Graduate School of Materials Research (GSMR)
Graduate School in Chemical Engineering (GSCE)
Department of Chemical Engineering (ÅA)

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

Program

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 *in situ* and *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.

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

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

the phenomenological perception → **understanding of the processes on molecular level**

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.**

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**.

Etymology

IN SITU

The term in situ spectroscopy is well established and widely used in the catalysis literature.

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

In situ

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.

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

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.).

---

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

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:

R.P. Eischens, S.A. Francis and W.A. Pliskin, *J. Phys. Chem.*, 60 (**1956**) 194.

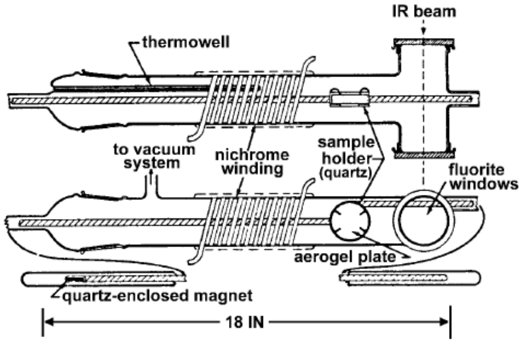
In order to reveal the relative strength of bonding for the chemisorbed CO contributing to each band or the effect of interaction on the band positions the spectra of **chemisorbed CO were studied as a function of surface coverage over silica-supported Pt, Pd and Ni**.

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.

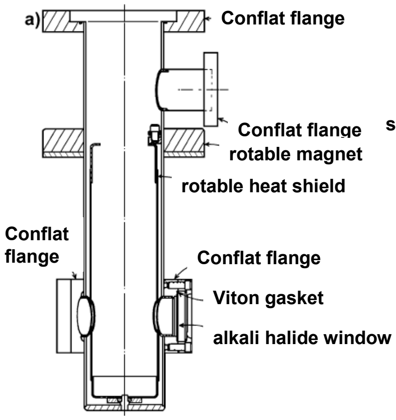
In catalytic research very often **"home-made"** IR cell reactors are used for the particular ***in situ*** studies.

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**

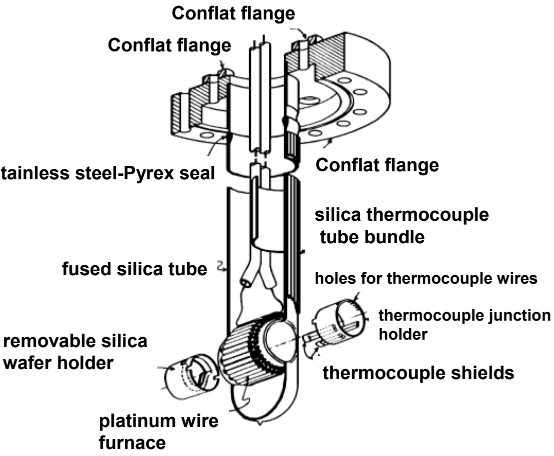


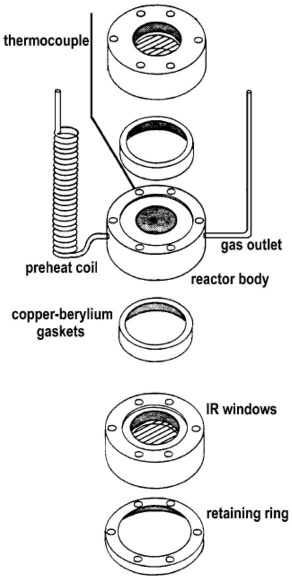
Ryason [P.R. Ryason, *Rev. Sci. Instrum.*, 44 (1973) 772.] has described a stainless **steel quartz cell** for IR transmission spectroscopy of catalyst wafers

cross section of infrared cell



cell insert

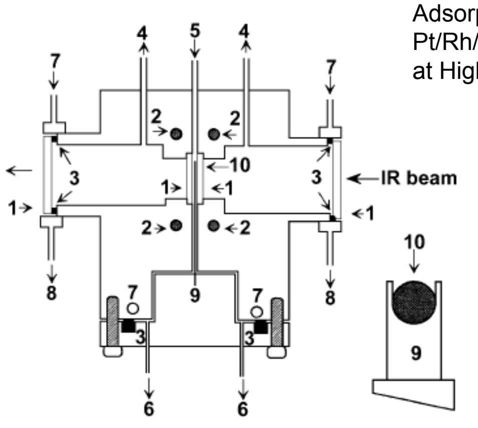




Prokopowicz *et al*. [R.A. Prokopowicz, P.L. Silveston, F.L. Baudais, D.E. Irish, R.R. Hudgins, *Appl. Spectrosc.*, **42** (1988) 385] have presented a design of a transmission IR cell for the high-temperature study of **transient adsorption and reaction in a flow system**

