TPDRO 1100
Advanced Catalyst Characterization

For Temperature Programmed Desorption, Reduction, Oxidation and Chemisorption

Metal supported catalysts

Oil industry catalytic processes

Catalytic converters

Materials surface acidity

Catalytic combustion

Environmental catalysis

Analyze • Detect • Measure • Control™

Thermo
ELECTRON CORPORATION

TPDRO 1100
Advanced Catalyst Characterization
For Temperature Programmed Desorption, Reduction, Oxidation and Chemisorption

TPDRO 1100:
A technological breakthrough for advanced

Catalysts improve our everyday life and help to preserve the environment

Catalysts are ubiquitously used in modern industrial processes such as in petrochemical plants, pharmaceutical,fine chemistry and food industry. Catalysts are typically composed of an active phase (usually a noble metal or an acid/base site) that is deposited and dispersed on a porous support (i.e. alumina, silica, etc.). The active phase in a solid catalyst has high affinity for the molecules of given reactants.
The molecules are first chemisorbed onto the active surface before reacting between themselves. The catalysts activity, for a given reaction, is usually proportional to the number of surface active sites. As for metal supported catalysts, the active sites are constituted by the exposed metallic surface.
There are several well known analytical techniques permitting an evaluation of parameters such as metal specific surface area, the metal dispersion and the average metal aggregate size. One of the fastest and reliable technique is the pulse chemisorption in flow. Additional studies related to catalysts, provide the determination of the energies involved in the chemisorption and desorption processes of the reactants and products. The above parameters can be obtained in an automated way by means of the TPDRO 1100 using the available techniques of thermal programmed desorption (TPD), reduction (TPR), oxidation (TPO) and pulse chemisorption.

Catalysts characterization now made easier and faster with the innovative TPDRO 1100

The complete characterization sequence of an active solid generally consists of two separate phases: the pre-treatment and the analysis. Depending on the type of analysis required, the sample needs to be activated before the test. For instance, when performing temperature programmed desorption, the surface of the catalyst must first be rid of pre-adsorbed gas species on its surface and then saturated with a suitable reactive gas. The pre-treatment procedure is usually a very time consuming and a delicate process as all the analytical results are pre-treatment sensitive.
A sequence of different gases flows through the catalyst bed at different temperatures. Heating rates must be performed with high precision to ensure reliable results.
The TPDRO 1100 features a fully automatic pre-treatment sequence with an unlimited selection of procedures. The settings of the activation procedures are memorized in the dedicated software database, which can be readily recalled and applied on similar samples therefore simplifying the setup process.

Metal Supported Catalysts • Oil Industry Catalytic Processes • Catalytic Converters

The development of catalysts has contributed enormously to change our everyday life.

catalyst characterization

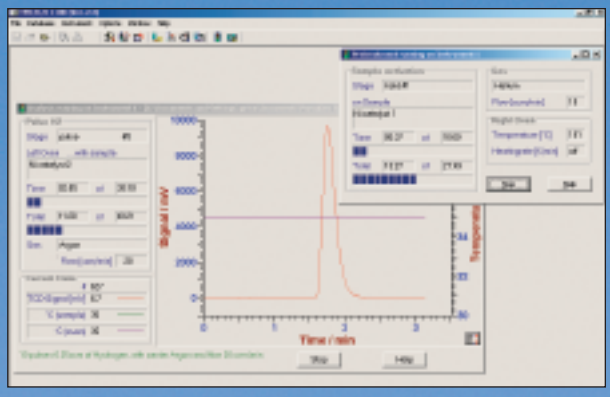
Catalyst activation and analysis: "parallel" is faster than "serial" !

Sometimes the pre-treatment procedure might lasts for hours, whereas the analyses are relatively short. Once the catalyst is activated for the analysis, it must not be exposed to any other reactive gases such as oxygen in the air, but should be kept under an inert gas. An innovative and proprietary reactor designed by Thermo Electron, circumvents this problem of sample exposure to atmospheric gases after the sample pretreatment step. The reactor can be closed and isolated from the environment after catalyst activation and the catalyst can be kept under an inert gas for subsequent operations. The user is able to transport the complete reactor along with the isolated and pretreated catalyst avoiding any risk of sample contamination prior to the analysis.

