對外合作組織與機構 動態報導

2017/8/3

UNCOVERING A MISSING LINK FROM METHANE TO METHANOL

揭開甲烷轉化甲醇反應的關鍵

By Steve Koppes • June 22, 2018

Microscopic crystalline structures called metal-organic frameworks (MOFs) may provide a way to solve one of the biggest problems in methane functionalization catalysis, an economically important chemical process.

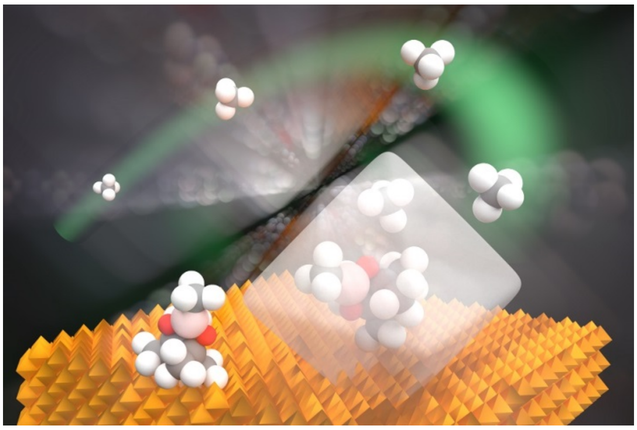
The nation's shale gas production boom of

報告摘要(KEY INFORMATION)

1. 被稱作金屬有機骨架材料(MOF)的微觀晶體結構，或可解決甲烷官能基催化反應的一大問題。這個在經濟上具十足潛力的化學反應，早因美國近年來頁岩石油氣的大量產出而備受矚目，但甲烷的高穩定性使反應難以進行；直到近來美國阿岡實驗室與西北大學研究學者以鋯催化劑進行實驗，終於有所突破。
2. 曾經幫車子換潤滑油的人想必都知道，減少金屬之間的摩擦力有多麼重要。阿岡國家實驗室的團隊已致力研究如何以石磨烯等固體潤滑油取代傳統潤滑油，不僅能節省成本，持續效果也較佳。
3. 美國退出伊朗核協議後，市場對地域危機的意識提高，為化解供應缺口，沙烏地阿拉伯與俄國將增加石油出口以維持市場供需平衡，同時美國也拉升其出口量，尤以頁岩石油氣為最。然而市場仍有各種不確定因素，包括 11 月選舉後川普政府可能改變稅率，及中東地區在伊朗受制裁後的緊張情勢。
4. 北美電力可靠度公司(NERC)夏季報告指出德州等區域將面臨電力供應短缺的困境。由於對可再生能源與天然氣火力發電的依賴性，當風能、太陽能無法發電，或天然氣因管線問題造成中斷，都可能產生危機。種種情況使能源多樣性之必要再受關注。
5. 總有一天，迷路的登山客可以不必再為沒有安全衛生的飲用水而苦惱。史丹佛大學團隊研發出一種新純化劑，可以在日照下還原氧氣、氧化水，產生過氧化氫(H2O2)，作為水中的抗菌劑。

recent years has led many researchers to look for new ways to functionalize methane — i.e., transform it into something more valuable. One such product could be methanol.

“There are a lot of ways to functionalize methane, but one form that would be cost effective and abundant is the transformation of methane to methanol,” said Max Delferro, the catalysis science program group leader at the U.S. Department of Energy’s (DOE) Argonne National Laboratory. “Unfortunately, methane is one of the most stable molecules. It’s difficult to activate methane.”



But now, a team led by Delferro and Omar Farha, associate professor of chemistry at Northwestern University, has demonstrated a new way to activate methane with MOFs, as a result of their joint efforts in the Inorganometallic Catalyst Design Center, a DOE-funded Energy Frontier Research Center. They and seven co-authors recently published their method in *Nature Catalysis*.

“This example showcases how designing crystalline materials, in particular MOFs, will lead to solutions of complex but exciting opportunities,” said Farha, who is also president and co-founder of NuMat Technologies.

A methane molecule consists of one carbon atom linked to four hydrogen atoms. But functionalizing carbon-hydrogen bonds in methane is a particularly challenging process that most known catalysts can achieve only under extremely acidic and/or oxidizing conditions.