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/CeO_2/Al_2O_3 Three-Way Catalyst at High Temperatures, JC,179,1998,503

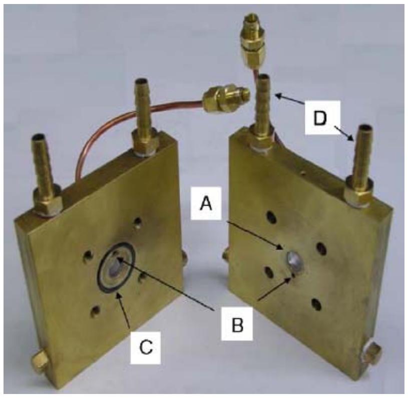


body of the cell sample holder

1 – CaF_2 windows,
2 – catridge heaters,
3 – Viton O-rings,
4 – vacuum line,
5 – gas inlet,
6 – gas outlet,
7-8 – cooling water inlet-outlet,
9 – sample holder,
10 – disk of catalyst

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.

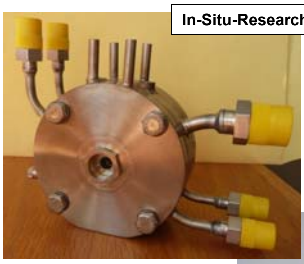


A cylindrical, CaF_2 rod (A) slides through internal O-rings located on both halves. A sample pellet is held between the CaF_2 rods when the two halves are bolted together. Gas flows into and out of the cell through small holes (B) and is contained within the volume sealed by the O-ring (C). Chilling 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

In-Situ-Research Instrument



Harrick High Temperature Cell

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

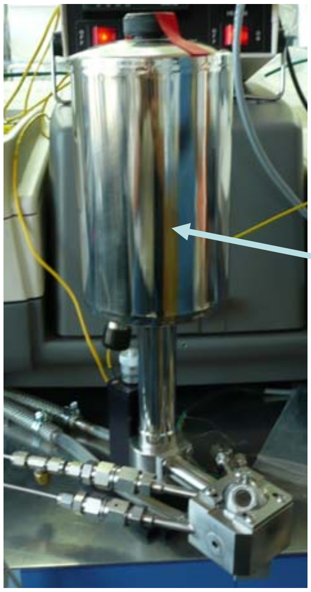
Catalyst Sample
Size 2 cm o.d., typically 80 mg of solid

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

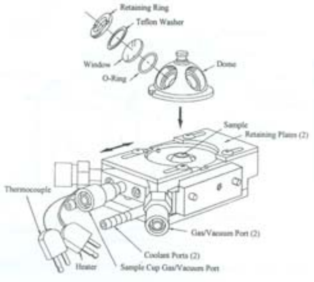
---

Commercial Reaction Chamber from Harrick Scientific for DRIFT analysis

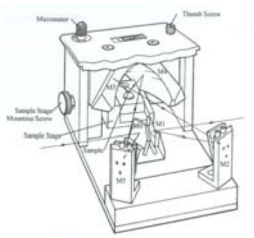


The Low Temperature Reaction Chamber, CHC-CHA, is designed for operation from **-150°C to 600°C under vacuum.**

In addition to the heater incorporated in the sample stage, the CHC also features a cooling conduit connected to a **dewar.**



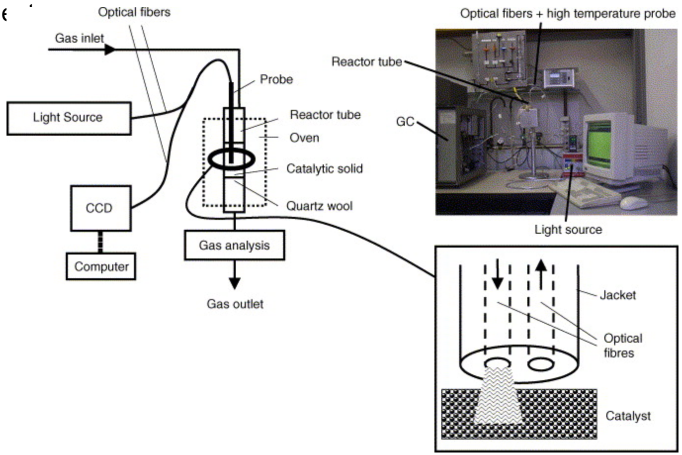
Main parts of Chamber



Optical accessories

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

c) “*Operando*” methodology describes “***in situ***” spectra under true catalytic operation as determined by ***simultaneous*** online activity/selectivity measureme



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”.

