Transforming gas into fuels with better alloys

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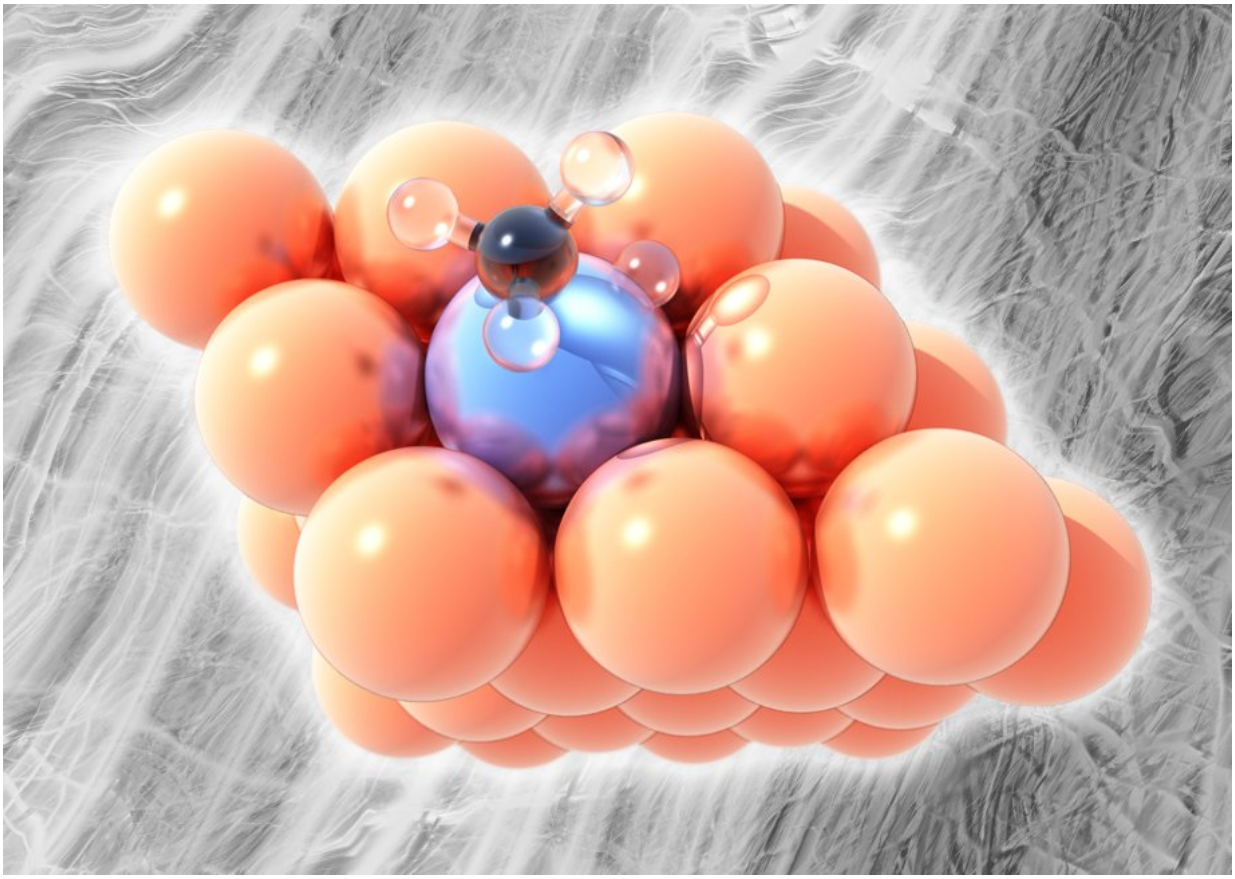

Pictured, the platinum–copper single-atom alloy. Copper (orange) is unable to break bonds between carbon (black) and hydrogen (clear) in methane derivatives except at higher temperatures, but a single atom of platinum (icy blue) in the surface layer of the alloy can break off hydrogen atoms at relatively low temperatures without forming coke. Credit: Michail Stamatakis, UCL

Technological advances in oil and gas well stimulation over the past decade now allow for the production of natural gas from shale gas trapped in rock formations underground. With the sudden increase in the availability of shale gas, scientists have regained interest in carbon–hydrogen (C–H) activation, the process of breaking C–H bonds from gases such as methane to form chains of hydrocarbons that can be used as fuel.

But scientists are a long way from gleaning these fuels from shale gas—most catalysts for C–H activation break off too many hydrogen atoms, leaving behind an unwanted carbon solid called coke.

Desiring a metal alloy that would function as a catalyst for C–H activation while remaining coke-resistant, a team led by Charles Sykes at Tufts University conceived of an alloy made from the reactive metal platinum and the inert metal copper. In a series of laboratory experiments, Sykes' team looked at pure copper, pure platinum, and a platinum–copper single-atom alloy (SAA) to determine each material's interactions with methane-derived hydrocarbons, molecules that are found naturally in shale gas. The team discovered that the platinum–copper SAA was resistant to coking.

Following this discovery, the Multiscale Computational Catalysis & Materials Science group led by Michail Stamatakis at the University College London used the high-performance computing (HPC) resources at the Oak Ridge Leadership Computing Facility (OLCF) to unmask details of the experiments via simulations. Matthew Darby, a postdoctorate at the time and now recipient of the UK's Engineering and Physical Science Research Council doctoral prize working in the Stamatakis group, performed the calculations for the project.

