

## TECHNICAL NOTE 1

## Applications of the Series 1500 Pulse Mass Analyzer in Catalyst Research

The essence of what a Series 1500 Pulse Mass Analyzer can do for researchers is to track temporary or permanent mass transfers from gaseous or vapor reactants to a porous catalyst flow-through bed. It can measure these mass changes in real time, with high mass and time resolution.

Until tapered element oscillating microbalance technology was applied to catalyst work, the mass transfer determination tools of the researcher were limited to volumetric or TGA methods. Most volumetric methods are indirect, non real time, require large samples, and are subject to many sources of error. TGA and hot microbalance methods are direct, but require very low gas flows, directed over a pile of catalyst rather than through a packed bed. In a TGA the percentage of the flow that actually contacts the bed is small and not accurately determined.

Volumetric methods and TGA methods can now be replaced with a direct reading, high flow, 100% contact method. Of particular interest are those processes which result in some portion of the reactants being retained in the bed as adsorbed gases, liquids, or solids. These particular experiments/studies in catalysis have as one of their major important variables a mass change:

- Coking/Deactivation
- Poisoning
- Characterization
- Competitive Adsorption
- Diffusion, Reaction and Adsorption Kinetics

## **COKING**

Coking is a major topic in contemporary catalyst research. Coking can be rapid and compensated by continuous regeneration, as in FCC catalysts, or slow and the subject of monthly or yearly maintenance, as in hydrotreating catalysts. The Pulse Mass Analyzer has both the short term mass resolution and long term stability needed to study these phenomena. Coking kinetics and the associated study of purging rates, conversion rates, regeneration rates, required temperatures, selectivity and yield can all benefit by knowing the mass changes of the catalyst bed very precisely in real time,

The usual method of determining coking by Leco test after an experimental run gives only the overall carbon retention due to all portions of the experiment. In order to get a picture of the rate of coking and how it varies with conditions, hundreds of identical experiments would have to be run, and each one interrupted at a different ending time. Even if the time were available, the variable end conditions of the truncated experiments would introduce errors.

One way of performing a coking experiment on an FCC catalyst with a PMA 1500 would be as follows:

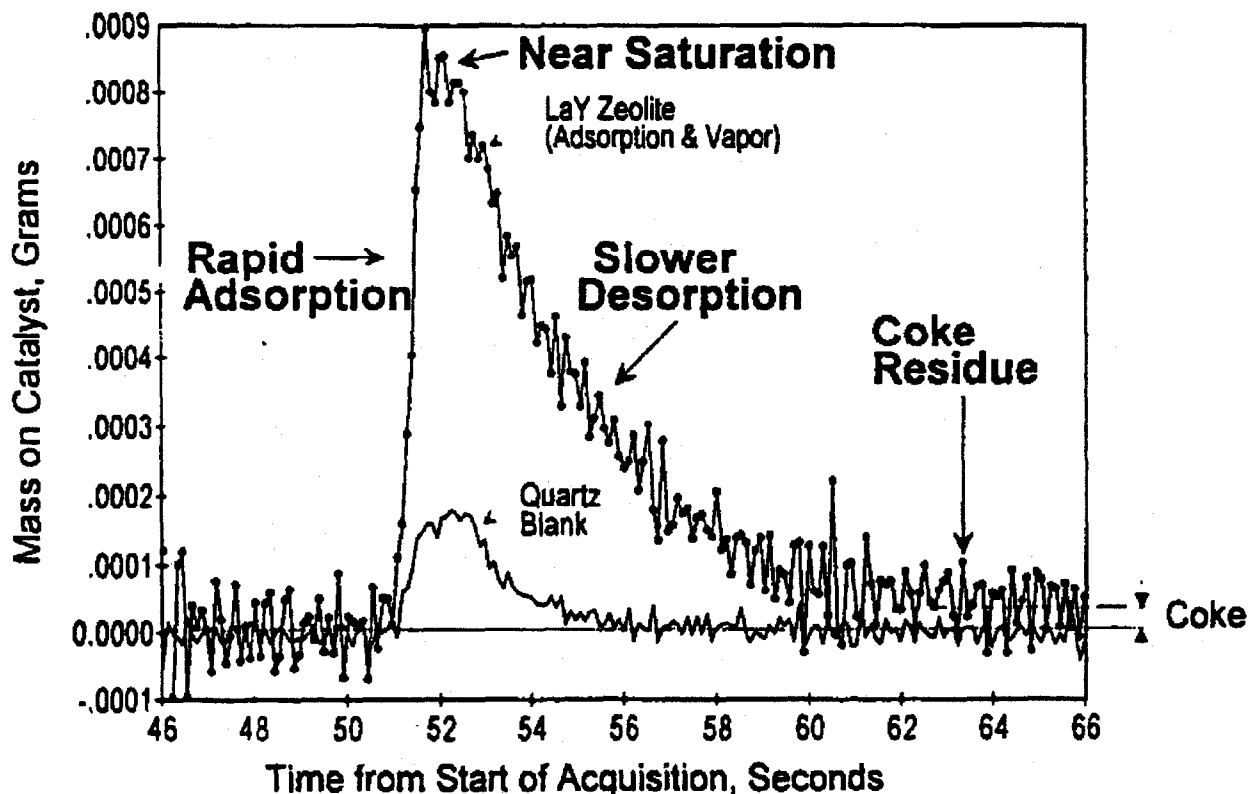
A measured pulse of heavy hydrocarbon vapor is inserted into an inert gas stream on a regular basis and sent to the catalyst bed. When the bed is fresh, the entire pulse mass will be seen to be adsorbed on the catalyst, reacted, and then most of it purged as product. The new information from the Series 1500 monitor after just a few pulses is dramatic. The rate of adsorption and the amount of adsorption can be found. The amount retained as residue can also be determined. The composition of the residue can be inferred by how much, if any, is lost before the next incoming pulse. Varying temperature will change some rates and total masses and not others, leading to good insights about both adsorption and desorption rates and reaction rates for both product and residue. Substituting an oxidizer gas stream for the inert gas/vapor pulse stream differentiates between metallic poison and carbonaceous coking residue. All of this occurs quickly, with high flow rates and quantitative results since 100% of each pulse interacts with the the catalyst bed. The experimenter can control the experiment while it is running, exploring variables at will in a browse mode, or holding variables at precise values long enough to get highly accurate data.

