dry reforming are two manifestations of the same reaction (Wei and Iglesia, 2004), and the kinetics are first order for methane and zero order for oxygen or carbon dioxide when using a nickel catalyst. It turns out, said Bell, that the kinetics of carbon accumulation, or coking, are also the same for steam and dry reforming of methane.

Given that coke formation is inevitable, the next question Bell addressed concerned where coke formation occurs. Experiments have shown that methane dissociation occurs preferentially at the steps on the catalyst surface, and the more steps present in the catalyst structure, the more carbon will form (Saadi et al., 2010; Sehested, 2006). At the same time, steps decrease the activation energy for methane dissociation, so what is good for catalytic activity is bad for coke formation, Bell explained. Experiments have also shown that carbon grows at steps as small graphene islands that eventually form graphene sheets and finally carbon nanotubes (Peng et al., 2012; Wu et al., 2016), and researchers have developed a thermodynamics-based explanation for why the steps are important and how wide they have to be to serve as nucleation sites for graphene growth (Saadi et al., 2010). These studies led to the prediction that introducing gold into the catalyst surface would inhibit this process, and indeed, experiments have shown that the presence of gold leads to smaller amounts of coke forming on the catalyst surface.

Turning to methane pyrolysis, Bell said that from a thermodynamic perspective, methane would prefer to form graphite and hydrogen rather than products such as ethylene and benzene. In fact, while molybdenum carbide nanoparticles in ZSM-5 zeolite or an iron on silica catalyst will produce some benzene and ethylene at temperatures exceeding 900 K, coke formation occurs rapidly resulting in catalyst deactivation. However, 2 years ago, researchers at the Dalian Institute of Chemical Physics showed that a catalyst in which iron atoms are isolated from one another in a silica structure is capable of avoiding coking and produces a mixture of ethylene, benzene, and naphthalene when operated at 1,363 K and at what Bell characterized as very high space velocities (Guo et al., 2014). This catalyst, the researchers report, is stable for 60 hours, which they attribute to the isolated iron carbide sites in the catalyst's silica framework. Bell noted that the presumed mechanism involves dissociating methane on the catalyst surface, with the resulting methyl radical then leaving the surface and reacting in the gas phase. While the chemistry is not fully understood, he suspects that these isolated iron sites are too small to nucleate the formation of graphene and that the reaction is run at such short contact time that there is rapid thermal quenching of the product gases, which would inhibit the gas-phase production of carbon.

As Tobin Marks from Northwestern University stated earlier, while the indirect conversion of methane to methanol via syngas is an important industrial process, the chemical industry would like to replace that energy-intensive process with one that directly oxidizes methane to methanol. Bell agreed that such a process would be of commercial interest, particularly if it could be run in a continuous manner. This latter feat has not been achieved yet, but researchers have shown that a copper-ZSM-5 catalyst will oxidize methane to methanol at relatively low temperatures. Catalyst reactivation, however, requires raising the temperature by several hundred degrees (Groothaert et al., 2005). Bell explained that three research teams each claim different copper structures that serve as the active catalytic site, indicating that further research to fully understand this chemistry is required.

Looking to the future, Bell listed several goals, including:

- Identify catalysts that operate at high temperature and are resistant to coke formation.
- Identify single-site catalysts that enable the continuous conversion of methane to methanol.
- Identify catalysts than can promote the oxidative dehydrogenation of alkanes to alkenes selectively.
- Understand the nature of oxygen species and what controls their activity.

During the ensuing discussion, Bala Subramaniam from the University of Kansas noted that because catalysts will increase the rate of conversion but not the equilibrium, process engineering in combination with catalyst development could be a powerful complement. Bell agreed that process engineering has to be part of the whole package of catalyst development, and that the two do go hand in hand. He noted that when engaging in process development, it does help to know what is happening locally at the catalyst. Bricker then asked if the tin in the platinum–tin catalysts was exerting a geometric or electronic effect, and Bell replied that quantum mechanical calculations show it to be an electronic effect in addition to the geometric effect of impacting nucleation sites.

HOMOGENEOUS CATALYSIS FOR CARBON–HYDROGEN BOND ACTIVATION

Homogeneous catalysts, said Shannon Stahl, have been used in numerous major industrial processes, and he wondered if the dividing line between homogeneous and heterogeneous catalysis is meaningful or if it is an artifact of the silos that separate chemistry and chemical engineering departments at most universities. Of greatest importance in his view are the molecular processes and concepts that are operating with a given catalyst regardless of the name it is given. Indeed, there is a great deal of opportunity for cross-fertilization and mechanistic understanding that spans homogeneous catalysis, heterogeneous catalysis, and electrocatalysis.

Some of the industrially important applications of homogeneous catalysis include the Shell higher olefin process for producing linear α-olefins from ethylene, the INEOS process for making higher α-olefins from syngas, The Dow Chemical Company's butadiene telomerization process, and Chevron Phillips's and Sasol's ethylene trimerization and tetramerization of ethylene processes, hydroformylation chemistry, and ethylene oxidation. Major applications for the products of these reactions are in linear low-density polyethylene (LLDPE), high-density polyethylene, detergent alcohols, and synthetic lubricants. Stahl noted that increasing 1-hexene use in LLDPE is expected to drive market growth (see Figure 4-9). Commenting on the slated construction of ethane crackers to produce ethylene, Stahl said, "If we are going to be awash in ethylene through ethane dehydrogenation, enhancing these types of processes could play an important role in terms of where we need to stimulate more activity in homogeneous catalysis."

Hydroformylation of α-olefins and syngas to produce linear and branched aldehydes is one example of a homogeneous catalysis process carried out on a massive scale, with production exceeding 18 billion pounds per year using primarily rhodium-based catalysts that were discovered in the 1960s (Cornils et al., 1994). Liquid-phase radical chain aerobic oxidation of hydrocarbons using a cobalt-manganese-bromine catalyst discovered in 1955 produces more than 100 billion pounds per year of chemicals such as terephthalic acid, which is used to make the plastic polyethylene terephthalate (PET) (Tomas et al., 2013). The Wacker process, discovered in 1959 and based on an organometallic catalyst, is used to convert ethylene into more than 1 billion pounds of acetaldehyde per year (Jira, 2009). Stahl noted that while this latter reaction appears to involve oxygen transfer, water is the source of the oxygen atom in acetaldehyde and molecular oxygen merely serves as an electron acceptor and reoxidizes the reduced copper (I) to copper (II).

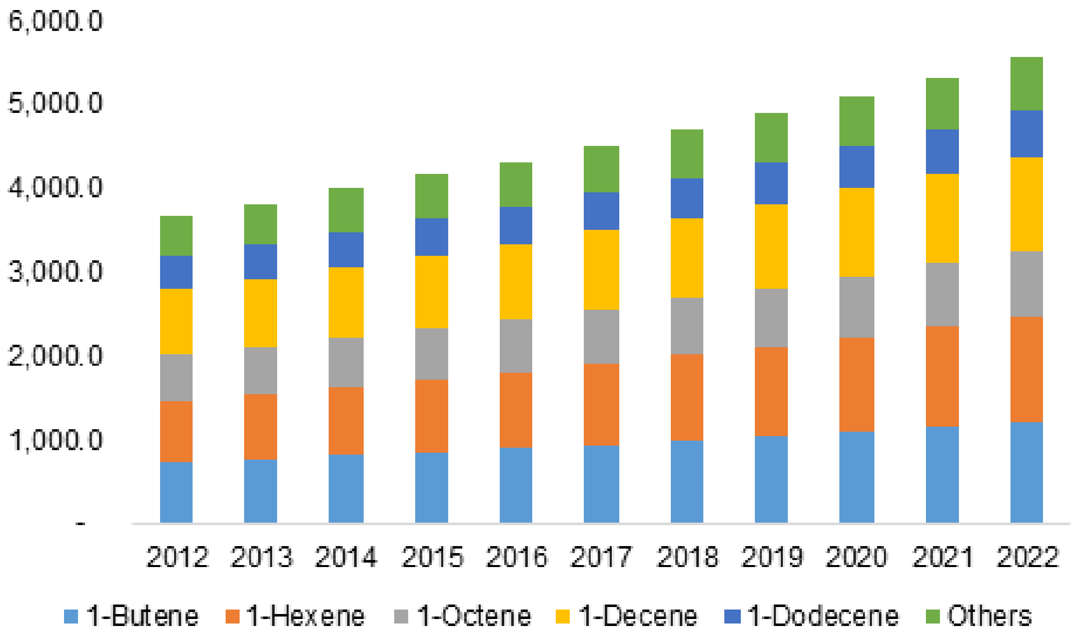

FIGURE 4-9 Projected growth of α-olefins.
NOTE: M = million.
SOURCE: Stahl, 2016. Reproduced with permission by Grand View Research.

One of the features of homogeneous catalysis that distinguishes it from heterogeneous catalysis is that soluble molecular complexes can often activate specific carbon–hydrogen bonds, not necessarily the weakest one. In that way, organometallic chemistry can drive a different reactivity pattern relative to that of traditional oxidation methods. While this selectivity may not play a critical role in the production of many commodity chemicals, Stahl noted it is capitalized on throughout organic chemistry and in particular in pharmaceutical synthesis. In fact, most of the research on homogeneous catalysis has focused on carbon–hydrogen bond functionalization as part of complex molecule synthesis and, to a lesser extent, fine chemicals synthesis. However, selectivity is crucial for alkane functionalization, with an example of preventing over-oxidation in the partial oxidation of methane to form methanol. As an aside, Stahl said in his opinion there has been a "brain drain" in the area of homogeneous catalysis directed toward hydrocarbon functionalization since the 1990s related to a lack of research funding from National Science Foundation (NSF) and the U.S. Department of Energy (DOE). Most of the research funding for homogeneous catalysis, he claimed, comes from the National Institutes of Health and goes toward pharmaceutical synthesis, rather than from NSF and DOE to study hydrocarbon functionalization.

The Shilov platinum chloride catalyst (Shilov and Shul'pin, 1997) is one of the more well-studied homogeneous catalysts for alkane functionalization that enables organometallic methane oxidation (see Figure 4-10). It is also possible to use oxygen as the oxidant using redox couples, and Stahl, and his collaborators have been studying that possibility in an electrocatalytic system (Gerken and Stahl, 2015; Joglekar et al., 2016).

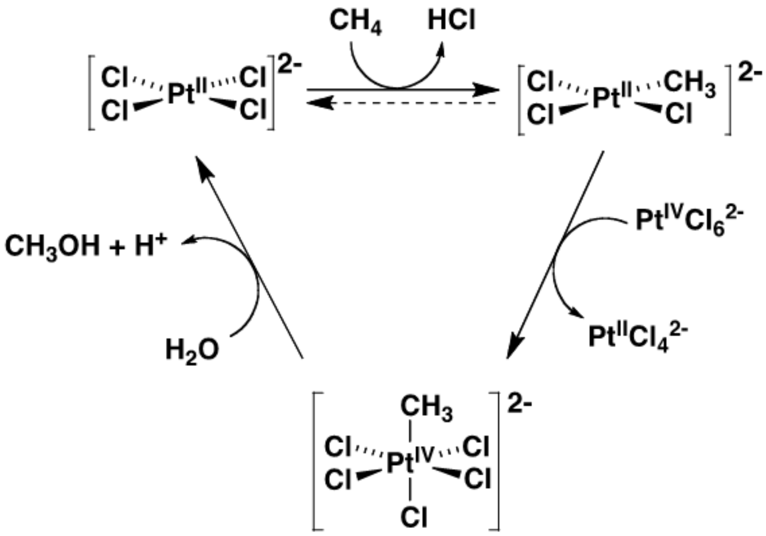

FIGURE 4-10 The Shilov system for methane oxidation.
SOURCE: Stahl, 2016.

Other uses of homogeneous catalysts include oxidative carbon–carbon coupling, which is used today to make polyimide resin from two aromatic molecules. The question, said Stahl, is whether this type of system could be used to couple two methane molecules to produce ethane, which would then undergo oxidative dehydrogenation on the same palladium catalyst to yield ethylene. In such a scheme, oxygen would act as a hydrogen acceptor in the ethane-to-ethylene reaction. Another possibility is to catalyze the non-oxidative conversion of hydrocarbons through the addition of methane to olefins (Sadow and Tilley, 2003).

Stahl noted that a team within the NSF Center for Chemical Innovation, the Center for Enabling New Technologies for Catalysis is exploring the idea of using homogeneous catalysis for converting natural gas liquids into longer-chain hydrocarbons that could be used as liquid fuels (Goldman et al., 2006, 2011). They are also studying routes for making aromatics from ethylene and alkanes (Brookhart et al., 2012; Goldman et al., 2011; Lyons et al., 2012). The key to developing these types of reactions, he said, is a willingness to work at elevated temperatures, which most researchers do not consider when studying homogenous catalysis because they worry about stability. This highlights the lack of sustained efforts to design homogeneous catalysts that are stable under conditions required for hydrocarbon functionalization.

During the discussion period, Matthew Neurock from the University of Minnesota noted that homogeneous catalysts offer the possibility of using analytical tools such as nuclear magnetic resonance spectroscopy to study well-defined molecules and their interactions with reactants in a way that is challenging with heterogeneous catalysts. These types of studies may not lead to an industrial process, but they can provide novel and useful information about how bonds are made, broken, and transformed through their interactions with the metal atoms in these catalysts.

WORKING GROUP SESSIONS

Following the presentations by Bricker, Bell, and Stahl, the workshop's participants broke into four predefined working groups, each of which explored an area in which catalysis could enable novel approaches to using natural gas and natural gas liquids. The subjects discussed by the four groups included light alkanes to alkenes and dienes, light alkanes to aromatics, emerging opportunities for novel approaches to natural gas conversion, and activation of natural gas using nontraditional oxidants. As was the case with the first set of working group discussions, each group, after hearing a short introductory presentation, was asked to answer a set of questions over the course of their of deliberation. Three of the four groups addressed the questions in Box 4-1.

BOX 4-1
Working Groups 1-3 Session Questions

1. What, if any, are the impediments to commercial viability of new technologies for converting light alkanes to alkenes and dienes or aromatics or for using nontraditional oxidants?
2. What are the top two to three well-established research approaches to making alkenes and dienes or aromatics or for activating natural gas with nontraditional oxidants viable and what are the challenges associated with them?
3. What are some promising but higher-risk novel approaches being undertaken?
4. What are the research opportunities that exist?
5. What should researchers be aware of in terms of industrial requirements and environmental constraints for new approaches to the utilization of natural gas?

The remaining fourth group, which discussed emerging opportunities for novel approaches to natural gas conversion, confronted a slightly different set of questions (see Box 4-2).

BOX 4-2
Working Group 4 Session Questions

1. What are the research-stage conversion processes for natural gas and ethane conversion that are currently under investigation?
2. What possibilities are there for entirely new, as yet unknown processes?
3. What are some incentives and impediments on the path to establishing the potential commercial viability of such novel approaches?
4. What are the opportunities for improvements in existing industrial processes?
5. What are the research opportunities that exist?

Following the 2-hour discussion period, each group's designated rapporteur summarized the group's work to the reassembled workshop participants. An open discussion followed the four reports.

Light Alkanes to Alkenes and Dienes

In her framing remarks to this working group, Angeliki Lemonidou, professor of chemical engineering and director of the Petrochemical Technology Laboratory at Aristotle University of Thessaloniki, recapped much of what earlier speakers had presented on the technologies used to convert light alkanes, primarily ethane and propane, to alkenes and dienes. She did, however, also note that while these dehydrogenation technologies are deployed on an enormous scale worldwide, there is still room for improving these processes. The three main drawbacks they suffer from include coke deposition; side reactions such as hydrogenolysis,[1] isomerization, and polymerization that produce unwanted byproducts; and thermodynamic limitations. Catalysis science, she said, can improve the performance of alkane dehydrogenation processes through the design of new or improved catalyst formulations and dopants based on fundamental understanding of coke formation routes and mechanism of side reactions. Research on catalysts can also aim to identify novel catalysts that replace toxic metal oxides with environmentally benign, catalytically active metals; and materials that selectively remove hydrogen from the reaction milieu by using hydrogen-permeable membranes.

With the shift from naphtha as a feedstock in the United States, butadiene production may not be able to meet future demand, so an area that Lemonidou believes merits special attention is butadiene synthesis from light alkanes. There is a desire, she said, to exploit new processes for butadiene production, and she suggested two potential routes: ethylene dimerization followed by oxidative dehydrogenation and a one-step oxidation of butane to butadiene. She also highlighted the lack of research on alternative oxidants for oxidative dehydrogenation, including the use of carbon dioxide as a mild oxidant (Ascoop et al., 2016; Koirala et al., 2015; Porosoff et al., 2015) and halogens (Upham et al., 2016).

Lemonidou concluded her remarks with her perspective on opportunities in this area. For propane to propylene, the immediate target should be to increase yield given that high selectivity is difficult with the known catalyst and using oxygen as the oxidant. For ethane to ethylene, there is immediacy for catalyst formulations that fulfill industry’s yield requirements and for scaling and testing promising catalysts under industrially relevant conditions. Current yields of butane to butadiene are low, so near-term work should focus on identifying catalysts that can boost yields to acceptable levels. The goal of all of this research on oxidative dehydrogenation, she said, should be to minimize the deep oxidation of alkanes and sequential oxidation of the resulting olefins. Approaches to achieving this goal include designing catalyst surfaces that adsorb weakly to the formed olefin, controlling active site density, and keeping the partial pressure of oxygen low, perhaps through the design of membrane-based reactors, or by decoupling the reduction and oxidation steps.

Discussion

The discussion that followed Lemonidou’s presentation, led by Tobin Marks, identified a number of impediments facing technologies for converting light alkanes into alkenes and dienes. A major obstacle is that the technologies currently used are mature with acceptable selectivity, and the capital costs of implementing a new technology are considerable. For PDH, one challenge is to develop enough of a knowledge base to enable the rational design of selective and stable catalysts, which Marks added is an overarching theme for the entire workshop. Another

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[1] Hydrogenolysis is a chemical reaction in which carbon–carbon bonds are cleaved by the addition of hydrogen.

challenge is to achieve similar selectivity but with a lower carbon footprint than oxidative dehydrogenation, and to do so with simpler reactors requiring smaller capital expenditures. For dienes, the discussion focused on direct routes from butane to butadiene.

With regard to the top two to three well-established research approaches to making alkenes and dienes, Marks reported that the group discussed identifying catalysts that would improve the carbon selectivity of oxidative dehydrogenation while maintaining acceptable turnover rates and frequencies. Alternative oxidants might be able to address this challenge, as might novel reactor designs such as circulating fluid bed and short-contact-time reactors.

The discussion on promising but higher-risk novel approaches produced a long list of ideas that Marks characterized as a good guide for developing a research program. The list included

- Biological routes for syngas fermentation to butadiene;
- Carbon-based catalysts, such as those using carbon nanotubes and graphene, for oxidative dehydrogenation at low temperatures;
- Oxygen activation and utilization bookkeeping in oxidative dehydrogenation reactions to improve selectivity and carbon efficiency; and
- Membrane reactor technology to separate hydrogen or remove products before further reaction occurs.

This group also identified a long list of new tools and scientific advances that are creating important research opportunities. This list included

- In situ observations of catalysts under a variety of dynamic reaction conditions;
- Theoretical methods for better understanding spectroscopy data and mechanisms of light alkane conversion;
- Tools for mechanistic studies of light alkane conversion, such as operando methods, labeling techniques, and Mossbauer and electron paramagnetic resonance spectroscopy; and
- Homogeneous catalysts for conversion of light alkanes as knowledge-based platforms for developing new concepts.

With regard to the industrial requirements and environmental constraints that researchers are responsible for knowing when developing new approaches to utilizing natural gas, an overarching impediment as reported by Marks is reducing the energy requirements of any process. With oxidative dehydrogenation reactor design, safety is a critical issue given how much heat these reactions produce. The group noted that the national laboratories have facilities to test novel reactor designs safely and that researchers could collaborate with those laboratories when it comes to testing design prototypes. When incorporating oxidative dehydrogenation chemistry with other processes, or considering the use of alternative oxidants, Marks added that there is value for researchers to think about scalability and environmental viability.

