Advanced techniques for characterization of heterogeneous catalysts

(4 credits/sp/op/Bologna)

Main lecturer:
Prof. Andrey Simakov
Centro de Nanociencias y Nanotecnologia
Universidad Nacional Autonoma de Mexico

Lecturers:
Prof. Tapio Salmi, Åbo Akademi
Prof. Dmitry Murzin, Åbo Akademi

Monday, 26.05
9.15 Opening remarks
The scope of the course.

*In situ* and *operando* spectroscopic techniques for characterization of heterogeneous catalysts.

Non-steady-state kinetic methods for heterogeneous catalysts characterization.

Concept of transient analysis. Main definitions.
Tuesday, 27.05
9.15 Transient analysis of catalytic reactions including \textit{in situ} and \textit{operando} spectroscopic measurements.

Wednesday, 28.05
9.15 Transient analysis of catalytic reactions using isotopes.

Applications of Temporal analysis of products (TAP) in analysis of catalytic reaction mechanisms.

Thursday, 29.05
9.15 Transient analysis of three-phase catalytic reactions.
Numerical aspects.
**The scope of the course**

**Non-steady-state** and **in situ** and **operando** experiments provide kinetic and spectroscopic information that is critical for

- comparison of non-steady-state performance of different catalysts,
- development of a dynamic kinetic model of catalytic transformations,
- design of efficient catalytic reactors particular those that work under non-steady-state conditions.

The goal of this course is to improve your skill in the application of these advanced methods for analysis of heterogeneous catalytic reactions and design new effective heterogeneous catalysts.

**Advanced techniques for characterization of heterogeneous catalysts. Part 1**

**In situ** and **operando** spectroscopic techniques for characterization of heterogeneous catalysts

*Advanced techniques for characterization of heterogeneous catalysts. Part 1*
In the beginning were steady-state kinetic experiments the generally applied experimental method, but nowadays the frontiers are the different kinds of surface spectroscopy with atomic scale resolution.

Catalysis, like other branches of chemistry, developed in its own way:

the phenomenological perception understanding of the processes on molecular level

In situ and operando spectroscopic techniques for characterization of heterogeneous catalysts. Part 1

Advanced techniques for characterization of heterogeneous catalysts. Part 1

Fundamental structure–activity/selectivity relationships are critical for the development of knowledge-based design of new and novel catalytic materials for different applications.

True fundamental understanding of the structure–activity/selectivity relationship requires molecular level characterization of catalytic materials under realistic catalytic operation conditions.
The term in situ spectroscopy is well established and widely used in the catalysis literature.

Etymologically, the term *in situ* has no temporal discrimination.

It is possible to describe several different types of *in situ studies*:

(a) *In situ* describes the collection of spectra of a catalytic sample in the same environment were it has been treated or pretreated and the temperature may no longer be that of the pretreatment.
b) Variable-programmed "in situ" spectra describes the spectra monitor the transformations occurring versus a variable.

Variable-programmed in situ studies may follow the materials under many conditions relevant to catalysis (pressure, temperature, reactant concentration, etc.).

c) "Reaction in situ" refers to in situ spectroscopic measurement under reaction conditions relevant to catalytic operation. Many in situ reactor cell designs may not be appropriate for true catalytic reaction kinetic studies because of complications from gas phase reaction due to large void volumes or heat and mass transfer gradients.

However, many IN SITU reactor cell designs may not be appropriate for TRUE catalytic reaction kinetic studies due to large void volumes or heat and mass transfer gradients.
After nearly 60 years of intensive application, infrared spectroscopy (IR) remains the most widely used, and usually most effective, spectroscopic method for characterization of surface chemistry of heterogeneous catalysts.

The IR cell in which the catalyst sample is pre-treated and subsequently studied is extremely important in surface studies.

The one of the first in situ cells for IR studies published in scientific literature was:


In order to reveal the relative strength of bonding for the chemisorbed CO contributing to each band or the effect of interaction on the band positions the spectra of chemisorbed CO were studied as a function of surface coverage over silica-supported Pt, Pd and Ni.

