Technology for Productivity

Application Note

Note #01/05

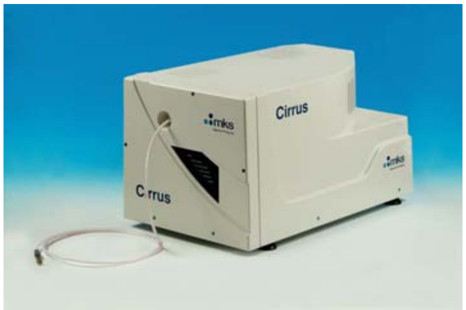
Overview of the Cirrus™ Gas Monitor in General Catalysis and Fuel Cell Applications

BACKGROUND

The development and use of catalysts covers a range of applications from the manufacture of fertilizers to fuel cells. A significant proportion of the use of catalysts relates to heterogeneous catalysis, where gases or liquids are passed over a solid catalyst to produce a gaseous or liquid product. The catalyst is usually in the form of a solid pellet or powder and normally functions at elevated temperatures. In contrast, homogenous catalysis is less widespread and often used to produce high value compounds (e.g. fine chemicals and pharmaceutical intermediates) by mixing the reactants together with the catalyst. The catalyst and reactant are both present in solution and subsequent processing stages are required to separate the product from the catalyst.

As a gas monitor that can rapidly analyze the concentration of a range of different gas species, the Cirrus™ system can prove valuable for those working in the field of heterogeneous catalysis in applications where gas phase reactants pass over a catalyst to produce a gaseous product. Heterogeneous catalysis can be sub-divided into a series of categories, including:

- Odor and combustion emissions abatement
- Production of precursors for the manufacture of fertilizers, fine chemicals and pharmaceuticals
- Generation of useful chemical intermediates
- Natural gas conversion
- Cracking of higher hydrocarbons (petrochemicals)



While the Cirrus gas monitor has been used in some abatement applications, its primary success has been in the use of catalysts for the production of chemical precursors and gas conversion, including fuel cells.

Fuel cells offer a cleaner, more efficient means of generating power. As well as the obvious environmental benefits, they also present a potential means of producing uninterrupted power, which is key to hospitals, airports and critical IT applications. Of the various types of fuel cells, the Cirrus system has been applied in the monitoring and study of PEMs and SOFCs with considerable success.

THE ROLE OF CIRRUS GAS MONITOR IN HETEROGENEOUS CATALYSIS

Within the field of catalysis, the specific role of the Cirrus gas monitor may vary from one application to another however, in general terms, it can be summarized under the following headings:

- Screening, development and optimization of catalysts
- Catalyst troubleshooting
- Optimization and monitoring of pre-treatment stages in the production of catalysts
- Optimization and monitoring of catalyst regeneration processes

Screening, development and optimization of catalysts

The fundamental purpose of a catalyst is to accelerate or facilitate the generation of products from a reactant stream. In this respect, one role of the Cirrus™ system is to assess the performance of the catalyst in terms of "activity" and "selectivity", i.e. measures of the "conversion efficiency" of the catalyst and its ability to convert reactants into product.

The performance of a catalyst is affected by several parameters that essentially impact upon the contact time between the catalyst and the reactant gas mixture. In terms of the physical structure of the catalyst, this would include the exposed surface area of the active material. In other words, issues relating to the concentration of active sites including support media, pellet/particle size and depth/size of catalyst bed. In terms of the reacting gas environment, these parameters also include temperature as well as the pressure and flow of reactants. Furthermore, certain species may "poison" a catalyst, thereby gradually reducing its efficiency. The concentration of such "poisons" in the reactant flow is therefore important.

As a real-time process monitor, the Cirrus system is able to measure both the reactant and product streams to measure conversion efficiency, while also being able to assess the impact of the aforementioned critical parameters on catalyst performance. Process Eye™ Professional, the software platform used to control the Cirrus monitor, has the ability to track these parameters and directly correlate them with the concentration of products species evolving from the catalyst bed. The Cirrus system can also monitor the level of "poisons" in the reactant stream and determine their impact upon catalyst activity. All of this information is essential when optimizing catalyst performance and establishing the best "windows of operation" with minimum "poisoning."

Using mass spectrometer based technology, the Cirrus system is able to monitor many different gas species over a range of compositions (from ppb to percentage levels). The system incorporates a triple-filter quadrupole analyzer with enclosed ion source. This sensor configuration allows the system to track ppb level "catalyst poisons" while simultaneously monitoring reactant or product species at significantly higher levels.

Catalyst troubleshooting

Catalytic reactors vary in size ranging from a micro-reactor, to a reactor used in full-scale production (sometimes with a side stream reactor for optimization tests). If a catalyst is under-performing, a sample is often tested under normal operational conditions in a lab reactor. The Cirrus gas monitor has proven to be a powerful tool when assessing catalyst performance as part of a troubleshooting exercise. It can quickly establish the conversion efficiency of a catalyst and is ideal for wider investigations where performance is tracked as other parameters are varied.

As mentioned earlier, the Cirrus system can also be used to monitor the level of "poisons" in the reactant stream that may serve to undermine the performance of a catalyst, e.g. sulphur containing species present in natural gas to provide the gas with an odor will "poison" a nickel catalyst.