According to Marks, the last constraint that researchers should consider is critically important in the real world of the chemical industry—the cost of capital. Specifically, this group suggested that lower capital costs in implementing a new technology compared with an existing technology could reduce the risk and produce a 15 to 20 percent return on investment.

Light Alkanes to Aromatics

In his opening presentation to this working group, Bruce Gates, distinguished professor of chemical engineering and materials science at the University of California, Davis, said that the conversion of propane to aromatics is less uphill thermodynamically than conversion of methane to aromatics, which had been discussed by one of the first four working groups. Various groups have reported success converting light alkanes to aromatics using acidic zeolites and zeolite-supported metals such as zinc, gallium, and molybdenum, but in his opinion these have been incompletely characterized. The metal atoms, for example, may be present as carbides or oxycarbides, or they may not be in a metallic state. It also appears, he said, that the metal atoms are both inside and outside of the zeolite pores. These catalysts, he added, coke rapidly and require frequent regeneration, which might contribute to catalyst deactivation.

The UOP CYCLAR™ process, developed by BP and UOP, produces aromatics from propane, butane, or a mixture of the two in a dehydrocyclodimerization reaction sequence (see Figure 4-11). Numerous authors, said Gates, have suggested that alkane dehydrogenation is a slow reaction catalyzed by molybdenum and that the subsequent oligomerization and cyclization are catalyzed by the acidic zeolite sites. The resulting product stream of benzene, toluene, and mixed xylenes can be recovered without an extraction unit or sent to an aromatics complex for conversion of the toluene and mixed xylenes into benzene and p-xylene. The yield of this process, said Gates, is reported to be 58 to 60 percent. Rapid catalyst deactivation requires continuous regeneration using UOP’s moving bed reactor and catalyst regenerator design incorporated in its Oleflex process, but the robust catalyst has a substantial lifetime.

An alternative process, Chevron’s Aromax® process, uses a platinum cluster-zeolite catalyst to produce benzene and toluene, but it is more suited to converting larger alkanes, such as hexane and heptane, into aromatics. Gates noted that this reaction resembles naphtha reforming but without the acidic function in the catalyst.

Gates noted there are opportunities for discovering improved catalysts, including the use of metal-containing molecular sieves that have been shown to catalyze reactions such as hydrogenation and dehydrogenation. This is a large and growing class of catalytic materials, he explained, though many of these materials have not been well characterized and are not uniform structurally. He also explained that catalytic performance in any alkane-to-aromatic reaction scheme developed so far depends strongly on the structure of the metal-containing species. As a result, there is an opportunity for chemists to explore that structure–activity relationship with an eye on improving catalyst design through the many synthetic routes that have been developed to tune catalyst structure and other properties that influence activity. These synthetic routes include organometallic syntheses and atomic layer deposition, the latter of which has been used to create zinc-containing catalysts that operate at atmospheric pressure and 823°C (Almutairi et al., 2012). Gates wondered if there were opportunities to use that type of approach for synthesizing well-defined catalysts containing metals such as zinc, gallium, and molybdenum in zeolites, and to create single-site catalysts.

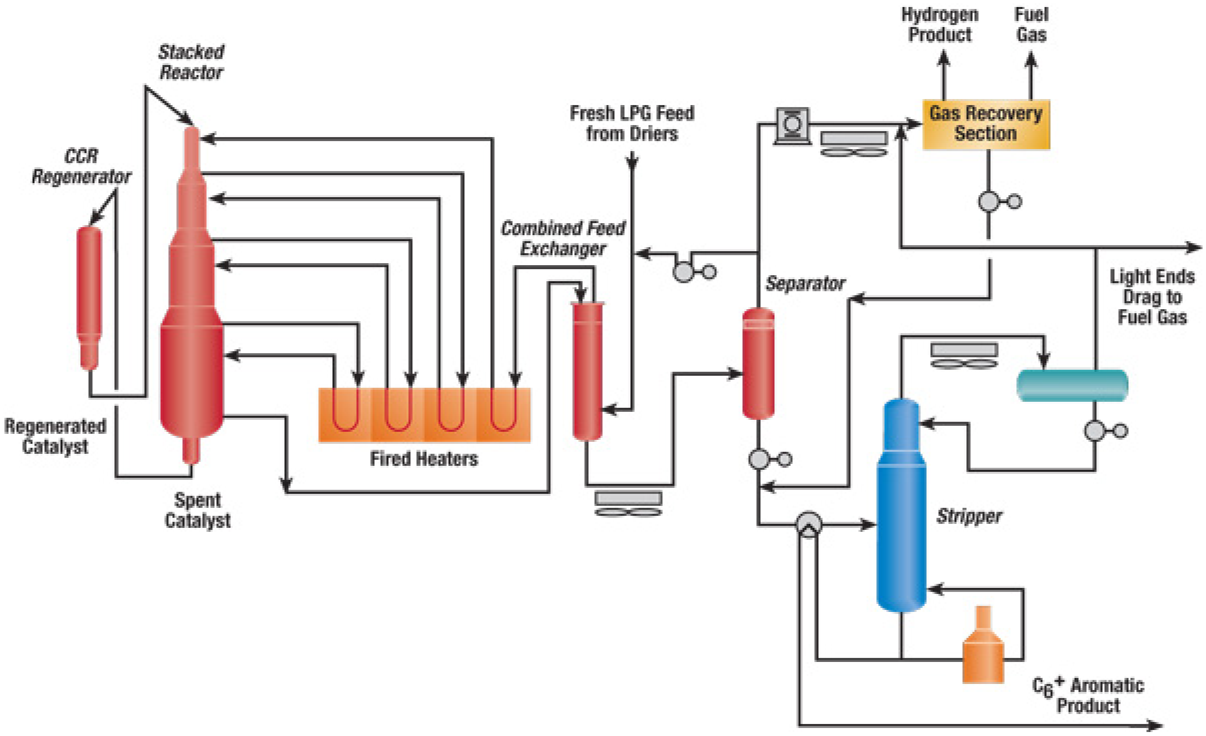


FIGURE 4-11 The UOP dehydrocyclodimerization process.
SOURCE: Bricker, 2016.

As a conclusion to his presentation, Gates enumerated several possible directions for research. One approach would be to vary the metal or combination of metals in molecular sieves of different pore structures and sizes. Another avenue for research would be to attempt to tailor metal-containing catalytic sites on or in a molecular sieve framework, either as single sites or multi-atom clusters. He also suggested a research effort aimed at understanding the chemistry of catalyst synthesis and at relating catalytic activity, selectivity, and stability to structure using theory and spectroscopy with functioning catalysts. Gates noted the lack of, repeated frequently during the workshop, developing a deeper characterization of catalysts. He also thought it worthwhile to investigate processes that would use methane in combination with other feedstocks to produce aromatics.

Discussion

Johannes Lercher from the Pacific Northwest National Laboratory, acting as this group's rapporteur, said the three major impediments to commercial viability of processes to convert light alkanes to aromatics are

1. yield, which the group thought was surprisingly low;
2. cracking, which produces methane and ethylene instead of aromatics; and
3. capital costs related in large part to the product separations required.

Research approaches that could make production of aromatics from alkanes viable included varying the metal in the zeolite, which the discussion noted has been the subject of several patents involving the use of rhenium and tungsten. Other approaches would be to vary the zeolite structure and to balance the metal and acid function in the zeolite. With regard to the second of these, the working group discussed the possibility of speeding up the rate-limiting dehydrogenation step by using a gallium or zinc catalyst, but then it speculated that perhaps it was important for this step to be slow so that too much olefin did not accumulate in the zeolite pores so as to prevent higher oligomerization and runaway reactions.

Promising but higher-risk novel approaches described by this working group included the use of confinement-based catalysts to steer selectivity, oxidative heating and aromatization to better manage energy use, and decoupling the dehydrogenation reaction and ring-closure reaction. With regard to this last possibility, Lercher noted there has been conflicting data in the literature so it was not clear whether this approach was a real possibility for industrial application or merely an interesting research project.

This working group discussed a long list of research opportunities, many of which, said Lercher, reiterate what other groups have proposed. These included

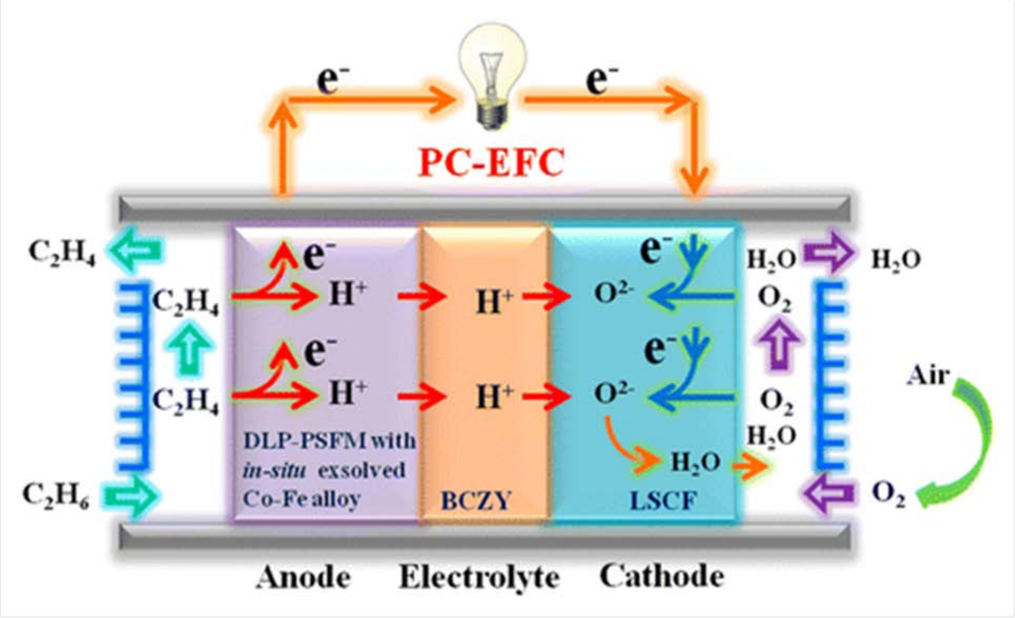
- Vary the metals, zeolites, and location of the active sites for the two reactions within the zeolites;
- Explore the chemical, structural, and mesoscopic properties of the zeolites across a wide range of structures and in a more exhaustive manner, particularly with regard to how well these structures stabilize or destabilize transitions states during dimerization and ring closure;
- Explore engineering approaches to optimize heat transfer for the endothermic reaction;
- Minimize cracking while maintaining dehydrogenation and cyclization activity, perhaps by better characterizing the role of cations in suppressing cracking;
- Determine the nature and mechanism of coke formation and devise strategies for limiting the sites at which coke is able to form or directing coke to form away from the active sites;
- Characterize the location of active sites in zeolite structures, their stability in the presence of reagents at process-relevant temperatures, and any factors that might increase the lifetime of the active sites;
- Explore other hydrothermally stable support systems beyond zeolites, such as tungsten-zirconia structures;
- Identify milder approaches to catalyst regeneration;
- Characterize the role of chemical potential on the active sites and how an active site might change as a function of the chemical potential within the reactor as a function of axial direction and reduction state;
- Develop methods for in situ operando high-temperature spectroscopy, pore size measurement, and microscopy; and
- Use theoretical methods to explore mechanisms and how active sites are maintained or change over time.

Emerging Opportunities for Novel Approaches

The working group heard two short presentations, one from independent consultant Guido Pez on electrochemically mediated catalysis, and the other on biocatalysis from Mattheos Koffas, the Dorothy and Fred Chau ’71 Career Development Constellation Professor in

Biocatalysis and Metabolic Engineering and professor of chemical and biological engineering and biological sciences at Rensselaer Polytechnic Institute. While electrochemical catalysis has potential as a means of converting hydrocarbons into value-added products, Pez said, one of its main limitations is the high relative cost of using electricity as a reagent to drive endothermic hydrocarbon conversion processes. Therefore, he explained, a more promising approach is to first conduct an exothermic, selective oxidation at the anode of an electrochemical system that would provide both electricity and chemicals from what has been called a "tailored" direct hydrocarbon fuel cell (Alcaide et al., 2006).

There are a number of thermodynamically feasible fuel cells for chemicals and energy cogeneration, said Pez. These include ethane plus oxygen to ethylene and water; methane coupling in the presence of oxygen to produce ethane and water or ethylene and water; and methane in the presence of oxygen to produce methanol. One group (Liu et al., 2016) has already demonstrated an ethane-to-ethylene fuel cell using a complex anode and cathode (see Figure 4-12). The published fuel cell was a 0.2 cm^2 button cell, and as configured it achieved selectivity exceeding 90 percent and yields approaching 40 percent at 750°C, with only methane and trace amounts of carbon monoxide as byproducts. This system produced no carbon dioxide, so in a zero-carbon environment, it is possible to consider such as a system as a replacement for steam cracking of ethane, said Pez.



Anode: $(Pr_{0.4}Sr_{0.6})_3(Fe_{0.85}Mo_{0.15})_2O_7$/Co-Fe alloy nanoparticles

$$C_2H_6 \rightarrow C_2H_4 + 2H^+ + 2e^-$$

H^+ **Electrolyte** : $BaCe_{0.7}Z_{r0.1}Y_{0.2}O_{3-\delta}$

Cathode: $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.20}Fe_{0.80}O_{3-\delta}$

$$O_2 + 2e- + 2H^+ \rightarrow 2H_2O$$

FIGURE 4-12 Ethane to ethylene fuel cell.
SOURCE: Liu et al., 2016.

A methane to ethane and ethylene fuel cell has also been reported (Kiatkittipong et al., 2004; Quddus et al., 2010) using a lanthanum-aluminum anode and a lanthanum-strontium-manganese cathode. This system achieved 91 percent selectivity for ethane and ethylene, with the relative amount of these two products varying with temperature. At 1,273 K, this fuel cell produces ethylene almost exclusively, with only trace amounts of ethane, carbon monoxide, and carbon dioxide. There are also published reports of electrocatalytic conversion of methane to methanol (Fan, 2015; Lee and Hibino, 2011; Spinner and Mustain, 2013), but these systems required energy input.

Electrocatalysis does not have to happen solely in the context of a fuel cell. It is possible, said Pez, for electrochemistry to promote catalysis or modify catalytic activity (Katsaounis, 2010). One group has developed what it calls “non-Faradaic electroreforming” of methane to syngas that produces a dramatic decrease in reaction temperature and an increase in yield that exceeds the calculated thermodynamic equivalent (Oshima et al., 2013; Sekine et al., 2011), though with electrical efficiency of only 15 to 25 percent. Others have used spark discharge (Kado et al., 2003) or corona discharge (Marafee et al., 1997) to convert methane into ethylene, though with substantial power input.

Turning to the subject of biocatalysis, Koffas said that methane is an excellent source of carbon and energy for microorganisms known as methanotrophs, which historically have been used for producing feed-grade biomass. These bacteria are capable, he explained, of converting methane into protein, alkanes, alcohols, sugars, dicarboxylic acids, and other higher-value chemicals such as carotenoid pigments and vitamins. Currently, a plant in Norway is producing 850,000 tons per year of methanol and 10,000 tons per year of protein for animal feed from crude methane using the microorganism *Methylococcus capsulatus*.

One area of industrially motivated research aims to produce carotenoid pigments and antioxidants using a microorganism known as *Methylomonas sp.* 16a. The genome of this organism has been sequenced, said Koffas, and this knowledge is being used to manipulate the organism’s metabolic pathways to produce different high-value carotenoids. He noted that prices for various carotenoids range from $500 per kilogram for β-carotene to $2,000 per kilogram for astaxanthin. Today, production is dominated by chemical synthesis, but researchers have engineered the organism to produce a variety of these valuable compounds and are now working to boost production to economically viable levels.

Discussion of Electrocatalysis

The discussion on electrocatalysis covered conversion of C1, C2, and C3 hydrocarbons to chemicals by use of electricity including limiting process economics. Methods covered were direct hydrocarbon fuels cells, electrically promoted catalysis, methane to syngas via electroreforming and methane to C2 hydrocarbons via electrical plasma processes.

In recapping the discussion on electrocatalysis, Monty Alger from Pennsylvania State University said that the outcome of discussion was straightforward: researchers are working on fuel cells, others are doing work on materials development, a third group is studying electrocatalysis, and none of these groups are talking to one another, a point that he noted had been raised throughout the workshop. As far as specifics, the working group voiced interest in these electrochemical processes but the concern was that these technologies may not be viable at an industrial scale because of the difficulty in scaling the electrocatalytic systems and operating them at scale. Another barrier to commercial viability is the high expected cost of building industrial scale electrocatalytic reactors, whether they are fuel cells or systems based on non-Faradaic electrochemical modification of catalytic activity.

At one point in the discussion, Alger recounted, it was mentioned that there has been a substantial body of work on ceramic membrane technology developed in recent years that could present an opportunity to advance an integrated solution for overall chemical conversion using electrochemical means. He noted that the opportunities that could result from merging membrane research and electrocatalysis are substantial and could lead to entirely new processes for chemical conversion. The discussion also pointed out that the drivers for fuel cell development are different than for catalysis.

Some in this working group stressed that the fuel cell community will not solve the challenges to developing industrial scale processes without collaborating with the catalyst, materials, and engineering communities. However, the group also recognized that funding is not available today for critical research on materials, such as transport membranes and mixed conductors, which will present challenges to collaboration. Others in the group also noted that the catalysts used in these systems could be improved.

Discussion of Biocatalysis

The discussion about biocatalysis began with working group members pointing out that biocatalysis is being used in small-scale commercial processes. Calysta, for example, is converting methane into protein feed to reduce the aquaculture industry’s need for fishmeal, and Newlight Technologies has a demonstration plant that uses biocatalysis to convert methane emissions into an engineering polymer. The group also noted that, at least theoretically, anything that can be made biologically could be made from methane given enough time and money to do the necessary metabolic engineering. The resulting challenge, then, will be to select the best opportunities to pursue. However, one qualifier for that selection would be that the resulting biocatalytic process converts methane into chemicals with no carbon dioxide generation. That would be a unique outcome with a unique value proposition, Alger reported. A possibility the group mentioned was to couple biocatalysis with electrocatalysis to invent processes that convert methane to chemicals without generating carbon dioxide or water. A challenge for research in this area is addressing overall economics to be viable for long-term commercialization.

One of the biggest impediments to commercialization of biocatalytic routes is their poor yield of product. Therefore, improving yields, kinetics, reaction rates, and process costs related to separations will be critical for any commercially viable process to come out of biocatalysis research. The working group raised the possibility that the organisms developed through this research could be tainted by the “genetically modified organism” label, which could limit the ability to export products made using these organisms to certain regions of the world, and the group noted the potential challenge of having chemically trained people running biological processes. Another confounding issue for biological systems is the potential impact of natural gas impurities on the microorganisms.

One potential advantage of biosynthetic approaches to alkane modification is the possibility of making materials not currently accessible in high volumes or entirely new materials for which markets could be developed. Such systems may also be more economically viable at smaller scales than current industrial chemical processes, which could be important for utilizing stranded and flared gas. Biocatalytic systems may also have lower energy demands, though the cost of separating product from a biological reactor could negate any energy-related savings.

Activation of Natural Gas Using Nontraditional Oxidants

One of the main drivers of developing nontraditional oxidants for activating natural gas is the benefit of eliminating carbon dioxide emissions associated with electricity production, transportation, and chemical, agricultural, and other industrial processes, said Eric McFarland, professor of chemical engineering at the University of California, Santa Barbara. In the area of alkane conversion, it has so far proven impossible to partially oxidize alkanes with oxygen at high rates and low cost without producing carbon dioxide, he noted. As an example, converting methane to syngas for the production of methanol and other chemicals produces between 0.5 and 1 ton of carbon dioxide per ton of methane. Aside from the issue of carbon dioxide emissions, McFarland said there is another reason to look at alternative oxidants for hydrocarbon conversion, which is to make the best use of the chemical potential stored in the carbon–hydrogen bond.