The authors wrote: "In order to carry out this work efficiently it was necessary to design apparatus in which the IR spectra could be obtained while the samples were subjected to a wide range of temperatures and pressures. Successful development of this in situ apparatus not only makes it possible to study the effect of surface coverage but also opens the way to IR studies of chemisorbed molecules while reactions are in progress".
The perfect, all-purpose cell has yet to be devised, and cell design is normally chosen to suit the purposes of a particular study.

In catalytic research very often "home-made" IR cell reactors are used for the particular in situ studies.

Peri and Hannan [J.B. Peri, R.B. Hannan, J. Phys. Chem., 64 (1962) 1526] designed an quartz IR cell for the determination of the surface hydroxyl groups on γ-alumina
Ryason [P.R. Ryason, Rev. Sci. Instrum., 44 (1973) 772] has described a stainless steel quartz cell for IR transmission spectroscopy of catalyst wafers.

Examples of IN SITU cells

Design of the high temperature IR cell for transient experiments

Set-up was designed for study of Heat of Adsorption of Carbon Monoxide on a Pt/Rh/CeO₂/Al₂O₃ Three-Way Catalyst at High Temperatures, JC, 179, 1996, 503

Examples of IN SITU cells

Advanced techniques for characterization of heterogeneous catalysts. Part 1

Home made FTIR cell for fast transients

In order to observe fast surface transients, it is required that the reactor has a low dead volume, and a reactor was constructed with this as a major design criterion.

A cylindrical, CaF₂ rod (A) slides through internal O-rings located on both halves. A sample pellet is held between the CaF₂ rods when the two halves are bolted together. Gas flows into and out of the cell through small holes (B) and is contained within the volume sealed by the O-ring (C). Chilling fluid is circulated through ports in the body of both halves (D).

The reactor volume surrounding the wafer is theoretically <0.05 cm³!!
Commercial In-Situ High-Low Pressure Infrared Reactor from IN-SITU-Research Instruments

Size o.d. 4", height 3.75"  
**Operating Pressures** 10-5 torr - 15 atm

Material  
Stainless Steel Windows CaF2 or any other standard IR transparent material

Catalyst Sample  
Size 2 cm o.d., typically 80 mg of solid

Temperature Control/Measurement  
One mini-thermocouple for reactor body temp control and one for sample surface measurement

Flow Pattern:  
Gases are flown parallel on both sides of the wafer Gaskets Viton O-rings

Commercial Reaction Chamber from Harrick Scientific for DRIFT analysis

The Low Temperature Reaction Chamber, CHC-CHA, is designed for operation from -150°C to 600°C under vacuum.

In addition to the heater incorporated in the sample stage, the CHC also features a cooling conduit connected to a dewar.
c) “Operando” methodology describes “in situ” spectra under true catalytic operation as determined by simultaneous online activity/selectivity measurements.

Operando spectroscopic methodology has just recently been introduced into the catalysis literature in 2002. This technique combines simultaneous in situ spectroscopy and kinetic measurements on the same sample and time.

Operando is borrowed from Latin, which means “working” or “operating” since the spectra are of an “operating” catalyst, whereas, “in situ” means “on site”.

Advanced techniques for characterization of heterogeneous catalysts. Part 1
Some historical remarks

- The first Operando Congress was celebrated in Lunteren, Netherlands, 2–6 March 2003.

- The Second Operando Congress was celebrated in Toledo, Spain, 23–27 April 2006.

- The Next Operando Congress will be celebrated in 2009.

Later we’ll consider

- An overview of the different multiple technique operando set-ups currently available for obtaining combined spectroscopic and catalytic information on heterogeneous catalytic systems.

- Also some difficulties, which can be encountered during the development of these set-ups, will be mentioned.