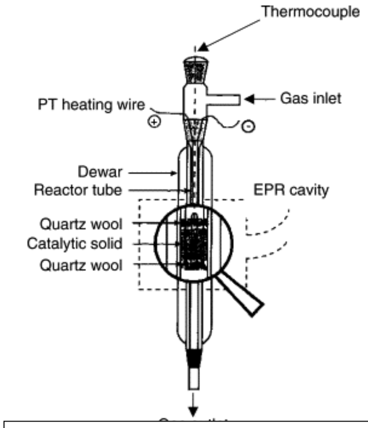
Some historical remaks

- ☐ 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.

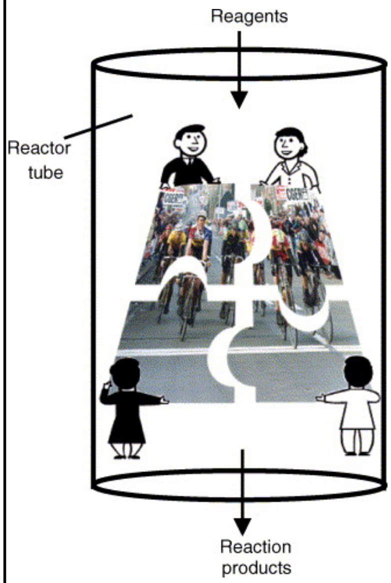
***Operando* ESR cell** developed in the group of Brückner (Berlin, Germany)



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 NO*x* over supported manganese oxide catalysts.

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



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

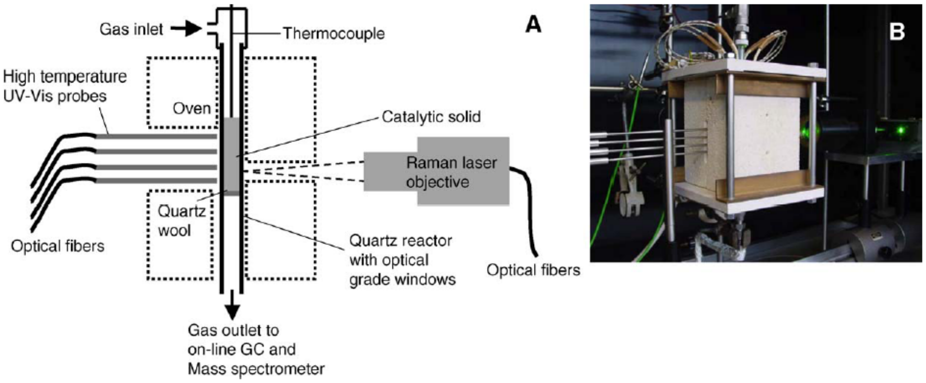
The adding additional spectroscopic techniques is most **valuable** if they provide **complementary information!!!**

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

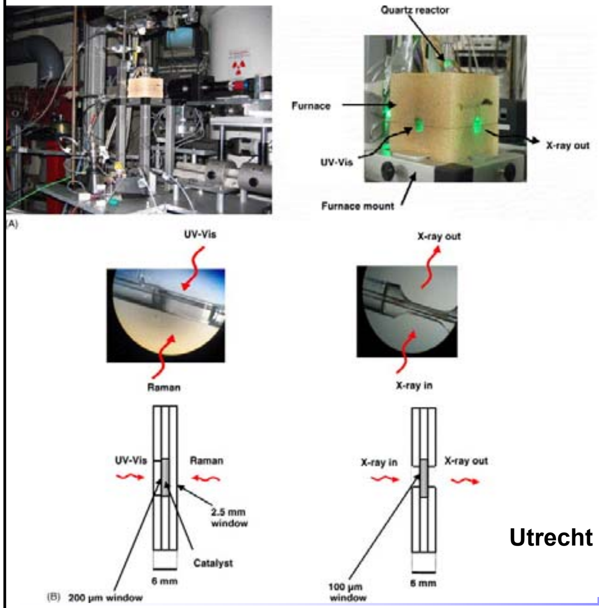
It would be **more advantageous** to look on catalytic systems from different perspectives by making use of **multiple characterization techniques**

An example of **two techniques** combined in one set-up



The *operando* UV–vis set-up allows to measure the d–d transitions and charge transfer transitions of supported transition metal oxides and the formation of organic molecules via their n–π* or π–π* transitions under working conditions

