UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Elucidating catalytic reaction mechanisms based on transient kinetic data: the Y-Procedure approach

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ERIC

Outline

- Introduction
  - Scope of the problem
  - Thin-Zone TAP experiments and the Y-Procedure
- Mechanism identification strategy:
  - Surface uptakes
  - Kinetic coherency
- Example: Adsorption vs. Impact mechanisms of CO oxidation
- Case study: CO oxidation on Au/SiO_2 catalysts
- Conclusions

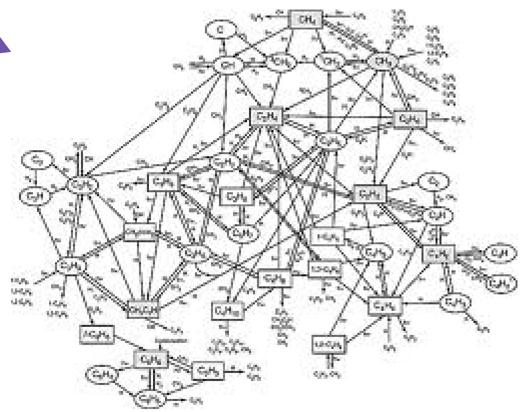
Scope of the problem

Given a collection of possible elementary steps,
how do we decide which particular combination of steps
is at work in our experiment?

Theoretical predictions

Prior knowledge

Combinatorics

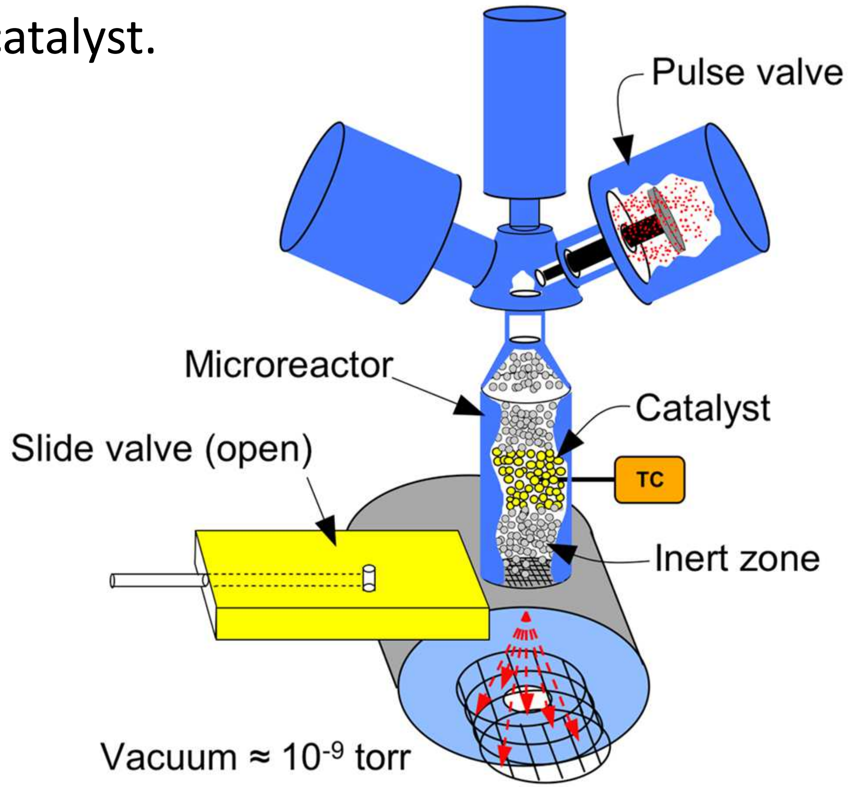


Exhaustive reaction network

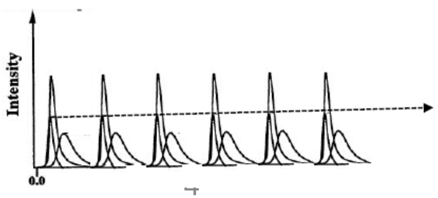
Which subset is kinetically important in my experiment?

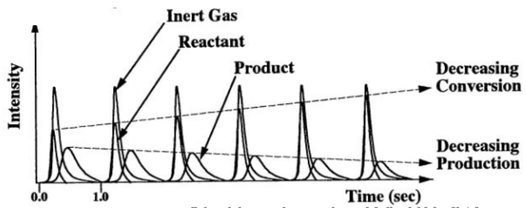
Thin-Zone Temporal Analysis of Products (TAP)

- **Microreactor** packed with real (technical) catalyst.
- Small (10^{14} molecules) and narrow (150 µs) **pulses of gas**.
- Transport of gas via well-defined **Knudsen diffusion**.
- Exit flows are measured with **millisecond temporal resolution**.
- Thin catalyst zone remains highly **uniform** during kinetic measurements**.**