- In a third part, it will be shown that there are, besides obtaining complementary information on the same catalyst system under identical reaction conditions, additional advantages for combining spectroscopic techniques.
**Operando ESR cell** developed in the group of Brückner (Berlin, Germany)

- It has been used to study for instance the behavior of
  - vanadium phosphate catalysts during the oxidation of \( n \)-butane,
  - the dehydrogenation of alkanes over supported chromium oxide catalysts
  - and the selective catalytic reduction of NOx over supported manganese oxide catalysts.

The operando ESR set-up probes paramagnetic transition metal ions or organic radicals present in the working catalytic solid.

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**Examples of Operando set-ups**

Each characterization technique allows obtaining additional information about the catalytic system positioned in the reactor tube.

The adding additional spectroscopic techniques is most valuable if they provide complementary information!!!

So, identical pieces would not display the whole picture of the catalytic problem and would not enable us to discriminate between active species (cyclists) and spectator species.
Combining operando techniques in one spectroscopic-reaction cell: New opportunities for elucidating the active site and related reaction mechanism in catalysis

It would be more advantageous to look on catalytic systems from different perspectives by making use of multiple characterization techniques.
Examples of Operando set-ups

An operando UV–vis/Raman/ED-XAFS set-up

for measuring supported metal oxide catalysts operating in gas-phase reactions at elevated temperatures and ambient pressures.

Detailed outline of the capillary reaction-spectroscopy cell for simultaneously measuring Raman/UV–vis (reflectance mode) and energy dispersive XAFS (transition mode), together with illustrative pictures

Utrecht University, The Netherlands

Advanced techniques for characterization of heterogeneous catalysts. Part 1

The setup for parallel operando EPR/UV–vis/Raman measurements

Built in the Institut für Angewandte Chemie Berlin, Germany

Advanced techniques for characterization of heterogeneous catalysts. Part 1
Overview of operando set-ups making use of multiple spectroscopic characterization techniques

Existing combinations of techniques for studying heterogeneous catalysts at work:

<table>
<thead>
<tr>
<th>Techniques combined</th>
<th>Application domain</th>
<th>Time resolution (s)</th>
<th>Information to be obtained</th>
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<tbody>
<tr>
<td>XRD</td>
<td>Heterogeneous catalyst</td>
<td>XRD: 30</td>
<td>XRD: long-range structural order</td>
</tr>
<tr>
<td>XAFS</td>
<td>XAFS: 90-30</td>
<td>XAFS: short-range structural order</td>
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</tr>
<tr>
<td>EPR</td>
<td>Heterogeneous catalyst</td>
<td>EPR: 60-300</td>
<td>EPR: paramagnetic transition metal ions</td>
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<tr>
<td>UV−vis</td>
<td>UV−vis: 0.01-1</td>
<td>UV−vis: electronic d-d and charge transfer transitions of transition metal ions</td>
<td></td>
</tr>
<tr>
<td>Raman</td>
<td>Raman: 2-120</td>
<td>Raman: vibrational spectra of metal oxides and organic deposits, such as coke</td>
<td></td>
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<tr>
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<td>UV−vis: 0.01-1</td>
<td>UV−vis: electronic d-d and charge transfer transitions of transition metal oxides</td>
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Advanced techniques for characterization of heterogeneous catalysts. Part 1
Overview of \textit{operando} set-ups making use of multiple spectroscopic characterization techniques