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

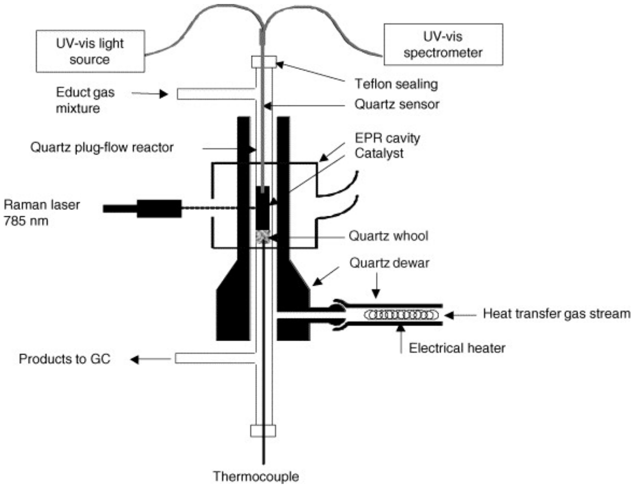


for measuring supported metal oxide catalysts operating in gas-phase reactions at elevated temperatures and ambient pressures.

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

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



Built in the Institut für Angewandte Chemie Berlin, Germany

Overview of *operando* set-ups making use of multiple spectroscopic characterization techniques

Existing combinations of techniques for studying heterogeneous catalysts at work:

Techniques combined	Application domain	Time resolution (s)	Information to be obtained
XRD XAFS	Heterogeneous catalysis	XRD: 30 XAFS: 10–30	XRD: long-range structural order XAFS: short-range structural order
EPR UV–vis	Heterogeneous catalysis	EPR: 60–300 UV–vis: 0.01–1	EPR: paramagnetic transition metal ions UV–vis: electronic d–d and charge transfer transitions of transition metal ions
Raman	Heterogeneous catalysis	Raman: 2–120	Raman: vibrational spectra of metal oxides and organic deposits, such as coke
UV–vis		UV–vis: 0.01–1	UV–vis: electronic d–d and charge transfer transitions of transition metal oxides

S. J. Tinnemans, J. G.Mesu, K.Kervinen, T.Visser, T. A. Nijhuis, A.M.Beale, D.E. Keller, Ad M.J. van der Eerden and B.M. Weckhuysen "Combining *operando* techniques in one spectroscopic-reaction cell: New opportunities for elucidating the active site and related reaction mechanism in catalysis" **Catalysis Today** V.113, I.1-2,2006, Pages 3-15

Overview of *operando* set-ups making use of multiple spectroscopic characterization techniques

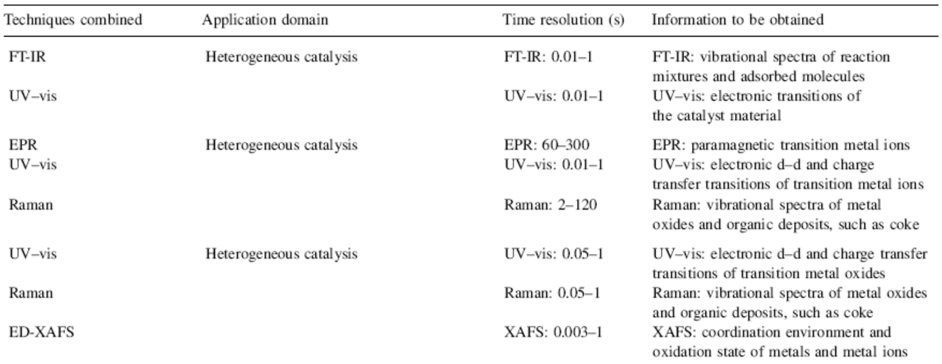
Existing combinations of techniques for studying heterogeneous catalysts at work:

Techniques combined	Application domain	Time resolution (s)	Information to be obtained
Raman FT-IR	Heterogeneous catalysis	Raman: 2–120 FT-IR: 0.01–1	Raman: vibrational spectra of metal oxides FT-IR: vibrational spectra of adsorbed species, such as NO
NMR	Heterogeneous catalysis	NMR: 7200	NMR: identification of organic molecules formed via chemical shift values
UV–vis		UV–vis: 0.01–1	UV–vis: electronic transitions ($n-\pi^*$ and $\pi-\pi^*$) of organic molecules
ED-XAFS	Heterogeneous catalysis	XAFS: 6	XAFS: coordination environment and oxidation state of metals and metal ions
FT-IR		FT-IR: 0.01–1	FT-IR: vibrational spectra of adsorbed species, such as CO and NO