- A combination of **State-defining** and **State-Altering** experiments**.**

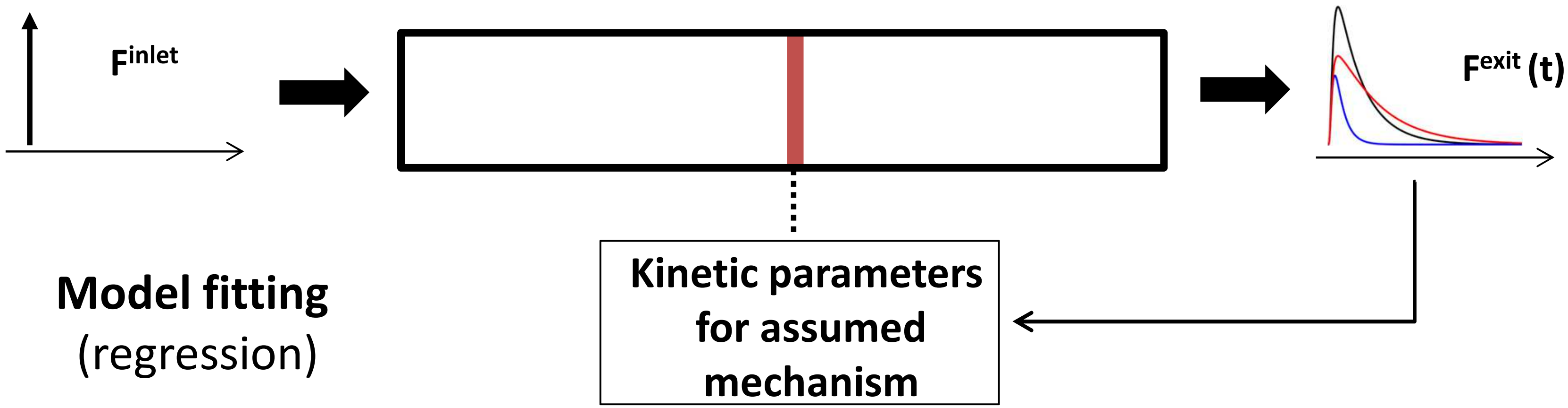




J. T. Gleaves et al., 1988

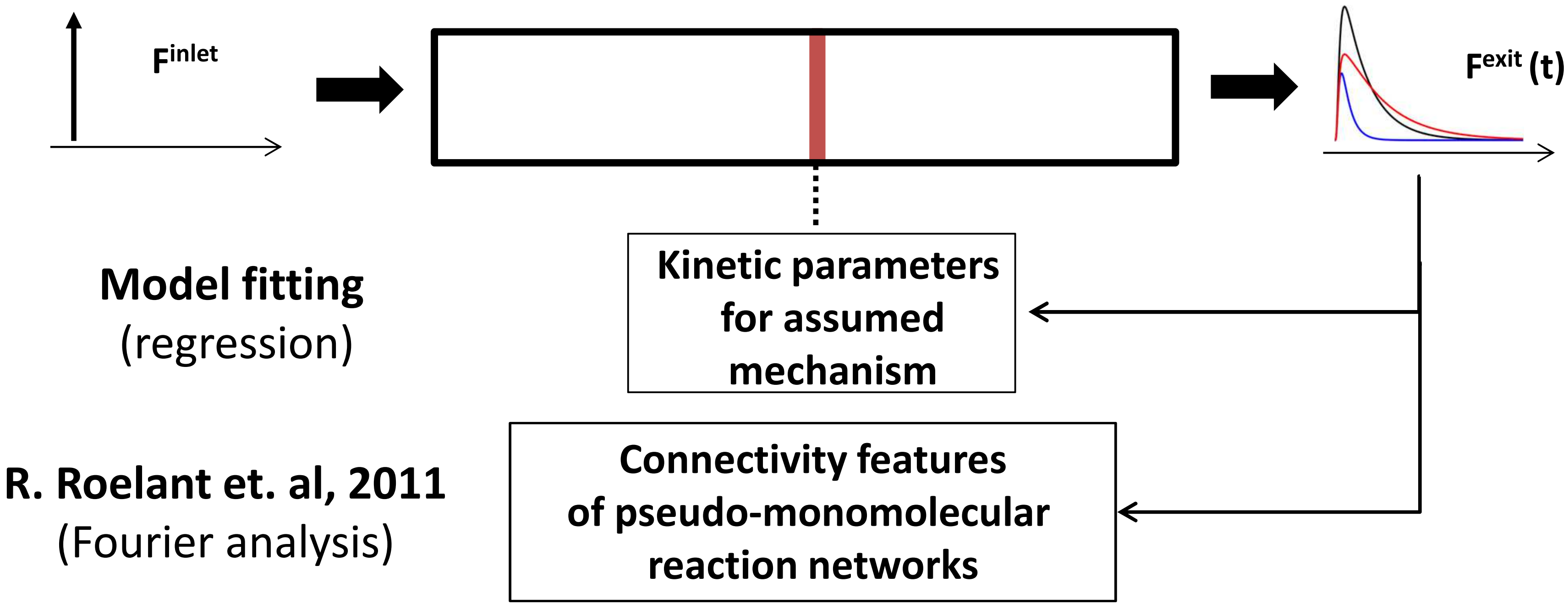
G. B. Marin and G. S. Yablonsky, 2011

Model fitting vs. the Y-Procedure

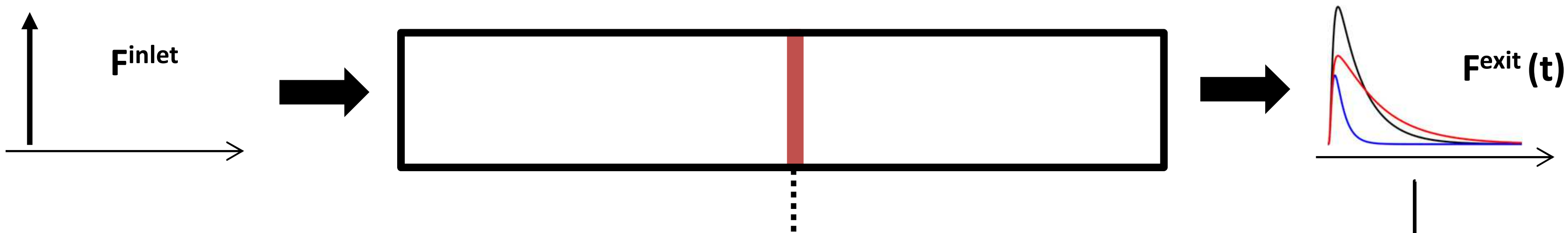


Model fitting
(regression)

Model fitting vs. the Y-Procedure

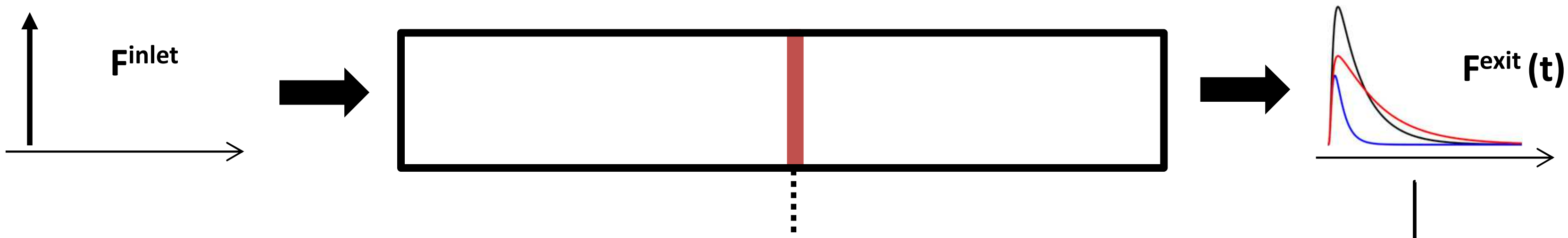


Model fitting vs. the Y-Procedure



Model fitting (regression)	**Kinetic parameters for assumed mechanism**
R. Roelant et. al, 2011 (Fourier analysis)	**Connectivity features of pseudo-monomolecular reaction networks**
Kinetically "model free" Y-Procedure (Fourier analysis) G. S. Yablonsky et. al, 2007	**$C_g(t)$ and $R(t)$**

Model fitting vs. the Y-Procedure



Model fitting
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Kinetic parameters for assumed mechanism

R. Roelant et. al, 2011
(Fourier analysis)

Connectivity features of pseudo-monomolecular reaction networks

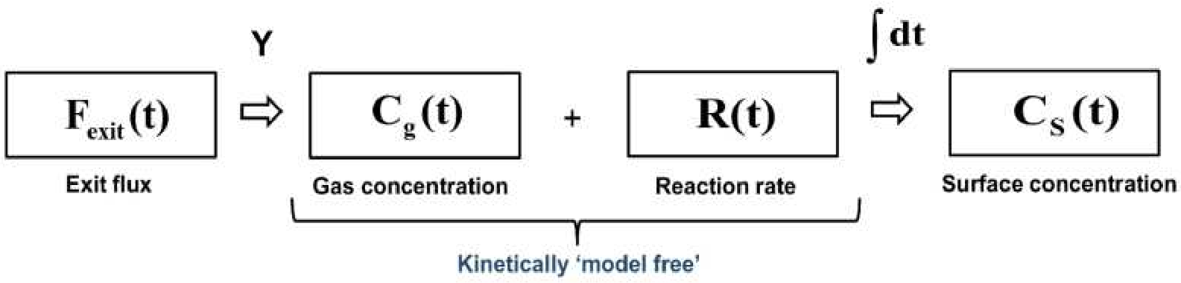
Kinetically "model free" Y-Procedure
(Fourier analysis)
G. S. Yablonsky et. al, 2007

$C_g(t)$ and R(t)

Need a **strategy** to interpret rates and concentrations with **minimum *a priori* mechanistic assumptions**.

Systematic strategy

A. For a given catalyst state:



1. Reconstruct gas concentrations and reaction rates

2. Evaluate <u>surface uptakes</u> based on gas rates

2. Explore how transient rates and concentrations behave relatively to each other (<u>temporal coherency/decoherency</u>)

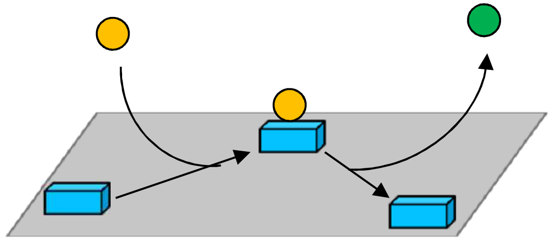
B. Repeat for evolving catalyst states

Concept

Surface Uptakes

Communication between gas and surface phases

1



- surface site Z
- gas molecule A or B

Molecular adsorption: Z + A = ZA

Dissociative adsorption: 2Z + A = 2ZA

Product release: ZA = Z + B

Communication between gas and surface phases

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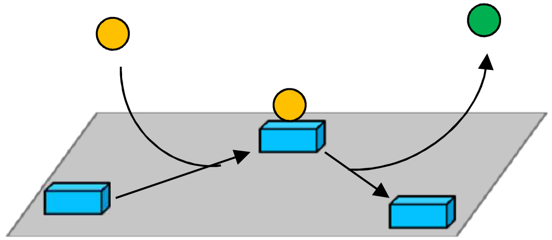

