Measure trace levels of impurities quickly and accurately.

Currently, performance evaluations for new catalysts require numerous types of analytical instruments to quantify all species of interest across a range of compositions and load conditions. The expense involved in purchasing and maintaining these instruments, as well as the difficulty in obtaining accurate measurements in a timely fashion, has driven researchers to look for alternatives. Two practical, cost-effective methods for rapid, accurate on-line gas analysis include mass spectrometry and Fourier transform infrared (FTIR) spectrometry. Together these gas analysis technologies enable catalyst researchers to quickly, accurately, and efficiently evaluate catalyst performance with minimal equipment and maintenance.

Catalyst R&D is strongly enabled by gas analysis technology that specifies and quantifies multiple species. In this article, we discuss the use of quadrupole mass spectrometry as a diagnostic tool for thermal programmed oxidation and thermal programmed reduction, and the use of Fourier transform infrared spectrometry for NOx and NH3 detection in catalytic reduction. Data will be presented to illustrate how these technologies can be used to provide accurate, chemically specific diagnostics of key catalyst processes.

**Quadrupole Mass Spectrometry Theory of Operation**

Mass spectrometers analyze gases by ionizing the atoms and molecules, usually with fragmentation, separating the ions by mass/charge (m/e) ratio, and displaying a mass spectrum (plot of m/e vs. peaks intensity). All the gas components are analyzed within a single scan and where identities of the major components are known, specific mass peaks can be monitored and calibration coefficients applied to derive the relative composition for each species present.

A quadrupole mass spectrometer (QMS) consists of an ionizer, a mass filter, and an ion detector. Various methods of ionization can be used, but electron-impact ionization is most common. Electrons emitted by a hot filament knock electrons off the incoming molecules and atoms to form positive ions. The ions are separated according to their m/e ratio by a quadrupole mass filter and are then detected with a Faraday cup or an electron multiplier. Since the quadrupole analyzer requires high vacuum for operation, a small turbomolecular vacuum pump and a pumped capillary inlet are used to deliver a small proportion of the atmospheric pressure sample stream to the ion source.

**QMS-based Gas Analysis Instrumentation**

An example of a QMS analyzer that has been specifically designed for real-time analysis of atmospheric pressure gases and gas streams is the MKS Spectra™ Mini-Lab™ (Photo 1), which analyzes gases and gas mixtures and monitors species across a wide range of compositions from part-per-billion (ppb) to percent levels. The mass spectrometer assembly is housed inside an oven with a radiant heater, which can be used to raise the chamber and inlet component temperature to 80°C during analysis, to ensure that sample species remain mobile and do not condense before being analyzed. A data collection interface, along with recipe-based control software, allows data to be accessed from other instruments and displayed along with gas composition data to aid in data analysis and reporting.

The pumped capillary inlet reduces the sample pressure from atmospheric pressure to the milliTorr range without contaminating or altering the sample in any way. A heated silica-
lined capillary is used for this purpose as it offers a low volume and inert surface, which together serve to maximize response speed while minimizing “previous sample” memory.

**QMS Systems in TPO and TPR**

On-line QMS gas analysis is frequently used in the study of fuel cells and in the catalytic conversion of methane and other higher hydrocarbons to hydrogen. Catalysts used in such processes are often subject to coking problems where the build-up of carbon deposits on the catalyst can impact performance. Removal of such carbon deposits can be achieved by temperature-programmed oxidation (TPO) where the catalyst is heated in the presence of an O₂/He gas mixture. **Figure 1** illustrates data acquired during a TPO process on an unreduced NiO/SiO₂ catalyst, in which the reactants and reaction products are monitored along with process temperature. By tracking the CO and CO₂ oxidation products, researchers were able to identify the temperature at which carbon removal began, the point at which the catalyst surface carbon was removed, and the total amount of carbon deposited on the catalyst.

The monitoring of temperature-programmed reduction (TPR) processes also provides useful information on catalyst behavior, including an insight into underlying reaction mechanisms and “activity sites” within the catalyst. By using the Mini-Lab to monitor water vapor composition as a function of temperature during the reduction of NiO, as illustrated in **Figure 2**, it is possible to identify the different temperatures at which reduction occurs. The well-defined “peaks” in the water composition plot illustrate the fact that there are different NiO reaction sites with different levels of reactivity. It is suggested that this relates to the difference between large NiO particles and NiO that is in direct contact with the silica catalyst support material.

The QMS instrumentation used during these studies provided catalyst researchers with several advantages over traditional analytical methods:

- Precise tracking of the reaction products along with temperature, in real time, all with a single analyzer
- Easy identification of the optimum temperature and conditions for catalyst treatment
- Straightforward identification when surface carbon had been removed from the catalyst along with a measure of the total carbon deposited

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**Figure 1**

TPR of 10% NiO/SiO₂ after 1 hour calcination at 600°C

**Figure 2**

TPR after isothermal POM over unreduced 10% NiO/SiO₂ (6 hrs; T=900°C; CH₄/O₂=6)
FTIR Theory of Operation