S. J. Tinnemans, J. G.Mesu, K.Kervinen, T.Visser, T. A. Nijhuis, A.M.Beale, D.E. Keller, Ad M.J. van der Eerden and B.M. Weckhuysen "Combining *operando* techniques in one spectroscopic-reaction cell: New opportunities for elucidating the active site and related reaction mechanism in catalysis" **Catalysis Today** V.113, I.1-2,2006, Pages 3-15

Overview of *operando* set-ups making use of multiple spectroscopic characterization techniques

Existing combinations of techniques for studying heterogeneous catalysts at work:



Techniques combined	Application domain	Time resolution (s)	Information to be obtained
FT-IR	Heterogeneous catalysis	FT-IR: 0.01–1	FT-IR: vibrational spectra of reaction mixtures and adsorbed molecules
UV–vis		UV–vis: 0.01–1	UV–vis: electronic transitions of the catalyst material
EPR	Heterogeneous catalysis	EPR: 60–300	EPR: paramagnetic transition metal ions
UV–vis		UV–vis: 0.01–1	UV–vis: electronic d–d and charge transfer transitions of transition metal ions
Raman		Raman: 2–120	Raman: vibrational spectra of metal oxides and organic deposits, such as coke
UV–vis	Heterogeneous catalysis	UV–vis: 0.05–1	UV–vis: electronic d–d and charge transfer transitions of transition metal oxides
Raman		Raman: 0.05–1	Raman: vibrational spectra of metal oxides and organic deposits, such as coke
ED-XAFS		XAFS: 0.003–1	XAFS: coordination environment and oxidation state of metals and metal ions

S. J. Tinnemans, J. G.Mesu, K.Kervinen, T.Visser, T. A. Nijhuis, A.M.Beale, D.E. Keller, Ad M.J. van der Eerden and B.M. Weckhuysen "Combining *operando* techniques in one spectroscopic-reaction cell: New opportunities for elucidating the active site and related reaction mechanism in catalysis" **Catalysis Today** V.113, I.1-2,2006, Pages 3-15

Some remarks

The first **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 **long-range ordering** information of the catalytic solid under investigation, whereas **EXAFS** is sensitive to the **short-range ordering** of the materials under study.

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

In the case of **magnetic resonance techniques** (NMR and EPR) more technical hurdles have to be taken to make the combined ***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.

Concluding remarks

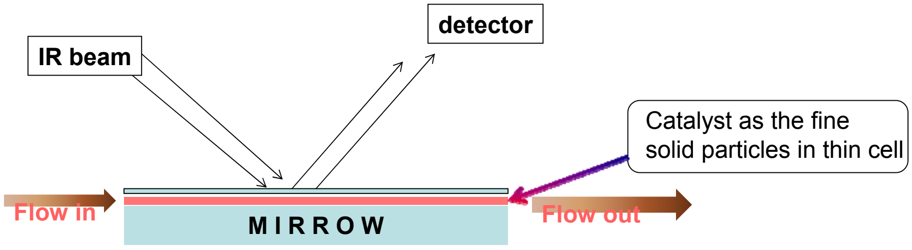
Evaluation of the still limited amount of literature reveals that there are – roughly speaking – **two types of research groups** working in the field of **operando** spectroscopy

1. **On one hand**, there are people focusing on the inorganic part of the catalyst material. *More in particularly, 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

---

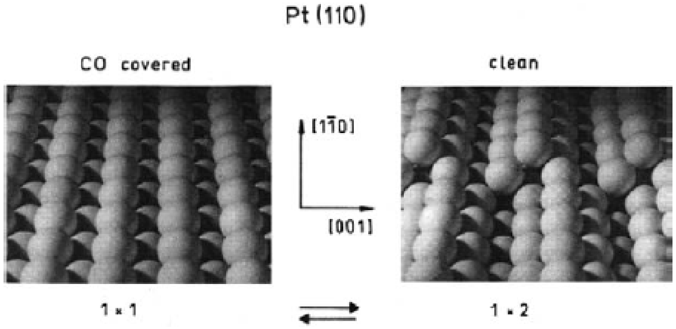
The classical approach is to perform **steady-state kinetic measurements** while obeying all these rules and guidelines and changing the experimental settings of **temperature, pressure or concentration, composition, space time**, etc. one by one, until the whole experimental space has been covered.

! 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 parallellization.**

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**.

