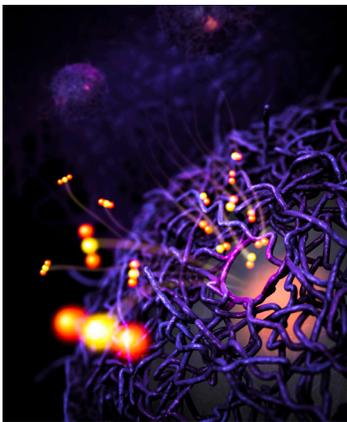


NATURAL GAS brief

OCTOBER 2020

Natural gas is an important resource and represents an opportunity to cost-effectively produce chemicals with lower greenhouse gas footprint compared to oil and coal. Scientific and industrial advances need to be made in order to realize the full potential of natural gas. NGI researchers are heavily involved in fundamental research on methane conversion that could enable these advances to become a reality.



Natural gas conversion to fuels and chemicals: opportunities and challenges

By Weixin Huang, Matteo Cargnello, Stanford University

In the natural gas and petroleum industries, flaring is currently the most utilized method to avoid hydrocarbon release in the atmosphere, wasting 3.5% of the world's natural-gas supply. Furthermore, emissions of pollutants from flaring may consist of toxic byproducts, such as NO_x and CO which are of public health and environmental concern.

The catalyzed conversion of methane (CH_4), the most abundant compound in natural gas, to liquid fuels and bulk chemicals provides an alternative to flaring and a solution to the expensive transportation of natural gas from remote locations. Some of the potential routes for methane conversion in this respect include, but are not limited to: (1) low-temperature direct oxidation to methanol and formaldehyde, (2) alternatives to steam reforming of methane ▶

ABOUT THE AUTHORS



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received his Ph.D. from the University of Notre Dame in 2018 and joined Prof. Matteo Cargnello's group at Stanford

University the same year as a postdoctoral scholar. His research focuses on the development of nanomaterials for the removal of hydrocarbons from contaminated gas streams.



Matteo Cargnello

is Assistant Professor of Chemical Engineering at Stanford since 2015. He obtained his Ph.D. at the University

of Trieste (Italy). His group research interests are in the preparation and use of uniform and engineered nanomaterials for heterogeneous catalysis and photocatalysis and the technological exploitation of nanoparticles and nanocrystals. Reactions of interest are related to sustainable energy generation and use, control of emissions of greenhouse gases, and better utilization of abundant building blocks (methane, biomass).

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with small footprint and low capital equipment, (3) oxidative coupling of methane to ethylene, and (4) non-oxidative coupling of methane to aromatics and hydrogen. In addition to these strategies, methane can also be seen as a transition fuel that can be produced from CO₂ and hydrogen using renewable energy, or through microbes in sustainable pathways. For these many reasons, methane is a resource presenting many opportunities to scientists and engineers.

NGI researchers are heavily involved in several of the above routes to convert methane into liquid compounds. There is a need for fundamental science and research to be performed to find successful methods for the selective activation and conversion of methane. Several ideas are being researched and this Brief highlights a few of the efforts in this area.

DIRECT CONVERSION OF METHANE TO METHANOL, OLEFINS AND VALUABLE CHEMICALS

The direct conversion of methane to liquid fuels and chemicals has received considerable research attention over the past decade. Methane-to-methanol, specifically, is a highly sought pathway in the natural gas industry because methanol is one of the most important starting materials to produce numerous commodity chemicals. In addition, the advantages of high energy density and easy storage make