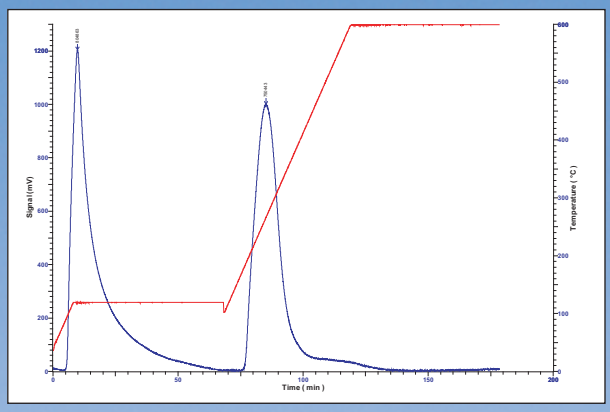
This important feature generates a number of additional possibilities:

- The catalyst activation can be performed in the TPDRO 1100 pre-treatment port or in another system (i.e. in a fume hood, inside a controlled environment, etc.)
- The TPDRO 1100 can simultaneously and independently perform the activation on a sample in the pre-treatment port and the analysis on another sample in the analysis port, saving valuable lab time and practically doubling the productivity

In addition to the above operations, TDPRO works sequentially, with no need to touch the reactor when moving from the pre-treatment to the analytical stage. The instrument will automatically perform the pre-treatment sequence of catalyst activation followed by the experiment, without any operator's intervention.



Simultaneous pre-treatment and analysis on two different catalysts



Unlimited automatic sequence of multiple preparation / analysis

parallel is faster than serial !

Key features of the TPDRO 1100

Precise gas control for high sensitivity detection	In the TPDRO the flow is regulated by a mass flow controller in a single gas line passing first to the TCD reference channel and then to the reactor and finally again to the TCD analytical channel. This configuration ensures that the flow is identical in both the TCD filaments, thus giving the ultimate in baseline stability and high sensitivity detection therefore more reliable results. Very low metal percentage catalysts can be tested easily, minimizing the sample load in the reactor and thus avoiding problems like re-adsorption and channelling effects.
Precise gas injection systems for pulse chemisorption	For calibration and pulse chemisorption, the probe gas can be injected into the reactor manually using a gas tight syringe or automatically through a high precision loop valve system. The loop selection can be as small as 0.15 cc and without "shutter" dead volume which is generating noise peaks in the baseline. Pulse gas can also be made of a low percentage mixture of a reactive gas in a suitable inert gas, thus permitting extremely small gas injections to test very low metal percentage catalysts.
Two independent ovens improve productivity	TPDRO features two separate and independent ovens. Both can be used independently for the sample activation (pre-treatment port) or the experiment (analysis port) up to 1100 °C. The ovens are anti-magnetic to avoid additional baseline noise when the carrier is polar. There is also a special fast cooling connection to compressed air to facilitate the cooling of the oven.
Temperature control both during the increase and decrease phases of the catalyst investigation	Oven temperature is raised linearly in a wide range of values. Rates of up to 40 °C/min is possible up to 750 °C or 20 °C/min up to 1100 °C extending the analytical performance especially in TPD experiments. In addition, a specially designed system permits to control the temperature rate also when decreasing the temperature. This allows detecting possible chemical reactions even during the sample cooling process.
Real sample temperature monitored continuously	A thermocouple is inserted into the special reactor directly over the sample or inside the catalyst bed. The probe is very thin, thus featuring a very fast response time to temperature variations. In addition, the sensor itself is protected by a quartz shield that avoids contact between the thermocouple and the reactive gases.
Additional analytical possibilities	Single point BET in flow analysis permits the "in-situ" evaluation of the total surface of the catalyst before and after the experiment, thus revealing immediately if morphological changes occurred to the sample during the course of the analysis.
External thermoregulation bath	The reactor can be fitted to a special recirculation bath for temperature control in the range of room temperature or even below zero degrees Celsius. The temperature can be precisely regulated by means of an external liquid circulation system during pulse chemisorption experiments.
Vapour generator optional kit	A number of organic vapours can be generated at constant temperature and injected quantitatively into the reactor, thus saturating the catalyst. The vapour can then be desorbed by TPD experiment.
Additional detectors for more comprehensive investigation of surface reactions	In sequence to the TCD detector, a suitable mass spectrometer can be connected to the TPDRO. The advantage is that the MS provides information of the gaseous species evolving from the catalyst, permitting, both a qualitative and quantitative determination

Special design reactor with built-in by-pass valve

A special reactor has been designed to insulate the catalyst from the enviroment after the activation. The unique reactor permits to prepare and measure simultaneously two catalysts, saving valuable lab time. In addition it is possible to prepare the catalyst in external preparation devices, especially when using dangerous or very corrosive gases for utmost safety of the operator. When the sample is ready, the sealed reactor can be transferred safely to the TPDRO for testing.