Darby found that at low temperatures, platinum rapidly strips hydrogens from methane, leading to the formation of carbon deposits; copper is

unable to break C–H bonds except at high temperatures. The team's platinum–copper alloy, however, was found to efficiently break C–H bonds at intermediate temperatures without forming coke. Like pure copper, the alloy was also able to form two- and three-molecule chains of methane—and could achieve this at a temperature more than 100 degrees Celsius cooler than what copper required.

"These calculations are very computationally expensive. For some, if you ran them on your laptop, it might take several months to run one calculation," Darby said. "At the OLCF, it can take maybe a day or two because you have hundreds of cores to work with."

Powerful supercomputers at the OLCF, a US Department of Energy (DOE) Office of Science User Facility located at DOE's Oak Ridge National Laboratory, solve complex scientific problems in energy, materials, chemistry, and many other scientific domains. The results of the team's simulations explain platinum and copper reactions with methane and offer a new coke-resistant catalyst.

Armed with this new knowledge, the experimentalists at Tufts created a microlevel replica of a real chemical plant's performance to gain even more insights into the process. The project demonstrates that theory can be used to refine experiments by providing fundamental understanding, setting the stage for larger-scale experimental work.

A coking problem

Common fuels that exist as chains of hydrocarbon molecules include propane, often used in furnaces for heat, and butane, the liquid found in most lighters. Using C–H activation, scientists can jumpstart reactions within the simplest hydrocarbon—methane—and thereby encourage these molecules to link together to form useful fuels. Because shale formations are abundant and sources of longer hydrocarbons (e.g., crude

oil) are running low, scientists are searching for ways to catalytically convert methane into these fuels.

Transition metals such as platinum and nickel are effective catalysts, but they also cause large amounts of obstructive coke deposits to form. This layer of carbon coats the top of the metal, rendering the remaining methane molecules unable to react with the rest of the metal material.

"Coke is a big problem in industrial chemistry," Darby said. "Once it's deposited, you have to take your metal out of the reactor, clean it off, and put it back in. That involves either shutting the giant chemical plant down or heating the metal to dangerously high temperatures."

Counterintuitive to their ability to rapidly break hydrogens away from methane, platinum and nickel are limited at making longer-chain hydrocarbons because of coking. Recently scientists have sought alloys made of an active metal such as platinum or nickel and an inert metal such as copper or silver. But even with these kinds of alloys, coking has continued to pose a problem.

Sykes' team developed a novel SAA, or single-atom alloy, with only 1 atom of platinum for every 100 atoms of copper, to combat the coking. The platinum atoms were isolated in the surface layer of the metal to ensure they wouldn't overly react. The experiments showed that single platinum atoms in copper still react to break C–H bonds but not to the extent that coke is formed.

Darby then simulated pure platinum, pure copper, and the SAA to determine which of the three surfaces a carbon atom binds to most strongly. He repeated this process with carbon bonded to one, two, three, and four hydrogens as well as hydrogen atoms on their own. He found that these molecules bind to copper with a higher affinity than to platinum, and much more energy is required for copper to break C–H

bonds. The results are key to explaining why copper is an ineffective catalyst.

"Platinum can break C–H bonds millions of times faster than copper, and the alloy is somewhere in between," Darby said. "Before this SAA, people couldn't get two or three methane molecules linked together at low temperatures without deactivating the metal. We've shown we can get as many as three."

The finding is important because there has never before been an alloy that could effectively break C–H bonds and also remain coke-resistant.

"Our SAA demonstrates that a solution to this problem could be possible," Darby said. "I hope this will help spur the chemistry community to try more SAA combinations and see if we can actually find the alloy that's going to be perfect for this."

Atom-sized particles

The simulations were performed on OLCF resources using the Vienna ab initio Simulation Package (VASP), a code designed for modeling materials at the atomic scale. VASP is the most popular of its kind and is perfectly tailored for use on high-performance parallel computers such as the ones at the OLCF.

"We model things on an atom level," Darby said. "We modeled 100 atom-sized particles: the catalyst and the methane molecules. We then calculated how much energy it takes to convert methane into something else."

By comparing these calculations to one another, Darby was able to explain the experimental findings. By reproducing everything in the experiment, the team could see down to the atom level and simulate the

number of times specific bonds would break—something that is impossible to count in an experiment.

The team's hope is that one day an alloy will be able to link up to eight methanes (the compound octane), which can then be used to fuel cars. The project results and the Stamatakis group's ongoing work will allow experimentalists to focus on the most important systems of alloys rather than testing random systems.

"With experiment, it's mostly trial and error," Darby said. "Simulations give us a roadmap."

More information: Matthew T. Darby et al. Elucidating the Stability and Reactivity of Surface Intermediates on Single-Atom Alloy Catalysts, *ACS Catalysis* (2018). DOI: 10.1021/acscatal.8b00881

Matthew D. Marcinkowski et al. Pt/Cu single-atom alloys as coke-resistant catalysts for efficient C–H activation, *Nature Chemistry* (2018). DOI: 10.1038/nchem.2915

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