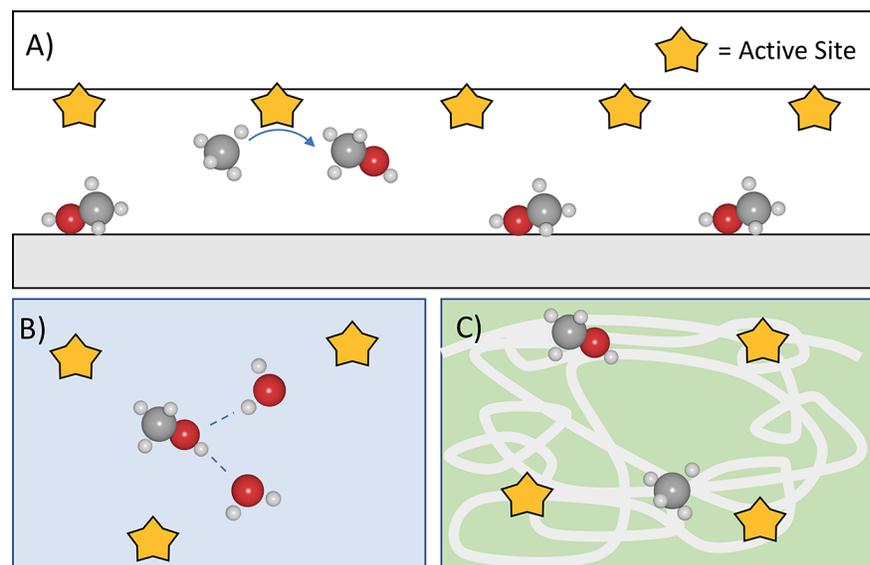
methanol one of the most promising sources for hydrogen production and fuel cell applications. Currently, the industrial route to methanol is an energy-intensive two-step process that involves the conversion of methane to syngas by steam reforming of methane, and the subsequent conversion of syngas to methanol. The production of syngas is performed at high temperatures of 700-1000 °C, which inevitably requires a significant amount of energy. An ideal approach for utilizing methane is the direct oxidation of methane into methanol under mild conditions.

Natural organisms can oxidize methane to methanol at ambient conditions. Methane monooxygenase (MMO), an enzyme in methanotrophic

bacteria, directly converts methane to methanol with 100% selectivity. This enzyme has copper and iron metal centers, forming angstrom-sized active sites with mono- and dinuclear species.¹ Besides the reactive sites, the local microenvironments can exert unique control over the catalytic process, utilizing weak interactions like hydrogen bonding and dispersion forces to achieve selectivity. It is known that the methane activation barriers on catalysts are generally high due to the strong C–H bond (4.5 eV). In addition, it is quite challenging to stop methanol from being further oxidized since C–H bonds in methanol have 0.4 eV lower dissociation energy than those in methane. To overcome these

Figure 1

Strategy for increased methanol yield in the methane-to-methanol conversion: A) methanol collector strategy; B) aqueous reaction conditions for methanol solvation; C) control of diffusion rates of methane and methanol.²