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<td>FT-IR</td>
<td>Heterogeneous catalysis</td>
<td>FT-IR: 0.00-1</td>
<td>FT-IR: vibrational spectra of reaction mixtures and adsorbed molecules</td>
</tr>
<tr>
<td>UV-vis</td>
<td></td>
<td>UV-vis: 0.01-1</td>
<td>UV-vis: electronic transitions of the catalyst material</td>
</tr>
<tr>
<td>EPR</td>
<td>Heterogeneous catalysis</td>
<td>EPR: 60–300</td>
<td>EPR: paramagnetic transition metal ions</td>
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<td>Heterogeneous catalysis</td>
<td>UV-vis: 0.05-1</td>
<td>UV-vis: electronic d–d and charge transfer transitions of transition metal oxides</td>
</tr>
<tr>
<td>Raman</td>
<td></td>
<td>Raman: 0.05–1</td>
<td>Raman: vibrational spectra of metal oxides and organic deposits, such as coke</td>
</tr>
<tr>
<td>ED-XAFS</td>
<td></td>
<td>XAFS: 0.003–1</td>
<td>XAFS: coordination environment and oxidation state of metals and metal ions</td>
</tr>
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Advanced techniques for characterization of heterogeneous catalysts. Part 1

Some remarks

The first \textit{operando} techniques combined in one set-up and reported in the open literature were X-ray diffraction (XRD) and X-ray absorption spectroscopy (EXAFS). XRD provides \textit{long-range ordering} information of the catalytic solid under investigation, whereas EXAFS is sensitive to the \textit{short-range ordering} of the materials under study.

Most combinations involve the use of vibrational (IR as well as Raman) and electronic (UV–vis) \textit{spectroscopies}.

In the case of \textit{magnetic resonance techniques} (NMR and EPR) more technical hurdles have to be taken to make the combined \textit{operando} set-up working.
Concluding remarks

The coupling approach in which two or more spectroscopic techniques are combined in one spectroscopic-reaction cell seems to be very powerful for elucidating the chemistry of catalyst materials, the mechanism of a catalytic reaction and the identification of active sites in heterogeneous catalysts.

This approach looks at first sight simple, but a lot of experimental hurdles have to be taken before a successful set-up can be applied to a particular catalytic problem. As an example the high intensity radiation, such as synchrotron sources for measuring XAFS data, may affect the catalytic process under investigation. By using a second technique, it is possible to evaluate the effect of such intense light sources on the investigated system.

Evaluation of the still limited amount of literature reveals that there are - roughly speaking - two types of research groups working in the field of operando spectroscopy

1. **On one hand**, there are people focusing on the inorganic part of the catalyst material. More in particular, these researchers make use of techniques, such as operando UV–vis and EPR spectroscopies, to test the oxidation state of a particular supported transition metal ion.

2. **On the other hand**, there are scientists putting more emphasis on the organic part of a catalytic reaction. These research groups use e.g. operando NMR and IR spectroscopies.
Concluding remarks

Finally, other fields of catalysis are still hardly explored. An example of an under developed area of research is the study of heterogeneous catalysts operating in the liquid phase. Only a limited number of studies report on the use of operando spectroscopy on catalytic solids in the liquid phase.

Perhaps, that the coupling of IR-ATR, in combination with other operando techniques, opens new avenues to gather detailed insight in these important catalytic processes.

Non-steady-state kinetic methods for heterogeneous catalysts characterization
Determination of intrinsic reaction kinetics of catalyzed reactions is of importance in the safe and economical design and control of industrial chemical and environmental processes, and in the development of new and improved catalysts.

Several criteria may be used to test the validity of the data for kinetic evaluation.

The classical approach is to perform steady-state kinetic measurements while obeying all these rules and guidelines and changing the experimental settings of temperature, pressure or concentration, composition, space time, etc. one by one, until the whole experimental space has been covered.

This activity is still time and money consuming, although the application of high-throughput methods developed in the last decades has reduced the amount of time and money involved by means of parallelization.
Steady-state experiments give valuable information about the overall rates of catalytic reactions, but they cannot reveal the underlying reaction mechanisms in an unequivocal way, because different reaction mechanisms give steady-state rate equations, which do not differ very much from each other.

Thus, the experimentally recorded kinetic data can typically be fitted to several kinetic equations and the true nature of the underlying catalytic surface reaction mechanism remains unknown.

However, interaction of the reaction medium with the catalyst sometime results in a reconstruction of the catalyst surface.

