Turning methane into valuable feedstock

BY KERRY GIBSON

PLENTIFUL NATURAL GAS HAS BEEN A BOON TO the U.S. energy sector. While it is fueling electrical power plants and providing heat for industry and homes, natural gas still can't hold a candle to petroleum as a feedstock when it comes to making other products, such as plastics, chemicals and other types of fuels.

The problem with natural gas is that it's primarily methane, along with some ethane and propane. Methane, comprised of one carbon atom and four hydrogen atoms, is tough to process because those hydrogen-carbon bonds are quite strong, and stronger than carbon-hydrogen and carbon-carbon bonds in valuable fuels and chemicals. But Ames Laboratory scientist Aaron Sadow hopes to develop catalysts that will break those bonds, yet control the outcome.

"The chemical industry can't use methane," Sadow says. "It can't go into high-value applications because it's difficult to efficiently and selectively convert. Ethane, by comparison, can easily be converted into ethylene, which is a precursor for a lot of chemicals and polymers."

"Before shale gas, companies were looking for alternative sources of ethylene, because the price of petroleum was going up and it wasn't economically feasible to use it for ethylene production," he continues. "Thanks to abundant natural gas, that's no longer the case. But if you look at other types of chemical feedstock that you can't get from shale gas, those prices have continued to climb."

But if methane could be unlocked as a source for those compounds, the value of natural gas would be increased and reliance on petroleum would be diminished.

Methane conversion has been tried for quite some time. However, methane reactions are hard to control and some of the intermediate products are unstable. In other words, once a reaction starts, it's hard to stop methane from breaking down all the way to carbon dioxide and water.

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A group of Ames Lab researchers, with collaboration from other national labs and private industry, has been looking for ways to control those reactions via catalysis. Within Ames Lab, Sadow's group has looked to Igor Slowing for help with high-surface-area metal oxides and to Marek Pruski's group to help characterize those materials via solid-state NMR. Theoretical groups led by Mark Gordon, Teresa Windus and Jim Evans are working to develop models for what's taking place.

"We (Sadow's group) had found some reactions where we were able to break what we thought were strong bonds with reducing reagents and that suggested a strategy for activating surfaces for bond activation chemistry," Sadow says. "Since these are dynamic systems, understanding how conversions happen will be really important. We had some recent results where we'd seen some molecular chemistry which suggested strategies for activating surfaces and high surface area materials towards bond activation."

"A lot of the general ideas are out in the literature, but what we bring is explicit insight into what goes on at single sites. We hope to then extrapolate that to high surface areas," he says. "We're well set up to try figure out what's taking place and how we might control it."

Sadow believes in teamwork

The current work relates somewhat to research Sadow did as a graduate student at the University of California-Berkeley.

"I was in Don Tilley's group where we were using organometallic molecules to activate methane," Sadow says. "Unfortunately the organometallic systems are delicate – they're very sensitive to air, moisture and temperature. In our current work, we're hopeful that a metal oxide surface with lots of sites will overcome that problem."

For Sadow, cracking the methane problem is both a chemical challenge and an economic imperative.

"Methane activation has been a challenge for 100 years," he says. "We know how to burn it and we can turn it into syngas under gasification conditions, but that's an inefficient pathway. At the same time, we also can't continue to rely on oil for all these chemical precursors."

"The group we have here at Ames Lab is in a unique position," he continues. "To be industrially useful, you need systems that are thermally stable. Fortunately, there have been tremendous advances in spectroscopic techniques for heterogeneous catalysis. The nano revolution has really given us new insight into what's on surfaces and how to think about surfaces and surface reactivity."

"Ames Lab has experts in materials, characterization, and expertise in trying to understand reactivity and develop single-site catalysts, so you bring it all together and we hope to affect some exciting changes."