

Prima BT and Prima PRO Process Mass Spectrometers

Fast, precise gas analysis mass spectrometry in catalysis research and development

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Keywords

- Heterogeneous
- Hydrogen
- Reforming
- Magnetic Sector

Introduction

For chemicals to react, their bonds must be rearranged, because the bonds in the products are different from those in the reactants. The slowest step in the bond rearrangement produces what is termed a transition state - a chemical species that is neither a reactant nor a product but is an intermediate between the two.

Reactant \rightleftharpoons Transition state \rightleftharpoons Products

Energy is required to form the transition state. This energy is called the activation energy, or E_a . In chemistry, heterogeneous catalysis also refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. Phase here refers not only to solid, liquid or gas but also immiscible liquids, e.g. oil and water. The majority of practical heterogeneous catalysts are solids, and the great majority of reactants are gases or liquids.



Heterogeneous catalysis is of paramount importance in many areas of the chemical and energy industries. Heterogeneous catalysis has attracted Nobel prizes for Fritz Haber in 1918, Carl Bosch in 1931, Irving Langmuir in 1932, and Gerhard Ertl in 2007.

Process analytical requirements

Catalysis is a crucial part of the chemical economy, with an abundance of chemical reactions being enabled by the addition of a suitable catalyst. The addition of a catalyst to a reaction mixture speeds up the reaction and causes a reaction to take place that without the catalyst, would never have taken place at all. This occurs as catalysts lower the activation energy required for a reaction to take place. Heterogeneous catalysis dates back hundreds of years and was a key driver in the industrial revolution¹. Heterogeneous catalysts are advanced resources, the preparation and activation of which are required at production scale. This involves a huge scientific and financial investment. An estimated 30% of global gross product relies on catalysis, and over 90% of chemicals and fuels produced worldwide involve heterogeneous catalysts, the economical and societal stake is huge².

Applications of Mass Spectrometers in the laboratory and in the process plant

Mass spectrometers have played an important role in catalyst development in recent years by providing fast, precise and accurate analysis of the off gases involved in such reactions. Gas analysis mass spectrometers offer fast, flexible analysis of a wide range of inorganic and organic gases, over an extremely wide range of concentrations and have been shown to be very robust and reliable.

It is often necessary to develop new analytical methods in the laboratory which are then transferred to the plant as a new process is 'scaled up'. It is therefore vital that the results from the laboratory MS correlate directly with those obtained from the Process MS. Although the external packaging of the two analyzers may be very different (the process MS should be capable of installation in a Hazardous Area, for example) the analytical performance should be identical.

Figure 1 shows our Prima BT laboratory magnetic sector MS capable of monitoring 16 gas streams, figure 2 shows our Prima PRO process magnetic sector MS capable of monitoring 64 gas streams.



Figure 1
Prima BT MS



Figure 2 Prima PRO Process MS

Benefits of Magnetic Sector Mass Spectrometry for Catalysis

Two main types of gas analysis mass spectrometers have been used for catalysis studies, with the magnetic sector MS providing greater stability and better precision than the quadrupole MS. Unlike the flat-topped peak generated by the magnetic sector, the quadrupole produces a Gaussian peak. So it is 'fault sensitive'—any drift in the mass scale will produce an error in the peak height measurement by measuring intensity on the shoulder of the peak rather than the peak maxima. This must be corrected for by more frequent calibration. Analysis by quadrupole can be useful for tracking reaction kinetics, but in many cases more precise quantitative analysis is required. Analysis of catalytic reactions provides another challenge for the more traditional, quadrupole-based mass spectrometers in that separation and differentiation of species with similar masses is difficult or impossible.

One particularly relevant example of this is Nitrogen and Carbon Monoxide, both are frequently present species in catalytic reactions, and both produce a molecular ion peak (N_2^+ , CO^+) at 28 atomic mass units (amu). Quantitative analysis therefore requires the analysis of a complex matrix of fragment peaks (e.g., C^+ at 12 amu, N^+ at 14 amu and

O+ at 16 amu). The fragmentation patterns produced by the magnetic sector analyzer are much more stable than those produced by the quadrupole, producing more stable, precise quantitative data. Typically, analytical precision is between 2 and 10 times better than a quadrupole analyzer, depending on the gases analyzed and complexity of the mixture. Other key advantages of magnetic sector analyzers include long intervals between calibrations and resistance to contamination. We produce both quadrupole and magnetic sector mass spectrometers; over thirty years of industrial experience have shown the magnetic sector analyzer offers the best performance for industrial online gas analysis. The magnetic sector analyzer used in both the Prima BT and the Prima PRO is shown in Figure 3.