- surface site Z
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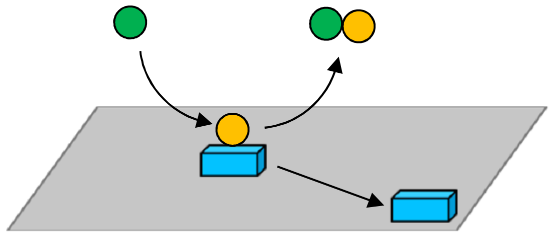
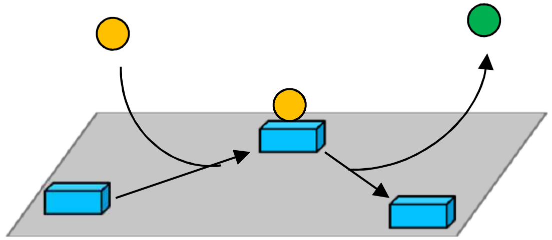


Impact reaction steps: ZA + B = Z + AB

Communication between gas and surface phases

1



[surface site icon] - surface site Z

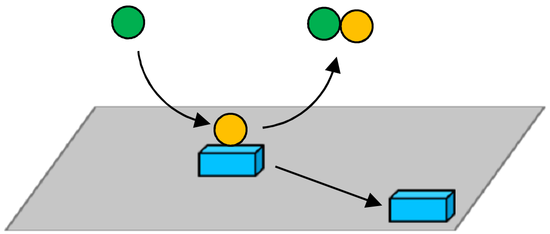
[yellow circle] - gas molecule A or B

Molecular adsorption: $Z + A = ZA$

Dissociative adsorption: $2Z + A = 2ZA$

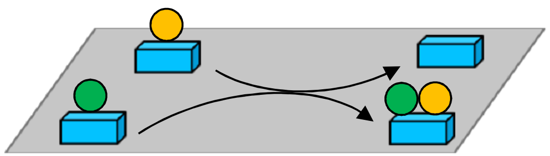
Product release: $ZA = Z + B$

2



Impact reaction steps: $ZA + B = Z + AB$

3



'Hidden' surface steps:

$ZA + ZB = Z + ZC$

$ZA = ZC$

$ZA + Z = Z_2A$

Evaluating surface uptakes

- Generally, it is **not** possible to express individual surface concentrations through gaseous rates.
- But when all elementary steps:

1) Exchange molecules with the gas phase (types 1 and 2)
2) Certain connectivity condition are fulfilled

It is **possible** to express surface concentrations through a linear combination of gaseous reaction rates:

$$C_s(t) = C_{s,init} + \underbrace{\int_0^t \sum_i \nu_i r_i^+(t')dt'}_{\textbf{Uptake}} - \underbrace{\int_0^t \sum_i \nu_i r_i^-(t')dt'}_{\textbf{Release}} = C_{s,init} + \underbrace{\int_0^t \sum_g \nu_g R_g(t')dt'}_{\textbf{Gas Rates}}$$

Concept

Kinetic coherency

Kinetic (de)coherency

Kinetic coherency – Every combination of elementary steps leads to synchronization of certain kinetic characteristics

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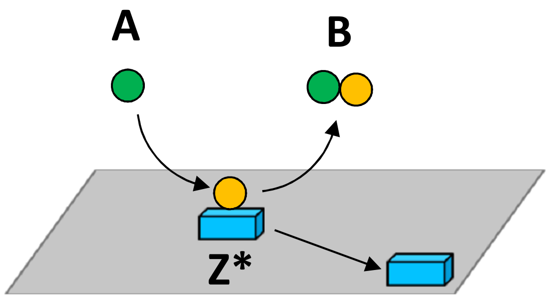


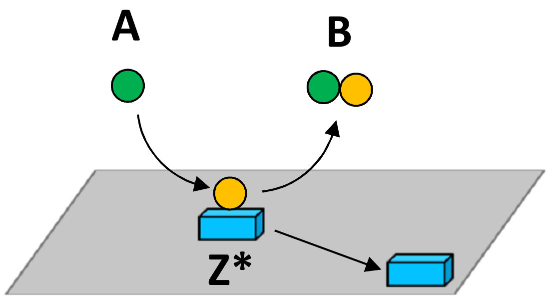
Rate-Rate coherency:

If A is consumed and B is produced in the same step, their rates must be synchronized (equal in this case):

$$R_A(t) = R_B(t)$$

Kinetic (de)coherency

Kinetic coherency – Every combination of elementary steps leads to synchronization of certain kinetic characteristics



Rate-Rate coherency:

If A is consumed and B is produced in the same step, their rates must be synchronized (equal in this case):

$$R_A(t) = R_B(t)$$

Rate-Concentration coherency:

Assuming the law of mass actions is valid, certain combinations of rates and concentrations must be synchronized, e.g:

$$R_{AB}(t) \,/\, C_A(t)C_{Z*}(t) \neq f(t)$$

Illustrative example

Model CO oxidation

Prototypical mechanism: CO oxidation

$$O_2 + 2Z \xrightarrow{k_1} 2ZO$$

$$CO + Z \underset{k_{-2}}{\overset{k_{+2}}{\rightleftarrows}} ZCO$$

$$ZO + CO \xrightarrow{k_3} Z + CO_2$$

$$ZO + ZCO \xrightarrow{k_4} 2Z + CO_2$$

Prototypical mechanism: CO oxidation

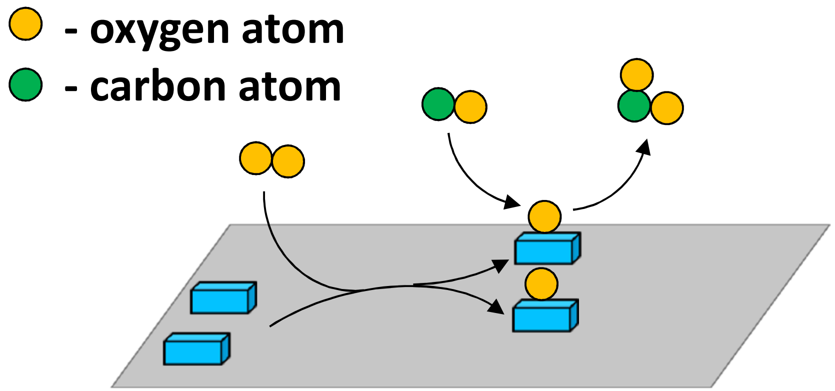
Impact mechanism or Eley-Rideal (ER)

$$O_2 + 2Z \xrightarrow{k_1} 2ZO$$

$$CO + Z \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} ZCO$$

$$ZO + CO \xrightarrow{k_3} Z + CO_2$$

$$ZO + ZCO \xrightarrow{k_4} 2Z + CO_2$$



Prototypical mechanism: CO oxidation

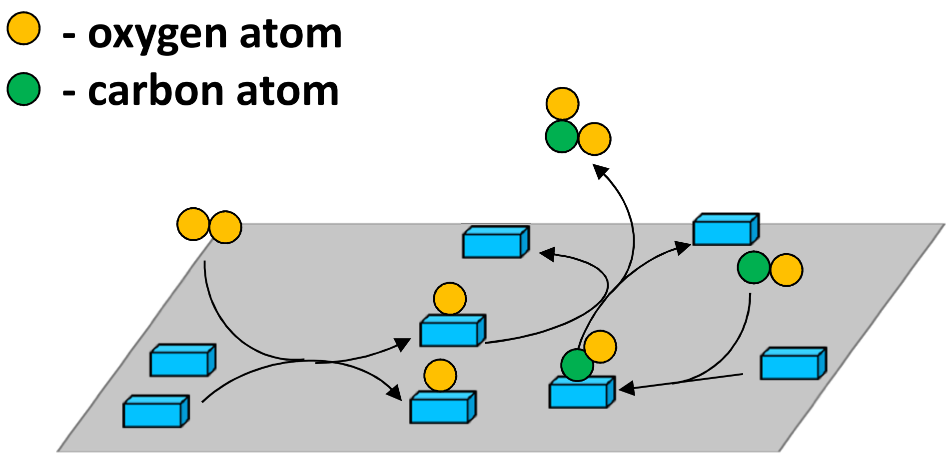
Adsorption mechanism or Langmuir-Hinshelwood (LH)