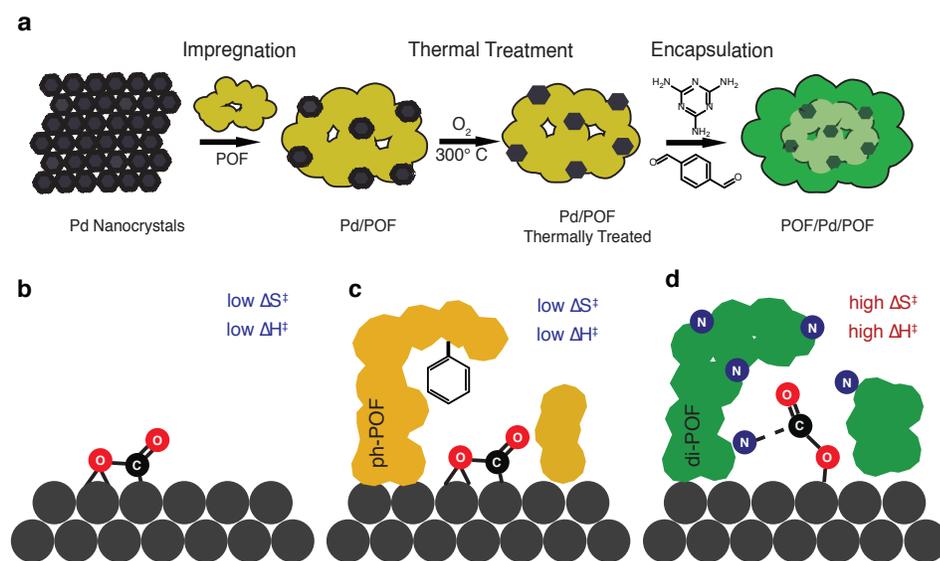


hurdles, Jens K. Nørskov and co-workers at Stanford University presented strategies developed through a simple kinetic model describing the selectivity–conversion tradeoff that limits continuous partial oxidation of methane to methanol (Figure 1).² Strategies include a methanol “collector”, aqueous reaction conditions, and diffusion-limited systems. A methanol “collector” is a material with strong methanol adsorption energy that can lower the partial pressure of methanol in the gas phase, thus stopping it from re-reacting on the catalyst active sites. Once the active sites are deactivated, methanol can be removed and the cycle restarted. Similarly, liquid water can act as a “collector” because of the favorable solvation of methanol in water, which makes aqueous solutions currently outperform gas-phase strategies. The issue is that these are batch processes with very limited conversions and yields. High methanol selectivity can also be achieved by restricting methanol diffusion to the active sites. These strategies provide new insight and suggestions to experimentalists in the field for designing active catalysts for direct methane to methanol.

In parallel to such theoretical efforts on methane-to-methanol catalysts, Matteo Cargnello’s group at Stanford designed systems where diffusion control can be exerted on reactants and products using encapsulated catalysts.³

Figure 2

Synthesis of polymer-confined Pd nanocatalysts. a) Step-wise scheme depicting the synthetic procedure of encapsulating Pd nanocrystals in polymer layers (POFs). b–c) Proposed transition state models in CO oxidation for exposed Pd surfaces (such as in Pd/Al₂O₃ and Pd/POF) as opposed to the polymer-coated catalysts with effective interactions (POF/Pd/POF, d).³



The materials were prepared by a step-by-step method as shown in Figure 2. Microenvironments created by the polymer encapsulation layers induced effects of confinement that were shown to control the diffusion of gas molecules, and CO₂ in particular. Such highly tunable chemistry and morphology of three-dimensional microenvironments were designed to modulate the activity and selectivity of CO oxidation used as a model reaction. In particular, it was found that the formation of CO₂ was controlled by diffusion, thus providing useful tools to design materials where methanol diffusion could control the methane-to-methanol production. This discovery could have implications in the engineering

of industrial catalysts capable of producing methanol since polymer layers can affect the transition state for methane-to-methanol and trap methanol before it burns.

Compact gas-to-liquid (GTL) systems are another potential solution to turn natural gas into fuels and commodity chemicals with small capital equipment footprint. GTL includes three main catalytic processes: syngas generation, Fischer–Tropsch synthesis and catalytic upgrading.⁴ A compact GTL system proposed by RTI consists of engine reformer technology as a syngas generator in conjunction with methanol synthesis.⁵ By optimizing the reformer’s engine performance, ▶

Natural gas chemistry continues to become more important as natural gas plays a larger role as an energy alternative to reduce dependence on oil and coal for meeting the increasing energy needs.

the system can reach 90% methane conversion with a syngas H_2/CO ratio greater than 1.8. The system can also achieve methanol yield greater than 50% from methane. Feeds of air and methane are utilized in the process, which reduces the cost of gas sourcing. Recently, the Gas Technology Institute (GTI) developed a new method, termed cool GTL, for converting CO_2 -containing natural gas to high-quality liquids efficiently and cheaply. The Cool GTL process integrates a low-temperature natural gas reformer and a novel Fischer-Tropsch reactor to make liquid hydrocarbons. By adjusting the amount of water and CO_2 in the feed, the catalyst can make synthesis gas at a 2:1 H_2/CO ratio which could then be converted into gasoline and diesel liquids using Fischer-Tropsch. The utility of an integrated conversion unit coupled with high yields for hydrocarbon liquids eliminates the production of waxes in the Fischer-Tropsch process.

Researchers have been also looking at alternative approaches for natural gas conversion. In comparison to traditional thermal catalytic processes, methane

photocatalytic oxidation is highly attractive since it utilizes photons to drive methane conversion. Arun Majumdar's group at Stanford is working on an effective and viable photocatalytic strategy for direct methane-to-methanol conversion at ambient conditions. Preliminary data show that semiconductor-metal-based photocatalysts produce methanol from methane under light illumination. Improvements in methanol yield are required and future directions for achieving higher photocatalytic efficiency include the modification of the semiconductor via phase, morphology, and doping control.