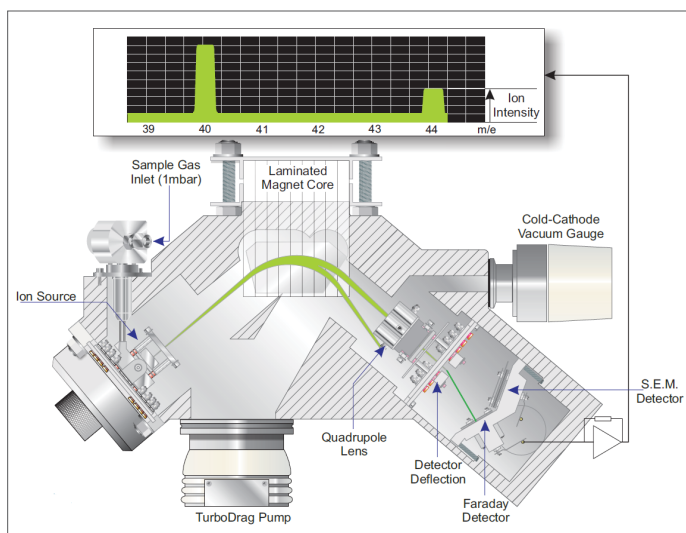


Figure 3 Magnetic sector analyzer used in Prima BT and Prima PRO

Rapid multistream sampling

If the MS is to monitor a series of reactor beds then a fast, reliable means of switching between streams is required. Solenoid valve manifolds have too much dead volume and rotary valves suffer from poor reliability, so we developed the unique RMS Rapid Multistream Sampler. It offers an unmatched combination of sampling speed and reliability and allows sample selection from 1 of 32 or 1 of 64 streams. Stream settling times are application dependent and completely user configurable. The RMS includes digital sample flow recording for every selected stream. This can be used to trigger an alarm if the sample flow drops, for example if a filter in the sample conditioning system becomes blocked.

Software

Thermo Scientific™ GasWorks™ software supports the analysis of an unlimited number of components per stream, and an unlimited number of user defined

calculations (Derived Values), such as Selectivity, and Carbon Balance. An unlimited number of analytical methods can be set up, so different analyses can be defined for different process streams. Serial Modbus and OPC are available for communicating with plant process control systems. Other protocols are available with the Prima PRO using optional protocol converters from serial Modbus.

Hydrogen

Hydrogen is seen by many as the medium of choice for energy storage. This is due to hydrogen possessing a very high energy content compared to its weight, and because it produces only water when combusted. However despite the ubiquitous nature of hydrogen, it is not naturally available as molecular hydrogen and must be chemically produced. Hydrogen can be produced using several methods and is a key component in several reactions for the creation of chemical feedstocks, including the ammonia process, methanol production and hydrogenation reactions. This prevalence of hydrogen poses a problem for the process control of catalytic reactions with quadrupole mass spectrometers. Quadrupole MS suffers from an effect known as 'zero blast', the RF amplitudes at low masses are too low to stop all ions from reaching the detector leading to a tail effect starting at 0 amu and extending as far as 4 amu. This noise from the zero blast, which is constantly changing, causes detection and resolution of the hydrogen peaks at mass 1 and 2 to be extremely difficult. The magnetic sector MS has a curved flight path for the ions, unlike the quadrupole which is straight. This means that it is impossible for ions to reach the detector when they should not, they must be bent by the magnet around to the detector. As a result of this, hydrogen resolution is superior on a Prima PRO or BT process mass spectrometer than on a quadrupole equivalent.

Performance specifications

We issue a guaranteed performance specification for Prima BT and Prima PRO based on an individual customer's specific stream details, with this performance being demonstrated during start-up by one of our trained engineers.

A set of typical performance specification for the Prima PRO on three very different process streams is shown in Table 1. This shows the 8-hour analysis precision (single standard deviation) based on an analysis time of 20 seconds including stream switching time. Thermo Scientific GasWorks software permits analysis optimization on a per-stream basis so we can select the most appropriate speed versus precision setting depending on process control requirements. Similarly, we can select the most efficient peak measurements for each stream and the most appropriate display units (% or ppm).

Table 1 Example of Prima PRO performance specification on three different gas streams.