$$O_2 + 2Z \xrightarrow{k_1} 2ZO$$

$$CO + Z \underset{k_{-2}}{\overset{k_{+2}}{\rightleftarrows}} ZCO$$

$$ZO + CO \xrightarrow{k_3} Z + CO_2$$

$$ZO + ZCO \xrightarrow{k_4} 2Z + CO_2$$



Prototypical mechanism: CO oxidation

ER + buffer CO adsorption

$$O_2 + 2Z \xrightarrow{k_1} 2ZO$$

$$CO + Z \underset{k_{-2}}{\overset{k_{+2}}{\rightleftarrows}} ZCO$$

$$ZO + CO \xrightarrow{k_3} Z + CO_2$$

$$ZO + ZCO \xrightarrow{k_4} 2Z + CO_2$$

Prototypical mechanism: CO oxidation

Combined mechanism or ER + LH

$$O_2 + 2Z \xrightarrow{k_1} 2ZO$$

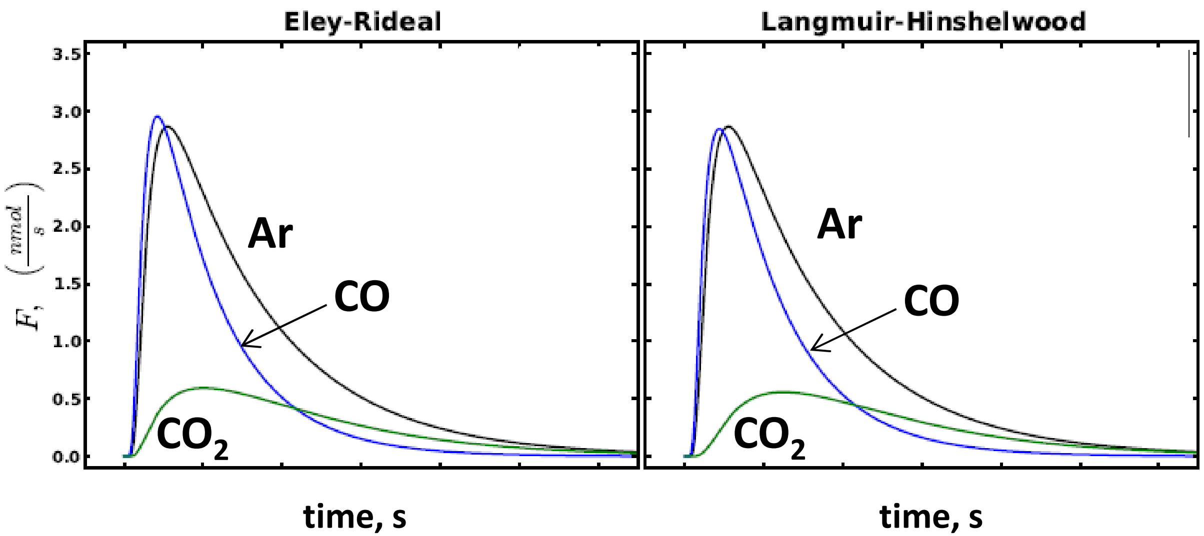
$$CO + Z \underset{k_{-2}}{\overset{k_{+2}}{\rightleftarrows}} ZCO$$