THE ROLE OF CIRRUS™ GAS MONITOR IN FUEL CELL APPLICATIONS

Optimization and monitoring of pre-treatment stages in the production of catalysts

The preparation of a catalyst may require a series of pre-treatment stages involving the passing of a gas stream over a catalyst at elevated temperatures. In such processes, the Cirrus gas monitor is able to provide useful information on:

- The optimum temperature and conditions to initiate such a treatment
- Confirmation that the treatment has reached completion
- An insight into the underlying reaction mechanism and "activity sites" within the catalyst

Figure 1 below illustrates how a Cirrus™ system can effectively monitor water generated during temperature-programmed reduction of a NiO/SiO_2 catalyst precursor. The ability to monitor high compositions of water in the product stream is attributed to the inlet design features of the Cirrus system. The capillary inlet is designed with an "inert" silica lining and the whole assembly may be heated to 150°C. Furthermore, the analyzer housing vacuum chamber and inlet interface components are enclosed in an oven with a radiant heater. When sample gases containing water are drawn into the Cirrus monitor, they are maintained at a constant, elevated temperature. This makes it possible to monitor changes in water composition (and other sticky/polar gases) in real time. A further attribute of the oven is that it allows easy access to the inlet components for maintenance purposes.

Optimization and monitoring of catalyst regeneration processes

Catalysts used in methane (or higher hydrocarbon) conversion are often subject to coking problems where a build-up of carbon deposits on the catalyst, impacts upon performance. Removal of such carbon deposits may be achieved by temperature programmed oxidation (TPO). In a similar way to temperature-programmed reduction, the Cirrus system is able to monitor the oxidation process and clearly identify the temperature associated with the onset of the oxidation reaction (see Figure 2 below). By monitoring the reaction products, it is also possible to identify both the total amount of carbon deposited on the catalyst, the temperatures at which carbon is removed from the catalyst and the point at which all of the carbon has been removed.

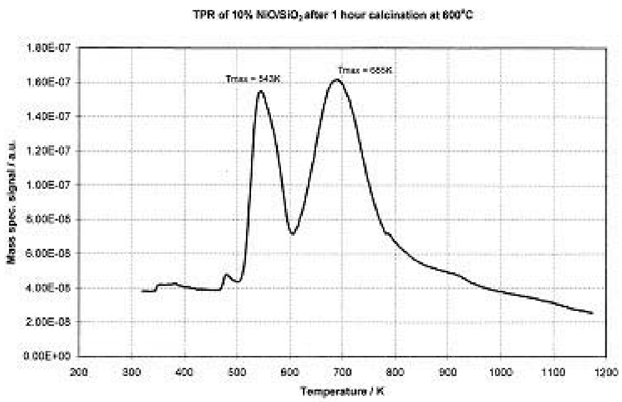


Figure 1: From the plot of water composition versus temperature, it is possible to clearly identify the different temperatures at which reduction occurs. It is evident that there are different NiO bond strengths and it is suggested that this relates to the difference between NiO existing as large particles and NiO in direct contact with the SiO_2 catalyst support material. Information provided courtesy of Keele University, UK.

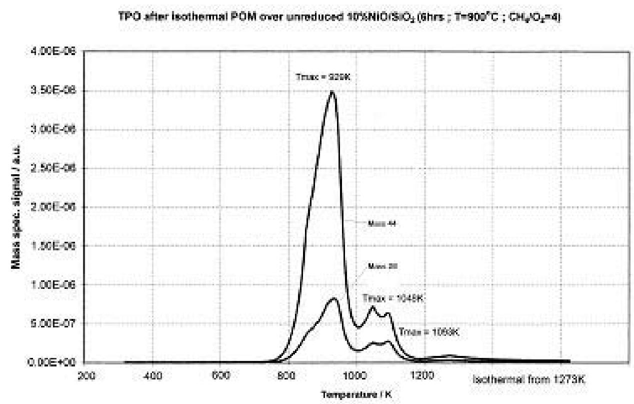


Figure 2: The above plot illustrates the information obtained from a Cirrus system monitoring a temperature-programmed oxidation. By tracking the oxidation products (CO and CO_2) it is possible to identify the temperature at which carbon removal begins and the point at which all carbon has been removed from the catalyst surface. Information provided courtesy of Keele University, UK.

COMPARISON WITH OTHER GAS MONITORING TECHNIQUES

The primary advantage of a Cirrus system in many catalytic gas-monitoring applications is its ability to provide a fast on-line analysis of a product gas stream and to respond rapidly to changes occurring as a result of the onset of a reaction. This, coupled with the ability to access pressure, flow rate and temperature information and correlate this directly with gas composition data, makes it a powerful tool for catalyst screening. There are, however, several other gas monitoring technologies that are routinely used including:

Gas Chromatography (GC)

Gas Chromatography (GC) is probably the main analytical technique used for catalytic gas monitoring. The primary disadvantage with GC is that it does not provide a fast, on-line measurement of gas composition for direct correlation with other critical parameters. It is however able to monitor a wide range of gases, including hydrocarbon species.

Gas Chromatography Mass Spectroscopy (GCMS)

As with GC, GCMS does not provide a fast, on-line analysis however the mass spectrometer is able to identify more complex hydrocarbon species within the product gas stream.

Fourier Transform Infrared (FTIR)

FTIR is suitable for on-line gas monitoring; however it cannot be used to monitor mono-atomic or symmetrical gas species.

CONCLUSION

Catalysts are used in virtually every industry, in a multitude of challenging applications. The Cirrus platform has demonstrated its performance capabilities in many of these fields. Its advanced spectrometer design delivers detection down to the part per billion (ppb) level. Available with a vast array of process control and system integration options, the Cirrus gas monitor offers the most flexible analytical system available today.

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