Stream	Natural gas (Primary Reformer Feed)		Primary Reformer Effluent		Synthesis Gas	
Component	Typical Composition % mol	Precision (Std Dev) % mol	Typical Composition % mol	Precision (Std Dev) % mol	Typical Composition % mol	Precision (Std Dev) % mol
Hydrogen	0 ~ 1	0.002	65 ~ 70	0.03	65 ~ 75	0.02
Methane	80 ~ 95	0.02	9 ~ 13	0.01	3 ~ 10	0.01
Nitrogen	2 ~ 5	0.01	0.1 ~ 3	0.02	20 ~ 26	0.01
Ethane	1 ~ 5	0.005				0.0
Argon			0.1 ~ 0.5	0.001	0.1 ~ 5	0.002
Carbon monoxide			9 ~ 10	0.03	4.8	0.0
Carbon dioxide	1 ~ 3	0.005	9 ~ 12	0.01	0.0	0.0
Propane	1 ~ 3	0.005				
i-Butane	0 ~ 1	0.005				
n-Butane	0 ~ 1	0.005				
i-Pentane	0 ~ 0.5	0.005				
n-Pentane	0 ~ 0.5	0.005				
Helium					0.5 ~ 1	0.002
n-Butane	0 ~ 1	0.005				

Examples of catalyst development using MS

Catalyst for dry reforming of methane

In principle, dry reforming of methane offers several advantages over conventional steam reforming, e.g., it produces a CO/H₂ ratio of around 1, compared to around 0.33 for steam reforming., which is extremely useful in several downstream production processes, including ammonia, alcohols and acetaldehydes. However, catalysts used for dry reforming have suffered from a number of problems, including deactivation by build-up of carbon residue on the catalyst surface.

A Prima BT was by one of our customers to obtain a US patent for catalysts able to catalyse dry reforming of methane³. Figures 4 and 5 are taken from that patent application, they show one variant of catalyst being tested at 20 bar pressure and 800°C. Gas feed containing 45% CH₄, 45% CO₂, and 10% Ar was passed over the catalyst for around 950 hours without recalibrating the Prima BT. Figure 4 shows the close correlation between CH₄ and CO₂ conversion; over the first 500 hours it was noted that the catalyst lost around 30% of its activity. This was then regenerated by removing methane from the stream so that the stream was pure carbon dioxide for a period of 5 hours. The catalyst was seen to regenerate fully.

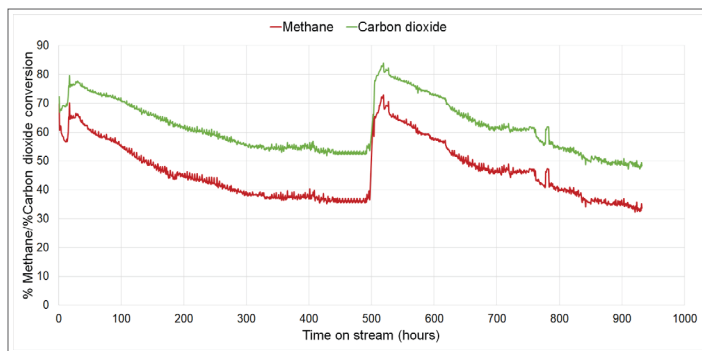


Figure 4 Methane and Carbon Dioxide conversion over 950 hours

Figure 5 shows a derived value outputted by the Prima BT, hydrogen to carbon monoxide ratio. This ratio also drops as the catalyst activity reduces.

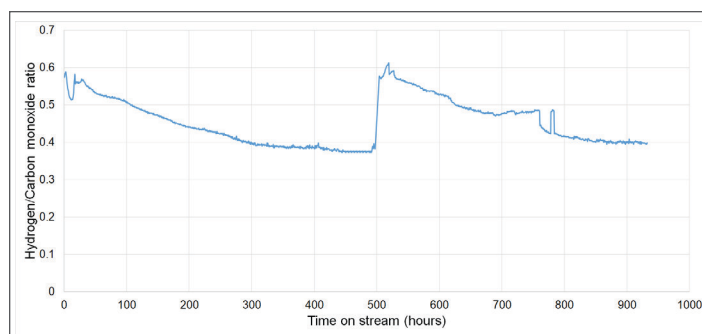


Figure 5 Hydrogen/Carbon monoxide ratio over 950 hours

The patent states that, by regenerating every 500 hours, or by using Fluid Catalytic Cracking (FCC) or moving bed technology, the catalyst can be used for high-pressure applications.

Production of synthesis gas by partial oxidation of methane

A Prima BT was used to evaluate catalysts for production of synthesis gas by partial oxidation of methane. The two temperature profile figures show the performance of two different catalysts undergoing the same reaction. They illustrate the need for fast analysis of complex mixtures when monitoring catalytic reactions—both these reactions span just eighty minutes.

The same reaction, starting with a cold reduced catalyst with a flow of methane and oxygen, is being carried out in both figures 6 and 7. Figure 6 shows a steady increase in CO₂ and water as total oxidation of some of the methane takes place. Above 800°C a ‘spark off’ is seen and the process switches to partial oxidation with syngas production. Figure 7 shows a completely different pathway with a much earlier transition to the desired partial oxidation reaction as a different catalyst is used. No complete combustion is seen, instead partial oxidation begins to occur at around 500°C with a steady increase in conversion up to 900°C.