Methane partial oxidation in the liquid phase can be driven by electrical potentials in addition to heat and light inputs. In this process, energy is released because of the favorable thermodynamics of breaking the C-H bonds in methane, so in principle a methane-to-methanol electrochemical pathway would be producing energy and an important liquid chemical at the same time. The challenge is still represented by the strength of the C-H bond and, in this case, also by the

very low solubility of methane gas in water. Thomas Jaramillo's group at Stanford used Pt surfaces to explore the possibility of directly oxidizing methane in water electrolytes.⁶ The work highlights the challenges in the process, but also the promise given that oxidized species are found to be produced under specific conditions of oxidation-reduction cycles on the model Pt electrode surface. Corroborated by DFT calculations from the Nørskov group, it was found that the critical step in C-H activation is thermochemical. Despite no methanol was produced, the method is promising at giving directions in the field for the direct, oxidative electrochemical conversion of methane.

In alternative approaches, liquid-phase reactions have been tested for the conversion of methane, but there are still challenges that need to be overcome for industrial applications. For instance, the use of strong oxidizing agents, such as selenic acid or oleum, cannot readily give efficient, closed catalytic cycles.⁷⁻⁸ As an environmentally friendly oxidant, hydrogen peroxide (H_2O_2) has been used for methane oxidation in the absence of strong acids. In industry, the current production of H_2O_2 is based on the well-established anthraquinone oxidation process, which is an indirect synthesis process. However, this method is not environmentally benign and requires high energy inputs. Hence, the direct synthesis of H_2O_2 needs to be more economical to enable ►

methane-to-methanol processes. Electrochemical production of H_2O_2 from water oxidation ideally solves the limitations associated with the anthraquinone oxidation process, because it provides a direct route for in-situ production of H_2O_2 . Xiaolin Zheng's and Jens K. Nørskov's groups at Stanford have been collaborating on developing catalysts for electrochemical H_2O_2 production that could then be used for methane oxidation. Density functional theory calculations explored active metal oxides for this reaction and suggested that $BiVO_4$ was the best catalyst for the two-electron water oxidation for H_2O_2 production among all the materials studied.⁹ This DFT result was further validated by experimental measurements, which showed that $BiVO_4$ produced the largest amount of H_2O_2 under dark among all the oxides and achieved the highest faraday efficiency of about 98% for H_2O_2 production. The next step is to use the produced H_2O_2 for methane conversion, and Xiaolin Zheng's group is currently working in this area.

METHANE FOR HYDROGEN PRODUCTION

Approximately 95% of hydrogen in the world is generated through steam reforming of methane, but the process is associated with high carbon emissions. Methane pyrolysis into solid carbon and hydrogen has recently emerged as an appealing process for CO_x -free hydrogen

production.¹⁰ Alongside hydrogen, the value-added carbon products that are generated through pyrolysis could find useful applications. For instance, carbon nanotubes (CNT) and fibers could be applied in steel and cement due to their strength and conductivity, although their cost of production must be drastically decreased to enable this application. Arun Majumdar, Matteo Cargnello and their research groups at Stanford are working on developing stable and efficient catalysts for methane pyrolysis and on investigating processes for recycling the catalysts without losing activity after multiple cycles of reaction (Figure 3). Oxide-supported catalysts have been selected for this reaction to develop

methods for the efficient separation of the catalyst from the deposited CNTs and recycling.

In addition to CNTs production from methane pyrolysis, Monolith Materials has been developing an electrical pyrolysis technology for producing carbon black. Instead of using naphtha as a feedstock, natural gas is used to produce a much purer carbon black with a yield greater than 99%. This approach is an opportunity to provide the market with needed carbon black in an environmentally and economically way, and pilot plant demonstrations are underway. The hydrogen produced can be used to power the plant, thus contributing to the lower environmental impact of this technology. ▶

Figure 3

Researchers in the Cargnello and Majumdar labs are developing processes for carbon-free hydrogen production from methane pyrolysis using heterogeneous catalysts.



