Cheaper, cleaner catalyst for burning methane created

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As the world's accessible oil reserves dwindle, natural gas has become an increasing important energy source. The primary component of natural gas is methane, which has the advantage of releasing less carbon dioxide when it's burned than do many other hydrocarbon fuels. But because of the very stable structure of the methane molecule, it can be difficult to access the energy stored within. When unburned methane escapes into the atmosphere, it's a greenhouse gas 20 times more powerful than carbon dioxide.

Now, researchers from the University of Pennsylvania, along with collaborators from Italy and Spain, have created a material that catalyzes the burning of methane 30 times better than do currently available catalysts.

The discovery offers a way to more completely exploit energy from methane, potentially reducing emissions of this powerful greenhouse gas from vehicles that run on natural gas. The catalyst may also offer a cleaner and cheaper way of generating energy from catalytic combustion in gas turbines.

"It's hard to come up with materials that are active enough and stable enough to withstand the harsh conditions of methane combustion," said Raymond J. Gorte, the Russell Pearce and Elizabeth Crimian Heuer Professor in Penn's Department of Chemical and Biomolecular Engineering. "Our materials look promising for some important applications."

Matteo Cargnello, now a postdoctoral fellow in Penn's Department of Chemistry, joined Gorte and Kevin Bakhmutsky, a former Ph.D. student in Gorte's lab, in the study. Their collaborators included Paolo Fornasiero and Tiziano Montini of Italy's University of Trieste and National Research Council and José J. Calvino, Juan José Delgado and Juan Carlos Hernández Garrido of the Universidad de Cádiz in Spain. The study is published in the journal *Science*.

Cargnello began work on this project while still an undergraduate at the University of Trieste, during a visit to Gorte's laboratory, and continued the collaboration as he pursued his doctoral degree at the Graduate School of Nanotechnology at the University of Trieste.

Catalysts are materials that make a chemical transformation quicker, easier, more energy-efficient and often safer. A car's catalytic converter, for example, transforms exhaust gases into innocuous products.

Catalysts that are currently available to burn methane, however, do not do so completely, leaving unburned methane to escape into the atmosphere and contribute to climate change.

"Particularly if you have a natural-gas engine, methane is going to be a major part of that tailpipe exhaust," Gorte said.

In addition, these conventional catalysts can require high temperatures of 600-700 degrees Celsius to encourage reactions to move along. Yet the catalysts themselves often lose their efficiency or deactivate when exposed to the high temperatures generated by methane combustion.

Additional environmental harm can result when methane is used to produce energy in a gas turbine. In this process, methane is typically burned at very high temperatures, in excess of 800 degrees C. When those temperatures rise to around 1,300 degrees C or higher, the reaction can produce harmful byproducts, including nitrogen oxides, sulfur oxides and carbon monoxide.

Conventional catalysts for methane combustion are composed of metal nanoparticles, and in particular palladium (Pd), deposited on oxides such as cerium oxide (CeO2). Tweaking that approach, the researchers instead used a method that relies on self-assembly of nanoparticles. They first built the palladium particles — just 1.8 nanometers in diameter — and then surrounded them with a protective porous shell made of cerium oxide, creating a collection of spherical structures with metallic cores.

Because small particles such as these tend to clump together when heated and because these clumps can reduce a catalyst's activity, the team deposited them on a hydrophobic surface composed of aluminum oxide to ensure they were evenly distributed.

"These techniques are common in the nanotechnology community, but I think it's a novel approach in making catalyst materials," Gorte said.

Testing the material's activity, the researchers found that their core-shell nanostructure performed 30 times better than the best methane combustion catalysts currently available, using the same amount of metal. It completely burned methane at 400 degrees C.

"It's possible to envision this catalyst contributing to pollution control from automotive exhaust and maybe even improving the efficiency of gas turbines," Cargnello said.

The researchers plan to further study the structure of the new catalyst to better understand why it works so well. And they will use similar methods to create new materials to test.

"We can use this assembly method to test different types of metals and oxides," Cargnello said. "That will allow us to prepare a whole library of materials, some of which might be very good at catalyzing reactions besides methane combustion."

More information: "Exceptional Activity for Methane Combustion over Modular Pd@CeO2 Subunits on Functionalized Al2O3," by M. Cargnello et al., *Science*, 2012.

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