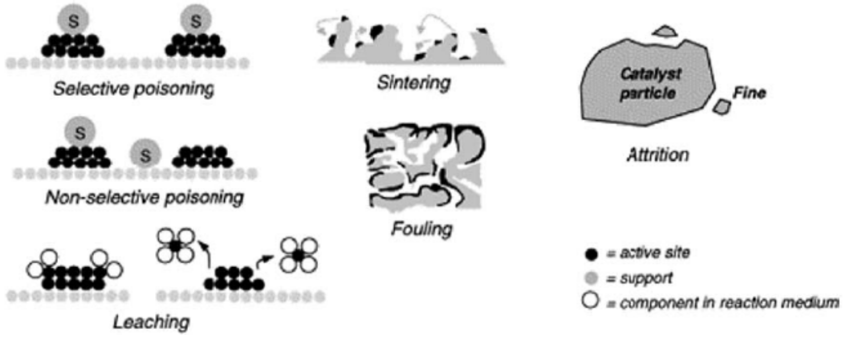


Reconstruction ofPt(110) surface due to CO adsorption

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

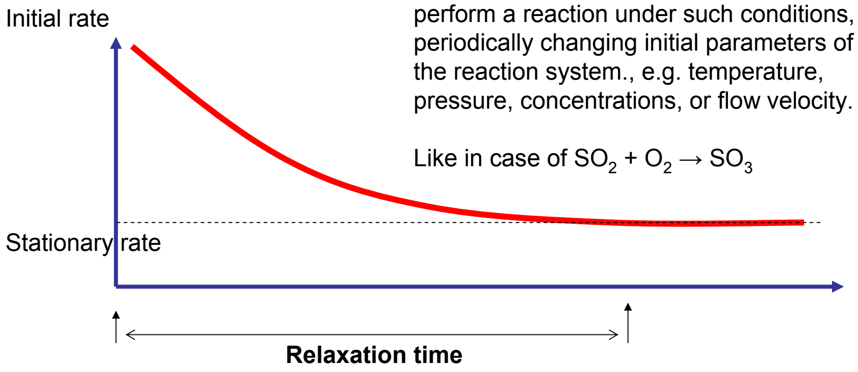
- the **surfaces**,
- but also changes in the **phase composition** of the catalyst and changes
- in the **bulk composition.**



Relaxation to steady-state

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 $SO_2 + O_2 \rightarrow SO_3$



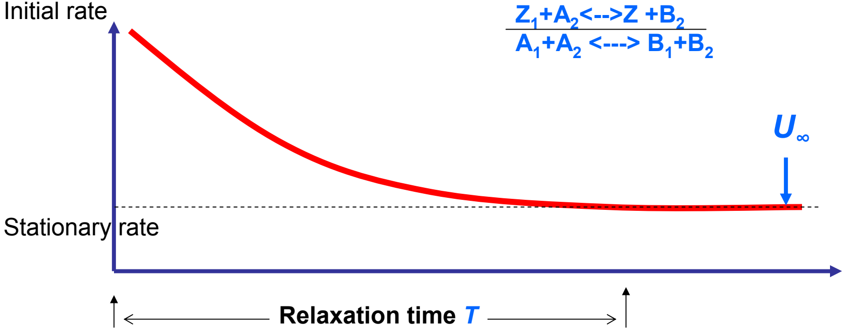
Under nonstationary conditions two types of processes could operate.

- 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.

Relaxation to steady-state

$$\begin{array}{l} Z+A_1 \text{<-->} Z_1 + B_1 \\ \underline{Z_1+A_2 \text{<-->} Z + B_2} \\ A_1+A_2 \text{<--->} B_1+B_2 \end{array}$$



$$T \leq \frac{1}{4} U_\infty$$

[According to D.Murzin, T. Salmi, *Catalytic Kinetics*, Elsevier Science and Technology Books, 2005]

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.**

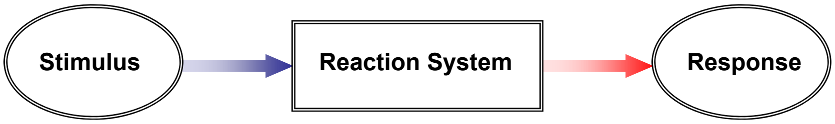
The basic ideas of the transient method applied to heterogeneous catalysis were set forth by K. Tamaru.

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.



Stimulus

Reaction System

Response

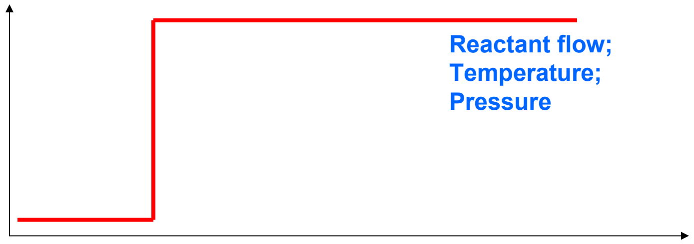
Stimuli

Three main stimuli are distinguished:

☐ a step function,
☐ a pulse,
☐ a time dependent function.