HETEROGENEOUS CO₂ REDUCTION TO METHANE AND LIQUID FUELS

In the United States, most of the natural gas is burned as a fuel for heating, transportation, and generating electricity with concurrent CO₂ production. Power-to-gas (PtG) technology is a viable option to turn the CO₂ back into methane and potentially create a carbon-neutral cycle.¹¹ To achieve this goal, hydrogen is required. As shown in Figure 4, power-to-gas hydrogen can be generated from water through an electrolysis process. It has been predicted that power-to-gas hydrogen generated from renewables will be cheaper than natural gas by 2030, proving power-to-gas hydrogen as a promising fuel of choice.¹² Power-to-gas methane (renewable natural gas) can be produced from power-to-gas hydrogen via methanation of CO₂ either in a bioreactor (single-celled

microorganisms) or in a chemical process known as Sabatier reaction. The CO₂ is captured from point sources or, hopefully in the near future, directly from the atmosphere. From this technology, renewable natural gas that contains a methane concentration of 90% or greater can be obtained. National Grid's research shows that renewable natural gas produced from their reactors can meet 16% of gas demand in four states: Massachusetts, New York, Rhode Island, and New Hampshire.¹³ It demonstrates that power-to-gas technology is a real and viable option to meet the clean energy needs of the future. Furthermore, power-to-gas technology is an exciting prospect for better integrating renewable energy sources in the electrical generation mix. It is known that global supplies of renewable electricity have grown greatly in recent years. Renewable energy sources like solar and wind,

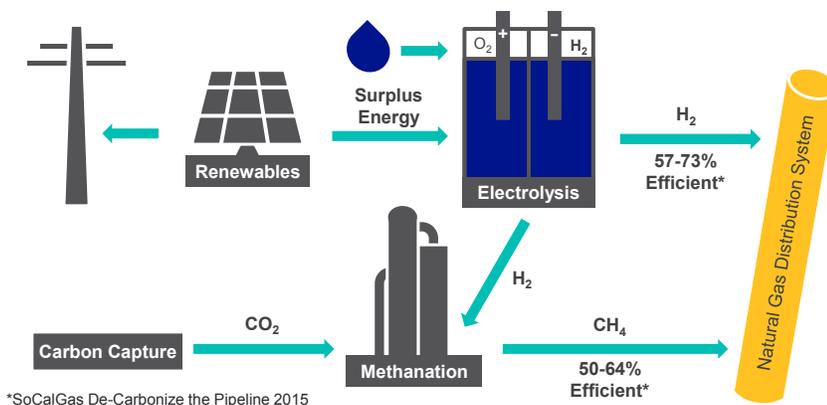
however, suffer from supply and demand imbalances, because their periods of production may not match electricity demand, causing a surplus of unused energy. To address this issue, surplus electricity can be used to produce power-to-gas hydrogen or methane, which can be stored and utilized in a future peak demand period. As such, it brings advantages in better matching the supply and demand of energy.

Power-to-liquids (P2L) technology is another viable option for reducing greenhouse gas emissions. In this process, renewable electricity, and water are used to produce liquid fuels via reverse water-gas shift reaction and Fischer-Tropsch synthesis. Liquid fuels could nearly be carbon neutral since the carbon capture and synthesis processes are from carbon-free electricity, such as solar and wind. Dr. Evan Sherwin, a post-doctoral scholar at Stanford in the group of Prof. Adam Brandt, used a techno-economic model to estimate the capital cost of liquid fuel production from variable renewable electricity. The analysis showed that liquid fuels production, which requires electrolyzers and fuel synthesis infrastructure, is not currently competitive with conventional fuel production. Such cost increase, however, could be politically acceptable as one of the mitigation pathways for reducing greenhouse gas emissions.

As an alternative to other conversion processes that rely on chemical, catalytic and

Figure 4

The conversion of excess renewable energy into a gas fuel (source: National Grid).¹³



electrocatalytic approaches, methanogens offer a promising route to produce methane from atmospheric carbon dioxide and clean electricity from solar, wind or nuclear power. Methanogens are organisms that naturally use methane in their metabolism. Prof. Alfred M. Spormann's group working with Prof. Craig Criddle's group at Stanford demonstrated how methanogens could be fed with electrons from solid electrode surfaces, producing methane gas and other chemicals sustainably.¹⁴ The whole microbial process has a net-zero carbon footprint and the microbial methane can be safely stored, thus minimizing leakage into the atmosphere. This methane-producing pathway could help efficiently utilize surplus electricity generated by wind farms and photovoltaic power stations just like the power-to-gas approach discussed above.