Among the potential alternative oxidants McFarland listed were sulfur (Zhu et al., 2013), carbon dioxide (Cavani et al., 2007; Wang et al., 1999), nitrogen oxides (Cavani et al., 2007), and sulfur oxides (Hristov and Ziegler, 2003; Mukhopadhyay et al., 2005; Periana et al., 1993), though he devoted most of his remarks to the use of chlorine, bromine, and iodine. The halogens—chlorine, bromine, and iodine—are quite effective, he said, at oxidative dehydrogenation, which is why they are used as flame retardants. This has been known, said McFarland, since the late 1940s (Rust and Vaughan, 1949). In the 1960s, Shell developed a dehydrogenation process using molten iodine salts (Sanborn et al., 1968), and more recently, researchers have demonstrated the production of light olefins from methane and ethane using chlorine as the oxidant (Shalygin et al., 2013). While working with halogens presents some engineering challenges, halogen chemistry is practiced safely and profitably on massive scales, McFarland noted.

Among the benefits of converting methane to methyl halogens are that it preserves the chemical potential stored in methane's carbon–hydrogen bond, the reaction product is easily separated from the reactants, and the hydrogen halide byproduct of the halogenation reaction also has value as an electron carrier. In fact, said McFarland, the catalytic reoxidation of the hydrogen halide by oxygen to produce the molecular halogen can be used to generate heat or electricity.

As an example of the halogen-mediated dehydrogenation reactions that he and his collaborators have explored, McFarland briefly described a process in which methane reacts with bromine at a moderate temperature of 400°C to produce methyl bromide, which is then catalytically coupled at 400°C to produce olefins, alcohols, aromatics, or ethers, depending on the catalyst. This mixture then passes over a solid metal oxide to absorb the hydrogen bromide. The resulting solid metal bromide is regenerated with oxygen to produce metal oxide plus bromine for reuse (Lorkovic et al., 2004; Zhang et al., 2011). This reaction scheme can be used to convert ethane to ethylene, propane to propylene, and butane to butene at greater than 95 percent selectivity. The unresolved issues with these processes include the ability to regenerate the solid metal oxide, the reactive capacity of the solid metal oxide, and hydrocarbon stability over the solids. To address these and other challenges, McFarland and his collaborators changed their approach, using a molten halogen salt to generate the halogen in situ (see Figure 4-13), to control heat exchange, and to absorb and transport bromine and oxygen. This approach reduced the system complexity, he explained.

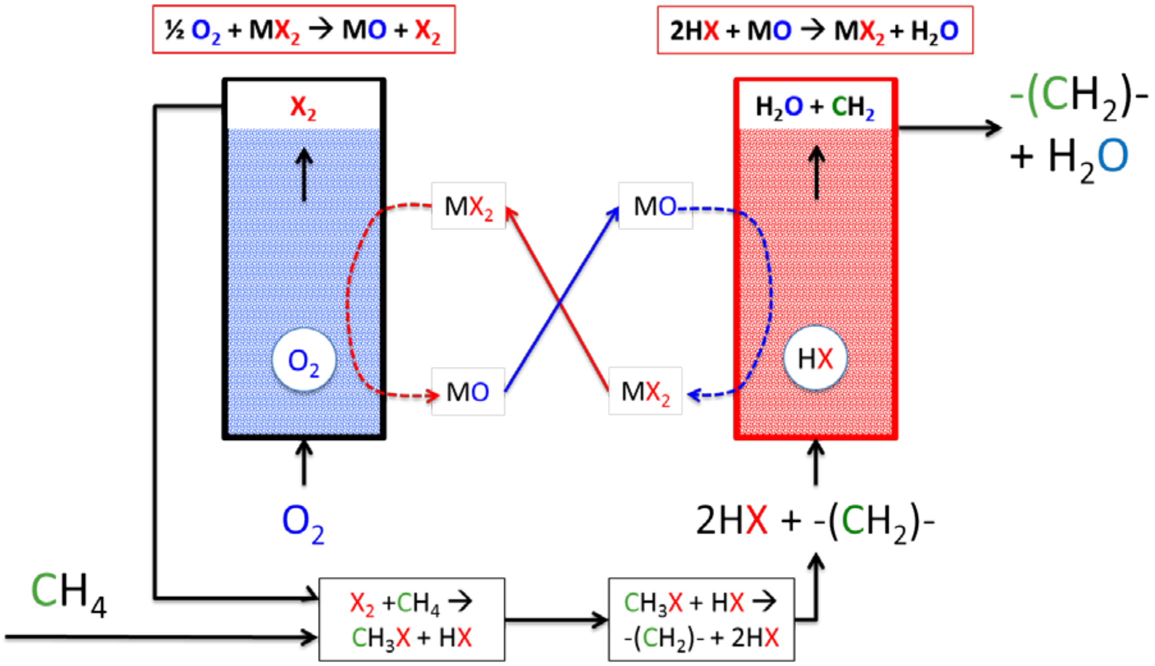


FIGURE 4-13 Methane conversion to methyl halide using a molten salt configuration.
SOURCE: McFarland, 2016.

Discussion

Group rapporteur James Stevens, recently retired as the Dow Distinguished Fellow at The Dow Chemical Company, began the discussion with the comment that over the years he had seen numerous examples of methane activation with non-traditional oxidants involving the conversion of methane to methyl-X, where X is a leaving group, and that if he were to poll the workshop participants, each one could probably identify one leaving group that someone in industry or academia had tried and even piloted for converting methane to other hydrocarbons via this route. His point was that this group's discussion was not so much about new science but rather about trying new ways of adapting existing science to meet specific needs. Having said that, he reported that the working group discussed a number of impediments for nontraditional oxidants to become commercially viable, including the lack of a tax on carbon dioxide emissions and the risk-aversive nature of the chemical industry with regard to new technology. The group also noted that current technology can work well in an environment where there is no penalty for emitting carbon dioxide. The group noted that dealing with corrosion issues in strong electrolyte environments raises the engineering and material demands and unknown safety issues, but these are not insurmountable if the economics become favorable. For example, the chemical industry has extensive experience in handling halogens and strong acids, and so the use of bromine to form methyl bromide and HBr, followed by coupling the methyl bromide to ethylene or other hydrocarbons would probably not be a technical challenge for industry. There was a discussion on the use of oxygen in a cycle to form more selective oxidants, thereby moderating the selectivity. However, the relative lack of research on how to use oxygen to form more selective oxidants at industrial scales was also noted in the discussion as an obstacle to progress.

With regard to well-established research approaches for activating natural gas with non-traditional oxidants, this group pointed out that processes using halogens to make, for example, methyl chloride and methyl bromide, which would serve as intermediates to make value-added hydrocarbon products have been piloted by numerous companies. The use of bromine as a non-traditional oxidant for methane coupling has several advantages, particularly because the heat of reaction of methane with bromine is much lower than that with oxygen, while still being an exothermic reaction, which has the potential to make the bromination reaction more selective. In addition, the use of halogens as non-traditional oxidants has the potential to make product separation easier. The use of halogens to convert methane to ethylene and other hydrocarbons has not been commercialized yet, primarily because of economic rather than technical reasons. Some major drawbacks with the use of bromine include the heat management and the large bromine recycle stream that would be necessary. Ultimately, the commercial use of non–traditional oxidants is disadvantaged over current technology, as long as there is no cost for producing and releasing carbon dioxide.

There was work in the 1940s on a commercial process for reacting methane with sulfur to form carbon disulfide and hydrogen sulfide, which were then reacted to form ethylene, regenerating sulfur. This area was recently developed further by the Marks group (Zhu et al., 2013). Sulfochlorination has also been demonstrated at scale, and again, economics are the only major impediment to commercial application. For promising but higher-risk approaches, the discussion noted that identifying new secondary regenerative and selective oxidants could have value, as could a process for selective mono–oxyhalogenation. Molten halide salt processes and solvents could offer an approach to recycle reactants and dissipate heat.

Research opportunities the group discussed as potential routes for overcoming obstacles for the use of non–traditional oxidants for natural gas included developing a more extensive knowledge base about strong electrolytes and identifying novel reactor and process materials for dealing with corrosive conditions. A better understanding of the kinetics of oxygen transfer and of multiphase reaction systems offers the possibility of improving oxidation reactions and the use of oxygen to form more selective methane oxidants and processes, while still using oxygen as the secondary oxidant. This was particularly noted for the formation of selective nitrogen-based oxidants and processes. The group also noted the lack of research on process engineering, including novel separations technologies. Each of these opportunities, the group pointed out, would be better addressed in collaborative efforts involving chemical engineers and chemists from industry, the national laboratories, and academia, which Stevens said was a common theme that others had mentioned throughout the day. This group also had a lengthy discussion, he reported, about how chemical engineering departments at U.S. universities may not be devoting enough attention today to teaching fundamental chemical engineering processes.

DISCUSSION

Alexander Orlov from the Institute for Advanced Computational Science at Stony Brook University pointed out there are two-dimensional materials, including graphene, carbides, and nitrides, that could hold promise as size-selective catalyst supports. Methods for scaling the production of such materials and research to develop those methods are lacking, which could perhaps tap into the funding opportunities associated with these materials.

Fabio Ribeiro from Purdue University said that this community can benefit from educating the public about the importance of making wise use of the nation's natural resources, referring to shale oil and natural gas. Lercher remarked that in his opinion, the way to make the argument to those who want to leave shale gas in the ground, since it is not a renewable resource, is to point out that shale oil and natural gas, which has a lower carbon footprint, can serve as a bridge to a zero-carbon industry. "This is not going to be the final solution, but a bridge that could last 30 to 50 years," said Lercher. Speaking from an industrial perspective, Stevens said that while many of these opportunities could be considered "basic blocking and tackling," it is becoming increasingly difficult to hire classically trained chemical engineers who know how to conduct these kinds of studies.

Bruce Gates turned the discussion to the subject of how to generalize the themes for how to go forward in catalysis research. Two themes that he heard repeatedly were to conduct operando characterization under more challenging conditions and to study single-site catalysts. Tobin Marks added developing more robust catalysts, and Lercher said studying carbon–hydrogen bond activation with the goal of creating more active and selective catalysts capable of operating at lower temperature. Moving forward, Mark Barteau from the University of Michigan suggested that the catalyst and process should be thought about as an integrated system. In Pez's opinion, electrode catalysis should be a theme given the possibility of using fuel cells to make both chemicals and electricity.

Carl Mesters from Shell said in his opinion, catalysis is a tool for chemistry to make products society needs, and perhaps chemistry is taking too narrow a view of what products it can make when taking advantage of the abundance of shale gas. One such product would be graphene for electrodes, but he also suggested that the carbon in natural gas could serve as a feedstock for making strong but lightweight materials for the building industry. What catalysis science has not done is look at ways of taking the carbon in methane and turning it into materials with specific properties beyond those available today. The challenge, he said, is to broaden the opportunity space and look into what catalysis can do beyond energy and existing chemicals. Orlov noted that he and his colleagues have been studying the use of carbon to reinforce polymer composites and as soil amendments that increase productivity. "There are some unusual applications, especially if you go outside the discipline and to people at the agriculture department or in materials science for incorporating carbon into existing products," said Orlov.

Alger voiced his support for that idea, but also cautioned that developing a new material is just the start of a process that has to include teaching the customer how to use the material and the virtues of a new material. Lercher noted that the chemical industry uses only 7 percent of the world's methane, with the rest being burned as a fuel. As a result, it would have to develop a host of revolutionary technologies to have even a modest impact on decarbonizing the global economy.

5

Environmental Impacts

The workshop's final session featured five panelists providing different perspectives of how advances in catalysis can have an impact on the environmental issues associated with greenhouse gas emissions. The five panelists were Carl Mesters, managing researcher and chief scientist at Shell; David Allen, the Gertz Regents Professor of Chemical Engineering and director of the Center for Energy and Environmental Resources at the University of Texas at Austin; Richard Helling, director of sustainable chemistry for The Dow Chemical Company; Bala Subramaniam, the Dan F. Servey Distinguished Professor of Chemical Engineering at the University of Kansas; and Klaus Harth, vice president for environmental catalysis research at BASF (Badische Anilin und Soda Fabrik).

In his introductory remarks, Monty Alger, director of the Pennsylvania State University Institute for Natural Gas Research and professor of Chemical Engineering noted that chemicals are a subset of the energy system, which can be a city, a campus, a company, a nation, or the world. Thinking of the energy system as a whole, and considering the majority of activities related to the energy using today's existing technologies, it is feasible to get to a zero-carbon state. The only obstacle would be the cost of investment. The real challenge is not just to become sustainable but to do so at the right level of cost-effectiveness and productivity cost; given that today there is no economic value proposition of moving to a zero-carbon world and creating the incentive to invest in a new infrastructure to support such a transition.

Another challenge, said Alger, is to create policy that incentivizes using the plentiful carbon resources this workshop has been considering in a way that generates the positive economic and environmental benefits that many of the technologies described and discussed at this workshop could enable. He cited several examples of policies and associated regulations—the Clean Air Act, the Clean Water Act, and policies banning the use of ozone-destroying chlorofluorocarbons—that triggered investment and transformation of systems using new and available technologies. Alger noted, though, that sustainability has to be built considering the entire value chain. So while one company might produce substantial carbon dioxide emissions, its products might enable other companies or industries to drastically reduce their emissions. Looking across the value chain can be challenging, because companies do not think horizontally to measure sustainability, but having said that, Alger noted that there is the capability and technology to measure what goes into the atmosphere in order to produce a total system measurement.

As a final comment, Alger said that the energy business in general and the chemical industry in particular are capital intensive. The best new technologies, then, will be ones that not only offer a benefit in terms of environmental impacts and operating costs, but also make use of existing infrastructure or reduce the cost of transitioning to a new infrastructure.

ENVIRONMENTAL IMPACTS ON ENERGY-MOBILITY CHEMICALS

The shale gas revolution, said Carl Mesters, has already enabled the United States to reduce its carbon emission by replacing coal with methane, since coal burning emits nearly twice the amount of carbon dioxide per unit of energy produced compared with burning natural gas to carbon dioxide and water (see Table 5-1). However, stated Mesters, the most efficient way to get energy from methane would be to convert methane to carbon and water, which would produce more energy per pound of methane but also eliminate carbon dioxide as byproduct. The challenges, then, are to develop the appropriate technology and to find a use for the carbon currently produced that would offset the cost of the carbon tax that would incentivize changing the way energy is produced from natural gas.

TABLE 5-1 Pounds of Carbon Dioxide Emitted per Million British Thermal Units (Btus) of Energy for Various Fuels

Fuel Source	CO_2 Emission (lb/mm Btu)
Coal (anthracite)	228.6
Coal (bituminous)	205.7
Coal (lignite)	215.4
Coal (subbituminous)	214.3
Diesel fuel and heating oil	161.3
Gasoline	157.2
Propane	139.0
Natural gas	117.0

SOURCE: http://www.eia.gov/tools/faqs/faq.cfm?id=73&t=11.

Another way in which natural gas could reduce harmful emissions, said Mesters, is by converting them to a liquid fuel that could substitute for diesel fuel made from oil. Shell, for example, is producing what it calls GTL (gas to liquid) Gasoil, a product that when burned in a properly tuned diesel engine produces significantly lower emissions of nitrogen oxides, particulate matter, hydrocarbons, and carbon monoxide.

With regard to converting methane into chemicals, Mesters said there are three basic routes to forming carbon–carbon bonds, all of which currently have drawbacks that integrated efforts in catalysis, process design, and separations science may be able to address. The direct pyrolysis of methane to olefins is energy intensive, produces a great deal of coke, and requires complex separations. Oxidative coupling suffers from competing kinetics and low methane conversion, generates a tremendous amount of heat, and can require complex separations. The indirect route via syngas or using alternative oxidants that first produce methyl-X compounds requires multiple chemical reactions in series, which drives up capital costs.

CHANGING THE SYSTEM OF CHEMICAL MANUFACTURING PROCESSES

Chemical manufacturing is a systems-based operation, said David Allen, and as the industry and policy makers begin to assess how the industry's environmental footprint will change with the transformations this workshop has discussed, it is important to do so from a systems perspective. For example, changing raw materials from petroleum to natural gas–based feedstocks changes the manufacturing system and creates new bottleneck processes, said Allen. In the case of butadiene, there are large effects on price and acetaldehyde becomes a bottleneck intermediate (DeRosa and Allen, 2015). Similarly, an analysis of methane-to-aromatics technologies identifies key cost points and maps cascading effects through the xylene and toluene supply chains.

He summarized the points he wanted the workshop to consider by saying that changing feedstocks, process chemistries, and process technologies changes the system of chemical manufacturing processes. As a result, the indirect impacts of changes in energy consumption, materials consumption, water use, and other measures of environmental impact can be larger than the direct impacts. Often, the net effect can be counterintuitive, he said.

LIFECYCLE ASSESSMENT

Lifecycle analysis, said Richard Helling, helps make good decisions and is a complementary tool to economic analysis when considering whether to deploy a new process technology. It can be a particularly powerful tool to use when looking at environmental impacts because it can account for the follow-on benefits that can result when a new chemical material enables changes outside of the chemical industry that have a positive environmental impact. For example, a new lightweight but strong material could have no net effect on chemical industry emissions, but it could make vehicles more energy efficient and reduce overall emissions significantly. However, calculating those benefits requires understanding how to determine the positive and negative environmental impacts of the new processes used to make that material.

Lifecycle analysis starts, then, with feedstocks and the first few steps of the reaction path to a new material, explained Helling, and proceeds through the entire lifecycle of a material to when it is disposed of or recycled. He also explained that thinking about the lifecycle of a product or material and using that information to influence purchases or investments, that is called "lifecyle thinking." Making that more quantitative, he said, is referred to as "lifecycle assessment" and it takes "a few orders of magnitude more work than lifecycle thinking," said Helling. At Dow, lifecycle thinking is used far more often than lifecycle assessment when making decisions.

One common metric used in lifecycle assessment is cumulative energy demand, which includes the energy content of a material, its fuel value, and the energy that goes into its manufacture. He said the simple rule of thumb is that the fuel value and energy for manufacturing are about equal, plus or minus 30 percent, though the uncertainty can get down to plus or minus 5 percent. "A priori, there is no way to dismiss one or the other fact as they both can be very important," said Helling.

Energetics alone, however, does not do justice to lifecycle assessment because it is fundamentally a multi-attribute assessment technique, and as Helling explained, it is rare that one option is better than an alternative in every way it can be examined. "There are almost always tradeoffs, and lifecycle assessment helps you understand quantitatively what those tradeoffs are," he said. As an example, a process might reduce greenhouse gas emissions but require more fresh water to do so, which might be a big problem in Texas but not in Michigan. As a result, while the calculations that go into a lifecycle assessment can be robust, Helling said, "it takes the values part of it to know what we do with the information and how we compare those things and come to a decision." Acknowledging that Dow does not do a full lifecycle assessment for every project, Helling concluded his remarks by promoting what he calls a 1-day lifecycle assessment. "That involves making enough assumptions that you can come to a directionally correct analysis as rapidly as possible," he explained.

QUANTITATIVE SUSTAINABILITY-GUIDED PROCESS DESIGN

The U.S. chemical industry uses approximately 5 billion British thermal units (BTUs) per year, accounting for 5.9 percent of the nation's energy use, and production of the top 18 commodity chemicals consume 80 percent of that energy and account for 75 percent of the industry's greenhouse gas emissions, said Bala Subramaniam. He noted that hydrogenations are the most energy-intensive processes, followed by cracking, oxidation, and carbon–carbon bond formation (see Figure 5-1). In his opinion, catalyst- and process-related improvements can reduce the industry's energy consumption and environmental impact. The challenge, he said, is to develop novel catalytic technologies that are not only economically viable, but also exhibit high carbon atom economy. Lifecycle analysis can help determine which technologies will meet both of those requirements (see Figure 5-2).