The Argonne-Northwestern team, however, has shown for the first time that MOFs can selectively produce a specific boron-infused methane product by shape-selective catalysis, a widely used industrial technique for chemicals synthesis and hydrocarbon processing. Shape-selective catalysis can distinguish between molecules that are slightly different in size and may selectively form only one desired chemical product. But for the technique to work, the pore space of the catalyst must be comparable to the size of the molecules involved in the reaction.

Since the 1960s, zeolites have been commonly used to perform this type of catalysis. Zeolites are microporous crystalline minerals that often include silicon, aluminum and oxygen. They are commonly used as commercial adsorbents and catalysts and have a cage-like framework in which reactant molecules can become trapped. But if the molecules are too big to fit inside the framework, no catalysis can occur.

In MOFs, organic molecules and metal oxide clusters serve as the links and nodes, respectively. MOFs are attractive candidates for performing shape-selective catalysis because they are structurally tunable, noted lead author Xuan Zhang of Northwestern and his colleagues in the *Nature Catalysis* article. Unlike zeolites, they can be synthesized with pore and aperture sizes tailor-made for targeted molecules.

"Max Delferro and Omar Farha are excellent scientists who benefit from the infrastructure offered by the Inorganometallic Catalyst Design Center to perform state-of-the-art research that will advance the knowledge and the economy of our nation," said Laura Gagliardi, director of the Inorganometallic Catalyst Design Center, based at the University of Minnesota.

The researchers drew inspiration for this work from two papers published back-to-back in the March 25, 2016, issue of *Science*, by teams at the University of Michigan and the University of Pennsylvania. Those teams showed how they could introduce a boron-based compound, in a process called borylation, and offer a promising route for methane activation under milder chemical conditions than would otherwise be possible.

The Michigan and Pennsylvania teams separately observed the borylation process yielding products that were both monoborylated (technologically valuable) and bisborylated (undesired). But by inserting an iridium-based catalyst (synthesized at Northwestern) inside the MOFs, the Argonne-Northwestern team was able to produce a reaction that formed only the monoborylated product; the pores of the MOFs were too small for the bisborylated product to form.

The Northwestern chemists also borylated the methane simultaneously under a variety of reaction conditions at Argonne's High-Throughput Research Laboratory. The team then documented details of the iridium catalyst's oxidation state in X-ray absorption experiments at the Materials Research Collaborative Access Team's (MR-CAT's) x-ray beamline within Argonne's Advanced Photon Source (APS), a DOE Office of Science User Facility.

In the next phase of their research, Delferro and Farha will attempt to activate methane with the same chemistry, but they will substitute Earth-abundant metals such as iron, cobalt, nickel and copper for iridium, which is rare and expensive.

"We're excited about the future for this chemistry," Delferro said. "If we can do the same chemistry with iron, then we're really in business."

The Nature Catalysis article "Catalytic Chemoselective Functionalization of Methane in a Metal-Organic Framework," also includes Argonne team members Zhiyuan Huang, Magali Ferrandon and Dali Yang as authors.

This work was supported as part of the Inorganometallic Catalyst Design Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. Use of the APS was also supported by the DOE, Office of Science. Operations of the Materials Research Collaborative Access Team at the APS are supported by the DOE and the MR-CAT member institutions. MR-CAT is a partnership of three universities (University of Notre Dame, University of Florida and the Illinois Institute of Technology), two Argonne divisions (Chemical Sciences and Engineering as well as Biosciences), the U.S. Environmental Protection Agency and two companies (BP and Honeywell UOP).

SLIPPERY WHEN DRY

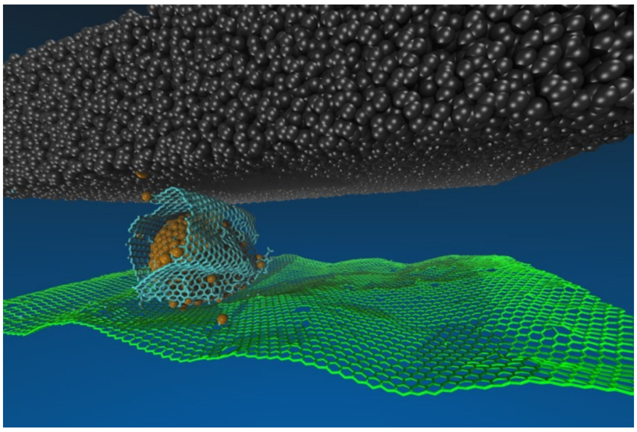
乾時潤滑

By Jo Napolitano • July 12, 2018

Anyone who has ever taken their car in for an oil change recognizes the importance of reducing the friction that arises when steel touches steel.