As the Pulse Mass Analyzer continues to operate in this mode, residue will continue to accumulate. Heating to a higher temperature would remove heavy product and restore activity but would not remove much carbon. This heating could be done with a product analyzer alone and show the same increases in activity, but only the Series 1500 monitor can tell you how much of the residue was there, how much was removed (by heating or oxidation), and then enable correlation of the quantity of deposit and removal with temperature, conversion, yield, selectivity, and efficiency changes:

Regeneration cycles that take into account temperature/time profiles and flow rates can now be formulated using the Pulse Mass Analyzer's deeper insight into the interaction of temperature and coking level with yield, selectivity, conversion, and efficiency. Cycles can be designed both to extend catalyst life and to minimize regeneration time. Once the cycles are formulated, the Series 1500 monitor can be used in a continuous flow mode as a superbly instrumented micro pilot plant. Using the temperature and valve sequence programming ability, one can test both the proposed use and regeneration cycles, specifying temperatures, gas compositions, gas flow rates, and step durations, with continuous coke monitoring. A continuous or spot-check product analyzer would be a valuable addition when running the Pulse Mass Analyzer as a micro pilot plant.

## Features of Transient Adsorption Trace

Cracking n-Decane over LaY Zeolite at 300°C,  
100 cc/min tie Carrier, 5 uL injection, 10 mg Zeolite



Data Courtesy of Dr. F. Hershkowitz,  
Exxon Research and Engineering Company

Studies of how temperature and pressure affect the retention of poison can be made, with real-time feedback of retention on a pulse-by-pulse basis. Long term tests with continuous reactant flow can take advantage of the monitor's automation and good long term stability to track slow accumulation of poisons out of actual process feedstock.

## **Poisoning**

Poisons and diffusion blockers can have similar effects on catalyst activity. Assigning cause to one or the other is an important first step in poisoning studies.

Poisons mask active sites or change the selectivity of the catalyst for particular reactants or reaction types. Diffusion blockers block access to particular activity centers or to entire passages of porous substrates. Poisons are usually metals or multiple bond light gas molecules. Diffusion blockers include carbon and the heavy products of the catalyst reaction itself.

The Series 1500 monitor can be used to determine the relative contributions of diffusion blockers and poisoning to a particular catalyst problem and explore possible solutions, or at least predict life based on feedstock composition.

To perform the measurements, a bed of catalyst is installed in the Pulse Mass Analyzer's sample holder, and then the catalyst is brought up to operating temperature and pressure in inert gas. Once conditions are established, a measured pulse of reactant gas is periodically inserted into the inert gas stream. When the bed is fresh, the entire pulse mass will be seen to be adsorbed on the catalyst and then some or all of it released as product. The first information from the Series 1500 monitor is how much of the pulse was adsorbed and how much residue was left behind.

As the instrument continues to operate in this mode, residue will continue to accumulate. This residue could be poison, carbon, or heavy product. Observing the rate of residue accumulation as well as changing rates of adsorption and desorption gives the first clues as to what is happening in the bed. Poisoning would be characterized by very small residue and small effects on adsorption and desorption rates, even though large conversion losses may occur (monitored by a gas analyzer).

To differentiate between poisoning and diffusion blocking, one would first increase the temperature. Heavy product residue will evaporate off with heating, leaving elemental carbon or poisoning as the culprit. Substituting an oxidizing gas for the inert gas would remove carbon at high temperature, but not metallic poisons. Such a treatment and the resulting mass and conversion data would show the relative contributions of poisoning, coking, and heavy product retention,

Once the problem is known to be poisoning and the amount has been quantified, poison spiked reactant gas can be introduced. The ability of the PMA 1500 sample bed holder to force 100% contact between reactant gas and catalyst makes quantitative work possible. The actual percentage of poison in feedstock retained can be calculated, as well as the effect of concentration on poisoning.