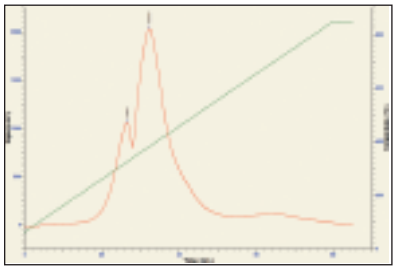
Materials Surface Acidity • Catalytic Combustion • Environmental Catalysis

Analytical techniques available on TPDRO 1100

Temperature programmed reduction and oxidation

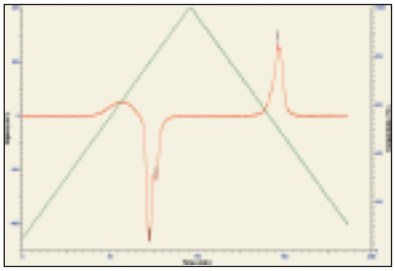
The objectives of this technique are essentially the following:

- To find the most efficient reduction/ oxidation conditions
- To identify the supported precursor phases and their interactions with the support
- To characterize complex systems, as bimetallic or doped catalyst, to determine the role of the second component and to establish alloy formation or promotion effects



TPR example on Co catalyst

In the TPR technique an oxidized catalyst is submitted to a programmed temperature increase, while a reducing gas mixture is passed over it (usually, hydrogen diluted in some inert gas as nitrogen or argon). In the TPO technique, the catalyst is in the reduced form and it is submitted to a programmed temperature increase, but in this case, an oxidizing mixture of gas (typically oxygen in helium) is passed over the sample.

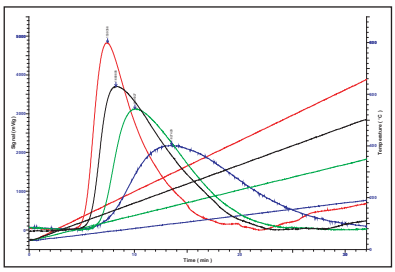


TPO example with temperature decrease control

Temperature programmed desorption

In the TPD studies the solid system is previously activated and then saturated with a probe reactive gas in isothermal conditions. During the temperature programmed desorption analysis, the sample is submitted to an increasing temperature at constant rate and it is swept by an inert gas such as helium, argon or nitrogen. The sample surface desorbs the gas that has been previously chemisorbed and the thermal conductivity detector monitors the process. The information produced by TPD experiments are related to:

- Energetic abundance of active sites
- Activation energy for desorption
- Free metal surface area