Subramaniam explained that his industry partners want this analysis to start early in process development and want to conduct a process scale simulation to perform the techno-economic analysis. As soon as he and his collaborators receive a process flow diagram, which includes stream and energy flows, they can conduct a lifecycle analysis that can even account for any environmental impacts that might accrue from producing the feedstock for the process. As examples, he discussed two processes, both for making the precursors to polyethylene terephthalate. The first analysis (Ghanta et al., 2013) compared a liquid-phase hydrogen peroxide–based process that eliminates carbon dioxide as a byproduct with a gas-phase oxygen-based silver–catalyzed process for ethylene epoxidation. The key question, he said, was whether the need to use hydrogen peroxide, which requires the use of methane, cancels the zero carbon dioxide benefit. This analysis identified performance metrics that could help yield an economically viable process and could show what parts of the process, including feedstock production, can be changed to reduce its environmental footprint. The analysis revealed that without such changes, the quantitative overall environmental impacts on air quality, water quality, and greenhouse gas emissions would be similar for both processes and lie within the uncertainties of such predictions.

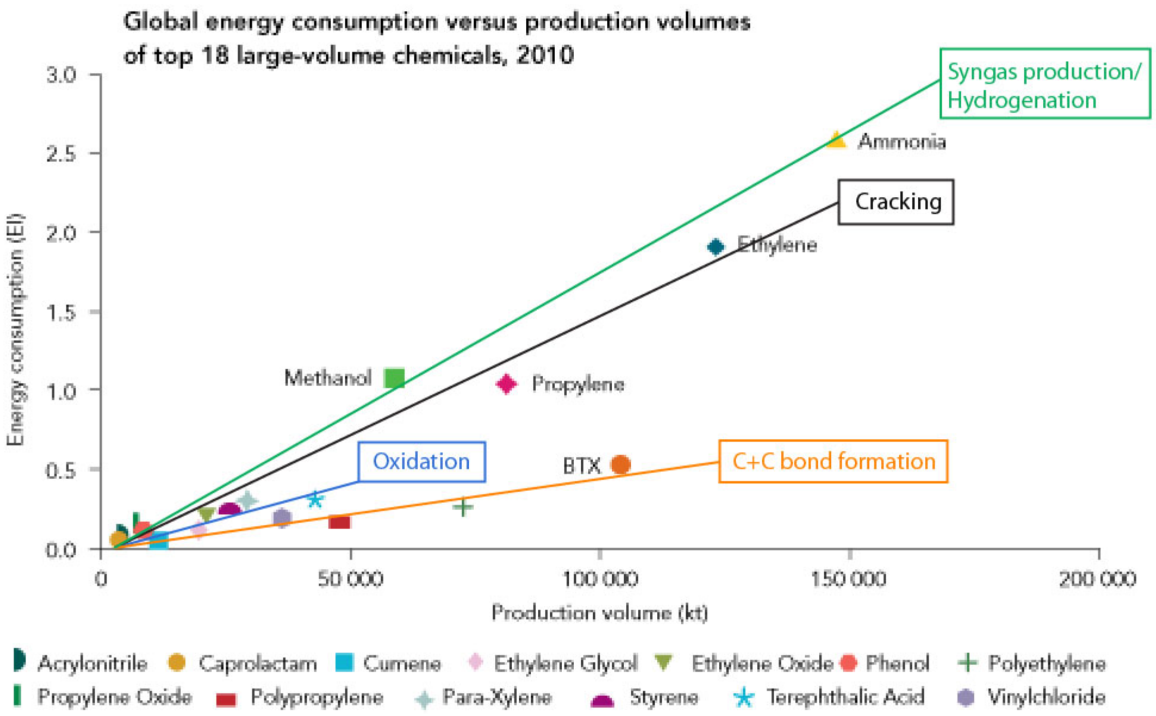


FIGURE 5-1 Global energy consumption versus production volumes of top 18 large-volume chemicals in 2010.
SOURCE: International Energy Agency, International Council of Chemical Associations, and DECHEMA, 2013.

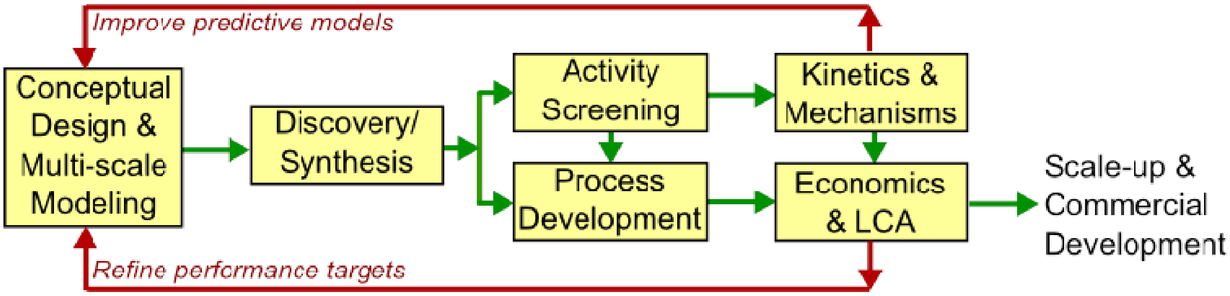


FIGURE 5-2 Quantitative sustainability analysis-aided discovery and development.
NOTE: LCA = lifecycle analysis.
SOURCE: Subramaniam, 2016.

In the second example, he and his collaborators compared terephthalic acid produced in a spray reactor process with the conventional process. This analysis showed there were clear economic and environmental advantages to the spray reactor process. The main economic advantages were a 50 percent reduction in capital costs arising from eliminating the hydrogenation step in the current process and a 15 percent reduction in operating costs, or approximately $0.07 per pound for a multi-billion pound compound. The main environmental advantage comes from reducing the amount of solvent burned, which would result in a substantial reduction in greenhouse gas emissions. He noted that his industry partners are now negotiating licenses for this process.

ENVIRONMENTAL CATALYSIS RELATED TO FEEDSTOCK CHANGE

Addressing the challenges raised during the workshop, said Klaus Harth, is of high importance to the chemical industry, particularly with regard to yield, energy utilization, capital investment, and sustainability. “We have to look at all of these criteria if we want to come up with the innovation and new processes based on shale gas,” said Harth. He reiterated, though, the message that others had made, which is that the impact of changes that the chemical industry makes will be important, but will nonetheless be small compared with changes required in the energy sector. How can catalysis impact the energy sector? Harth said that having catalysts that can oxidize natural gas, which occurs in auto exhaust, would provide a great environmental benefit.

DISCUSSION

Mark Barteau from the University of Michigan commenting on Subramaniam’s figure showing the energy intensity of the top 18 commodity chemicals (see Figure 5-2), noted that he draws a different conclusion from that figure. Two-thirds of the carbon footprint of the hydrogenation processes, he said, comes from generating hydrogen, and the cracking processes are endothermic, so discounting those two curves by the things that catalysis cannot change suggests, in his opinion, that the industry has figured out the optimal inefficiency for a wide variety of processes across the chemical industry that is independent of feedstock variations, price fluctuations, inversion of processes, and any other factors. Subramaniam said that where catalysis can change that equilibrium is by maximizing carbon atom efficiency. Helling agreed with Barteau and said that putting a firmer value on carbon emissions will make decisions easier because instead of them being made on the basis of complex value judgments, there will be a true, measurable economic cost. Mark Jones from The Dow Chemical Company said he agreed with both Barteau and Subramaniam and noted that in his opinion, Subramaniam is arguing that running processes at maximum carbon efficiency will be good regardless of policy.

Helling then noted that the U.S. chemical industry’s switch to shale gas as its major feedstock has already made it more sustainable, but that improvements are required to be among the natural gas producers who are using older technology. He suggested something akin to a “cash for clunkers” program that would encourage producers to use equipment that would greatly reduce the current methane leakage rates. Allen added that the latest data he has seen show the average leakage rate is between 1 and 1.5 percent of the methane extracted from a shale gas well is released into the atmosphere before it is used and that leakage is dominated by what he called “super-emitters.” Two percent of the sites in the Barnett shale formation, he said, accounts for 50 percent of the methane emissions (Zavala-Araiza et al., 2015).

Along the same lines, Pallavi Chitta, from the University of Utah, noted that natural gas flaring is wasting approximately $1 billion of natural gas per year and the energy equivalent of approximately 20 percent of U.S. electricity generation while emitting carbon dioxide equivalent to the emissions of approximately 1 million cars per year during the environmental panel open discussion. He added, and Helling agreed, that flaring was a better option than simply venting methane given that methane is approximately 25 times more potent than carbon dioxide as a greenhouse gas, but the better option still would be to make something from that natural gas. Helling added that naphtha accounts only for approximately 8 percent of U.S. chemical feedstocks, though globally that percentage is still as high as 40 percent.

Wayne Schammel from Siluria Technologies commented that process efficiency is a key aspect of sustainability, but that efficiency has to encompass an entire process developed in conjunction by chemists and chemical engineers. As an example, he cited a process for oxidizing p-xylene to terephthalic acid that achieves 100 percent conversion with 98 percent selectivity, but that generates methyl bromide, a greenhouse gas, and uses a dual water–acetic acid solvent. The most energy-intensive step in this process involves converting 80 percent acetic acid to 95 percent acetic acid for reuse. His point was that if someone developed a different process for oxidizing p-xylene terephthalic acid that eliminated methyl bromide production and operated at room temperature instead of 200°C, it would not be of much use because it would also eliminate the generation of heat that is used in the process's dehydration tower. Mesters added that efficiency optimization modeling today does not include carbon dioxide emissions and often ignores water, too, which must change going forward.

6

Summary of Key Points

Over the course of the 2-day workshop, the presentations and discussions in the breakout groups highlighted several key points and broad challenges and opportunities where advances in catalysis could enable optimal use of the nation's shale gas for the benefit of the chemical industry. Many of the key points captured from individual breakout groups overlapped one another. These key points are summarized here.

As discussed in the opening chapters of this report, reevaluating the focus of research in catalysis was inspired from the current shift in petrochemical feedstocks to lighter hydrocarbons. This shift is a result of technological advances in hydraulic fracturing and horizontal drilling that have enabled access to abundant reserves of natural gas. In evaluating what this new research focus might look like, other important factors were mentioned at the workshop. Chief among these include lowering energy and resource intensive catalytic processes, with a particular focus on reduced carbon dioxide emissions.

During the course of the workshop, several routes were identified by which methane or other light alkanes could be converted to higher-value chemicals. The most promising routes involve the conversion of the light alkane (principally ethane and propane) to olefins. The development of a commercially viable process for the direct conversion of methane to higher-value chemicals was recognized to be a continuing challenge notwithstanding impressive research and technological advances made in recent years. It was also recognized that further research, both with regard to the design and development of catalysts, reactors, and overall process schemes, can contribute in achieving economically viable processes, a goal to be pursued vigorously in order to maintain the competitive advantage that shale gas offers the U.S. chemical industry.

Many of the research opportunities identified and discussed amongst participants during the workshop are not unique to lighter feedstocks. Nevertheless they remain important challenges to address in order to enable the development of successful catalytic processes for these feedstocks, as well as to benefit the field of catalysis more broadly. These include:

- A concerted basic research effort combining kinetics, spectroscopy, and theory aimed at increasing understanding of the catalytic process on an atomic and molecular level that could be used to guide the development of catalysts with precisely tailored properties that can retain their integrity under industrial operating conditions.
- Development of advanced analytical capabilities to enable the structural and chemical characterization of catalysts in a temporally and spatially resolved manner and under realistic operating conditions.
- Design and development of more selective catalysts that produce fewer byproducts and thereby reduce the energy demand and capital costs for post-reaction separations.
- Identification of ways to manage carbon flow so that carbon ends up preferentially in products rather than in coke. Increased understanding and new approaches for solving this issue would increase reaction productivity, reduce energy use, and extend catalyst lifetime.
- Increased collaboration among among materials scientists, chemists, and reaction engineers working in industrial, academic, and national laboratories in order to accelerate the development of highly selective and robust catalysts that could withstand real operating conditions.
- A portion of the national research portfolio devoted to novel, high-risk approaches would enable transformative discovery and technology.

In addition to the general research challenges for catalysis, specific research challenges and opportunities that are specific to lighter feedstocks were identified. Earlier chapters in the report provide details on previous and current research approaches to address the catalytic conversion of methane and light alkanes. However, ongoing research efforts to maximize the full potential for catalytic conversion of methane and light alkanes were mentioned. Those captured during the workshop include:

- Acquiring fundamental knowledge that would enable the rational design of selective and stable catalysts for conversion of methane and condensable components of natural gas to chemical intermediates, in particular, C_4 alkenes and dienes and aromatics;
- Novel (small-scale catalytic) processes to convert natural gas streams associated with untapped reserves of stranded gas;
- Identifying and developing new oxidants that can replace oxygen, but be easily produced from oxygen (or, more ideally, air) in alkane oxidation reactions and new processes for managing oxygen in a cost-efficient manner;
- Researching a detailed understanding of chemical looping and using that knowledge to develop novel catalysts and reactor designs to enable a more efficient approach to methane utilization;
- Exploration of biosynthetic routes for converting methane into entirely new materials with novel properties;
- Applying metabolic engineering to boost yields from microorganisms capable of converting methane into chemicals with no carbon dioxide production;
- Investigating processes that couple biocatalysis with electrocatalysis to convert methane to chemicals without carbon dioxide or water production;

- Identifying single-site catalysts that enable continuous conversion of methane to methanol; and
- Studying metal-organic frameworks as potential solutions to the challenges of separating products from reactants in an energy- and cost-efficient manner.

To realize the greatest potential of recently more available and increasingly lower-cost natural gas as a feedstock for chemical production requires finding new catalysts that exhibit higher stability and selectivity with fewer byproducts than those currently available. Combined with novel product-separation approaches, cost and energy-efficient processes may be achieved. Participants noted that even with better design and improved engineering processes, a remaining problem is the production of greenhouse gases. To move toward a low carbon world, much of what happens in the future is dependent on thinking holistically and creating catalysts that assist in the transformation of natural gas to higher value chemicals while reducing any negative environmental effects. The pursuit of this challenge will be accelerated by collaborations amongst chemists, chemical engineers, materials scientists, physicists, and biologists from academia, industry, and national laboratories.

References

Alcaide, F., P.-L. Cabot, and E. Brillas. 2006. Fuel cells for chemicals and energy cogeneration. *Journal of Power Sources* 153(1):47-60.

Almutairi, S. M. T., B. Mezari, P. C. M. M. Magusin, E. A. Pidko, and E. J. M. Hensen. 2012. Structure and reactivity of Zn-modified ZSM-5 zeolites: The importance of clustered cationic Zn complexes. *ACS Catalysis* 2(1):71-83.

Alvarez-Galvan, M. C., N. Mota, M. Ojeda, S. Rojas, R. M. Navarro, and J. L. G. Fierro. 2011. Direct methane conversion routes to chemicals and fuels. *Catalysis Today* 171(1):15-23.

American Chemistry Council. 2013a. *Shale gas, competitiveness, and new US chemical industry investment: An analysis based on announced projects.* Washington, DC: American Chemistry Council.

———. 2013b.Year-end 2013 chemical industry situation and outlook: American chemistry is back in the game. Washington, DC: American Chemistry Council.

———. 2014. American chemistry: Growing the U.S. economy, providing jobs, enhancing safety. Washington, DC: American Chemistry Council. Available at https://blog.americanchemistry.com/2014/06/american-chemistry-growing-the-u-s-economy-providing-jobs-enhancing-safety [accessed March 7, 2016].

———. 2015a. The rising competitive advantage of U.S. plastics. Washington, DC: American Chemistry Council.

———. 2015b. Guide to the business of chemistry—2015. Washington, DC: American Chemistry Council.

———. 2016. Shale gas and new U.S. Chemical industry investment: $164 billion and counting. Washington, DC: American Chemistry Council. Available at https://www.americanchemistry.com/Policy/Energy/Shale-Gas/Slides-Shale-Gas-and-New-US-Chemical-Industry-Investment.pdf [accessed March 7, 2016].

ARPA-E (Advanced Research Projects Agency-Energy). 2012. *Efficient natural gas-to-methanol conversion*. Available at http://arpa-e.energy.gov/?q=slick-sheet-project/efficient-natural-gas-methanol-conversion [accessed April 13, 2016].

Ascoop, I., V. V. Galvita, K. Alexopoulos, M.-F. Reyniers, P. Van Der Voort, V. Bliznuk, and G. B. Marin. 2016. The role of CO_2 in the dehydrogenation of propane over WO_x–VO_x/SiO_2. *Journal of Catalysis* 335:1-10.

Au, C.-T., T.-J. Jhou, W.-J. Lai, and C.-F. Ng. 1997. An ab initio study of methane activation on lanthanide oxide. *Catalysis Letters* 49(1-2):53-58.

Banerjee, R., Y. Proshlyakov, J. D. Lipscomb, and D. A. Proshlyakov. 2015. Structure of the key species in the enzymatic oxidation of methane to methanol. *Nature* 518(7539):431-434.

Basset, J.M., C. Coperet, D. Soulivong, M.Taoufik, J. Thivolle Cazat. 2010. Metathesis of Alkanes and Related Reactions, *Accounts of Chemical Research* 43: 323-334.

Beck, B., V. Fleischer, S. Arndt, M. G. Hevia, A. Urakawa, P. Hugo, and R. Schomäcker. 2014. Oxidative coupling of methane—A complex surface/gas phase mechanism with strong impact on the reaction engineering. *Catalysis Today* 228:212-218.

Bell, A. 2016. "Conversion of Methane and Light Alkanes to Chemicals over Hetergeneous Catalysts-Lessons Learned from Experinment and Theory." Presented at the Board on Chemical Sciences and Technology Workshop on The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis, Washington, DC, March 7-9, 2016.

Bodke, A. S., D. A. Olschki, L. D. Schmidt, and E. Ranzi. 1999. High selectivities to ethylene by partial oxidation of ethane. *Science* 285(5428):712-715.

Botella, P., E. García-González, A. Dejoz, J. M. López Nieto, M. I. Vázquez, and J. González-Calbet. 2004. Selective oxidative dehydrogenation of ethane on movtenbo mixed metal oxide catalysts. *Journal of Catalysis* 225(2):428-438.

Bricker, J. 2016. "History and State of the Art of Ethane/Propane Dehydrogenation Catalysis." Presented at the Board on Chemical Sciences and Technology Workshop on The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis, Washington, DC, March 7-9, 2016.

Brookhart, M., M. Findlater, D. Guironnet, and T. W. Lyons. 2012. Synthesis of para-xylene and toluene. Filed and issued.

Brown, M. J., and N. D. Parkyns. 1991. Progress in the partial oxidation of methane to methanol and formaldehyde. *Catalysis Today* 8(3):305-335.

Cavani, F., N. Ballarini, and A. Cericola. 2007. Oxidative dehydrogenation of ethane and propane: How far from commercial implementation? *Catalysis Today* 127(1-4):113-131.

Chan, S. I., and S. S. F. Yu. 2008. Controlled oxidation of hydrocarbons by the membrane-bound methane monooxygenase: The case for a tricopper cluster. *Accounts of Chemical Research* 41(8):969-979.

Chin, Y.-H., C. Buda, M. Neurock, and E. Iglesia. 2013. Consequences of metal–oxide interconversion for C-H bond activation during CH_4 reactions on Pd catalysts. *Journal of the American Chemical Society* 135(41):15425-15442.

Cornils, B., W. A. Herrmann, and M. Rasch. 1994. Otto Roelen, pioneer in industrial homogeneous catalysis. *Angewandte Chemie International Edition in English* 33(21): 2144-2163.

Cui, Y., X. Shao, M. Baldofski, J. Sauer, N. Nilius, and H. J. Freund. 2013. Adsorption, activation, and dissociation of oxygen on doped oxides. *Angewandte Chemie, International Edition in English* 52(43):11385-11387.

