Fuels, Engines, and Emissions

Quantitative Surface Species Identification on Catalysts under Realistic Engine Conditions

Background

Oak Ridge National Laboratory (ORNL) is developing and applying unique measurement capabilities, as demonstrated recently with the spatially resolved capillary-inlet mass spectrometer (SpaciMS) and with phosphor thermography. These instruments have provided key insights into several performance barriers of diesel emissions-control catalysts with regard to the chemical speciation and temperature of the gas phase. However, little is known about the chemistry and formulations on the surface of the catalysts in these vehicles. A diffuse reflectance infrared Fourier transform spectrometer (DRIFTS) reactor with high sensitivity enables this type of catalyst characterization, which is critical to the development of emission-compliant high-efficiency engines.

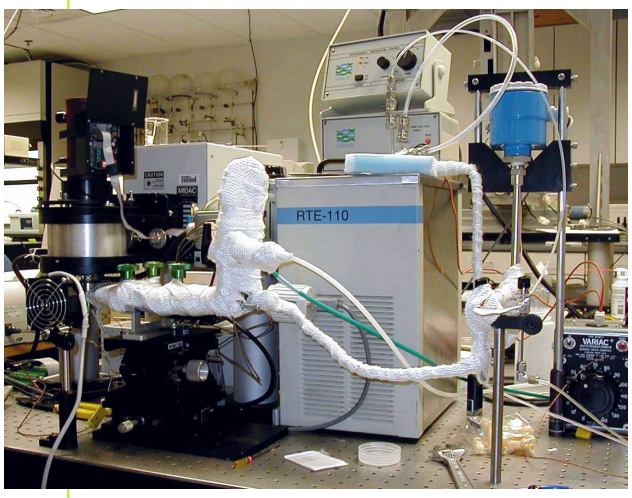
The Technology

The DRIFTS reactor at ORNL enables characterization of surface species on a catalyst under realistic exhaust conditions. It is highly sensitive and, when used in conjunction with chemisorption measurements, allows identification of quantifiable surface species on some nitrogen oxide (NO_x) adsorber catalysts.

The technology is based on a 2.5- to 25-μm-wavelength infrared (IR) beam that is focused on the surface of the catalyst. Chemical bonds characteristically absorb wavelengths of the IR beam due to dipole moments of the bonds, such that when the reflected beam is directed to the detector, the missing wavenumbers are determined and the characteristic functional groups can be determined.

Because the beam is focused at the catalyst surface, one can determine both the chemical and the gas-phase species on the catalyst surface. Typically, these are the only determinations done in most DRIFTS laboratories. However, it is also possible to calibrate the amount of light that is missing from the beam to quantify the surface species based on Beer's Law of absorption. We are able to perform this additional analysis in our lab with our "barrel ellipse" DRIFTS attachment, which enables collection of the diffusely

Less dependence on foreign oil, and eventual transition to an emissions-free, petroleum-free vehicle



DRIFTS reactor with heated gas lines for inclusion of steam. The chemisorption system is on the wall in the background.

reflected IR beam over 330°. (The most common "off-the-shelf" DRIFTS equipment collects less than 90° of reflection.) This attachment, developed at the Y-12 National Security Complex in conjunction with Harrick Scientific over 10 years ago, is being given new life in a new research area. The calibrated values are determined with chemisorption measurements and are enabled with the high sensitivity of the measurements. The sensitivity is especially important when water is used in the reactor because H_2O interferes with adsorbed NO_x species.

The ORNL reactor was used to study $Pt/K/Al_2O_3$, a NO_x absorber catalyst, during the storage phase at temperatures up to 400°C. The primary NO_x storage form is an ionically bound nitrate, NO_3^-, on the K-phase. The Al_2O_3 support has NO_x adsorption behavior, but the amount stored on Al_2O_3 is minimal when H_2O is present; however, H_2O adsorbed on alumina dramatically affects the adsorption chemistry on the K phase by shifting the competition between NO_x and CO_2 for adsorber sites in favor of NO_X by 64%. Analysis at 150-400°C shows that $Pt/K/Al_2O_3$ is limited by kinetics below 200°C and by available sites above 350°C.

Commercialization

The barrel ellipse DRIFTS attachment is commercially available from Harrick Scientific. The attachment is being used in materials studies at ORNL and other national laboratories. ORNL's application of this commercial technology to catalyst research and development is considered to be unique.

Benefits

- In situ measurements of realistic catalysts under realistic conditions
- Quantifiable measurements made possible by high resolution
- Identification of surface species crucial for understanding chemical processes and modeling efforts

Where Can I Find More Information?

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