Reconstruction of Pt(110) surface due to CO adsorption

Where the driving force for reconstruction of clean surfaces is minimization of the surface energy.
Changes in the catalyst activity could be not only due to changes in

- the surfaces,
- but also changes in the phase composition of the catalyst and changes
- in the bulk composition.
Sometimes it could be even beneficial to perform a reaction under such conditions, periodically changing initial parameters of the reaction system, e.g. temperature, pressure, concentrations, or flow velocity. Like in case of $\text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3$.

Under nonstationary conditions two types of processes could operate.

- The concentrations of intermediates in the catalytic cycles are at non steady and such changes are due to the *intrinsic reaction mechanism*.
- The changes in the rate constants of some elementary steps are associated with the *side reactions*, not catalytic cycles.

So, the non stationary behavior is associated with the rate of the chemical reaction while the relaxation time of side processes could be higher than the relaxation time of the reaction itself.
The application of unsteady-state techniques has already been known for decades [M. Kobayashi, Chem. Eng. Sci. 37 (1982) 393–401].

As an example, in chemical engineering, tracer techniques have been used to characterize reactor systems by residence times and their distributions.

The basic ideas of the transient method applied to heterogeneous catalysis were set forth by K. Tamaru.

In general, the term "transient" refers to changing one or more of the system parameters. In transient kinetic studies, a dynamic change is introduced into a reactor system, and the response of a reaction quantity is observed.
In catalysis research the temporal response of the reaction system is followed upon an imposed change in a reaction variables:

- temperature,
- flow,
- concentration,
- labeled components

Three elements need to be considered, a 'stimulus', a reaction system and an analysis system to follow the time dependent 'response' or 'relaxation' of the system.

### Stimuli

Three main stimuli are distinguished:

- a step function,
- a pulse,
- a time dependent function.
The step function is most well known as it marks the start of a reaction in batch operation after the injection of reactant(s), of the catalyst, a rapid temperature or pressure increase, or in continuous operation a change in flow rate.

Reactant flow; Temperature; Pressure

The pulse injection, well-known from chromatography, may be the injection of a reactant in an inert flow through a reactor or of a labeled compound in a reacting environment.
The time dependent functions comprise linear or periodical programmed changes. In most cases the temperature (temperature programming techniques) or concentration is varied.

**Stimuli**

**Temperature, Concentration**

See TPD simulation

Responses

Depending on the rate of change of the variable that is used to detect the response of the reaction system upon the stimulus, a suitable analysis technique should be chosen.

Mass spectrometry (MS) is generally preferred for labeled components and/or rapid changes, but it cannot discriminate between isomers.

Gas chromatography (GC) is an attractive option, and especially the modern miniaturized fast systems with analyses on the tens of seconds scale.

The spectroscopy (IR, Raman, UV–vis, etc) is a good alternative since nowadays it may yield (nearly) continuous data, like a thermal conductivity detector (TCD) does.

The catalyst can be studied also by different techniques to be presented later in the second lecture.
Reaction system—operation

Transient techniques can be applied under unsteady-state as well as steady-state operation of the catalytic reaction system.

**Steady-state operation** applies if the reacting system is not disturbed by the stimulus (when isotopically labeled species is introduced into the system. This technique is called **Steady-State Isotopic Transient Kinetic Analysis (SSITKA)** and applies to continuous flow operation. The total concentrations of reactants and products and the adsorbed intermediates do not change, only their isotopic composition does).

**Transient operation occurs** when the operational variables change in time and the catalyst experiences different conditions like upon a step change or pulse injection of a reactant.

Examples of reactant and product responses for a typical step-response experiment and an irreversible reaction with adsorption.

![Graph showing concentration change over time during transient operation](image)
An example

An irreversible reaction $A \rightarrow B$ takes place with competitive adsorption.

At $t_1$ the feed concentration is stepped up and at $t_2$ it is stepped down. Curve I represents the blank reactor response without catalyst, while II and III are the concentrations of $A$ and $B$ in the reactor outlet with catalyst.