A complementary method to QMS is Fourier transform infrared spectrometry (FTIR). This technique exploits the phenomenon of molecular IR absorption to generate an accurate real-time measurement of gas concentrations in complex mixtures. In a typical IR gas analyzer, an IR beam is passed through a gas sample in a cell. The various gas molecules in the path of the beam interact with the IR radiation by absorbing the light at molecule specific wavelengths. Each gas species has a unique “fingerprint” absorption spectrum related to the vibrational and rotational energy levels characteristic of the molecule. Since no two chemical species produce the same IR absorption spectrum, IR is useful for gas analysis. The only gases to which IR is not sensitive are the noble gases such as xenon and argon, and homomolecular diatomics such as O₂ and N₂. For other gases, IR spectroscopy is recognized as a powerful and flexible analytic technique. Because the technique employs measurement of absorbance, an intrinsic gas property, it is especially well suited to applications where quantitative analysis of concentrations is required. In the examples below, we will illustrate applications where the instrument calibrations are permanent, stable, and transferable from instrument to instrument, a key advantage in industrial applications.

When analyzing mixtures of gases, it is usually necessary to collect IR data at multiple wavelengths. A preferred method for this type of IR analysis is FTIR spectrometry, in which an interferometer is used to encode the IR light by modulating each frequency of light at a different audio frequency. This encoded light is known as an “interferogram” because it is generated using interference. This modulated light is then passed through the gas sample, to allow spectral absorption to occur. A Fourier transform is applied to this time-varying interference pattern to generate the IR spectrum. Automated analysis software usually converts the spectrum to an absorbance spectrum, which in turn is analyzed via multivariate techniques into concentrations of the constituent gases. The data are most often presented in terms of concentration or partial pressure timelines.

FTIR-based Gas Analysis Instrumentation for Catalytic Performance Evaluations

A versatile FTIR-based analyzer specifically designed for real-time gas analysis is the MKS On-Line™ MultiGas™ 2030 Analyzer (Photo 2). The instrument is composed of a rugged process FTIR spectrometer, a high throughput optical sampling cell, application-specific analysis software, and an instrument-independent quantitative spectral library. The FTIR spectrometer has a spectral resolution of 0.5-128 cm⁻¹ with a measurement range from ppb to percent. The spectrometer is coupled to a small vol-
FTIR-based Gas Analysis for Catalytic Performance Evaluations

FTIR-based gas analyzers have been used in catalyst evaluations where differentiation among hydrocarbons and direct measurement of NO, NO₂, HNO₃, SO₂, SO₃, H₂O, CO, CO₂, NH₃ and other components found in combustion or catalytic streams at sub-ppm levels are important. Historically each compound or compound group was measured on an individual analyzer, many requiring water removal that added complexity and uncertainty to the measurement. For example, most commercially available instruments suffer from considerable measurement errors when NOₓ is measured in the presence of significant moisture concentrations. Consequently, many users install expensive and often unreliable driers in the gas stream as a preconditioner to measuring NOₓ. With proper algorithms and measurements acquired at sufficiently high spectral resolution, however, it is relatively easy to measure nitrogen oxide gases in the presence of significant quantities of water vapor. Figure 3 illustrates the analyzer’s capabilities in measuring trace levels of NO in a gas stream containing a high percentage of moisture, without sample conditioning.

Using conventional technology, some gases, such as ammonia, cannot be measured directly and are typically converted to NOₓ and then analyzed. This adds even more complexity and greater potential for systematic error. Direct measurements of such compounds can be made accurately by FTIR instruments with advanced algorithms and high spectral resolution.

Figure 4 illustrates the output that was used to track sub-ppm levels of components directly without conversion, including NOₓ, ammonia, and hydrocarbons for a catalyst performance evaluation. The FTIR gas analyzer in these studies provided catalyst researchers with an effective alternative to traditional analytical methods with:

- Monitoring of catalytic byproducts directly, including NH₃, SO₂, and SO₃, all with a single analyzer
- Sub-ppm of NOₓ in high moisture levels, without expensive sample conditioning
- Speciation (differentiation) of hydrocarbons

From a maintenance perspective, the analyzer requires only periodic gas cell cleaning when utilized continuously, as compared to extensive maintenance needed on numerous traditional analytical analyzers. It also maintains permanent stable calibrations, reducing the time and need for constant calibration checks.

Conclusion

Until now, evaluations for new catalysts required numerous analytical instruments to quantify all species of interest across a range of compositions and load conditions. The studies above demonstrate that catalyst researchers have two practical and cost effective methods for accurate and rapid on-line gas analysis—mass and FTIR spectrometry. Together these technologies enable users to quickly and efficiently evaluate catalyst performance without sacrificing accuracy, and with minimal equipment and maintenance.

Tim Robinson (Tim_Robinson@mksinst.com) is General Manager, MKS Spectra Products; Peter Rosenthal, Ph.D. (Peter_Rosenthal@mksinst.com) is General Manager, MKS On-Line Products; Martin L. Spartz, Ph.D. (Martin_Spartz@mksinst.com) is Director of Technical Marketing, MKS On-Line Products, MKS Instruments, Inc. 6 Shattuck Road, Andover, MA 01810; 800-227-8766; fax, 978-975-0093. MKS is a manufacturer of instruments, components, and subsystems for vacuum- and gas-based processes.