$$ZO + CO \xrightarrow{k_3} Z + CO_2$$

$$ZO + ZCO \xrightarrow{k_4} 2Z + CO_2$$

Numerical example: CO oxidation

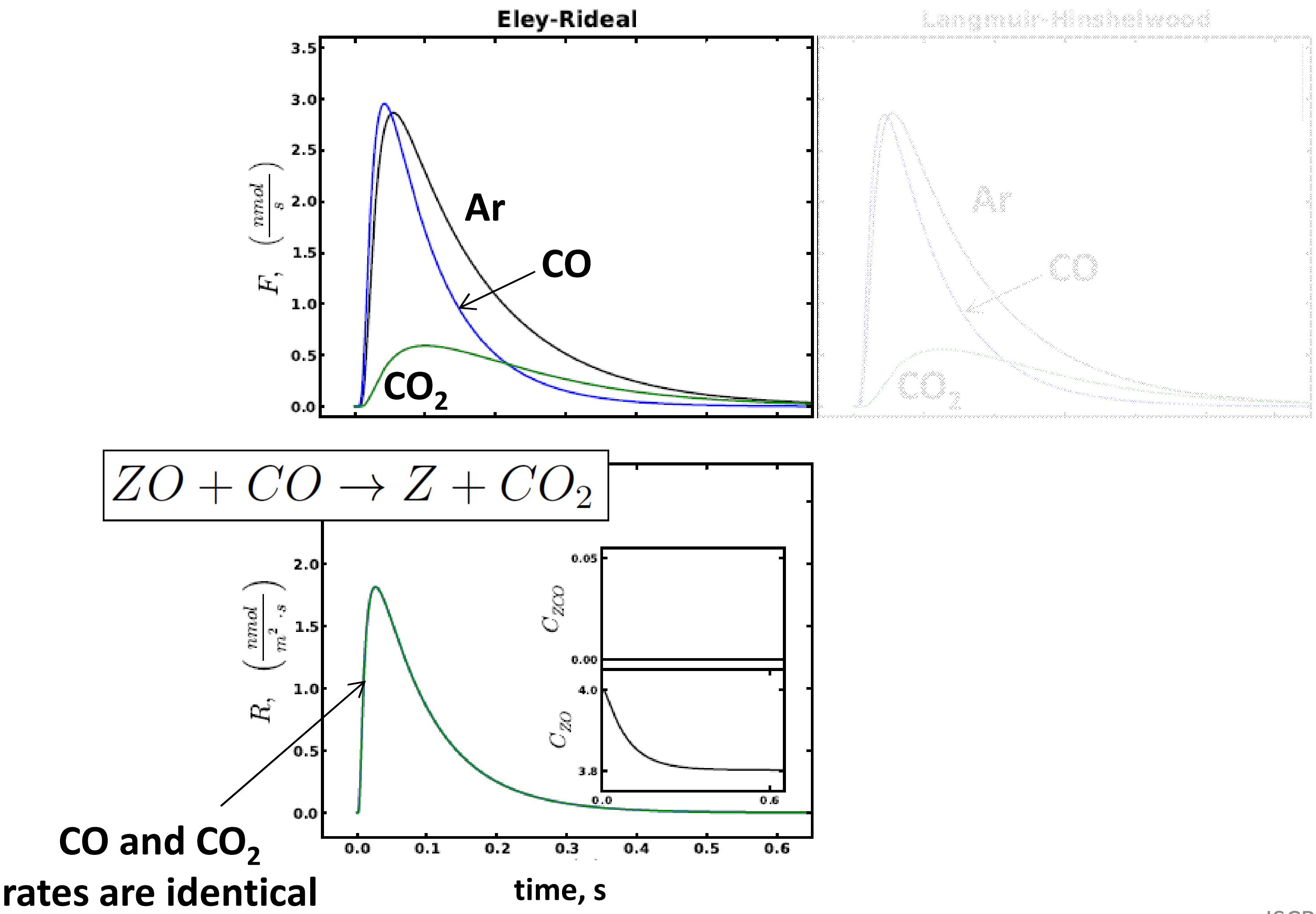
CO pulse over fully oxidized surface



Mechanism discrimination is challenging based on exit-flow data

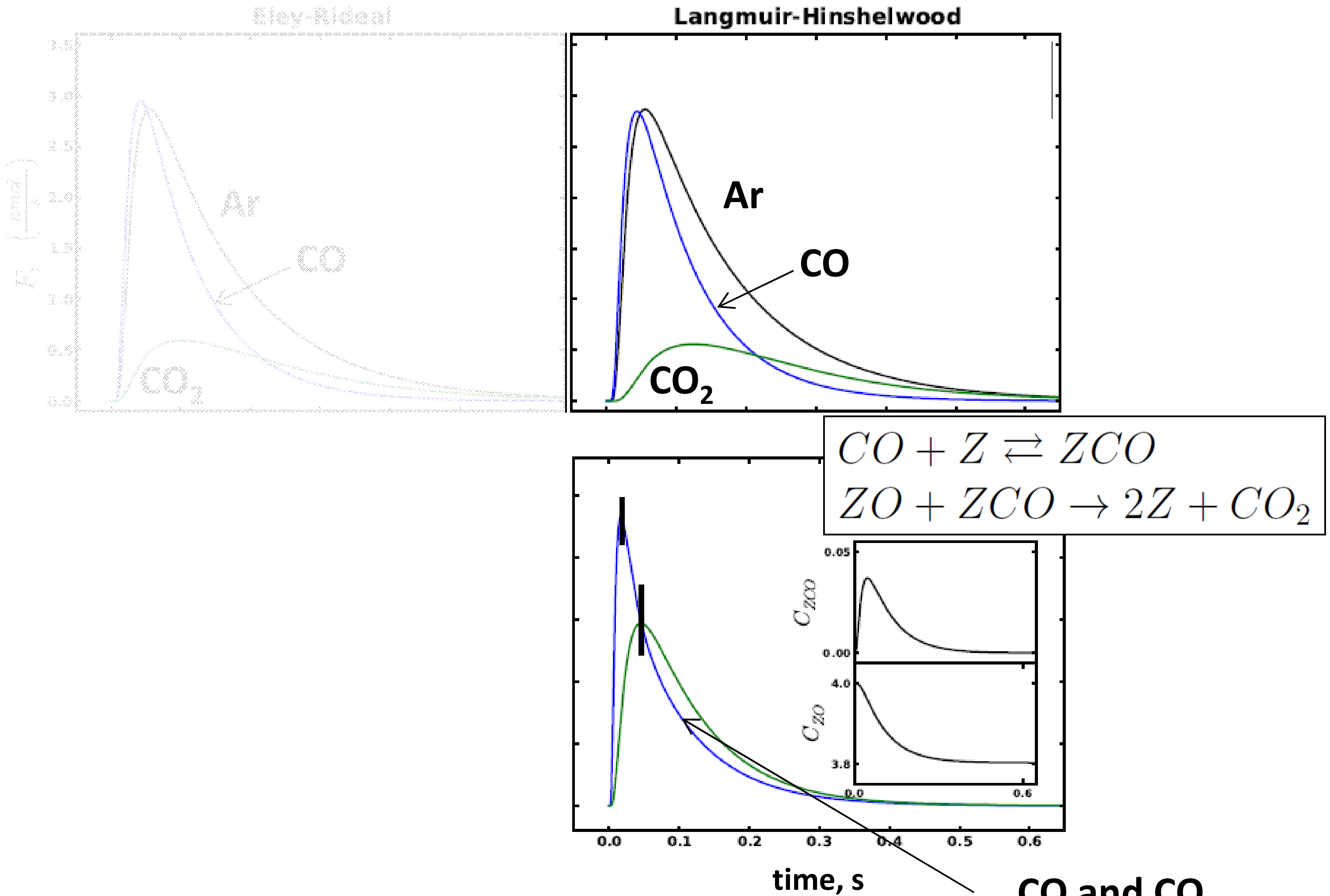
Numerical example: CO oxidation

CO pulse over fully oxidized surface



Numerical example: CO oxidation

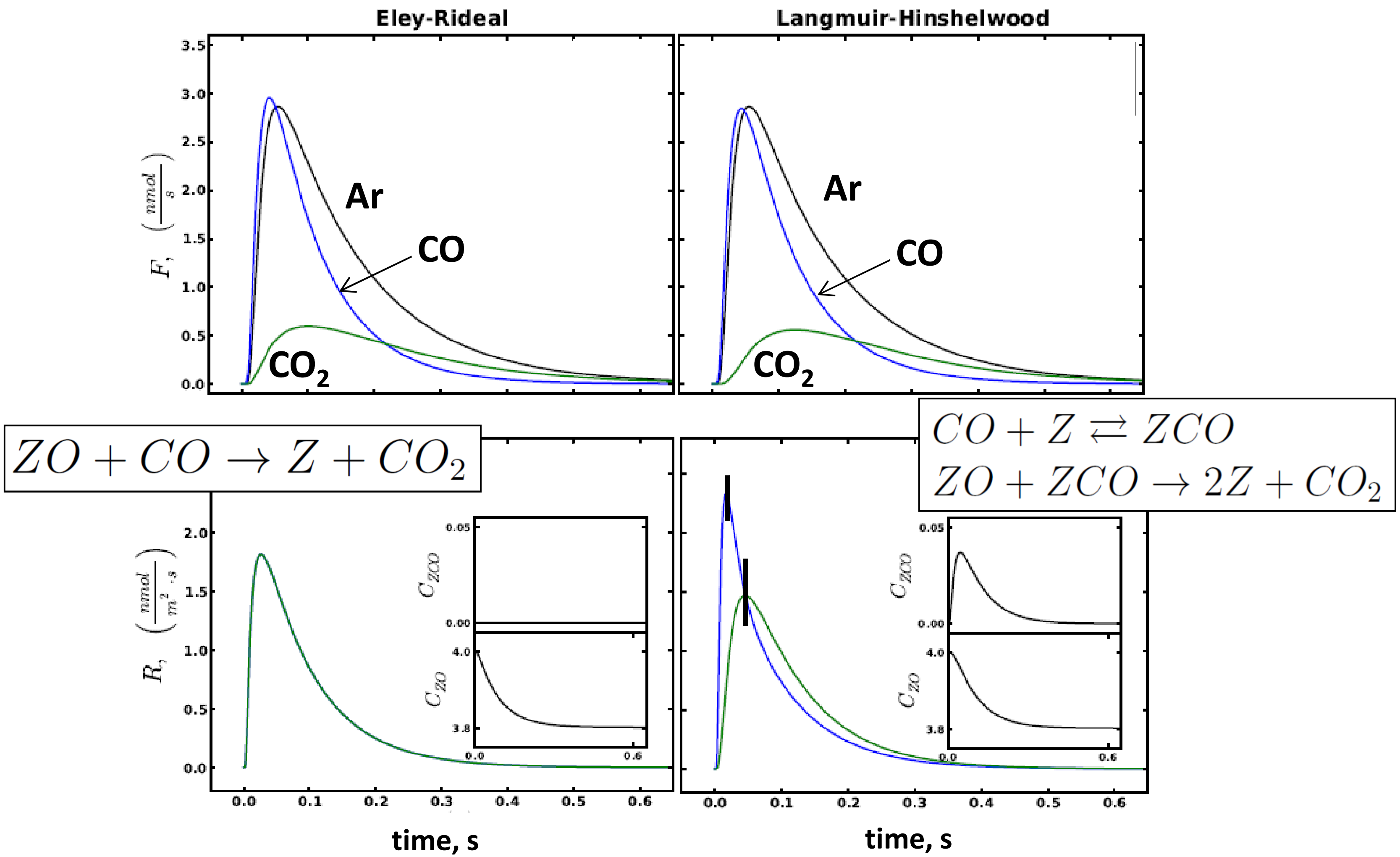
CO pulse over fully oxidized surface



CO and CO_2 rates are different

Numerical example: CO oxidation

CO pulse over fully oxidized surface