The difference curve for the step up, the blank response minus the reactive response, represents the 'missing' concentration in the reactor outlet.

The two areas under the indicated difference curves equal the total amount of $A$ and $B$ present on the catalyst, so in principle from both stimuli this information can be collected. It depends on the response which of the two is more accurate. A too fast concentration increase or a too tailing decay may hamper the correct determination.

Example of transients for CO+O$_2$ over oxidized Au-CeO$_2$ catalyst
Non-steady-state kinetic methods for heterogeneous catalysts characterization

Example of transients for CO+O₂ over prereduced Au-CeO₂ catalyst

**Example of transients for CO+O₂ over prereduced Au-CeO₂ catalyst**

- Adsorption of O₂
- Reaction of CO with formed oxygen species

**Advanced techniques for characterization of heterogeneous catalysts. Part 1**


- Instantaneous: a) Surface reaction
  b) Adsorption
- Monotonic: c) Desorption
  or combination of a) and c); b) and c)
- Overshoot response: d) Regeneration of active surface species
  e) Competitive adsorption of reaction components
- S-shape response: h) Presence of some stable intermediates

**Advanced techniques for characterization of heterogeneous catalysts. Part 1**
Non-steady-state kinetic methods for heterogeneous catalysts characterization

Typical flow scheme of an experimental set-up for transient experiments

The four-way valve is used to switch between two flow lines, e.g. between inert and reaction mixture (situation drawn here) or between reaction mixtures of which one contains a labeled component.

Characteristics of most commonly used reactor systems for transient investigations in heterogeneous catalysis

(Semi-)batch reactor

<table>
<thead>
<tr>
<th>Application</th>
<th>Mostly liquid–solid, gas–liquid–solid (slurry, fixed bed)</th>
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<tbody>
<tr>
<td>Pressure</td>
<td>Atmospheric to high pressures (gas: semi-batch)</td>
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<tr>
<td>Analysis</td>
<td>GC (discrete points)</td>
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<tr>
<td></td>
<td>DSC, gas supply rate (continuous)</td>
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<tr>
<td></td>
<td>New developments: IR and Raman spectroscopy</td>
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<tr>
<td>Information</td>
<td>Concentration versus time—several runs needed for kinetics</td>
</tr>
<tr>
<td></td>
<td>Low time resolution: minutes</td>
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<td></td>
<td>Many data points composition</td>
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<td></td>
<td>Deactivation not noticed, multiple runs needed with same sample</td>
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</tbody>
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Non-steady-state kinetic methods for heterogeneous catalysts characterization

Characteristics of most commonly used reactor systems for transient investigations in heterogeneous catalysis

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<th>Fixed-bed tubular reactor</th>
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<tr>
<td><strong>Application</strong></td>
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<tr>
<td><strong>Pressure</strong></td>
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<td><strong>Techniques</strong></td>
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<tr>
<td><strong>Transient</strong></td>
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<tr>
<td><strong>Steady state</strong></td>
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<td><strong>Information</strong></td>
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<td><strong>Analysis</strong></td>
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Advanced techniques for characterization of heterogeneous catalysts. Part 1

Transient state methods have applications in:
- reactor modeling,
- optimization
- control.

By measuring the concentrations as a function of time at the catalytic reactor outlet qualitative conclusions concerning the surface reaction mechanisms can be drawn and the kinetic parameters included in the rate equations for the surface reaction steps can be estimated from the data by using non-linear regression analysis.

Transient techniques have been recognized as useful tools for studying the mechanisms of heterogeneous catalysis. They give more information about the surface reaction mechanism than is deducible from an equivalent number of stationary measurements and they are useful, especially for preliminary screening to definitely limit the number of possible mechanisms that are selected for a further evaluation.

Later we’ll consider examples of combinations of several transient techniques with spectroscopic measurements IN SITU and OPERANDO, as well as, application of isotopes and TAP reactor.