Czuprat, O., S. Werth, S. Schirrmeister, T. Schiestel, and J. Caro. 2009. Olefin production by a multistep oxidative dehydrogenation in a perovskite hollow-fiber membrane reactor. *ChemCatChem* 1(3):401-405.

DeRosa, S. E., and D. T. Allen. 2015. Impact of natural gas and natural gas liquids supplies on the United States chemical manufacturing industry: Production cost effects and identification of bottleneck intermediates. *ACS Sustainable Chemistry & Engineering* 3(3):451-459.

Dubois, J.-L., M. Bisiaux, H. Mimoun, and C. J. Cameron. 1990. X-ray photoelectron spectroscopic studies of lanthanum oxide based oxidative coupling of methane catalysts *Chemistry Letters* 19(6):967-970.

Duff, B. 2012. U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy presentation at the National Academies of Sciences, Engineering, and Medicine's Board on Chemical Sciences and Technology's Chemical Sciences Roundtable Workshop, May 31, 2012.

EIA (U.S. Energy Information Administration). 2015. U.S. Crude Oil and Natural Gas Proved Reserves. Available at https://www.eia.gov/naturalgas/crudeoilreserves [accessed March 7, 2016].

———. 2016. *Short-term outlook for hydrocarbon gas liquids.* Washington, DC: U.S. Department of Energy.

EPA (U.S. Environmental Protection Agency). 2010. *Methane and nitrous oxide emissions from natural sources.* Available at https://www3.epa.gov/climatechange/ghgemissions/gases/ch4.html [accessed May 31, 2016].

Fan, Q. 2015. Non-Faradaic electrochemical promotion of catalytic methane reforming for methanol production. Filed and issued.

Fang, X., S. Li, J. Gu, and D. Yang. 1992. Preparation and characterization of W-Mn catalyst for oxidative coupling of methane. *Journal of Molecular Catalysis (China)* 6:255-261.

Feng, X., J. Wu, A. T. Bell, and M. Salmeron. 2015. An atomic-scale view of the nucleation and growth of graphene islands on Pt surfaces. *The Journal of Physical Chemistry C* 119(13):7124-7129.

Ferreira, V. J., P. Tavares, J. L. Figueiredo, and J. L. Faria. 2013. Ce-doped La_2O_3-based catalyst for the oxidative coupling of methane. *Catalysis Communications* 42:50-53.

Forde, M. M., R. D. Armstrong, C. Hammond, Q. He, R. L. Jenkins, S. A. Kondrat, N. Dimitratos, J. A. Lopez-Sanchez, S. H. Taylor, D. Willock, C. J. Kiely, and G. J. Hutchings. 2013. Partial Oxidation of Ethane to Oxygenates Using Fe- and Cu-Containing ZSM-5. *Journal of the American Chemical Society* 135(30):11087-11099.

Galvita, V., G. Siddiqi, P. Sun, and A. T. Bell. 2010. Ethane dehydrogenation on Pt/Mg(Al)O and PtSn/Mg(Al)O catalysts. *Journal of Catalysis* 271(2):209-219.

Gao, J., Y. Zheng, G. B. Fitzgerald, J. de Joannis, Y. Tang, I. E. Wachs, and S. G. Podkolzin. 2014. Structure of Mo_2C_x and Mo_4C_x molybdenum carbide nanoparticles and their anchoring sites on ZSM-5 zeolites. *The Journal of Physical Chemistry C* 118(9):4670-4679.

Gao, J., Y. Zheng, J. M. Jehng, Y. Tang, I. E. Wachs, and S. G. Podkolzin. 2015. Catalysis. Identification of molybdenum oxide nanostructures on zeolites for natural gas conversion. *Science* 348(6235):686-690.

Gärtner, C. A., A. C. van Veen, and J. A. Lercher. 2013. Oxidative dehydrogenation of ethane: Common principles and mechanistic aspects. *ChemCatChem* 5(11):3196-3217.

———. 2014. Oxidative dehydrogenation of ethane on dynamically rearranging supported chloride catalysts. *Journal of the American Chemical Society* 136(36):12691-12701.

Gaspar, N. J., I. S. Pasternak, and M. Vadekar. 1974. H_2S promoted oxidative dehydrogenation of hydrocarbons in molten media. *The Canadian Journal of Chemical Engineering* 52(6):793-797.

Gerken, J. B., and S. S. Stahl. 2015. High-potential electrocatalytic O_2 reduction with Nitroxyl/NO_x mediators: Implications for fuel cells and aerobic oxidation catalysis. *ACS Central Science* 1(5):234-243.

German, E. D., and M. Sheintuch. 2013. Predicting CH_4 dissociation kinetics on metals: Trends, sticking coefficients, H tunneling, and kinetic isotope effect. *The Journal of Physical Chemistry C* 117(44):22811-22826.

Gesser, H. D., N. R. Hunter, and C. B. Prakash. 1985. The direct conversion of methane to methanol by controlled oxidation. *Chemical Reviews* 85(4):235-244.

Ghanta, M., T. Ruddy, D. Fahey, D. Busch, and B. Subramaniam. 2013. Is the liquid-phase H_2O_2-based ethylene oxide process more economical and greener than the gas-phase O_2-based silver-catalyzed process? *Industrial & Engineering Chemistry Research* 52(1):18-29.

Goldman, A. S., A. H. Roy, Z. Huang, R. Ahuja, W. Schinski, and M. Brookhart. 2006. Catalytic alkane metathesis by tandem alkane dehydrogenation-olefin metathesis. *Science* 312(5771):257-261.

Goldman, A. S., M. Brookhart, A. H. Roy, R. Ahuja, and Z. Huang. 2011. Dual catalyst system for alkane metathesis. Filed and issued.

Groothaert, M. H., P. J. Smeets, B. F. Sels, P. A. Jacobs, and R. A. Schoonheydt. 2005. Selective oxidation of methane by the bis(μ-oxo)dicopper core stabilized on ZSM-5 and mordenite zeolites. *Journal of the American Chemical Society* 127(5):1394-1395.

Grundner, S., M. A. C. Markovits, G. Li, M. Tromp, E. A. Pidko, E. J. M. Hensen, A. Jentys, M. Sanchez-Sanchez, and J. A. Lercher. 2015. Single-site trinuclear copper oxygen clusters in mordenite for selective conversion of methane to methanol. *Nature Communications* 6:7546.

Guo, X., G. Fang, G. Li, H. Ma, H. Fan, L. Yu, C. Ma, X. Wu, D. Deng, M. Wei, D. Tan, R. Si, S. Zhang, J. Li, L. Sun, Z. Tang, X. Pan, and X. Bao. 2014. Direct, nonoxidative conversion of methane to ethylene, aromatics, and hydrogen. *Science* 344(6184):616-619.

Hammond, C., M. M. Forde, M. H. Ab Rahim, A. Thetford, Q. He, R. L. Jenkins, N. Dimitratos, J. A. Lopez-Sanchez, N. F. Dummer, D. M. Murphy, A. F. Carley, S. H. Taylor, D. J. Willock, E. E. Stangland, J. Kang, H. Hagen, C. J. Kiely, and G. J. Hutchings. 2012. Direct catalytic conversion of methane to methanol in an aqueous medium by using copper-promoted Fe-ZSM-5. *Angewandte Chemie, International Edition in English* 51(21):5129-5133.

Hammond, C., N. Dimitratos, J. A. Lopez-Sanchez, R. L. Jenkins, G. Whiting, S. A. Kondrat, M. H. ab Rahim, M. M. Forde, A. Thetford, H. Hagen, E. E. Stangland, J. M. Moulijn, S. H. Taylor, D. J. Willock, and G. J. Hutchings. 2013. Aqueous-phase methane oxidation over FeMFI zeolites; promotion through isomorphous framework substitution. *ACS Catalysis* 3(8):1835-1844.

Hashiguchi, B. G., S. M. Bischof, M. M. Konnick, and R. A. Periana. 2012. Designing catalysts for functionalization of unactivated C-H bonds based on the CH activation reaction. *Accounts of Chemical Research* 45(6):885-898.

Hinsen, W. W., and M. Baerns. 1983. Oxidative coupling of methane to C2 hydrocarbons in the presence of different catalysts. *Chemiker-Zeitung* 107:223-226.

Holmen, A. 2009. Direct conversion of methane to fuels and chemicals. *Catalysis Today* 142(1–2):2-8.

Hristov, I. H., and T. Ziegler. 2003. The possible role of SO_3 as an oxidizing agent in methane functionalization by the catalytica process. A density functional theory study. *Organometallics* 22(8):1668-1674.

Jira, R. 2009. Acetaldehyde from ethylene: A retrospective on the discovery of theWwacker process. *Angewandte Chemie, International Edition in English* 48(48):9034-9037.

Joglekar, M., V. Nguyen, S. Pylypenko, C. Ngo, Q. Li, M. E. O'Reilly, T. S. Gray, W. A. Hubbard, T. B. Gunnoe, A. M. Herring, and B. G. Trewyn. 2016. Organometallic complexes anchored to conductive carbon for electrocatalytic oxidation of methane at low temperature. *Journal of the American Chemical Society* 138(1):116-125.

Jones, C. A., J. J. Leonard, and J. A. Sofranko. 1984. Methane conversion. Filed and issued.

Jones, G., J. G. Jakobsen, S. S. Shim, J. Kleis, M. P. Andersson, J. Rossmeisl, F. Abild-Pedersen, T. Bligaard, S. Helveg, B. Hinnemann, J. R. Rostrup-Nielsen, I. Chorkendorff, J. Sehested, and J. K. Nørskov. 2008. First principles calculations and experimental insight into methane steam reforming over transition metal catalysts. *Journal of Catalysis* 259(1):147-160.

Jones, M. 2016. "Overview of the Shale Gas Boom and its Impact on the Chemical Industry." Presented at the Board on Chemical Sciences and Technology Workshop on The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis, Washington, DC, March 7-9, 2016.

Kado, S., K. Urasaki, Y. Sekine, and K. Fujimoto. 2003. Direct conversion of methane to acetylene or syngas at room temperature using non-equilibrium pulsed discharge. *Fuel* 82(11):1377-1385.

Kalyuzhnaya, M. G., A. W. Puri, and M. E. Lidstrom. 2015. Metabolic engineering in methanotrophic bacteria. *Metabolic Engineering* 29:142-152.

Katsaounis, A. 2010. Recent developments and trends in the electrochemical promotion of catalysis (epoc). *Journal of Applied Electrochemistry* 40(5):885-902.

Keller, A. 2012. NGL 101- The Basics. Available at http://www.eia.gov/conference/ngl_virtual/eia-ngl_workshop-anne-keller.pdf [accessed June 2016].

Keller, G. E., and M. M. Bhasin. 1982. Synthesis of ethylene via oxidative coupling of methane: I. Determination of active catalysts. *Journal of Catalysis* 73(1):9-19.

Kiatkittipong, W., T. Tagawa, S. Goto, S. Assabumrungrat, and P. Praserthdam. 2004. Oxidative coupling of methane in the LSM/YSZ/LaAIO SOFC reactor. *Journal of Chemical Engineering of Japan* 37(12):1461-1470.

Koirala, R., R. Buechel, F. Krumeich, S. E. Pratsinis, and A. Baiker. 2015. Oxidative dehydrogenation of ethane with CO_2 over flame-made Ga-loaded TiO_2. *ACS Catalysis* 5(2):690-702.

Kumar, C. P., S. Gaab, T. E. Muller, and J. A. Lercher. 2008. Oxidative dehydrogenation of light alkanes on supported molten alkali metal chloride catalysts. *Topics in Catalysis* 50(1):156-167.

Kwapien, K., J. Paier, J. Sauer, M. Geske, U. Zavyalova, R. Horn, P. Schwach, A. Trunschke, and R. Schlogl. 2014. Sites for methane activation on lithium-doped magnesium oxide surfaces. *Angewandte Chemie, International Edition in English* 53(33):8774-8778.

Labinger, J. A., and J. E. Bercaw. 2002. Understanding and exploiting C-H bond activation. *Nature* 417(6888):507-514.

———. 2015. Mechanistic studies on the Shilov system: A retrospective. *Journal of Organometallic Chemistry* 793:47-53.

Lee, B., and T. Hibino. 2011. Efficient and selective formation of methanol from methane in a fuel cell-type reactor. *Journal of Catalysis* 279(2):233-240.

Lercher, J. 2016. “Lighter Feedstocks-Implications and chances for catalysis.” Presented at the Board on Chemical Sciences and Technology Workshop on The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis, Washington, DC, March 7-9, 2016.

Levan, T., M. Che, J. M. Tatibouet, and M. Kermarec. 1993. Infrared study of the formation and stability of $La_2O_2CO_3$ during the oxidative coupling of methane on La_2O_3. *Journal of Catalysis* 142(1):18-26.

Lieberman, R. L., and A. C. Rosenzweig. 2005. Crystal structure of a membrane-bound metalloenzyme that catalyses the biological oxidation of methane. *Nature* 434(7030):177-182.

Lin, C. H., K. D. Campbell, J. X. Wang, and J. H. Lunsford. 1986. Oxidative dimerization of methane over lanthanum oxide. *Journal of Physical Chemistry* 90(4):534-537.

Liu, S., L. Wang, R. Ohnishi, and M. Ichikawa. 1999. Bifunctional catalysis of Mo/HZSM-5 in the dehydroaromatization of methane to benzene and naphthalene XAFS/TG/DTA/MASS/FTIR characterization and supporting effects. *Journal of Catalysis* 181(2):175-188.

Liu, S., K. T. Chuang, and J.-L. Luo. 2016. Double-layered perovskite anode with in situ exsolution of a Co–Fe alloy to cogenerate ethylene and electricity in a proton-conducting ethane fuel cell. *ACS Catalysis* 6(2):760-768.

Lorkovic, I. M., A. Yilmaz, G. A. Yilmaz, X.-P. Zhou, L. E. Laverman, S. Sun, D. J. Schaefer, M. Weiss, M. L. Noy, C. I. Cutler, J. H. Sherman, E. W. McFarland, G. D. Stucky, and P. C. Ford. 2004. A novel integrated process for the functionalization of methane and ethane: Bromine as mediator. *Catalysis Today* 98(1–2):317-322.

Louis, C., T. L. Chang, M. Kermarec, T. L. Van, J. M. Tatibuët, and M. Che. 1993. EPR study of the stability of the O^{-}_{2} species on La_2O_3 and of their role in the oxidative coupling of methane. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 72:217-228.

Lunsford, J. H. 1995. The catalytic oxidative coupling of methane. *Angewandte Chemie, International Edition in English* 34(9):970-980.

———. 2000. Catalytic conversion of methane to more useful chemicals and fuels: A challenge for the 21st century. *Catalysis Today* 63(2-4):165-174.

Lyons, T. W., D. Guironnet, M. Findlater, and M. Brookhart. 2012. Synthesis of p-xylene from ethylene. *Journal of the American Chemical Society* 134(38):15708-15711.

Marafee, A., C. Liu, G. Xu, R. Mallinson, and L. Lobban. 1997. An experimental study on the oxidative coupling of methane in a direct current corona discharge reactor over Sr/La_2O_3 catalyst. *Industrial & Engineering Chemistry Research* 36(3):632-637.

Maughon, B. 2016. “Methane to Ethylene: Drivers, History, Challenges, and Current Developments.” Presented at the Board on Chemical Sciences and Technology Workshop on The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis, Washington, DC, March 7-9, 2016.

McFarland, E. 2016. “Activation of Natural Gas Using Nontraditional Oxidants.” Presented at the Board on Chemical Sciences and Technology Workshop on The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis, Washington, DC, March 7-9, 2016.

Melzer, D., P. Xu, D. Hartmann, Y. Zhu, N. D. Browning, M. Sanchez-Sanchez, and J. A. Lercher. 2016. Atomic-scale determination of active facets on the MoVTeNb oxide M1 phase and their intrinsic catalytic activity for ethane oxidative dehydrogenation. *Angewandte Chemie, International Edition in English*.

Mukhopadhyay, S., M. Zerella, and A. T. Bell. 2005. A high-yield, liquid-phase approach for the partial oxidation of methane to methanol using SO_3 as the oxidant. *Advanced Synthesis & Catalysis* 347(9):1203-1206.

Oshima, K., T. Shinagawa, M. Haraguchi, and Y. Sekine. 2013. Low temperature hydrogen production by catalytic steam reforming of methane in an electric field. *International Journal of Hydrogen Energy* 38(7):3003-3011.

Palkovits, R., M. Antonietti, P. Kuhn, A. Thomas, and F. Schüth. 2009. Solid catalysts for the selective low-temperature oxidation of methane to methanol. *Angewandte Chemie International Edition in English* 48(37):6909-6912.

Palmer, M. S., M. Neurock, and M. M. Olken. 2002. Periodic density functional theory study of methane activation over La_2O_3: Activity of O^{2-}, O^{-}, O_2^{2-}, oxygen point defect, and Sr^{2+}-doped surface sites. *Journal of the American Chemical Society* 124(28):8452-8461.

Peng, Z., F. Somodi, S. Helveg, C. Kisielowski, P. Specht, and A. T. Bell. 2012. High-resolution in situ and ex situ TEM studies on graphene formation and growth on Pt nanoparticles. *Journal of Catalysis* 286:22-29.

Periana, R. A., D. J. Taube, E. R. Evitt, D. G. Loffler, P. R. Wentrcek, G. Voss, and T. Masuda. 1993. A mercury-catalyzed, high-yield system for the oxidation of methane to methanol. *Science* 259(5093):340-343.

Periana, R. A., D. J. Taube, S. Gamble, H. Taube, T. Satoh, and H. Fujii. 1998. Platinum catalysts for the high-yield oxidation of methane to a methanol derivative. *Science* 280(5363):560-564.

Periana, R. A., O. Mironov, D. Taube, G. Bhalla, and C. Jones. 2003. Catalytic, oxidative condensation of CH_4 to CH_3COOH in one step via CH activation. *Science* 301(5634):814-818.

Porosoff, M. D., M. N. Myint, S. Kattel, Z. Xie, E. Gomez, P. Liu, and J. G. Chen. 2015. Identifying different types of catalysts for CO_2 reduction by ethane through dry reforming and oxidative dehydrogenation. *Angewandte Chemie, International Edition in English* 54(51):15501-15505.

Quddus, M. R., Y. Zhang, and A. K. Ray. 2010. Multi-objective optimization in solid oxide fuel cell for oxidative coupling of methane. *Chemical Engineering Journal* 165(2):639-648.

Ramos, R., M. Menéndez, and J. Santamaría. 2000. Oxidative dehydrogenation of propane in an inert membrane reactor. *Catalysis Today* 56(1-3):239-245.

Rebeilleau-Dassonneville, M., S. Rosini, A. C. v. Veen, D. Farrusseng, and C. Mirodatos. 2005. Oxidative activation of ethane on catalytic modified dense ionic oxygen conducting membranes. *Catalysis Today* 104(2-4):131-137.

Rust, F. F., and W. E. Vaughan. 1949. Oxidation of hydrocarbons catalyzed by hydrogen bromide - Summary. *Industrial & Engineering Chemistry* 41(11):2595-2597.

Saadi, S., F. Abild-Pedersen, S. Helveg, J. Sehested, B. Hinnemann, C. C. Appel, and J. K. Nørskov. 2010. On the role of metal step-edges in graphene growth. *The Journal of Physical Chemistry C* 114(25):11221-11227.

Sadow, A. D., and T. D. Tilley. 2003. Homogeneous catalysis with methane. A strategy for the hydromethylation of olefins based on the nondegenerate exchange of alkyl groups and sigma-bond metathesis at scandium. *Journal of the American Chemical Society* 125(26):7971-7977.

Salehi, M.-S., M. Askarishahi, H. R. Godini, O. Görke, and G. Wozny. 2016. Sustainable process design for oxidative coupling of methane (OCM): Comprehensive reactor engineering via computational fluid dynamics (CFD) analysis of OCM packed-bed membrane reactors. *Industrial & Engineering Chemistry Research*.