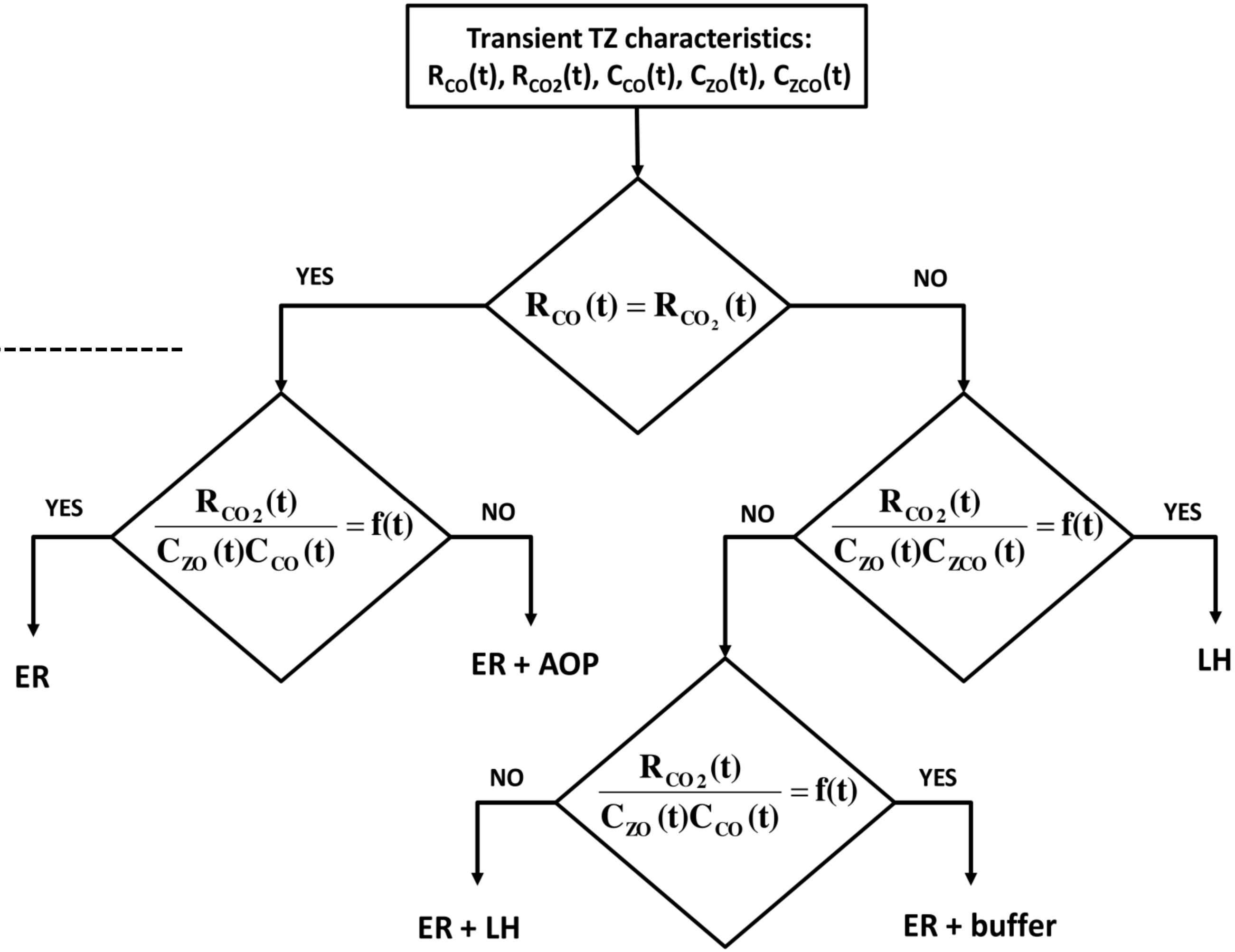


Y-Procedure facilitates mechanism discrimination

Decision tree: CO oxidation

Rate - Rate coherency

Rate - Concentration coherency



Case study

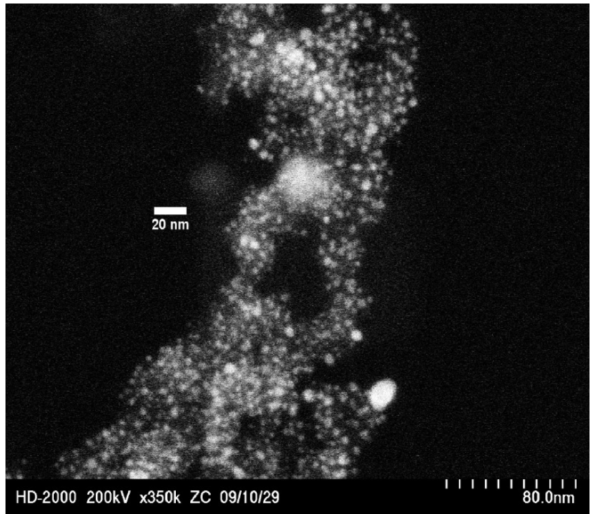
CO oxidation on Au catalyst

Case study: CO oxidation on Au/SiO_2

Au/SiO_2 catalyst prepared by magnetron sputtering is a useful model system:

- Non-reducible carrier eliminates support effects
- Gold NPs supported on silica are thermally stable
- High weight loading (~10%) which has not been investigated previously
- Not contaminated by chemical precursors