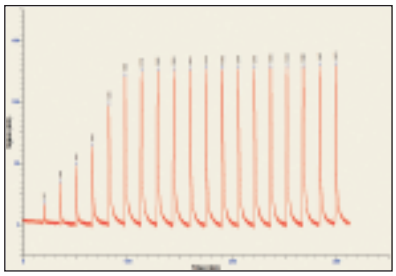


Ammonia TPD spectra at different temperature rates

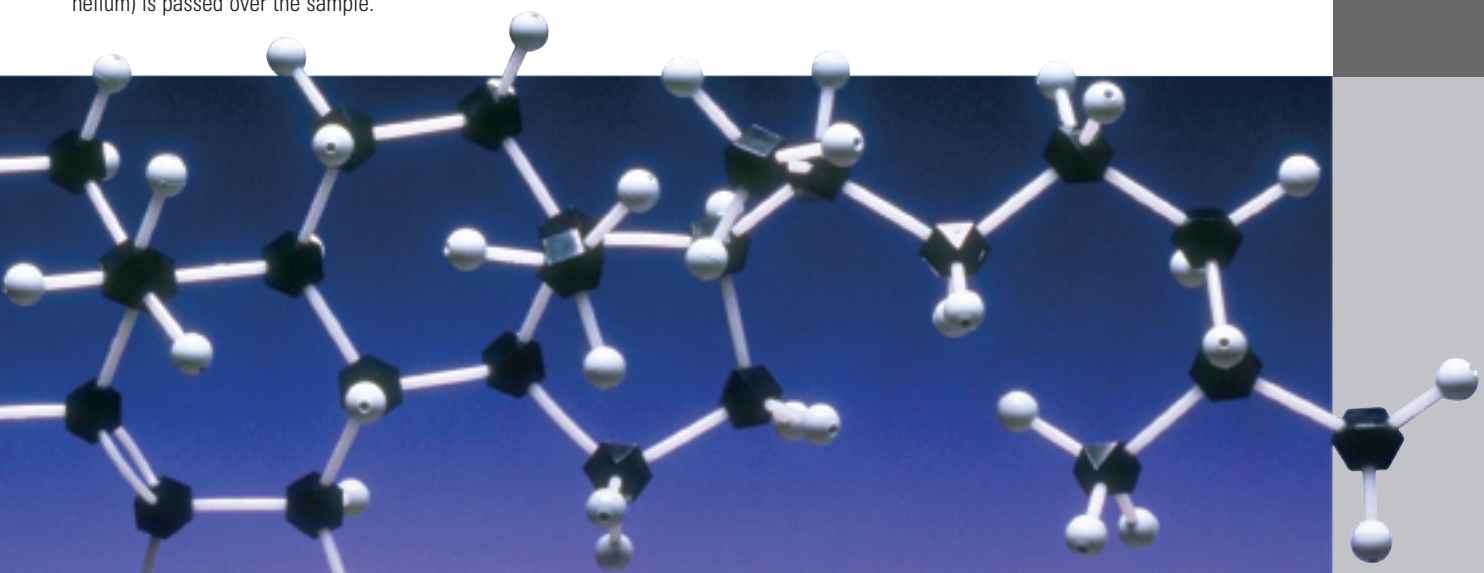
Example of hydrogen TPD

Pulse chemisorption in flow

The chemisorption analysis in a flow system is denoted Pulse Chemisorption. The gas to be chemisorbed is introduced as a pulse, via a calibrated loop valve, into the stream of the inert carrier gas flowing through the reactor and the sample. The catalyst is previously activated by an appropriate pre-treatment procedure and then submitted to chemisorption. The result is demonstrated like a series of peaks with increasing peak height. The software then automatically calculates the exposed metal area and metal dispersion.



Hydrogen 5% pulses on Pt catalyst



TPDRO for

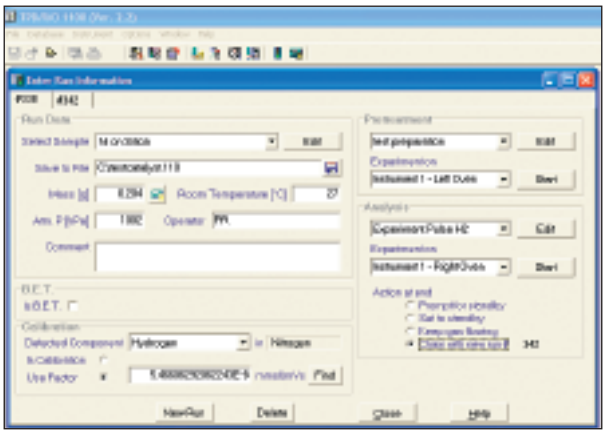
- Total chemisorbed / desorbed gas specific volume
- Metal specific surface area
- Metal dispersion percentage
- Peaks automatic or manual integration, integration limits, maximum peak temperature, etc.
- Calculation of metal percentage from TPR experiments
- Calculation of desorption activation energy from TPD
- Calculation of mass / metal percentage correction in multiple experiments
- TPR/TPO temperature/time profiles

Graphs

TCD signal (mV or mV/g), oven and sample temperatures versus time
TCD signal (mV or mV/g) versus oven or sample temperature
Plot of activation energy for desorption
Overlay of multiple experiments on a single graph with multiple calculations

Special design software

The software of TPDRO has been specifically designed to run the sample preparation and analyses automatically store data in real time, generate graphs, reports and calculations. All the operations required for processing the data are contained in the TPDRO software suite, like baseline subtraction, automatic peaks integration routine, tabular results, overlay of different experiments as well as printout of results. Reports can also be generated directly in the rtf format. The software is integrated with a number of databases containing all the essential information related to gases and gas-vapour mixtures, reactions, samples, metals, reaction stoichiometry, preparation and analytical methods.



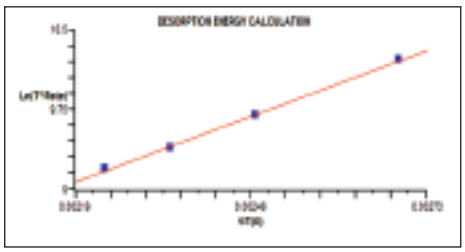
Desorption Energy Calculation from ammonia TPD

DESORPTION ENERGY CALCULATION

Sample: **32.63**

File	Pk	Rate (°C/min)	Peak T(°C)	1/T(K)	Ln(T_/Rate)
TpdNH3_20C.110	1	20	173	0.00224	9.2
TpdNH3_15C.110	1	15	153	0.00234	9.4
TpdNH3_10C.110	1	10	131	0.00247	9.7
TpdNH3_5C.110	1	5	98	0.00269	10.22

Gas constant (J/mol K):	8.314451
Correlation Factor:	0.9989
Slope:	2270.2316
Intercept:	4.0927
Energy of des.(Kj/mol):	18.8757
Arrhenius prefactor:	37.898



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