Sanborn, C. E., E. A. Anderson, and H. H. Engel. 1968. Iodinative dehydrogenation and iodine recovery. US3405195 A, filed October 8, 1968, and issued.

Schäfer, R., M. Noack, P. Kölsch, M. Stöhr, and J. Caro. 2003. Comparison of different catalysts in the membrane-supported dehydrogenation of propane. *Catalysis Today* 82(1-4):15-23.

Schwach, P., M. G. Willinger, A. Trunschke, and R. Schlogl. 2013. Methane coupling over magnesium oxide: How doping can work. *Angewandte Chemie, International Edition in English* 52(43):11381-11384.

Schwach, P., W. Frandsen, M.-G. Willinger, R. Schlögl, and A. Trunschke. 2015. Structure sensitivity of the oxidative activation of methane over MgO model catalysts: I. Kinetic study. *Journal of Catalysis* 329:560-573.

Sehested, J. 2006. Four challenges for nickel steam-reforming catalysts. *Catalysis Today* 111(1-2):103-110.

Sekine, Y., K. Tanaka, M. Matsukata, and E. Kikuchi. 2009. Oxidative coupling of methane on Fe-doped La_2O_3 catalyst. *Energy & Fuels* 23(2):613-616.

Sekine, Y., M. Haraguchi, M. Matsukata, and E. Kikuchi. 2011. Low temperature steam reforming of methane over metal catalyst supported on $Ce_xZr_{1-X}O_2$ in an electric field. *Catalysis Today* 171(1):116-125.

Shah, N. N., M. L. Hanna, and R. T. Taylor. 1996. Batch cultivation of Methylosinus trichosporium OB3b: V. Characterization of poly-β-hydroxybutyrate production under methane-dependent growth conditions. *Biotechnology and Bioengineering* 49:161-171.

Shalygin, A., E. Paukshtis, E. Kovalyov, and B. Bal'zhinimaev. 2013. Light olefins synthesis from C1-C2 paraffins via oxychlorination processes. *Frontiers of Chemical Science and Engineering* 7(3):279-288.

Shilov, A. E. and G. B. Shul'pin. 1997. Activation of C-H bonds by metal complexes. *Chemical Reviews* 97(8): 2879-2932.

Silberova, B., M. Fathi, and A. Holmen. 2004. Oxidative dehydrogenation of ethane and propane at short contact time. *Applied Catalysis A: General* 276(1-2):17-28.

Simon, U., O. Görke, A. Berthold, S. Arndt, R. Schomäcker, and H. Schubert. 2011. Fluidized bed processing of sodium tungsten manganese catalysts for the oxidative coupling of methane. *Chemical Engineering Journal* 168(3):1352-1359.

Somodi, F., Z. Peng, A. B. Getsoian, and A. T. Bell. 2011. Effects of the synthesis parameters on the size and composition of Pt–Sn nanoparticles prepared by the polyalcohol reduction method. *The Journal of Physical Chemistry C* 115(39):19084-19090.

Somodi, F., S. Werner, Z. Peng, A. B. Getsoian, A. N. Mlinar, B. S. Yeo, and A. T. Bell. 2012. Size and composition control of Pt-In nanoparticles prepared by seed-mediated growth using bimetallic seeds. *Langmuir* 28(7):3345-3349.

Soorholtz, M., R. J. White, T. Zimmermann, M.-M. Titirici, M. Antonietti, R. Palkovits, and F. Schuth. 2013. Direct methane oxidation over Pt-modified nitrogen-doped carbons. *Chemical Communications* 49(3):240-242.

Soulivong, D., C. Copéret, J. Thivolle-Cazat, J.-M. Basset, B. M. Maunders, R. B. A. Pardy, and G. J. Sunley. 2004. Cross-metathesis of propane and methane: A catalytic reaction of C-C bond cleavage of a higher alkane by methane. *Angewandte Chemie International Edition in English* 43(40):5366-5369.

Spinner, N., and W. E. Mustain. 2013. Electrochemical methane activation and conversion to oxygenates at room temperature. *Journal of the Electrochemical Society* 160(11):F1275-F1281.

Stahl, S. 2016. “Homogeneous Catalysis for C-H Activation and Other Approaches to Shale Gas Utilization.” Presented at the Board on Chemical Sciences and Technology Workshop on The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis, Washington, DC, March 7-9, 2016.

Stansch, Z., L. Mleczko, and M. Baerns. 1997. Comprehensive kinetics of oxidative coupling of methane over the La_2O_3/CaO catalyst. *Industrial & Engineering Chemistry Research* 36(7):2568-2579.

Strong, P. J., S. Xie, and W. P. Clarke. 2015. Methane as a resource: Can the methanotrophs add value? *Environmental Science & Technology* 49(7):4001-4018.

Subramaniam, B. 2016. “Environmental Impacts.” Presented at the Board on Chemical Sciences and Technology Workshop on The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis, Washington, DC, March 7-9, 2016.

Sun, P., G. Siddiqi, W. C. Vining, M. Chi, and A. T. Bell. 2011. Novel Pt/Mg(In)(Al)O catalysts for ethane and propane dehydrogenation. *Journal of Catalysis* 282(1):165-174.

Tabata, K., Y. Teng, T. Takemoto, E. Suzuki, M. A. Bañares, M. A. Peña, and J. L. G. Fierro. 2002. Activation of methane by oxygen and nitrogen oxides. *Catalysis Reviews* 44(1):1-58.

Tomás, R. A., J. C. M. Bordado, and J. F. P. Gomes. p-Xylene oxidation to terephthalic acid: A literature review oriented toward process optimization and development. *Chemical Reviews* 113(10):7421-7469.

Upham, D. C., M. J. Gordon, H. Metiu, and E. W. McFarland. 2016. Halogen-mediated oxidative dehydrogenation of propane using iodine or molten lithium iodide. *Catalysis Letters* 146(4):744-754.

U.S. International Energy Agency, International Council of Chemical Associations, and DECHEMA. 2013. Technology Roadmap—Energy and GHG Reductions in the Chemical Industry via Catalytics Processes. Available at www.iea.org/publications/freepublications/publication/Chemical_Roadmap_2013_Final_WEB.pdf) [accessed March 7, 2016]. Copyright © 2013 OECD/IEA, 9 rue de la Fédération, 75739 Paris Cedex 15, France and The International Association for Chemical Associations, [Avenue E. Van Nieuwenhuyse 4, box 1, B-1160 Brussels, Belgium] and Gesellschaft für Chemische Technik und Biotechnologie e.V. (DECHEMA), [Theodor-Heuss-Allee 25, 60486 Frankfurt am Main]. License: www.iea.org/t&c.

Wang, S.-G., X.-Y. Liao, J. Hu, D.-B. Cao, Y.-W. Li, J. Wang, and H. Jiao. 2007. Kinetic aspect of CO_2 reforming of CH_4 on Ni(111): A density functional theory calculation. *Surface Science* 601(5):1271-1284.

Wang, W., A. D. Liang, and S. J. Lippard. 2015. Coupling oxygen consumption with hydrocarbon oxidation in bacterial multicomponent monooxygenases. *Accounts of Chemical Research* 48(9):2632-2639.

Wang, Y., Y. Takahashi, and Y. Ohtsuka. 1999. Carbon dioxide as oxidant for the conversion of methane to ethane and ethylene using modified CeO_2 catalysts. *Journal of Catalysis* 186(1):160-168.

Wei, J., and E. Iglesia. 2004. Isotopic and kinetic assessment of the mechanism of reactions of CH_4 with CO_2 or H_2O to form synthesis gas and carbon on nickel catalysts. *Journal of Catalysis* 224(2):370-383.

Woertink, J. S., P. J. Smeets, M. H. Groothaert, M. A. Vance, B. F. Sels, R. A. Schoonheydt, and E. I. Solomon. 2009. A $[Cu_2O]^{2+}$ core in CuZSM-5, the active site in the oxidation of methane to methanol. *Proceedings of the National Academy of Sciences* 106(45):18908-18913.

Wood, B. R., J. A. Reimer, M. T. Janicke, and K. C. Ott, and A. T. Bell. 2004. Methanol formation of Fe/Al-MFI via the oxidation of methane by nitrous oxide. *Journal of Catalysis* 225:300-306.

Wu, J., Z. Peng, and A. T. Bell. 2014a. Effects of composition and metal particle size on ethane dehydrogenation over Pt_xSn_{100-x}/Mg(Al)O ($70 \leqslant x \leqslant 100$). *Journal of Catalysis* 311:161-168.

Wu, J., Z. Peng, P. Sun, and A. T. Bell. 2014b. N-butane dehydrogenation over Pt/Mg(In)(Al)O. *Applied Catalysis A: General* 470:208-214.

Wu, J., S. Mallikarjun Sharada, C. Ho, A. W. Hauser, M. Head-Gordon, and A. T. Bell. 2015. Ethane and propane dehydrogenation over Pt/Mg(In)(Al)O. *Applied Catalysis A: General* 506:25-32.

Wu, J., S. Helveg, S. Ullman, Z. Peng, and A. T. Bell. 2016. Growth of encapsulating carbon on supported Pt nanoparticles studied by in situ TEM. *Journal of Catalysis* 338:295-304.

Yildiz, M., Y. Aksu, U. Simon, K. Kailasam, O. Goerke, F. Rosowski, R. Schomacker, A. Thomas, and S. Arndt. 2014a. Enhanced catalytic performance of Mn_xO_y-Na_2WO_4/SiO_2 for the oxidative coupling of methane using an ordered mesoporous silica support. *Chemical Communications (Cambridge)* 50(92):14440-14442.

Yildiz, M., U. Simon, T. Otremba, Y. Aksu, K. Kailasam, A. Thomas, R. Schomäcker, and S. Arndt. 2014b. Support material variation for the Mn_xO_y-Na_2WO_4/SiO_2 catalyst. *Catalysis Today* 228:5-14.

Zavala-Araiza, D., D. R. Lyon, R. A. Alvarez, K. J. Davis, R. Harriss, S. C. Herndon, A. Karion, E. A. Kort, B. K. Lamb, X. Lan, A. J. Marchese, S. W. Pacala, A. L. Robinson, P. B. Shepson, C. Sweeney, R. Talbot, A. Townsend-Small, T. I. Yacovitch, D. J. Zimmerle, and S. P. Hamburg. 2015. Reconciling divergent estimates of oil and gas methane emissions. *Proceedings of the National Academy of Sciences* 112(51):15597-15602.

Zavyalova, U., Holena, M., Schlogl, R., and M. Baerns. 2011. Statistical Analysis of Past Catalytic Data on Oxidative Methane Coupling for New Insights into the Composition of High-Performance Catalysts. *ChemCatChem*. 3: 1935-1947. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

Zboray, M., A. T. Bell, and E. Iglesia. 2009. Role of C-H bond strength in the rate and selectivity of oxidative dehydrogenation of alkanes. *The Journal of Physical Chemistry C* 113(28):12380-12386.

Zhang, A., S. Sun, Z. J. A. Komon, N. Osterwalder, S. Gadewar, P. Stoimenov, D. J. Auerbach, G. D. Stucky, and E. W. McFarland. 2011. Improved light olefin yield from methyl bromide coupling over modified SAPO-34 molecular sieves. *Physical Chemistry Chemical Physics* 13(7):2550-2555.

Zhu, Q., S. L. Wegener, C. Xie, O. Uche, M. Neurock, and T. J. Marks. 2013. Sulfur as a selective “soft” oxidant for catalytic methane conversion probed by experiment and theory. *Nature Chemistry* 5(2):104-109.

Appendix A

Workshop Agenda

The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production Implications for Catalysis: A Workshop

March 7-8, 2016
National Academy of Sciences Building
2101 Constitution Avenue Northwest, Washington, DC 20418

March 7, 2016 (Lecture Room)
Open Session

8:45 am Doors open

9:00 am Welcome and Introduction
Alexis T. Bell (Chair), University of California, Berkeley

9:15 am *Overview of Shale Gas Boom and Its Impact on the Chemical Industry*
Mark Jones, The Dow Chemical Company

10:00 am *Implications for Catalysis*
Johannes Lercher, Pacific Northwest National Laboratory

10:45 am Break

11:15 am *Hydrocarbons to Chemicals and Fuels via Engineered Microbes*
Greg Stephanopoulos, Massachusetts Institute of Technology

12:00 pm Lunch on your own

Session 1: Methane Catalysis
Chair: Johannes Lercher

1:00 pm *Is oxidative coupling the royal road for the valorization of methane to olefins?*
Reinhard Schomäcker, Technische Universität Berlin

1:45 pm Instructions for Breakout Groups
Johannes Lercher, Pacific Northwest National Laboratory

Group A - Methane to Syngas – Board Room
Speaker: **Jan Lerou**, Jan Lerou Consulting, LLC
Discussion Leader: **Maria Flytzani-Stephanopoulos**, Tufts University

Group B - Methane to Ethylene – Room 125
Speaker: **Bob Maughon**, The Dow Chemical Company
Discussion Leader: **Anne Gaffney**, Idaho National Laboratory

Group C - Methane to Aromatics – Room 118
Speaker: **Israel Wachs**, Lehigh University
Discussion Leader: **Monty Alger**, The Pennsylvania State University

Group D - Methane to Methanol – Lecture Room
Speaker: **Tobin Marks**, Northwestern University
Discussion Leader: **Karen Goldberg**, University of Washington

3:45 pm Break

4:15 pm Report Back and Discussion

5:30 pm Open session adjourn

March 8, 2016 (Lecture Room)
Open Session

Session 2: Ethane/Propane Catalysis Chair: Maria Flytzani-Stephanopoulos

8:15 am Doors open

8:30 am *History and State of the Art of Ethane and Propane Catalysis*
Jeffery Bricker, UOP LLC, A Honeywell Company

9:15 am *Conversion of Methane and Light Alkanes to Chemicals Over Heterogeneous Catalysts: Lessons Learned from Experiment and Theory*
Alexis T. Bell, University of California, Berkeley

9:45 am *Homogeneous Catalysts for C-H Activation and Other Approaches to Shale Gas Utilization*
Shannon Stahl, University of Wisconsin–Madison

10:15 am Break

10:30 am Instructions for Breakout Groups
T. Brent Gunnoe, University of Virginia

Group A - Light Alkanes to Alkenes and Dienes – Board Room
Speaker: **Angeliki Lemonidou**, Aristotle University of Thessaloniki, Greece
Discussion Leader: **Angela Belcher**, Massachusetts Institute of Technology

Group B - Light Alkanes to Aromatics – Room 125
Speaker: **Bruce Gates**, University of California, Davis
Discussion Leader: **Johannes Lercher**, Pacific Northwest National Laboratory

Group C - Emerging Opportunities for Novel Approaches to Natural Gas Conversion – Room 118
Speakers:
Biocatalysis: **Mattheos A. G. Koffas**, Rensselaer Polytechnic Institute
Electrocatalysis: **Guido Pez**, consultant
Discussion Leader: **Monty Alger**, The Pennsylvania State University

Group D - Activation of Natural Gas Using Nontraditional Oxidants – Lecture Room
Speaker: **Eric McFarland**, University of California, Santa Barbara
Discussion Leader: **Jim Stevens**, The Dow Chemical Company (retired)

12:30 pm Lunch on your own

1:30 pm	Report Out and Discussion
2:30 pm	Break

Session 3: Environmental Impacts
Chair: Monty Alger

2:45 pm	Panel Discussions **David Allen**, University of Texas, Austin **Richard Helling**, The Dow Chemical Company **Bala Subramaniam**, University of Kansas **Carl Mesters**, Shell **Klaus Harth**, Badische Anilin und Soda Fabrik (BASF)

Session 4: Opportunities
Chair: Jim Stevens

4:30 pm	Workshop Summary **Alexis T. Bell** (chair), University of California, Berkeley
5:00 pm	Open Discussion
5:30 pm	Open session adjourn

Appendix B

Biographic Sketches of Workshop Speakers and Organizing Committee Members

Monty Alger, *Pennsylvania State University*
Dr. Alger is the Director of the Pennsylvania State Institute for Natural Gas Research and Professor of Chemical Engineering. Prior to Penn State, Dr. Alger was vice president and chief technology officer with Air Products and Chemicals, Inc. responsible for Research and Development. He worked 23 years at General Electric (GE) where he led technology development at the Global Research Center, GE Plastics, and was the Technology General Manager for the Advanced Materials Business. Before GE, Dr. Alger was an assistant professor and director of the Massachusetts Institute of Technology's Chemical Engineering Practice School stationed at GE Plastics. He received his Ph.D. from the University of Illinois at Urbana-Champaign and his S.M. in Chemical Engineering Practice from the Massachusetts Institute of Technology. He is a member of the National Academy of Engineering and serves on several external and university chemical engineering advisory councils.

David Allen, *University of Texas at Austin*
Dr. Allen is the Gertz Regents Professor of Chemical Engineering and the Director of the Center for Energy and Environmental Resources, at the University of Texas at Austin. He is the author of 7 books and more than 200 papers. His recent work has focused primarily on air quality, and the engineering of sustainable systems. Dr. Allen has been a lead investigator for multiple air quality measurement studies, which have had a substantial impact on the direction of air-quality policies. Over the past 3 years, with support from Environmental Defense Fund and a group of natural gas producers, he has been leading a team measuring methane emissions from natural gas production sites. He has served on a variety of governmental advisory panels and from 2012 to 2015 chaired the U.S. Environmental Protection Agency's Science Advisory Board. He has won multiple awards for his research and teaching awards at the University of Texas and University of California, Los Angeles (UCLA). Dr. Allen received his B.S. degree in Chemical Engineering, with distinction, from Cornell University in 1979. His M.S. and Ph.D. degrees in Chemical Engineering were awarded by the California Institute of Technology in 1981 and 1983, respectively. He has held visiting faculty appointments at the California Institute of Technology, the University of California, Santa Barbara, and the U.S. Department of Energy.

Angela Belcher, *Massachusetts Institute of Technology*
Prof. Belcher attended the University of California, Santa Barbara, for her undergraduate and graduate degrees. She obtained her B.S. in creative studies in 1991 and her Ph.D. in chemistry in 1997, unraveling the ways in which proteins can direct the material properties of minerals. Dr. Belcher joined the Massachusetts Institute of Technology faculty in 2001 as Professor in the

Departments of Biological Engineering and Materials Science and Engineering. Dr. Belcher's lab seeks to understand and harness nature's own processes in order to design technologically important materials and devices for energy, the environment, and medicine. Ancient organisms have evolved to make exquisite nanostructures like shells and glassy diatoms. Using directed evolution, the laboratory engineers organisms to grow and assemble novel hybrid organic-inorganic electronic, magnetic, and catalytic materials. In doing so, the group capitalizes on many of the wonderful properties of biology—using only non-toxic materials, employing self-repair mechanisms, self-assembling precisely and over longer ranges, adapting and evolving to become better over time. These materials have been used in applications as varied as solar cells, batteries, medical diagnostics, and basic single-molecule interactions related to disease.