CHALLENGES

There are numerous options for the utilization of methane and natural gas and their conversion into valuable fuels and chemicals. Finding catalysts able to activate methane and directly produce chemicals could be economical and environmentally useful. However, the main challenge

for commercial applications of these catalysts and novel processes is selectivity: currently, we do not have systems that selectively produce desired compounds in appropriate yields required for commercialization. The situation is similar for higher alkanes such as ethane and propane. C–H activation is not the only obstacle. Being more polar than methane, most target products with C–H and O–H bonds are highly vulnerable to cascade-like overoxidation under reaction conditions, which results in a large fraction of unwanted byproducts, e.g. CO₂. Thus, the challenge lies in increasing the reaction selectivity by preventing downhill overoxidation reactions.

Another limitation for developing methods for the catalytic functionalization of methane on an industrial scale is capital costs. Typically, the catalytic conversion section of the value chain is the largest contributor to capital costs and could be as high as 35-40% of the total costs.¹⁵ To reduce capital investment, further efforts are needed to improve catalyst design to achieve high activity and stability. Furthermore, novel reactors and conversions schemes could help reduce the burden of capital costs.

For example, small and modular chemical reactors could lead to reduced capital costs and overall better economic landscape. However, the development of modular chemical conversion units still requires fundamental and applied research on the conversion processes, and possibly new schemes that have not been explored yet.

CONCLUSIONS AND PERSPECTIVES

Natural gas chemistry continues to become more important as natural gas plays a larger role as an energy alternative to reduce dependence on oil and coal for meeting the increasing energy needs. Apart from direct combustion, methane functionalization is becoming highly desirable due to its greater environmental benefits and more promising process economics. As described in this brief, attempts made in direct partial functionalization of methane to replace current routes via syngas are being investigated within the Natural Gas Initiative at Stanford. Developing such reaction processes with high selectivity is the most important hurdle to overcome in this area. Therefore, this calls for more efforts in a challenging but worthwhile research area for years to come. ■ ►

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THE NATURAL GAS INITIATIVE AT STANFORD

Major advances in natural gas production and growth of natural gas resources and infrastructure globally have fundamentally changed the energy outlook in the United States and much of the world. These changes have impacted U.S. and global energy markets, and influenced decisions about energy systems and the use of natural gas, coal, and other fuels. This natural gas revolution has led to beneficial outcomes, like falling U.S. carbon dioxide emissions as a result of coal to gas fuel switching in electrical generation, opportunities for lower-cost energy, rejuvenated manufacturing, and environmental benefits worldwide, but has also raised concerns about global energy, the world economy, and the environment.

The Natural Gas Initiative (NGI) at Stanford brings together the university's scientists, engineers, and social scientists to advance research, discussion, and understanding of natural gas. The initiative spans from the development of natural gas resources to the ultimate uses of natural gas, and includes focus on the environmental, climate, and social impacts of natural gas use and development, as well as work on energy markets, commercial structures, and policies that influence choices about natural gas.

The objective of the Stanford Natural Gas Initiative is to ensure that natural gas is developed and used in ways that are economically, environmentally, and socially optimal. In the context of Stanford's innovative and entrepreneurial culture, the initiative supports, improves, and extends the university's ongoing efforts related to energy and the environment.



Join NGI

The Stanford Natural Gas Initiative develops relationships with other organizations to ensure that the work of the university's researchers is focused on important problems and has immediate impact. Organizations that are interested in supporting the initiative and cooperating with Stanford University in this area are invited to join the corporate affiliates program of the Natural Gas Initiative or contact us to discuss other ways to become involved. More information about NGI is available at ngi.stanford.edu or by contacting the managing director of the initiative, Naomi Boness, Ph.D. at naomi.boness@stanford.edu.