Researchers at the U.S. Department of Energy's (DOE) Argonne National Laboratory have been working for years to replace oil with solid lubricants such as graphene, which is a cheaper and more efficient substitute, one that lasts significantly longer.

Argonne's Laboratory Directed Research and Development (LDRD) Program, which gave them the seed money they needed to begin their experimentation, initially funded the work of Argonne researchers Anirudha Sumant and Ali Erdemir.



Graphene can also be used to better protect ball bearings, which can corrode over time when exposed to water, the process commonly referred to as tribo-corrosion. The Argonne-developed process based on graphene has shown that a few layers of graphene not only reduces friction in steel rubbing against steel by seven times and the wear by 10,000 times but also significantly reduces the tribo-corrosion problem.

"That's a significant improvement over any other existing solid lubricants coating available today," Sumant said. "Also, the amount of graphene needed is very small and therefore cost is much lower and eliminating oil waste would be more environmental friendly, which is a great side benefit."

Sumant and his colleagues' work has far reaching implications both inside and outside the automobile industry. It could help wind turbines move with greater ease, allowing them to produce more energy. It also can better seal off machinery as it pumps oil or gas from the ground or out at sea.

The Argonne team, led by Sumant, who is a researcher at the Center for Nanoscale Materials, went on to win two additional grants totaling $1.4 million from the U.S. Department of Energy.

It was through the initial LDRD funding that they recognized graphene as an emerging solid lubricant, one that works differently than existing oil-based and other solid lubricants, including graphite lube and even diamond-like carbon.

Not only does graphene perform better, it's more affordable. Even moderate quality graphene works great for tribological applications, which is not the case for various electronics and sensor applications.

Most of the cost in conventional solid lubricant coatings relates to the infrastructure needed to apply it, including the electricity to run the related machinery and the machines' maintenance. Not so with graphene, which can be applied by spraying a solution in the air and can coat any complicated shape or size — and over a large surface area.

In an effort to bring their finding to the marketplace, Sumant and his team are currently working with two different companies in vastly different industries.

The first is one of the world's leading providers of mechanical pump seals. It is working with the scientists to replace its silicon carbide seals with graphene, which would reduce wear and friction.

The team also plans to work with another company from the automobile sector, which uses molds to create car parts, including door panels. Argonne researchers are seeking to develop a new lubricant that could reduce friction in metal forming applications and thereby bring down the cost of automobile manufacturing.

Vivian Sullivan, LDRD program manager at Argonne, said the graphene experiment is an excellent example of how basic science can be used for practical means outside the laboratory.

"Discoveries like this have real-world applications, which is exactly what the DOE is looking for," she said. "It's why the department threw its support behind this project after the initial round of LDRD funding."

LDRD supports high-risk, potentially high-value research and development. It encourages the creation of novel technical concepts and enhances the national laboratories' ability to pursue their own strategic goals as well as those of federal funding agencies.

"It's one of the main ways the labs continually revitalize their research," said Supratik Guha, Argonne's Senior Science Advisor and director of the Nanoscience and Technology division and Center for Nanoscale Materials, a DOE Office of Science User Facility.

LDRD monies also helped Sumant and his team acquire a high-temperature stage for their unique, multifunction tribometer, which helps study friction, wear and force between two surfaces at an almost immeasurable level.

RECENT DEVELOPMENTS IN THE OIL MARKET

石油市場的近期發展

By Tetsuo Morikawa

At an OPEC meeting on June 22 followed by a ministerial meeting of OPEC and non- OPEC parties to the joint production cut on June 23, it was decided to ease the supply cuts from July. On the basis of the production cut of approx. 1.2 mb/d for OPEC and 0.6 mb/d for ten non-OPEC countries agreed at the end of 2016, the compliance rate as of May stands at 152% for OPEC countries (a reduction of 1.8 mb/d) and 147% overall including the non-OPEC parties to the production cut. Regarding the decision, Khalid Al-Falih, the Saudi Minister of Energy, Industry and Mineral Resources, said that a production increase of around 1 mb/d would be necessary. However, as this amount may be insufficient to avoid a supply-demand crunch, on June 22 Brent climbed 3% from the previous day to $75.55/bbl. It rose further to $75.31 on June 27 after the United States called on major countries to stop importing oil from Iran.