Alexis T. Bell, *University of California, Berkeley*
Dr. Bell is the Dow Professor of Sustainable Energy at University of California, Berkeley and Faculty Senior Scientist at Lawrence Berkeley National Laboratory. He earned his undergraduate and doctoral degrees at the Massachusetts Institute of Technology. His research specialty is catalysis and chemical reaction engineering. He studies reaction mechanisms in order to identify factors limiting the activity and selectivity of catalysts. Reaction systems being investigated by his group include the synthesis of oxygenated compounds from CO_x ($x = 1, 2$), the conversion of alkanes to olefins and oxygenated products under oxidizing conditions, and the reduction of nitric oxide under oxidizing conditions. The objectives of his program are pursued through a combination of experimental and theoretical methods. Spectroscopic techniques, including IR, Raman, NMR, UV-Visible, and EXAFS, are used to characterize catalyst structure and adsorbed species under actual conditions of catalysis. Isotopic tracers and temperature-programmed desorption and reaction techniques are used to elucidate the pathways via which catalyzed reactions occur. Quantum chemical calculations are conducted to define the structure and energetics of adsorbed species and the pathways by which such species are transformed. The combined use of theory and experimental methods enables the attainment of a deeper understanding of the core issues of interest than can be achieved by the use of either approach alone. His research honors include the Curtis W. McGraw Award for Research from the American Association of Engineering Education; the Professional Progress, R. H. Wilhelm, and William H. Walker Award from the American Institute of Chemical Engineers; the Paul H. Emmett Award in Fundamental Catalysis; the Michel Boudart Award for the Advancement of Catalysis from the Catalysis Society; and the American Chemical Society Gabor A. Samorjai Award for Creative Research in Homogeneous or Heterogeneous Catalysis and the Goerge Olah Award in Petroleum or Hydrocarbon Chemistry from the American Chemical Society. Dr. Bell is a member of the National Academy of Sciences, the National Academy of Engineering, a Fellow of the American Association for the Advancement of Science, and an elected member of the American Academy of Arts and Sciences. He also holds an Honorary Professor title in the Siberian Branch of the Russian Academy of Sciences.

Jeffery Bricker, *UOP LLC, A Honeywell Company*
Dr. Bricker is the Senior Director of Research at UOP, which conducts research in the areas of New Materials, Catalysis, Advanced Characterization, Membranes, Renewable Fuels, and Exploratory Platforms. He received a B.S. in mathematics and chemistry from Heidelberg University in 1979 and a Ph.D. in Chemistry from The Ohio State University in 1983. He started at UOP as a catalyst scientist working in paraffin dehydrogenation, selective hydrogenations,

natural gas utilization, and selective oxidation. He has held a variety of positions in Refining, Petrochemical, and Separations research and development, and has had a key role in development of several UOP technologies and products. In his current role, he is accountable for UOP's longer-range research programs and capabilities development. He has been awarded 55 U.S. patents. He is a member of the North American Catalysis Society and the American Chemical Society. He frequently lectures on catalysis around the world. He has received a number of awards including the UOP Stine Star, 2006 Honeywell Growth and Innovation Award the 2011 ACS National Award in Creative Invention, and was the 2008 Devon Meek Lecturer

Maria Flytzani-Stephanopoulos, *Tufts University*
Dr. Flytzani-Stephanopoulos is Distinguished Professor and the Robert and Marcy Haber Endowed Professor in Energy Sustainability in the School of Engineering at Tufts University. She directs the Tufts Nano Catalysis and Energy Laboratory, which investigates new catalyst materials for the production of hydrogen and 'green' chemicals. Pioneering work from her lab has demonstrated the use of single atom catalysts for reactions of interest to fuel processing, which entails efficient and sustainable use of precious metals in clean energy production, and in the commodity and value-added chemicals production with improved yields and reduced carbon footprint. Dr. Flytzani-Stephanopoulos joined the Chemical Engineering faculty at Tufts in 1994. She holds 10 patents and has written more than 150 technical papers. She has been an editor of the journal *Applied Catalysis B: Environmental* since 2002, and is an associate editor of *Science Advances*. She is the recipient of a number of awards, including the Tufts Distinguished Scholar award, the Henry J. Albert Award of the International Precious Metals Institute (IPMI), the Giuseppe Parravano Memorial Award of the Michigan Catalysis Society, the Graduate Teaching and Mentoring Award of the Tufts School of Engineering, and the Carol Tyler Award of the IPMI. She is a member of the National Academy of Engineering and a Fellow of the American Association for the Advancement of Science and the American Institute of Chemical Engineers.

Anne M. Gaffney, *Idaho National Laboratory*
Dr. Gaffney received her B.A in chemistry and mathematics from Mount Holyoke College in 1976 and her Ph.D. in physical organic chemistry in 1981. She has been working in the chemical industry for nearly 30 years in areas of process chemistry, catalysis, selective oxidation, "green chemistry," clean energy, and sustainability. She recently retired from Lummus Technology in March 2010, where she held the position of vice president of technology and was responsible for leading the commercialization of new catalysts and improved metathesis processing of olefins. At Lummus Technology, Dr. Gaffney also developed a new alkylation process called AlkyClean with a "green" heterogeneous catalyst; this process was acknowledged with the 2009 American Chemical Society (ACS) Award for Affordable Green Chemistry. Prior to Lummus Technology, Dr. Gaffney was a senior research fellow, where she worked on developing new catalysts and processes for the selective oxidation of hydrocarbons. Anne has more than 200 patents and patent applications, more than 80 publications, and has given close to 90 seminars. She was selected as an ACS Fellow in 2010 and received the ACS Distinguished Service Award in Petroleum Chemistry, also in 2010. She co-founded the Catalysis Division of ACS in 2009. Since her retirement from Lummus Technology, Dr. Gaffney has founded AMG Chemistry and Catalysis Consulting, LLC, co-founded the Langmuir Research Institute, and has consulted for various companies, including Air Liquide, Anellotech, and NanoSelect. In January 2011, she became the research and development director of specialty materials at Invista.

Bruce Gates, *University of California, Davis*
Dr. Gates studied chemical engineering at the University of California, Berkeley (B.S., 1961), and the University of Washington (Ph.D., 1966), and with a Fulbright grant did postdoctoral research at the Ludwig Maximilians University of Munich. He worked for 2 years as a research engineer at Chevron Research Company and began as an assistant professor at the University of Delaware in 1969, becoming the H. Rodney Sharp Professor of Chemical Engineering and Professor of Chemistry. In 1992, he joined the University of California, Davis, where he is Distinguished Professor in the Department of Chemical Engineering and Materials Science. He has spent 4 sabbatical years at the Ludwig Maximilians University of Munich and was recently a guest professor at Hokkaido University. Dr. Gates's research is focused on catalysis, with an emphasis on essentially molecular metal complex and metal cluster catalysts anchored to solid surfaces and on catalytic conversion of biomass-derived compounds. He authored the textbook Catalytic Chemistry and co-authored Chemistry of Catalytic Processes. He edits the monograph Advances in Catalysis. He serves on the U.S. Department of Energy's Basic Energy Sciences Advisory Board. He has been recognized with awards from the American Chemical Society, American Institute of Chemical Engineers, the North American Catalysis Society, and the Council for Chemical Research. He is a member of the National Academy of Engineering.

Karen Goldberg, *University of Washington*
Dr. Goldberg received her A.B. degree in 1983 from Barnard College of Columbia University in New York City. She did undergraduate research with Professors Roald Hoffmann (Cornell University) and Stephen Lippard (Columbia University) and with Drs. Tom Graedel and Steven Bertz (AT&T Laboratories). She then went on to the University of California, Berkeley, where she earned her Ph.D. in chemistry in 1988 with Professor Robert Bergman. Following a postdoctoral year with Professor Bruce Bursten (The Ohio State University), she joined the faculty at Illinois State University, a primarily undergraduate institution in 1989. In 1995, she moved to the University of Washington in Seattle as assistant professor of chemistry. She was awarded tenure and promoted to associate professor in 2000. In 2003, she was promoted to full professor, in 2007 was named Lawton Distinguished Scholar in Chemistry, and in 2010 became the Nicole A. Boand Endowed Professor in Chemistry. Dr. Goldberg currently serves as director of the NSF Phase II Center for Chemical Innovation, the Center for Enabling New Technologies through Catalysis (CENTC), a collaborative effort among 19 principal investigators and their students at 14 institutions across North America (www.nsfcentc.org). CENTC also has an industrial affiliates program involving major chemical, petrochemical, and pharmaceutical companies. She has served on the Advisory Boards of the American Chemical Society (ACS) journals Inorganic Chemistry, and Accounts of Chemical Research and Organometallics, and as co-chair of the 2012 Gordon Research Conference on Green Chemistry. Dr. Goldberg also serves as a member of the Chemistry Selection Committee for Sloan Research Fellowships. She was elected a Fellow of the American Association for the Advancement of Science and a member of the Washington State Academy of Science in 2012. In 2015, she received the Carol Tyler Award from the International Precious Metal Institute and will receive the 2016 ACS Award in Organometallic Chemistry in March 2016. Dr. Goldberg is best known for her work developing mechanistic understanding of fundamental organometallic reactions.

T. Brent Gunnoe, *University of Virginia*
Dr. Gunnoe is a professor of chemistry at the University of Virginia. With a focus on the environmental and economic challenges of developing more efficient synthetic methods, his research interests span the fields of inorganic and organic chemistry. His research group focuses on the preparation and characterization of new transition-metal complexes that are capable of activating organic molecules toward novel reactivity. By concentrating on fundamental aspects of inorganic and organometallic chemistry, his efforts are ultimately directed toward the rational design of single-site catalysts that form the foundation of new homogeneous synthetic methodologies. Dr. Gunnoe's publications are extensive and have appeared in the Journal of the American Chemical Society, Inorganic Chemistry, and Dalton Transactions, among many others. He received his B.A. from West Virginia University and his Ph.D. from the University of North Carolina at Chapel Hill.

Klaus Harth, *BASF*
Dr. Harth is vice president for environmental catalysis research at BASF. He is currently responsible for the global research and development (R&D) of BASF's Mobile Emissions Catalyst business. Dr. Harth is located in Iselin, New Jersey. Prior to this role, he was vice president for process catalysis research, for BASF SE in Ludwigshafen, Germany, and served as divisional technology officer for BASF's Petrochemical Division. Since joining BASF in 1987, he has worked in different R&D and business roles including an assignment as regional business manager for catalysts in Hong Kong, China. He earned his Ph.D. in physics from the University of Kaiserslautern, Germany.

Richard Helling, *The Dow Chemical Company*
Dr. Helling is director of sustainable chemistry for The Dow Chemical Company, located in Midland, Michigan. He leads the Sustainable Chemistry expert community at Dow, which supports Dow businesses on the use of lifecycle assessment (LCA), the Sustainable Chemistry Index (SCI), and related tools to identify opportunities for innovation, differentiating products in the marketplace, and creating sustainable value for Dow. He was a member of the State of Michigan's Green Chemistry Roundtable and the Green Chemistry & Commerce Council, and is currently on the board of the American Center for Life Cycle Assessment and active in working groups of The Sustainability Consortium. Dr. Helling joined Dow in 1987 and has held a variety of roles in process research, development, and manufacturing. He developed and improved technologies at Dow's Pittsburg, California, manufacturing site for waste reduction, reaction selectivity, and purification of chlorinated pyridines that are used in a broad range of Dow AgroSciences products, becoming the leader for Process and Environmental Technology in Pittsburg. He led the process development for SiLK™ dielectric materials in Midland, Michigan, and was the Dow AgroSciences European contract synthesis leader and fungicides technology leader when based in Drusenheim, France. He returned to Midland in 2003, when he began his use of LCA to complement economic evaluations of new technologies, especially the use of renewable feedstocks for chemical production, becoming an associate research and development director. Dr. Helling holds a bachelor's degree from Harvey Mudd College, with majors in engineering and history, a master's degree in chemical engineering practice from the Massachusetts Institute of Technology (MIT), and a doctorate in chemical engineering, also from MIT. He was an assistant professor with the MIT Chemical Engineering Practice School prior to

joining Dow. He is an author of 23 papers, holds 2 patents, is a registered Professional Engineer in Michigan, and is an LCA Certified Professional.

Mark Jones, *The Dow Chemical Company*
Dr. Jones, currently executive external strategy and communications fellow for The Dow Chemical Company, reporting directly to Dr. A.N. Sreeram, corporate vice president of research & development (R&D). Since assuming this role in September 2011, supporting then Dow chief technology officer Bill Banholzer, Dr. Jones has performed technical assessments, developed external communications, and enhanced Dow efforts in external awards. He is a frequent speaker at a variety of industry events on various industry related topics. He continues to providing technical support for Dow's Renewable Chemistries Expertise Center. He is on the Board of Directors of the BIO Industrial and Environmental Section (IES), and frequent contributor to both American Chemistry Council and World Economic Forum teams focused on renewable and sustainable chemistry. He represents Dow Chemical on the American Chemical Society (ACS) Corporation Associates, hosts ACS webinars with some regularity, and regularly blogs for the ACS's Industry Insights. The White House's Advanced Manufacturing Partnership has been a recent focus, looking both at technology options and improving scale-up of new technologies. Dr. Jones has recently assumed responsibility for next-generation sustainability goals associated with innovation. He spent most of his career developing catalytic processes. He is currently a member of a National Research Council team reviewing the Advanced Research Projects Agency-Energy (ARPA-E) program. He is a co-author on the recently released National Research Council report Sustainable Development of Algal Biofuels in the United States. Dr. Jones joined Dow in 1990 following a graduate career that had very little to do with his ultimate career path. After graduating with a B.S. in chemistry from Randolph-Macon College, he received his Ph.D. in physical chemistry with Barney Ellison at the University of Colorado Boulder, where he studied gas-phase ion molecule chemistry—not an area of great industrial interest. Dr. Jones was introduced to catalysis during his postdoctoral research with Bruce Koel, then at the Cooperative Institute for Research in Environmental Science in Boulder. He spent his early career in the Catalysis department in what is now Core R&D. He left Core R&D in 2006 to take the Strategy Fellow role in Hydrocarbons, Energy, and Basic Chemicals. He is the author of more than 12 issued U.S. patents and numerous publications.

Mattheos Koffas, *Renesselaer Polytechnic Institute*
Dr. Koffas is the Dorothy and Fred Chau '71 Endowed Professor in the departments of Chemical and Biological Engineering and Biological Sciences at Rensselaer Polytechnic Institute and the Career Development Professor of the Biocatalysis Constellation at Rensselaer Polytechnic Institute since 2011. He received his Ph.D. from the Massachusetts Institute of Technology (MIT) in 2001, where he worked on amino acid biosynthesis in Corynebacterium glutamicum. He was a visiting research scientist at DuPont Central Research from 2001 to 2002. During that time, he worked on developing a process for the conversion of natural gas to high-value chemicals. Dr. Koffas joined the Department of Chemical and Biological Engineering at SUNY Buffalo in 2002 as tenure-track assistant professor and was promoted to associate professor in 2008. He works in the field of metabolic engineering and systems biotechnology with particular emphasis on the biosynthesis of natural products. Some of his work includes the biosynthesis of high-value phytochemical such as polyphenols, the production of mammalian polysaccharides with pharmaceutical and nutraceutical properties, and the development of electrobiochemical

reactors for the production of reducing equivalents. Dr. Koffas currently serves on the editorial board of several journals, including *Current Opinion in Biotechnology*, *BMC Plant Biology*, *Metabolic Engineering Communications and Biotechnology*, and *Bioprocess Engineering*. He has published more than 70 peer-review papers and holds a number of patents some of which have been commercialized.

Angeliki Lemonidou, *Aristotle University*
Professor Lemonidou, is professor of chemical engineering at the Aristotle University of Thessaloniki and Director of the Petrochemical Technology Laboratory. She got her Ph.D. with honors from the Chemical Engineering Department in 1990. Her thesis titled "Catalytic Steam Cracking for Ethylene Production" was supervised by Professor Iacovos Vasalos. Since then she has served the same department from many positions as lecturer, assistant professor, and associate professor. Professor Lemonidou is deputy head of the newly founded Center for Interdisciplinary Research and Innovation of Aristotle University and a collaborating faculty member of the Chemical Process Energy Resources Institute (CPERI/CERTH). Professor Lemonidou has developed long collaborations with universities and research centers in Greece and also with international universities, such as the Technical University of Munich (TUM), the University of California, Berkeley, and the University of Delaware. Professor Lemonidou's research activities are the area of catalysis and more specifically on the development of active and selective nano-structured materials for reactions related to transformation of hydrocarbons and bio-based compounds. The target reactions she currently studies are the selective oxidation of lower alkanes, the sustainable production of hydrogen through advanced steam reforming of natural gas, the CO_2 capture, and the hydrodeoxygenation of biomass derived oxygenates. Her expertise lies in the preparation of nanomaterials via advanced preparation techniques, the structural and morphological characterization using various physicochemical techniques, as well as detailed kinetic and mechanistic studies of catalytic materials under reaction conditions. She has made substantial contributions with the work of her group on ethane oxidative dehydrogenation and the in-depth study of the Ni-Nb-Ox catalytic materials for the reaction. She has numerous publications (more than 100) in scientific journals and conference proceedings. Her work has been highly appreciated by the scientific community with more than 3,500 citations and h-factor 35. Professor Lemonidou has been invited as keynote speaker to many conferences and academic institutions to deliver lectures, has organized national and international conferences, and has served as a member of editorial boards and as a guest editor of peer-review journals. She is national delegate from Greece at the European Federation of Catalysis Societies and a member at large of the European Federation of Catalysis Societies Council.

Johannes A. Lercher, *Pacific Northwest National Laboratory*
Dr. Lercher, studied chemistry at Technische Universität Wein (TU Wien), receiving his Ph.D. in 1981 at the same institution. After a visiting lectureship at Yale University, he joined TU Wien as a lecturer, and later an associate professor. In 1993, he was appointed professor in the Department of Chemical Technology at the University Twente, the Netherlands, and in 1998 in the Department of Chemistry of TU München, Germany. Since 2011 he has served as director of the Institute for Integrated Catalysis at the Pacific Northwest National Laboratory. He is external member of the Austrian Academy of Sciences and a member of the Academia Europae and the European Academy of Sciences, as well as honorary professor at several institutions in China.

Author of about 510 papers and 17 patents, he is currently president of the European Federation of Catalysis Societies and editor-in-chief of the *Journal of Catalysis*. Recent awards include the Kozo Tanabe Award for Acid-Base Catalysis, the Robert Burwell Lectureship of the North American Catalysis Society, the Francois Gault Lectureship of the Federation of European Catalysis Societies, and the R.B. Anderson Award of the Canadian Catalysis Society. His interests are related to catalysis in zeolites as well as on nanostructured oxides and sulfides, focusing on bifunctional and concerted catalysis, as well as understanding the influence of the steric and chemical environment on the properties of active centers in a catalytic site.

Jan Lerou, *Jan Lerou Consulting, LLC*
Dr. Lerou is principal of Jan Lerou Consulting, LLC, which offers consulting in a wide variety of heterogeneous catalytic processes. He has more than 40 years of experience in chemical reaction engineering in academia, large chemical industries, and start-up companies. He is also adjunct professor of chemical engineering at Pennsylvania State University. He recently retired as group chief technology officer of Oxford Catalysts, Ltd., and Velocys, Inc., subsidiaries of Oxford Catalysts Group, PLC (now Velocys, PLC).

Tobin Marks, *Northwestern University*
Dr. Marks is Vladimir N. Ipatieff Professor of Chemistry and Professor of Materials Science and Engineering at Northwestern University, and Distinguished Adjunct Professor at Texas A&M University at Qatar and at Korea University. He received a B.S. degree in chemistry from the University of Maryland (1966) and a Ph.D. from the Massachusetts Institute of Technology (1971) in inorganic chemistry. His research interests include transition metal and f element organometallic chemistry; catalysis; vibrational spectroscopy; synthetic facsimiles of metalloprotein active sites; carcinostatic metal complexes; solid state chemistry and low-dimensional molecular metals; nonlinear optical materials; polymer chemistry; tetrahydroborate coordination chemistry; macrocycle coordination chemistry; molecular electro-optics; metal-organic chemical vapor deposition; polymerization catalysis; printed flexible electronics; solar energy; and transparent conductors. Dr. Marks has received numerous American Chemical Society National Awards including MacDiarmid Medal, University of Pennsylvania, 2013; Wilkinson Medal, Royal Society of Chemistry U.K., 2014; Sacconi Medal, Italian Chemical Society, 2015; Materials for Industry Award, Royal Society of Chemistry U.K., 2015; and Honorary Foreign Member, Chinese Chemical Society. Dr. Marks received a doctor of science degrees honoris causa from the Hong Kong University of Science and Technology in 2011, the University of South Carolina in 2011, and The Ohio State University in 2012.
Peer-reviewed publications: 1,155; h-index = 136 on 71,000 citations; issued U.S. patents: 234.

