Curbing Nitric Oxide In Car Exhaust

Smog and acid rain could be reduced in large cities if nitric oxide could be removed from car exhaust.

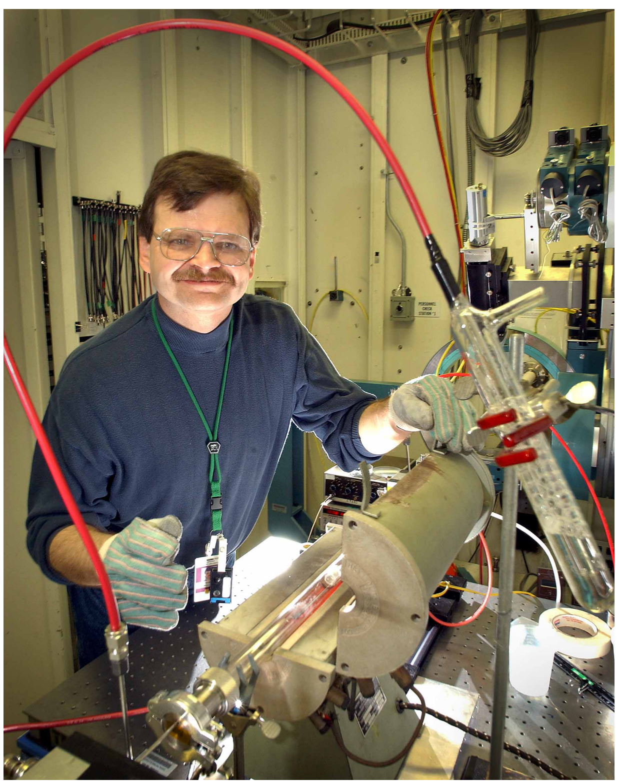
Nitric oxide, which also causes skin irritation and blood damage, is usually destroyed inside a car's catalytic converter, but existing catalysts are unable to meet new standards for pollution control and fuel efficiency.

Now, funded by DOE's Division of Chemical Sciences, Geosciences & Biosciences in the Office of Basic Energy Sciences, Oak Ridge National Laboratory (ORNL) scientists working at the NSLS have unveiled some of the inner workings of a compound that promises to curb cars' nitric oxide emissions more efficiently.

For the last four years, led by ORNL chemist Dave Mullins, the scientists have been looking at how a catalyst - a material used to accelerate chemical reactions - made of cerium oxide and rhodium, could be improved to destroy nitric oxide in car catalytic converters.

"In a car's catalytic converter, nitric oxide is broken down into nitrogen gas and oxygen," Mullins says. "Until now, catalysts have been selected hit or miss, so very little is known about how they actually work."

The scientists use model catalysts either powders made of cerium oxide and very finely dispersed particles of rhodium or thin oxide films grown in vacuum and pass reactant gases over them. Then they direct x-rays produced by the NSLS toward the samples while adjusting the sample temperature or reactant gas composition. Acting as a camera, the x-rays produced "snapshots" of how the catalyst broke the nitric oxide gas apart.



Dave Mullins

Two processes, called photoemission and photoabsorption, allowed the scientists to get a glimpse at the nitric oxide breakup mechanism.

In the photoemission process, light absorbed by the compounds ejects tiny particles called electrons. By measuring the energies of these electrons, the scientists can determine the identities of gases adsorbed on the catalyst. In the photoabsorption process, light that is absorbed by the catalyst provides complementary information about the composition of the catalyst itself. These experiments confirm that the rhodium particles are the movers and shakers responsible for destroying nitric oxide.

"The rhodium particles first weaken the bond between nitrogen and oxygen," Mullins explains. "Then the nitrogen is released as a gas, and the oxygen goes into the cerium oxide or reacts with surrounding hydrogen and carbon, leading to water and carbon dioxide, respectively."

Much to their surprise, the scientists also found that the rhodium particles were being influenced by the cerium oxide.

"We thought that a rhodium particle and the cerium oxide were as independent as an object sitting on a table," Mullins says, "but you can get indirect interactions between the powder and the particles."

The interaction between the rhodium and the cerium oxide makes the rhodium more active, increasing its ability to break the nitrogen-oxygen bond, Mullins adds.

Adding impurities in the cerium oxide can also make it work better, the scientists observed. After trying various types of impurities, they noticed that zirconium, a steel-gray metal used in alloys and ceramics, "dramatically improved the ability of the cerium oxide to exchange oxygen," Mullins says.

The scientists also looked for ways to reduce the temperature at which nitric oxide is broken down. Much of the pollution emitted by an automobile is produced just after a car is started, before the engine and catalyst reach their operating temperature. Reducing the temperature for nitric oxide decomposition will improve the catalysts performance during the warm-up period. As it turned out, the added zirconium lowered the temperature at which cerium oxide exchanges oxygen by about 100 degrees Celsius.

Mullins and his collaborators are now investigating the mechanisms by which zirconium improves the catalytic properties of cerium oxide. They are also studying the action of other impurities such as dysprosium.

"The research efforts needed to optimize the destruction of nitric oxide in car exhaust are extensive," admits Mullins, "but the knowledge that we have gained so far will lead to more new discoveries."

-Patrice Pages

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