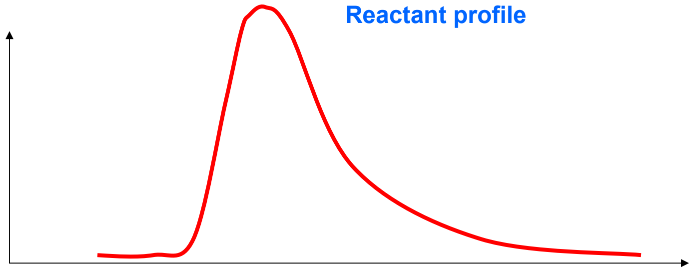
Stimuli

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.



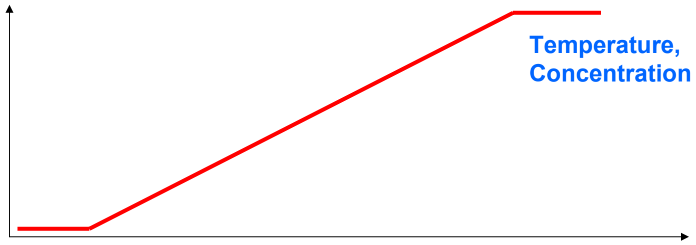
Stimuli

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.



Stimuli

The time dependent functions comprise linear or periodical programmed changes. In most cases the temperature (temperature programming techniques) or concentration is varied.



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

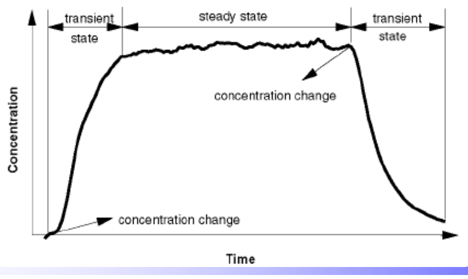
Transient techniques can be applied under unsteady-state as well as steady-state operation of the catalytic reaction system.

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**).

Reaction system—operation

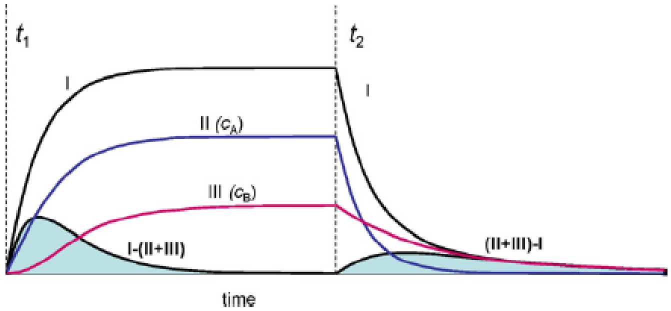
Transient operation occurs when the operational variables change in time and the catalyst experiences different conditions like upon a step change or pulse injection of a reactant.

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



An example

An irreversible reaction **A** → **B** takes place with competitive adsorption

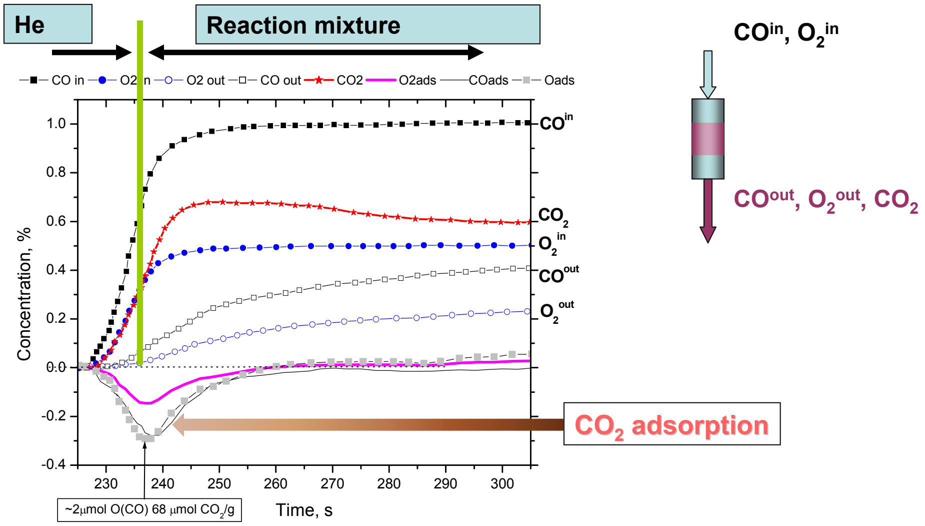


At t1 the feed concentration is **stepped up** and at t2 it is **stepped down**. Curve I represents the blank reactor response without catalyst, while II and III are the concentrations of **A** and **B** in the reactor outlet with catalyst.