Bob Maughon, *The Dow Chemical Company*
Dr. Maughon is the research and development (R&D) vice president for performance plastics and hydrocarbons at The Dow Chemical Company. Prior to this role, he was the senior R&D director for Dow Pharma & Food Solutions in the Functional Materials Business Group. Dr. Maughon began his career with Dow in 1998, working in the central research laboratories on a variety of programs ranging from heterogeneous hydrogenation catalysis, ring-opening polymerization, and homogeneous catalysis. In 2004, he assumed leadership for the chemical feedstocks research area, focusing on breakthrough technologies for utilization of methane and coal as Dow feedstocks for olefins. He subsequently became the technical leader for the catalytic

chemistry group of Core R&D in 2005. In 2006, he was named the director of inorganic chemistry & catalysis, where he was responsible for leading inorganic chemistry, homogeneous and heterogeneous catalysis, and high-throughput research with responsibilities for the development of new technologies for chemical and renewable feedstocks and advantaged catalytic processes. From 2008 to 2010, he served as the lead R&D director for the Hydrocarbons and Energy Business. He is director and president of Dow International Technology Corporation and director of the Union Carbide Polyolefins Development Company, Impact Analytical, and the Council of Chemical Research. He also serves on the University of Michigan Engineering Advisory Council. Dr. Maughon earned his bachelor's degree in chemistry from Rice University in 1993 and his doctorate in organic chemistry from the California Institute of Technology in 1998.

Eric McFarland, *University of California, Santa Barbara*
After his undergraduate studies in Nuclear Engineering at University of California, Berkeley, Dr. McFarland moved to the Massachusetts Institute of Technology (MIT), where he studied nuclear science and completed his Ph.D., investigating the measurement of complex chemical reaction kinetics using nuclear phenomena. While a graduate student, Dr. McFarland was a member of a team at Field Effects, Inc., that designed and built the first permanent ring magnet–based magnetic resonance imaging system. He received an M.D. from Harvard Medical School and, after post-graduate training in general surgery, worked part-time in Emergency Medicine. He joined the Department of Nuclear Engineering at MIT and then later moved to the University of California, Santa Barbara, where his research interests moved to chemical kinetics and catalysis specifically related to energy production. He was recently completed a 2-year position as the inaugural director of the Dow Centre for Sustainable Engineering Innovation and Dow Chemical chair in chemical engineering at the University of Queensland. He has broad-ranging research interests with direct links to industrial problems and has published more than 170 papers and is the inventor on more than 30 patents. Dr. McFarland has taken several leaves of absence from the University in industry, he was a founding technical director of Symyx Technologies, and as a member of the management team, helped grow the company from 3 to more than 150 employees and eventually a successful public offering. He has been on the board of directors of several chemical and technology companies and served for 8 years as president and CEO of GRT, Inc., a technology company developing a new process for the production of liquid fuels and chemicals from natural gas and as president and CEO of an advanced battery start-up.

Carl Mesters, *Shell International Exploration & Production, Inc.*
Dr. Mesters is a Dutch national. He joined Shell in 1984, where he currently works as managing researcher in PTI/D at the Shell Technology Center in Houston. In 2005, he was appointed Shell's chief scientist for chemistry & catalysis. He has been active in catalysis and process research and development (R&D) across many areas, including selective catalytic reduction of NOx, ethylene oxide, gas-to-liquids, catalytic dewaxing, aromatic hydrogenation, and xylene isomerization, among others, resulting in more than 70 patents filed; and is currently working on heavy oil conversion and gas to chemicals. Dr. Mesters has been chairman of the Catalysis Society of the Royal Dutch Chemical Society. He holds a degree in physical and inorganic chemistry from the University of Utrecht, the Netherlands, where he also completed a research Ph.D.

Guido Pez, *Consultant*
Dr. Pez was born in Italy but acquired most of his education in Australia. He graduated with a Ph.D. in chemistry from Monash University and following a postdoc in Canada he joined Allied Chemical (now Honeywell), then worked for most of his career at Air Products & Chemicals (Allentown, Pennsylvania), where he held the position of chief scientist in inorganic chemistry, until he retired in 2009. Dr. Pez has authored or co-authored 78 scientific publications; he is named as an inventor on 64 U.S. patents and was the recipient in 1994 of the American Chemistry Society Award in Inorganic Chemistry. His research interests have ranged from catalysis, gas separations, fluorine chemistry, hydrogen storage, and electrochemistry in the context of new electrolytes for phosphoric acid fuel cells and Li ion batteries. In now his "second career," he has taught inorganic chemistry at Barnard College of Columbia University, and is continuing to pursue his research interests in catalysis and electrochemistry.

Reinhard Schomäcker, *Technische Universität Berlin*
Dr. Schomäcker studied chemistry at the University of Bielefeld. He received his diploma in 1984 and a doctoral degree in physical chemistry in 1987. In 1990, he finished a habilitation thesis at the Max-Planck-Institute for Biophysical Chemistry in Göttingen. Also in 1990, he joined the chemical engineering group of the Central Research Laboratories of the Bayer AG in Leverkusen. In 1992, Dr. Schomäcker became Privatdozent for physical chemistry at the University of Cologne in addition to his appointment with the Bayer AG. Since 1996 he has served as professor of technical chemistry at the Technische Universität Berlin (TU Berlin). His mayor research interests are catalysis, reaction engineering, and colloidal systems. With projects in these fields, his research group is involved in the cluster of excellence UNICAT and different collaborative research centers funded by the German Research Foundation. In research and university administration, he served as managing director of the chemistry department of TU Berlin and head of the graduate school BIG-NSE.

Shannon Stahl, *University of Wisconsin–Madison*
Dr. Stahl is a John and Dorothy Vozza Research Professor of Chemistry at the University of Wisconsin–Madison. The central theme of his research group is catalysis, with an emphasis on catalytic aerobic oxidation reactions. This work includes the discovery, development and mechanistic characterization of catalytic methods for selective oxidation of organic chemicals with O2. His research program includes a focus on the chemistry of molecular oxygen related to energy conversion, including fuel cells and solar energy conversion. He was an undergraduate at the University of Illinois at Urbana–Champaign. His subsequent training at the California Institute of Technology (Ph.D., 1997), where he was a National Science Foundation (NSF) Predoctoral Fellow with Prof. John E. Bercaw, and the Massachusetts Institute of Technology (postdoc, 1997-1999), where he was an NSF Postdoctoral Fellow with Prof. Stephen J. Lippard, focused on selective oxidation of methane to methanol.

Gregory Stephanopoulos, *Massachusetts Institute of Technology*
Dr. Stephanopoulos is the W.H. Dow Professor of Chemical Engineering and Biotechnology at the Massachusetts Institute of Technology (MIT). He received his B.S. from the National Technical University of Athens, his M.S. from the University of Florida, and his Ph.D. from the University of Minnesota, all in chemical engineering. He joined, upon finishing his doctorate in 1978, the chemical engineering faculty of the California Institute of Technology (Caltech) and

in 1985 he was appointed professor of chemical engineering at MIT, where he has been ever since. He served as associate director of the Biotechnology Process Engineering Center (1990-1997) and member of the International Faculty of the Technical University of Denmark (2001-2005). He was also the Taplin Professor of HST (2001-2012), and serves presently as instructor of bioengineering at HMS (1997-present). Dr. Stephanopoulos's current research focuses on metabolic engineering and its applications to the production of fuels, biochemicals, and specialty chemicals, as well as mammalian cell physiology as it pertains to diabetes and metabolism. Dr. Stephanopoulos has coauthored or edited 5 books and more than 400 papers and 50 U.S. patents. He has supervised 110 graduate postdoctoral students and is the editor-in-chief of the journal Metabolic Engineering and Current Opinion in Biotechnology; he also serves on the editorial boards of seven scientific journals. He has delivered approximately 30 named lectures and has been recognized with many awards, including the William H. Walker Award of AIChE (2014); the John Fritz Medal of AAES (2013); the Eni Prize in Renewable Energy (2011); the ACS E.V. Murphree Award (2010); the AIChE Founders (2007) and Wilhelm (2001) Awards; and the Merck (2002), Amgen (2009), and George Washington Carver (2010) Awards. He was elected member of the National Academy of Engineering in 2003 and corresponding member of the Academy of Athens in 2011, and is serving presently as president of AIChE. Prof. Stephanopoulos has taught a variety of undergraduate and graduate courses at Caltech and MIT and co-authored the first textbook on the subject of metabolic engineering. He introduced and directed three MIT summer courses on the subjects of metabolic engineering (1995-1999), bioinformatics (2000-2004) and biomass-to-biofuels conversion (2008-present). He is a fellow of the American Institute of Medical and Biological Engineering, AIChE, and the American Association for the Advancement of Science.

James Stevens, *The Dow Chemical Company (retired)*
Dr. Stevens recently retired as the Dow Distinguished Fellow in the Core Research and Development Department of The Dow Chemical Company, where he worked for more than 35 years. Distinguished Fellow is the highest technical position at Dow. His primary field of research is in the area of new polymeric materials, catalysts, and the high-throughput discovery of organometallic single-site catalysts. Dr. Stevens is an inventor on more than 100 issued U.S. patents, more than 1,100 global patents, 18 publications, and two books. He has won a Dow Inventor of the Year Award five times, and was presented the Dow Central Research Excellence in Science Award. Other awards he has received include the United States National Inventor of the Year Award; the American Chemical Society (ACS) Delaware Section Carothers Award; the ACS Award in Industrial Chemistry; the Herbert H. Dow Medal, the highest honor Dow awards to the company's scientists and researchers; the Perkin Medal; and the 2011 North American Catalysis Society Houdry Award. Dr. Stevens received a B.A. in chemistry from The College of Wooster in 1975. He obtained a Ph.D. in inorganic chemistry from The Ohio State University in 1979. He is an advisor on the National Science Foundation Center for Chemical Innovation, Solar Fuels based at the California Institute of Technology. He is a member of the National Academy of Engineering; the Academy of Medicine, Engineering, and Science of Texas; and is a Fellow of the American Association for the Advancement of Science.

Bala Subramaniam, *University of Kansas*
Dr. Subramaniam is the Dan F. Servey Distinguished Professor of Chemical Engineering at The University of Kansas (KU). Dr. Subramaniam earned a B.S. in chemical engineering from the

University of Madras, India, and his Ph.D. in chemical engineering from the University of Notre Dame. He has also held visiting professorships at the University of Nottingham, United Kingdom, and the Institute of Process Engineering, ETH, Zürich, Switzerland. Dr. Subramaniam's research interests are in catalysis, reaction engineering, and crystallization. In particular, his research harnesses the pressure-tunable physicochemical properties of unconventional solvents such as supercritical fluids and gas-expanded liquids in multiphase catalysis to develop resource-efficient technologies with reduced environmental footprint. He has more than 160 publications and 27 issued U.S. patents, and has edited 2 books. He is the founding director of the Center for Environmentally Beneficial Catalysis (CEBC), a unique university/industry consortium that is developing and providing licensing opportunities for novel sustainable technologies related to fuels and chemicals. Dr. Subramaniam is associate editor of the American Chemical Society Sustainable Chemistry and Engineering journal and chair-elect of the 2018 Gordon Research Conference on Green Chemistry. He has also served as the president of the International Symposia in Chemical Reaction Engineering (ISCRE, Inc.) and serves on the board of directors of the Organic Chemical Reactions Society (OCRS). His honors include ASEE's Dow Outstanding Young Faculty Award, Indian Institute of Chemical Engineers' Chemcon Lectureship Award, and KU's Higuchi Research Achievement Award. Dr. Subramaniam is a Fellow of the AIChE, the ACS Industrial & Engineering Chemistry Division, and the National Academy of Inventors.

Israel Wachs, *Lehigh University*
In a career spanning three decades, Dr. Wachs has earned international renown for research into heterogeneous catalysis. His research focuses on the catalysis science of mixed-metal oxides (supported metal oxides, bulk metal oxides, polyoxometalates, zeolites, and molecular sieves) for numerous catalytic applications (selective oxidation for manufacture of value-added chemicals), environmental catalysis (selective catalytic reduction of NOx and SOx), hydrocarbon conversion by solid acid catalysts for increased fuel energy content, olefin metathesis for on-demand production of scarce propylene, olefin polymerization, conversion of methane to liquid aromatic fuels, biomass pyrolysis, water-gas shift for production of clean hydrogen, and photocatalytic splitting of water to clean hydrogen. The research aims to identify the catalytic active sites present on the heterogeneous catalyst surface to allow establishment of fundamental structure-activity/selectivity relationships that will guide the rational design of advanced catalysts. The research approach taken by the Wachs group is to simultaneously monitor the surface of the catalyst with spectroscopy under reaction conditions and online analysis of reactant conversion and product selectivity with online GC/mass spectrometer analysis. This new methodology has been termed "operando spectroscopy" and is allowing for the unprecedented development of molecular-level structure-activity/selectivity relationships for catalysts. The spectroscopic techniques employed by the Wachs group for determination of the catalytic active sites and surface reaction intermediates are Raman, infrared (IR), ultra violet–visible (UV-vis), X-ray absorption spectroscopy (XANES/EXAFS), nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and temperature-programmed surface reaction (TPSR). Isotopic labeling of deuterium, oxygen-18 and carbon-13 is also used to track reaction pathways, determine rate-determining steps and distinguish between spectator species and actual surface reaction intermediates. The U.S. Environmental Protection Agency has honored Dr. Wachs with a Clean Air Excellence Award for a catalytic process he invented that converts paper-mill pollutants into formaldehyde. The American Chemical Society (ACS) has given Dr. Wachs the

George A. Olah Award for achievements in hydrocarbon and petroleum chemistry, and the American Institute of Chemical Engineering (AIChE) has honored him with the Catalysis and Reaction Engineering Division Practice Award. He is the recipient of multiple awards from local catalysis societies (Michigan, New York, Chicago, and Philadelphia). In 2011, he was named a Fellow of the ACS, the highest honor bestowed by the society. In 2012, he was recognized by the German Alexander von Humbolt Foundation with a Humboldt Research Award, and the International Vanadium Chemistry Organization with its Vanadis Award. Dr. Wachs has published more than 300 highly cited technical articles (approximately 24,000 citations and H-index of approximately 90) and holds more than 36 U.S. patents.

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Appendix C

Participant List[1]

First Name	Last Name	Affiliation	Role
Montgomery	Alger	Pennsylvania State University	Committee member
David	Allen	University of Texas	Speaker
Brian	Anderson	West Virginia University	
Jonas	Baltrusaitis	Lehigh University	
Mark	Barteau	University of Michigan	
Angela	Belcher	Massachusetts Institute of Technology	Discussion leader
Alexis	Bell	University of California, Berkeley	Committee member
Aditya	Bhan	University of Minnesota	
Nazeer	Bhore	ExxonMobil Research and Engineering	
James	Bielenberg	ExxonMobil Research and Engineering	
Jeffery	Bricker	UOP	Speaker
Phillip	Britt	Oak Ridge National Laboratory	
Carlos Alberto	Carrero Marquez	University of Wisconsin–Madison	
Marco	Castaldi	City College, City University of New York	
Pallavi	Chitta	University of Utah	
Pamela	Chu	National Institute of Standards and Technology	
Ronald	Cimini	ExxonMobil	
Rob	Crane	ExxonMobil Chemical	
Thomas	Degnan	University of Notre Dame	
James	Dumesic	University of Wisconsin	

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[1] This list does not include those joining the workshop via webcast.

First Name	Last Name	Affiliation	Role
William	Epling	University of Houston	
Wei	Fan	University of Massachusetts Amherst	
Maria	Flytzani-Stephanopoulos	Tufts University	Committee member
Rebecca	Fushimi	Idaho National Laboratory	
Anne	Gaffney	Idaho National Laboratory	Discussion leader
Bruce	Garrett	Pacific Northwest National Laboratory	
Bruce	Gates	University of California, Davis	Speaker
John	Gilje	National Science Foundation	
Karen	Goldberg	Washington	Discussion leader
Carlos	Gonzalez	National Institute of Standards and Technology	
Raymond	Gorte	University of Pennsylvania	
Lars	Grabow	University of Houston	
Damien	Guironnet	University of Illinois at Urbana-Champaign	
T. Brent	Gunnoe	University of Virginia	Committee member
Robert	Hart	The Shepherd Chemical Company	
Klaus	Harth	Badische Anilin und Soda Fabrik	Speaker
Richard	Helling	The Dow Chemical Company	Speaker
Andrew	Herring	Colorado School of Mines	
Sudhakar	Jale	W.R. Grace & Co.	
George	Janini	National Science Foundation	
Mark	Jones	The Dow Chemical Company	Speaker
William	Jones	University of Rochester	
Zakya	Kafafi	National Science Foundation	
Mukund	Karanjikar	Technology Holding LLC	
Alexander	Katz	University of California, Berkeley	
Mattheos	Koffas	Rensselaer Polytechnic Institute	Speaker
Theodore	Krause	Argonne National Laboratory	
Marjorie	Langell	National Science Foundation	
Peter	Legzdins	The University of British Columbia	
Angeliki	Lemonidou	Aristotle University	Speaker

First Name	Last Name	Affiliation	Role
Johannes	Lercher	Pacific Northwest National Laboratory	Committee member
Jan	Lerou	Consultant	Speaker
JoAnn	Lighty	National Science Foundation	
Suljo	Linic	University of Michigan	
Dongxia	Liu	University of Maryland	
Lance	Lobban	University of Oklahoma	
Tobin	Marks	Northwestern University	Speaker
David	Marler	ExxonMobil Research and Engineering	
Christopher	Marshall	Argonne National Laboratory	
Bob	Maughon	The Dow Chemical Company	Speaker
Manos	Mavrikakis	University of Wisconsin	
Robert	McCabe	National Science Foundation	
Eric	McFarland	University of California, Santa Barbara	Speaker
Patrick	McGrath	Advanced Research Projects Agency-Energy	
Carl	Mesters	Shell	Speaker
Horia	Metiu	University of California, Santa Barbara	
Raul	Miranda	Department of Energy	
Scott	Mitchell	Saudi Arabia Basic Industries Corporation	
Triantafillos	Mountziaris	National Science Foundation	
Matthew	Neurock	University of Minnesota	
Alexander	Orlov	Institute for Advanced Computational Science	
Charles	Peden	U.S. Department of Energy	
Guido	Pez	Consultant	Speaker
Mark	Pouy	Booz Allen Hamilton / ARPA-E	
Sohi	Rastegar	National Science Foundation	
Fabio	Ribeiro	Purdue University	
Pat	Rizzuto	Bloomberg Bureau of National Affairs	
Ali	Rownaghi	Missouri University of Science and	

First Name	Last Name	Affiliation	Role
		Technology	
Ron	Runnebaum	University of California, Davis	
Scott	Rychnovsky	National Science Foundation	
Basudeb	Saha	University of Delaware	
José	Santiesteban	ExxonMobil Research and Engineering	
Wayne	Schammel	Siluria Technologies	
Reinhard	Schomacker	Technical University of Berlin	Speaker
Viviane	Schwartz	U.S. Department of Energy	
Shannon	Stahl	University of Wisconsin	Speaker
Eric	Stangland	The Dow Chemical Company	
Addison	Stark	Advanced Research Projects Agency-Energy	
Greg	Stephanopoulos	Massachusetts Institute of Technology	Speaker
James	Stevens	The Dow Chemical Company (retired)	Committee member
Bala	Subramaniam	University of Kansas	Speaker
Jean-Philippe	Tessonnier	Iowa State University	
Don	Tilley	University of California, Berkeley	
YuYe	Tong	Georgetown University	
Dionisios	Vlachos	University of Delaware	
Israel	Wachs	Lehigh University	Speaker
Eric	Wachsman	University of Maryland	
Yong	Wang	Washington State University/PNNL	
Teng	Xu	ExxonMobil Chemical	