Both figures illustrate the magnetic sector MS’s ability to analyze complex reaction mixtures containing compounds that produce overlapping spectral peaks, e.g., carbon dioxide contributing to the signal measured for carbon monoxide at mass 28, also its ability to analyze water with little or no visible tail on the water signals.

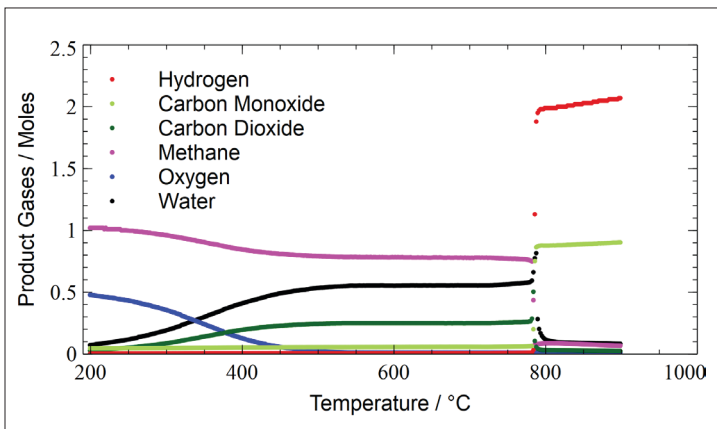


Figure 6 Temperature profile, catalyst A

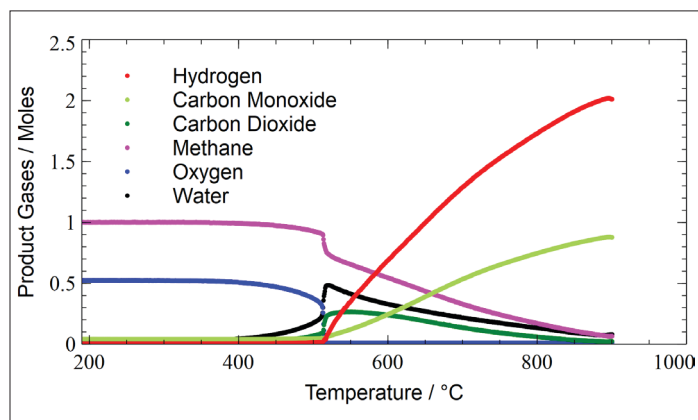


Figure 7 Temperature profile, catalyst B

Sulfur Analysis

Sulfur containing compounds are poisonous to many different catalysts. The sulfur compounds occupy active sites that are used to speed up the rate of the reaction, and as a result these sites are not available for the desired reaction pathway. This poisoning effect is observed when sulfur compounds are a little as ppm concentrations in the reaction mixture.

Our mass spectrometers can measure several sulfur compounds down to ppm levels; typical performance figures are shown in Table 2. Analysis time is less than 30 seconds, including stream switching time and standard deviations are measured over 8 hours. The Prima can be used to raise an alarm when the concentration of specified sulfur compounds increases above a set tolerance, this can be used to divert the sample away from the often-expensive catalyst to protect it from the poisoning effects.

Table 2 Analysis of ppm level sulfur compounds with Prima PRO

Component	Typical composition ppm	Precision of analysis by Prima PRO (single standard deviation) \leq
Hydrogen sulfide	3 ppm	0.5 ppm
Methyl mercaptan	10 ppm	0.5 ppm
Ethyl mercaptan	10 ppm	0.5 ppm
n-Propyl mercaptan	10 ppm	0.5 ppm
n-Butyl mercaptan	10 ppm	0.5 ppm

Summary

Magnetic sector mass spectrometers have demonstrated the highest levels of precision for catalyst studies by combining high speed with excellent stability, the magnetic sector analyzer lends itself ideally to this demanding application. Thermo Fisher Scientific's gas analysis MS product range, Prima BT and Prima PRO, provide fast and precise off-gas analysis through laboratory research, to pilot plant and to full scale production. Prima BT provides a bench-top solution for laboratory scale reactors, being configured with 15 sample and 6 calibration ports. Prima PRO is equipped to monitor 60+ reactors and is available for Zone 1 and Class 1 Division 2 hazardous area installation. The highly precise and complete gas composition measurements provided by both models are easily incorporated into the process control system.

Acknowledgements

Dr Lawrence D'Souza, Staff Scientist, SABIC Corporate Research and Innovation Centre, Thuwal, Saudi Arabia

Dr John Staniforth, Research Associate, Keele University Chemistry Dept., UK

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