## **Diffusion, Reaction, and Adsorption Kinetics**

Choosing a catalyst requires the selection of a geometry for the carrier, as well as the selection of a chemical composition. The success of the choice depends in part on identifying which step or steps control the speed of the overall reaction and then optimizing the structure, geometry and chemical composition using that knowledge.

To perform this analysis, the Series 1500 monitor should be loaded with a trial catalyst and set up in pulse mode. A small quantity of reactive gas is periodically introduced into a flowing stream of inert carrier gas.

The basic steps in a catalytic reaction are well known but poorly understood. The first and last steps, diffusion into and out of the bed, are influenced only by the fluid dynamics of diffusion processes. These are physical processes, not chemical. The second and fourth steps, adsorption and desorption, deal with mass transfer at a surface. Only the middle step deals with an actual chemical reaction involving identifiable reactants and products. Up until now one could only study this five-step process by measuring the chemical composition of the input and output of the reactor bed. This could be likened to seeing only the footprints of an elephant. One knows it must be big and which way it was going, but footprints alone would be very tenuous information on which to base guesses about how healthy it is or how to take care of it. One could draw a finer analogy about feedstock and products, but let's leave that to the imagination, since the conclusion is the same: The easiest way to learn about an elephant is to weigh and measure the elephant itself.

Steps 2 and 4, adsorption and desorption, can be studied directly using the microgram and 0.1 second resolutions of the Pulse Mass Analyzer. A mass peak is produced as the catalyst adsorbs the reactant, reacts with it, and desorbs it. In cases in which steps 1 and 5 (diffusion) occur quickly, the leading and trailing edges of the mass peak show the rates of steps 2 and 4. Some manipulation of the pulse size and temperature might be necessary to obtain a full peak. If the peak mass is less than the total mass injected, then either the reaction step 3 is very fast (some desorption of product takes place while adsorption is still occurring) or some of the reactant passed through unchanged. Analysis of the products would tell which has occurred, and is necessary to get a complete picture. In general, step 3 is much more sensitive to temperature than steps 1, 2, 4, or 5, and this fact can be used to study the relative rates.

Steps 1 and 5 are sensitive to flow rate, so manipulation of the carrier gas flow rate while monitoring mass accumulation and product composition can sort out the speed of these steps. The same size reactive gas pulse in a faster stream of carrier gas has less time to diffuse into the inner pores of the catalyst granules. In a diffusion limited reaction, the mass peak decreases, and the portion of the reactant gas that passes through unchanged would increase with carrier gas flow rate. A reaction time limited reaction (step 3) would show the same mass peak over a wide range of carrier flow rates, and the portion of unreacted gas would be small and steady. Once again, both the pulse size and temperature may have

to be manipulated to obtain clear peaks and avoid the case in which slow diffusion is made up for by the pulse just traveling further into the bed. The pulse should be sized so that a large fraction of the available surface area is used, and a series of ever larger pulses can show this very graphically as mass peaks get bigger and bigger, eventually leveling off.

While the study of the relative speed of the five steps on a single carrier/catalyst combination is interesting, the real power of the Pulse Mass Analyzer is in comparing the performance of similar catalysts. Using conventional methods, only the overall conversion, yield, and efficiency could be determined, and only at the specific conditions used. The literature is full of warnings about the folly of assuming a one-to-one correspondence between lab reactor performance and pilot or production reaction performance.

Using the Series 1500 monitor, the researcher can know both which catalyst is best under laboratory conditions and many of the reasons why it is best. Flow and diffusion conditions in a production bed are quite different from those in an isothermal plug flow laboratory reactor. Some of the differences are known, and having rate information about some or all of the five critical steps can be effectively used to predict production reactor performance based on laboratory tests.

Once the relative speeds of the five critical steps are known, scaling up from laboratory to pilot, and from pilot to production, can be a safer and more predictable process.

## **Typical Associated Equipment for Complete Experimental Setups**

### Gas Preparation and Cleanup:

- Regulators
- Driers
  - Drier regenerators
- Molecular sieves
  - Molecular sieve regenerators
- Flow controllers
- Gas switching valves
- Sampling valves
- Simple TCD (thermal conductivity detector) for timing
- Hot well evaporator for liquid HC's
- Automated injector for liquids
- Pressure gauge

### Sample Preparation

- Balance to pre-weigh samples
- Weighing and loading utensils
  - Spare standard size tapered element in protective holders for quicker turn-around
- Custom tapered elements in protective holders with user-specified volume and shape sample cavities

### Downstream Equipment

- Backpressure regulator and/or pressure gauge
- Gas switching valves
- Flow dividers
- Heat tracing
- Sample valves
- Vacuum pump
- Gas analyzers
  - Gas chromatograph
  - Mass spectrometer
  - Combination GC/MS
  - FTIR
- Titration
- Flow Counter

### Software

- Curve fitting and scaling
- Spreadsheet and graphing