



Contact: Peter Genzer, (631) 344-3174 | Written by Laura Mgrdichian-West

New Catalyst Recycles Methane Emissions at Room Temperature

Brookhaven-led collaboration develops an inexpensive catalyst to convert methane emissions into useable products without the need for ultra-high temperatures

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UPTON, N.Y. — Natural gas is a fossil fuel that is widely used in the U.S. for heating, cooking, and electricity generation and it is also used as a chemical feedstock for the manufacture of plastics and other products. But because it consists primarily of the greenhouse gas methane, natural gas is one of the leading sources of methane emissions.

To recycle methane in the atmosphere, researchers worldwide are studying catalysts that can convert methane into useable fuels and other products. Recently, a research collaboration led by scientists at the U.S. Department of Energy's (DOE) Brookhaven National Laboratory developed an inexpensive catalyst that performs well and — critically — works at, or near, room temperature, which is key to developing real-life, widespread methane recycling applications.

The work is featured on the cover of the Oct. 15, 2024, edition of the journal *ACS Nano*.

"Researchers have been continually searching for a catalyst that can achieve methane conversion at moderate temperatures," said Brookhaven chemist Arephin Islam, the paper's lead author. "Our catalyst does not require temperatures well above 500 K (about 440 degrees Fahrenheit), as many others do. It is also efficient and uses common, low-cost materials, making it potentially scalable to commercial applications."

The catalyst consists of magnesium oxide nanoparticles — each just about half a billionth of a meter in diameter — embedded within a very thin layer of copper oxide, which, in turn, sits upon a layer of copper. Although bulk magnesium oxide is not a good methane conversion catalyst on its own, researchers have learned that it is activated by the addition of certain metals or metal oxides. This was one factor that led to this investigation, but the group was also guided by a theoretical study conducted by Brookhaven chemists Ping Liu and Erwei Huang, which published in May of this year. That work determined that integrating nanostructured magnesium oxide with copper oxide could be a successful catalytic approach for methane conversion at mild temperatures.

"It was worth investigating how magnesium oxide in nanoparticle form could be more reactive toward methane, particularly when combined with copper, which is known to have the ability to catalyze methane conversion," said Brookhaven chemist Jose Rodriguez, principal investigator of the research.

Studying the system with light and electrons

The group studied the performance of catalyst samples that were synthesized with different concentrations of magnesium oxide applied to the copper oxide surface. They used several techniques, including an X-ray method known as ambient-pressure x-ray photoelectron spectroscopy (AP-XPS), which yielded information on chemical composition and the chemical interactions taking place on the catalyst surface. This work was performed at the National Synchrotron Light Source II (NSLS-II), a DOE Office of Science user facility located at Brookhaven that produces intense beams of X ray light for studying a wide variety of materials and biological samples.

At NSLS-II, the group used state-of-the-art instrumentation at the In Situ and Operando X-ray Spectroscopy (IOS) beamline, which allows scientists to study samples “at work” in real time and under realistic operating conditions. and under realistic operating conditions.

At the beamline’s AP-XPS endstation, the team prepared catalyst samples via a process called physical vapor deposition, which allows ultra-thin layers of a material to be deposited onto a substrate. Next, they exposed each sample to reactant gases at realistic pressures and directed X-rays at its surface. The X-ray light caused electrons to be ejected from the surface via the photoelectric effect, and these ejected electrons were then analyzed to determine their kinetic energies. These energies, in turn, revealed the binding energies of electrons from specific atoms in the sample and allowed the researchers to identify specific chemical elements as well as their oxidation states and chemical environments — information that is key to understanding a catalyst’s behavior.

AP-XPS is an excellent technique to use in this type of study because it allows real-time surface analysis of materials during reactions, bridging the gap between controlled lab studies and practical industrial applications.

To see how the reactions had changed the magnesium oxide/copper oxide catalyst surface of each sample, the researchers employed a powerful imaging technique called scanning tunneling microscopy (STM), which creates a visual map of a sample’s surface by sweeping across it with an extremely sharp conducting tip. A voltage between the surface and tip causes electrons to “tunnel” across the tiny gap between the tip and the surface, and the currents created by those electrons are measured and translated into an image.

The AP-XPS and STM measurements collectively showed that the catalyst system activates methane at room temperature, breaking its carbon-hydrogen bonds and converting it to ethane, which is used for a variety of commercial purposes, including refrigerants and the production of fuels. Overall, the new catalyst’s performance rivals that of expensive catalysts based on platinum and other metals in that group, such as palladium.

Beyond methane

In another recent Brookhaven-led study published in April, members of the group determined that this catalyst system is also successful at converting carbon dioxide, another greenhouse gas, at room temperature.

Using the same two methods, synchrotron-based AP-XPS at the IOS beamline and STM, they showed that nanoclusters of magnesium oxide on a copper oxide/copper surface can dissociate carbon dioxide into carbon monoxide and other carbon species. This ability opens reaction channels that could lead to the formation of oxygenates and light alkanes, two chemical groups that are involved in the production of fuels.

“Together, these findings are a significant step toward sustainable conversion of two potent greenhouse gases and carbon mitigation strategies,” said Islam.

This study is a collaboration between scientists at Brookhaven, Stony Brook University, the University of Michigan, and the Central University of Venezuela. It was funded by the DOE Office of Science.

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