New Bifunctional Catalysts Promise Dramatic NO_x Reductions for Heavy Vehicles

Challenge

The U.S. Environmental Protection Agency (EPA) typically aims the start date of a new standard toward a point in the future when it projects that the technologies designed to meet the standard will become commercialized. So it was in December 2000, when the agency ruled that a 95% cut in allowed nitrogen oxide (NO_x) emissions — which contribute to the formation of smog and acid rain — would take effect in 2007. The exhaust aftertreatment technology to meet that standard does not currently exist (Figure 1). But there is a growing consensus that a technology called "selective catalytic NO_x reduction" will make an ideal aftertreatment approach if it can be developed and implemented in time.

A number of catalysts have shown promise over the years in systems used to treat diesel exhaust, including the metal-exchanged zeolite Cu-ZSM-5. But the catalysts often lose activity when exposed to the amounts of water vapor typically present in diesel exhaust. They also tend to require temperatures that are too high and produce relatively large amounts of undesired side products, including nitrous oxide (N_2O) and carbon monoxide (CO).

Argonne Solution

Argonne researchers recently developed a series of bifunctional catalysts that overcome all of the show-stopping drawbacks of other catalysts. The bifunctional catalysts can operate at the temperatures encountered in diesel exhaust and are *more* effective at NO_x removal when water vapor is present. In addition, NO_x reduction selectivities under lean-burn conditions range from 95% to nearly 100% and are accompanied by few or no NO_x side products and virtually no hydrocarbon slippage. Carbon monoxide levels remain higher than the researchers would like, but they have been cut to about 25% of those obtained using Cu-ZSM-5 alone, and work continues to reduce the amount even more. The researchers' goal is to develop an efficient NO_x reduction system that operates passively, using waste heat and a minimal slipstream of unburned hydrocarbons.

Figure 1. Truck manufacturers will need new technologies to help them meet EPA regulations that require a 95% cut in allowed NO_x emissions by 2007.

How the Catalysts Work

The new catalysts are bimodal, meaning that they consist of two different components, a base metal-exchanged zeolite, such as Cu-ZSM-5, and a special oxide additive. The term "bifunctional" indicates that different types of reactions occur at two different sites. The metal zeolite phase provides the catalytic sites that are responsible for NO_x reduction, while the additive phase improves oxidation performance and possibly contributes to oxidizing NO to form NO_2, which is more easily reduced. As a bonus, the additive improves the water stability of the catalyst. This apparently results from the formation of an active third phase caused by an interaction between the additive and copper. The researchers are also working with several other metal-exchanged zeolites and additive materials and have demonstrated similar NO_x reduction improvements with many of them.

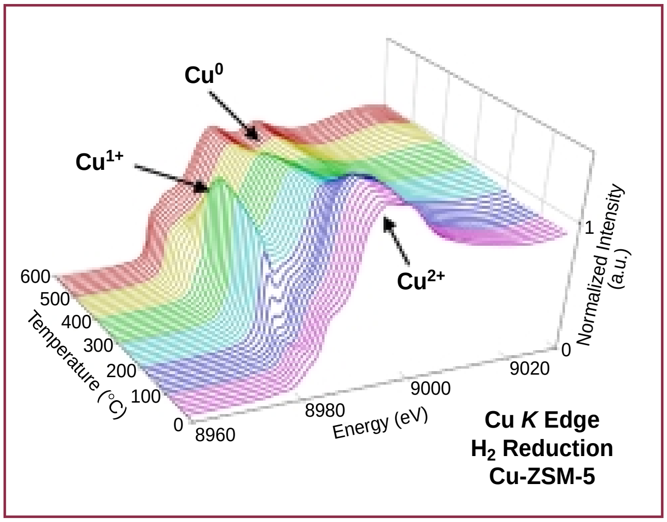

Figure 2. Researchers are using x-ray absorption spectroscopy at Argonne's Advanced Photon Source to trace the state of copper on Cu-ZSM-5 during H_2 reduction as copper moves from Cu^{2+} to a metallic-like state that can be undesirable for NO_x aftertreatment. Tools such as these are bringing new understanding of the catalyst's structure and interactions.

Future Plans

Research continues to improve the performance of these bifunctional catalysts, using rational catalyst design principles to alter the initial reagents, synthesis methods, and treatment conditions that are involved in fabricating these materials. Basic research also continues by means of a variety of *in situ* analytical techniques, including infrared (IR) spectroscopy, extended x-ray absorption fine structure (EXAFS), and x-ray absorption near-edge spectroscopy (XANES). The *in situ* x-ray methods are being employed at the Advanced Photon Source (Figure 2). XANES is used to determine the oxidation states of the metal sites, while EXAFS provides information on their local environments. IR spectroscopy opens a window to the bonding of intermediate species, such as CO, on the surfaces of the catalysts.

The researchers plan to test the long-term stability of the materials under reaction conditions and evaluate their resistance to the presence of sulfur oxides (SO_x), which pose potential problems because they interact with various metals and, together with water vapor, yield sulfuric acid. The catalysts and support materials the researchers are using, however, can tolerate high sulfur levels and high acid strength, both of which are improbable, given that the EPA has mandated severe cuts in the sulfur content of diesel fuel. Argonne's bifunctional catalysts have attracted the interest of major diesel engine manufacturers and have led to a Cooperative Research and Development Agreement (CRADA) with BP.

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