This decision was surely backed by soaring oil prices in April and May. With the achievement of rebalancing and the rising market awareness of geopolitical risks in May such as the exit of the US from the Iran nuclear agreement, WTI reached $70/bbl on May 7 and Brent surpassed $80/bbl on May 22, both reaching their highest levels for three and a half years. Saudi Arabia and Russia were willing to continue the joint production cut in 2019 as of April, but as prices soared, a possible easing of the production cut was mentioned when Saudi Energy Minister Khalid Al-Falih and Russian Energy Minister Alexander Novak met on May 22. US pressure on Saudi Arabia, its partner in countering Iran, to boost production reportedly affected the decision on the easing.

Meanwhile, US oil output continues to increase, reaching 14.9 mb/d as of May 2018 from an average of 13.09 mb/d in 2017. Shale oil, which accounts for most of the increase, is improving in productivity, albeit moderately, as is the rig count. The US Energy Information Administration remains bullish, forecasting an annual average output of 15.13 mb/d for 2018 (up 2 mb/d yoy) and 16.5 mb/d for 2019 (up 1.4 mb/d yoy).

Saudi Arabia, Russia, and other countries that agreed to ease the production cut in the meetings on June 22 and 23 will boost their output and try to maintain the supply-demand balance. Meanwhile, the outlook for the global economy is uncertain amid fears of worsening trade friction if the Trump administration imposes further tariffs ahead of the US mid-term election in November. The situation in the Middle East remains tense with the return of sanctions against Iran. There will be much speculation ahead of the next OPEC meeting on December 3, which will discuss how to coordinate the production cut policy for 2019. Accordingly, the market is likely to become even more nervous, resulting in high price volatility.

US: RISK OF A SUPPLY SHORTAGE IN THE US POWER MARKET

美國電力市場的供應短缺危機

By Junichi Ogasawara

On May 30, North American Electric Reliability Corporation (NERC), the oversight and assessment organization for maintaining the reliability of North America's power systems, released their summer reliability report. The report expressed concern over a supply shortage in Texas this summer. The supply margin of 18.9% stated in the 2017 summer reliability report is expected to shrink to 10.9%, below the 13.75% margin required for a stable supply, as more coal-fired thermal power plants close, the start of new power plants is delayed, and more power plants stop operation. This, if combined with normal levels of unplanned outages of thermal power plants, very hot weather, or a reduction in wind power output, could result in a negative supply margin.

Further, the Midcontinent Independent Transmission System Operator (MISO), which is experiencing significant growth in wind power, says that it is often necessary to take emergency procedures due to frequent demand response and adjustment of BTMG (behind-the-meter-generation: on-site generation behind the meter) output. California's ISO also points out the possibility of a shortage of operation reserve capacity, with the risk rising particularly if the water level for hydropower and solar PV output drop concurrently. Supply risks in gas pipelines could also elevate the risk.

As all these regions have increased their levels of renewable electricity and are highly dependent on gas thermal power, problems emerge when the supply capacity of both energies comes under threat. Renewable energies have the risk of a simultaneous drop in output while gas thermal power may face a stoppage of gas supply facilities such as gas pipelines under abnormal weather conditions.

Coincidentally, according to media reports, President Trump has ordered the Department of Energy to consider measures to avoid closures of nuclear and coal power plants. While the order was issued to address any impact on employment, it may have also been caused by the mounting risk of supply disruptions due to an imbalance in supply capacity. So far, the reliability assessment for power has not been considering gas supply facilities. However, with the recent rise in dependency on gas in the US, information has begun to be gathered on the adequacy of gas procurement, and a method of evaluating the risk of gas supply disruptions is being studied. However, the method is yet to be fully established.

In 2017, President Trump ordered a study on a plan to subsidize nuclear power to make the power grid more reliable and resilient, but in January 2018, the Federal Energy Regulatory Commission declared the end of the study saying that it was not possible to ensure consistency with market procedures. Should a supply shortage emerge this summer due to the supply capacity imbalance, however, the importance of a diversified power mix could come under the spotlight again.