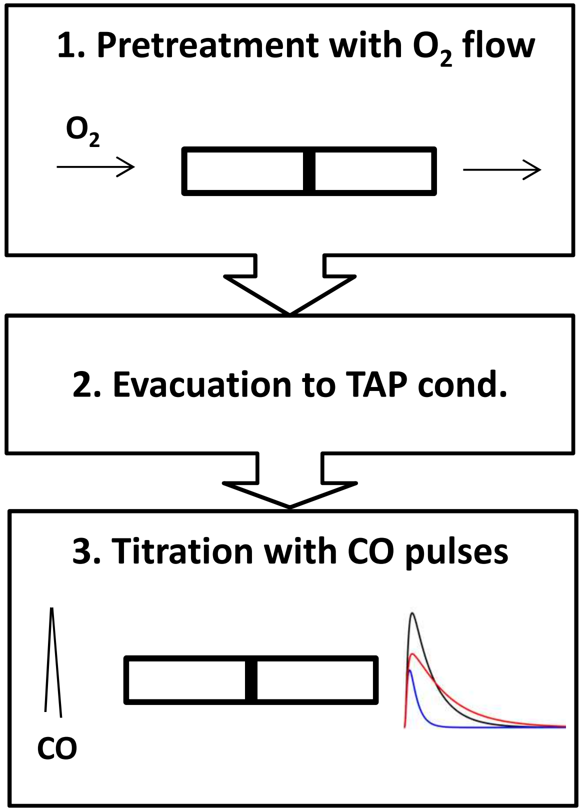
Avg. particle size 3.20 nm



X. Zheng et al., 2010

Case study: CO oxidation on Au/SiO_2

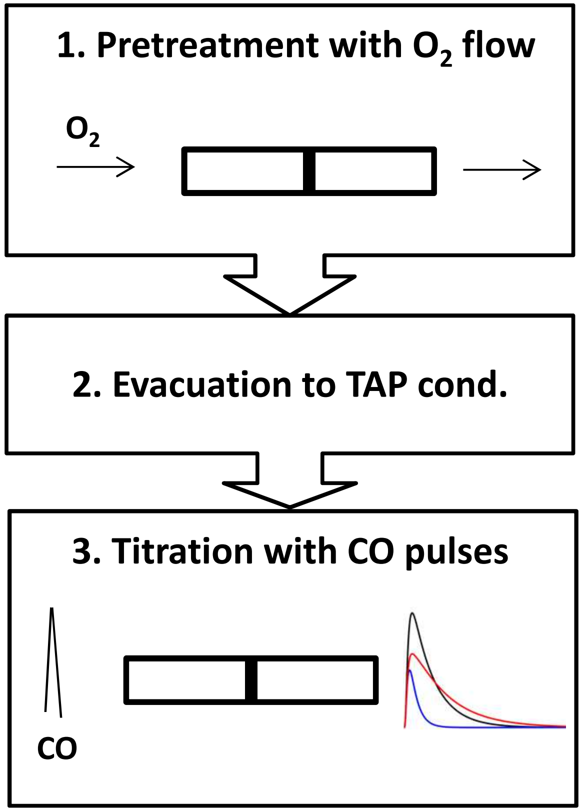
Experiment

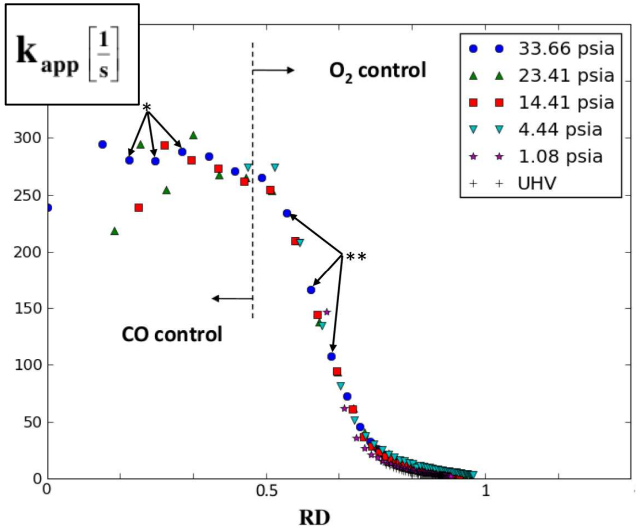


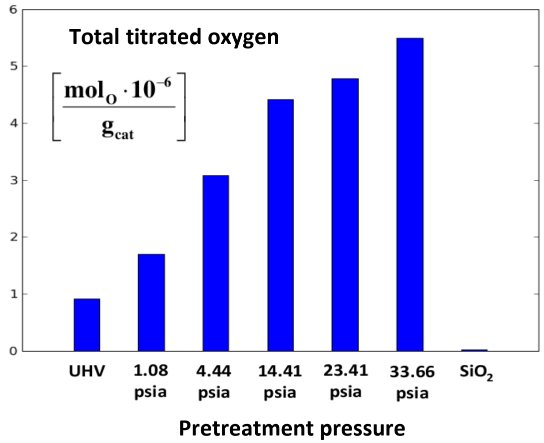
X. Zheng et al., 2010

Case study: CO oxidation on Au/SiO_2

Experiment | **Global analysis**



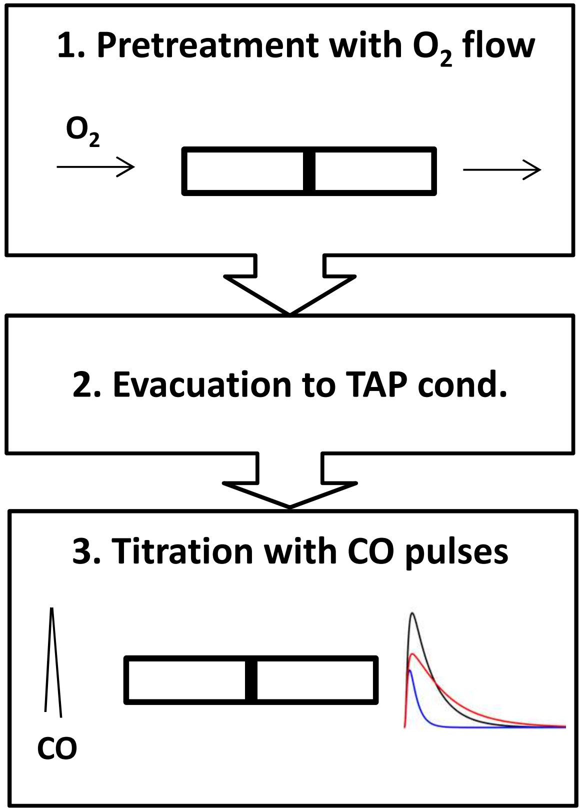


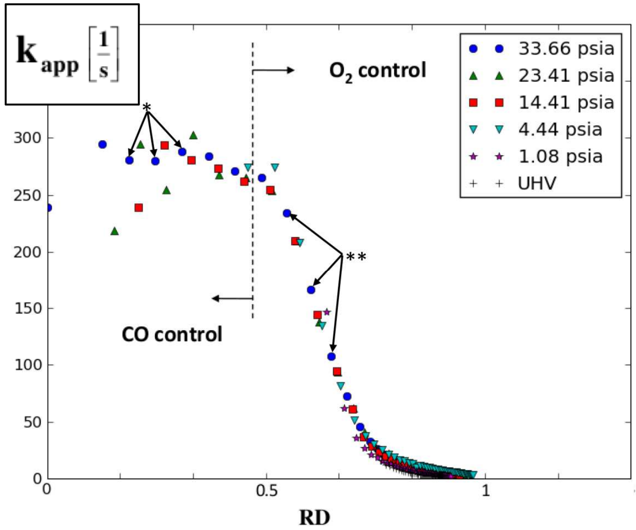


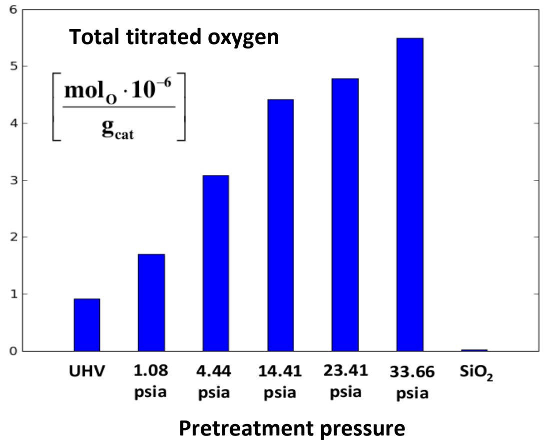
X. Zheng et al., 2010

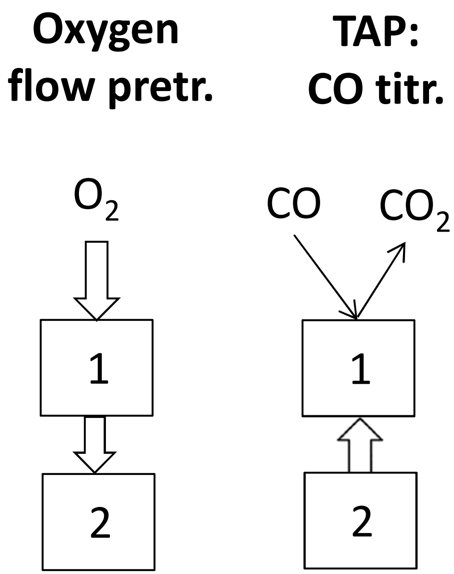
Case study: CO oxidation on Au/SiO_2

Experiment | **Global analysis** | **Mechanistic hypothesis**







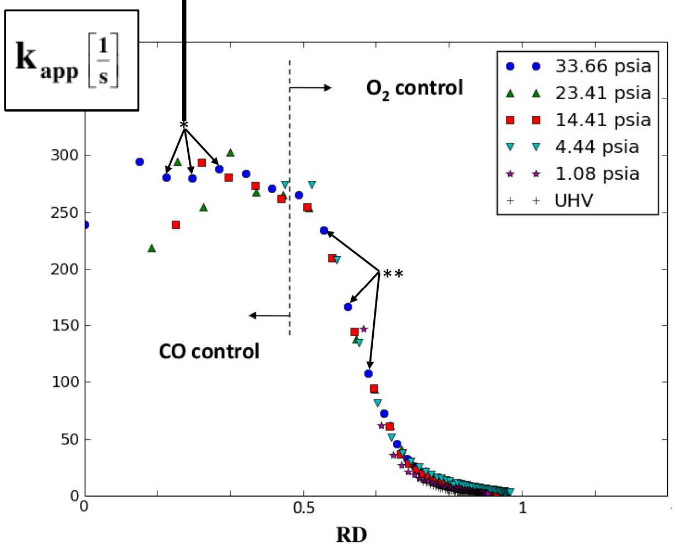


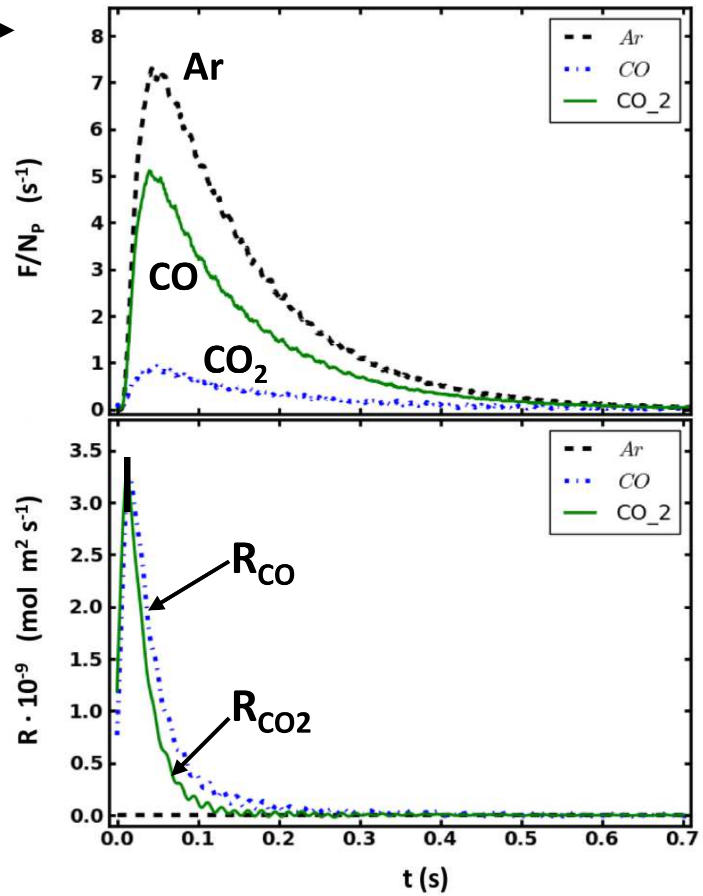
Two kinetically distinct "reservoirs" exchanging oxygen