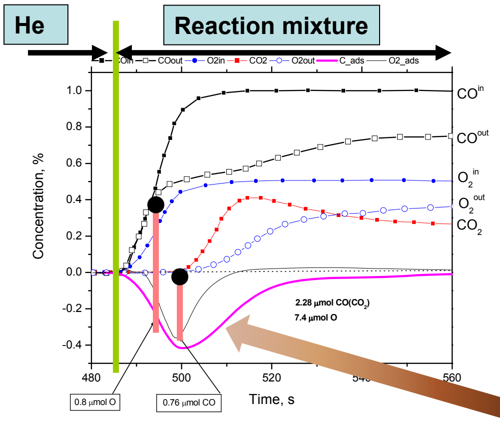
The difference curve for the step up, the blank response minus the reactive response, represents the '**missing' concentration** in the reactor outlet.

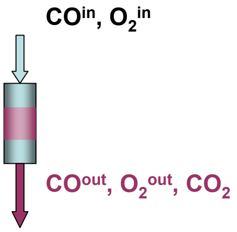
The two areas under the indicated difference curves equal the **total amount** of **A** and **B** present on the catalyst, so in principle from both stimuli this information can be collected. It depends on the response which of the two is more accurate. A too fast concentration increase or a too tailing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

Example of transients for CO+O_2 over oxidized Au-CeO_2 catalyst



Example of transients for CO+O_2 over prereduced Au-CeO_2 catalyst





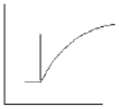
- Adsorption of O_2
- Reaction of CO with formed oxygen species

Typical responses (M. Kobayashi, Characterization of transient response curves in heterogeneous catalysis--I. Classification of the curves. *Chemical Engineering Science,* 37 (1982) 393).

Instantaneous

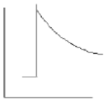
a)Surface reaction
b)Adsorption

Monotonic



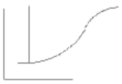
c)Desorption
or combination of a) and c); b) and c)

Overshoot response



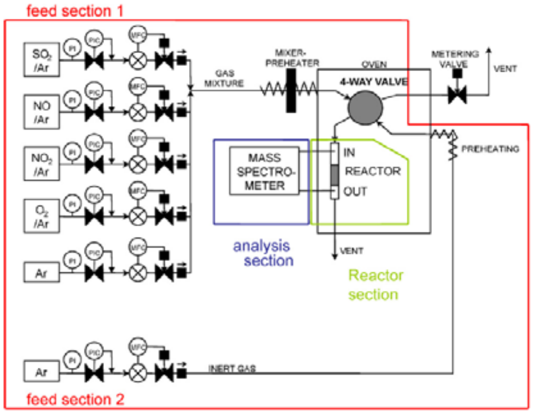
d)Regeneration of active surface species
e)Competitive adsorption of reaction components

S-shape response



h)Presence of some stable intermediates

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
Application	**Mostly liquid–solid, gas–liquid–solid (slurry, fixed bed)**
Pressure	**Atmospheric** to high pressures (gas: semi-batch)
Analysis	**GC (discrete points)** **DSC, gas supply rate (continuous)** **New developments: IR and Raman spectroscopy**
Information	**Concentration versus time—several runs needed for kinetics** **Low time resolution: minutes** **Many data points composition** **Deactivation not noticed, multiple runs needed with same sample**

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

	Fixed-bed tubular reactor
Application	Gas–solid (mostly), liquid–solid, gas–liquid–solid
Pressure	Vacuum to high pressures
Techniques	*Transient* Pulse in carrier or vacuum (TAP) Concentration steps *Steady state* Pulse of labeled species into unlabelled flow Steps from labeled to unlabelled
Information	Concentration at fixed space time, pressure, temperature, feed composition Time resolution: >0.1 s to >10 s Deactivation directly noticed Mechanistic information, titration of surface species and surface sites, kinetics, diffusion, concentration along bed length, sample mass
Analysis	GC, MS, GC–MS (discrete points) Tomography (axial profiles) TEOM (mass changes) DSC (integral reactor performance)

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.