A SOLAR PURIFIER CREATES ITS OWN DISINFECTANT FROM WATER AND SUNLIGHT

當登山客受困又脫水時，該飲用泥濘水嗎？

By Andrew Myers・June 22, 2018

A hiker gets disoriented while on a desert trek when she comes upon a drying puddle left by a recent rain.

Consumed by thirst, miles from home, the hiker must decide whether to drink and risk infection from whatever bacteria are in the puddle, or endure dehydration. But that hiker might one day be able to drink worry free, thanks to a new kind of water purifier that uses sunlight and water to produce hydrogen peroxide, a powerful and common antiseptic.

The experimental water purifier, developed in the lab of Xiaolin Zheng, associate professor of mechanical engineering, is a variant of the better-known process of using solar energy to split water into hydrogen, a clean-burning fuel, and oxygen, a life-sustaining element. But, as the team describes in the journal Advanced Energy Materials, instead of fully splitting oxygen and hydrogen, the new process reduces oxygen and oxidizes water to produce hydrogen peroxide, or H_2O_2.

Even just a small amount will purify the water, she says. Hydrogen peroxide disinfects water at a level of tens of parts per million. That's about two tablespoons in 25 gallons of water. In tests using tap water, the Stanford system easily reached well over 400 parts per million of H_2O_2 in five hours.

Zheng says the team will have to change some of the materials in the process to make its blend of ordinary water and hydrogen peroxide safe to drink. But they think that one day, a person in desperate thirst could pull out their lightweight solar purifier, pour in some suspect H_2O and, given enough time, produce enough H_2O_2 through the sun-activated process to turn any fresh water into a veritable oasis.

In addition to future drinking water applications, Zheng and Xinjian Shi, the graduate student leading the project, also imagine that their system might be adapted into self-sustaining swimming pools purified with solar-created hydrogen peroxide rather than chlorine, or solar-powered water purification stations for use in developing regions where fresh water is a precious commodity.

Plentiful raw materials

The prototype consisted of two electrodes, an anode and a cathode, thrust into water. The anode was made of bismuth vanadate ($BiVO_4$), a photosensitive semiconductor. Simple carbon served as the cathode. When exposed to sunlight, the bismuth vanadate semiconductor sent negatively charged electrons flowing toward the cathode, while positively charged carriers — or "holes" as they are known in physics — flowed back toward the anode. The flow of electrons turned oxygen into hydrogen peroxide while the holes acted to transform water into hydrogen peroxide, forming the purifying compound at both electrodes.

It is a new take on what is known in engineering circles as a photoelectrochemical (PEC) system. PEC systems have been much studied since the 1970s for their ability to convert sunlight to fuel and other useful chemicals, like hydrogen and oxygen. Prior PEC experiments have produced hydrogen peroxide but none of these previous experiments has been as successful as the present research.

"Ours is an unassisted system," Shi says, "It requires zero energy input and only light, water and oxygen to work. Water is the 'fuel' of our system. In fact, it works with tap water."

Intriguingly, the system produces hydrogen peroxide on both sides of the reaction, at the anode and the cathode. At the end of it all, there's even a small amount of electricity remaining, due to the efficiency of the chemical reactions. While not a great amount, that additional energy might be used to light an LED bulb as an indicator that the system is working properly, the researchers say, letting the thirsty owner drink with confidence.

"We think that this is a new direction in PEC water splitting, which usually requires additional energy inputs to work," Zheng says.

Work ahead

The researchers consider this paper as a proof of concept and say much work remains before hydrogen peroxide-producing purifiers can become commonplace. Most importantly, bismuth vanadate — the anode — is itself toxic and would need to be replaced by another equally photosensitive material.

Dr. Samira Siahrostami, a co-author on the study and a research engineer at the SUNCAT Center for Interface Science and Catalysis at Stanford, selected bismuth vanadate as the anode for this prototype due to its efficiency and ability to generate hydrogen peroxide. Going forward, the researchers plan to identify other anode materials that are stable, efficient and safe for water purification.

Zheng and Shi also suggest that they might replace the carbon cathode with a different material that is also photosensitive (carbon is not). Such a design would harness a greater range of solar light to further enhance efficiency of the system.