X. Zheng et al., 2010

Case study: CO oxidation on Au/SiO_2

Intra-pulse analysis (Y-Procedure)





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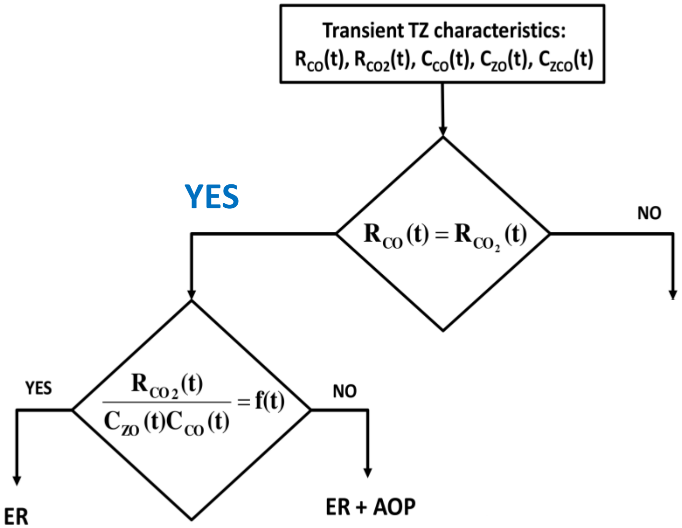
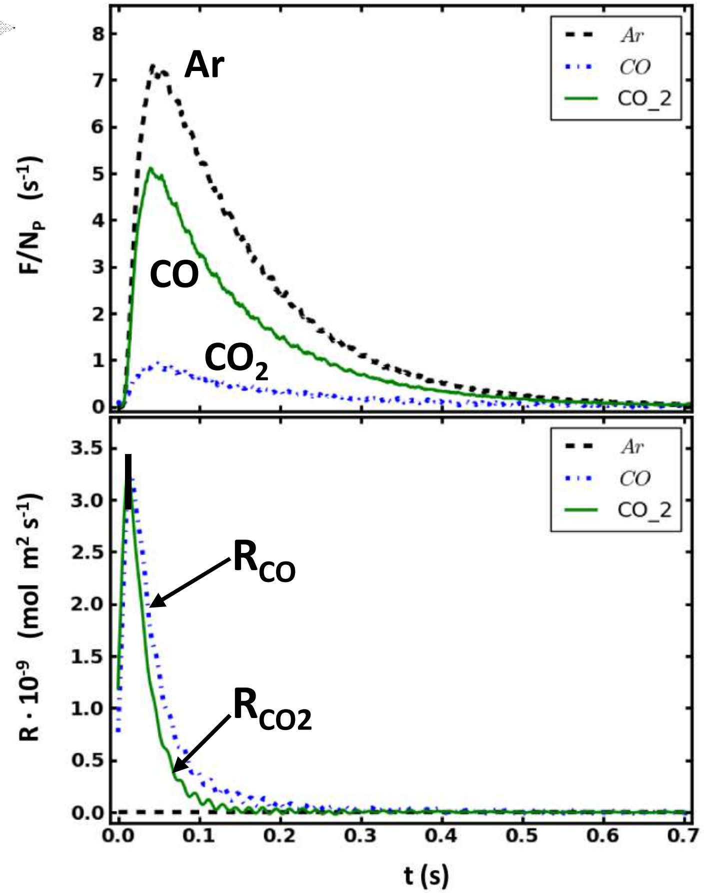
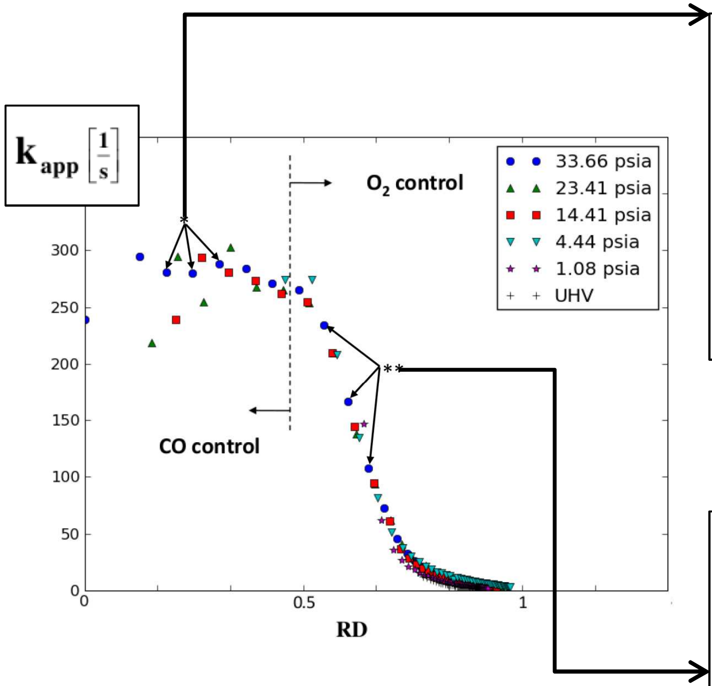


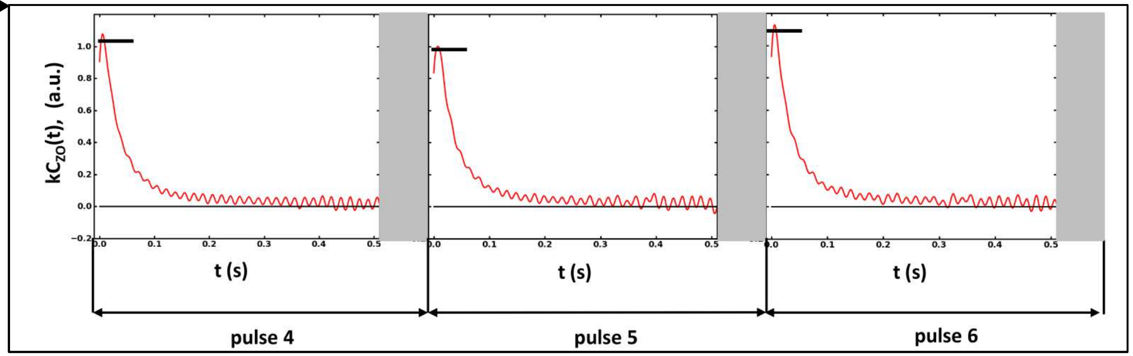


Case study: CO oxidation on Au/SiO_2

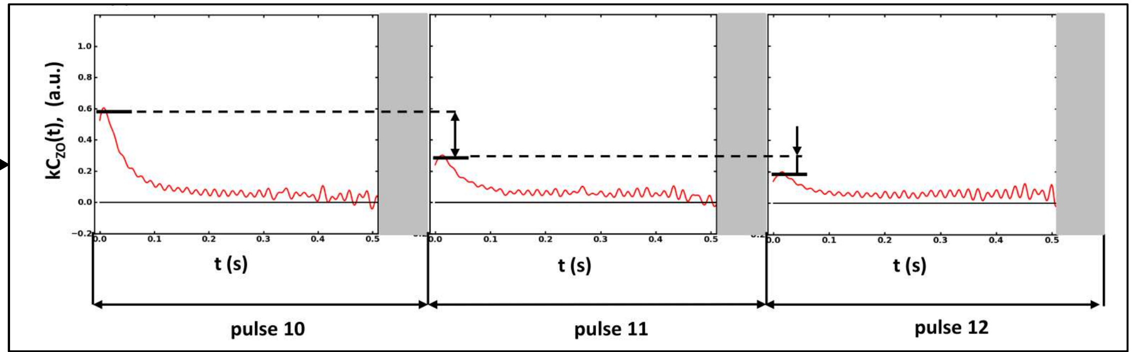
Intra-pulse analysis (sub-second time scale)



Apparent oxidation constant drops within each pulse,
but recovers its value by the beginning of the next pulse



Apparent oxidation constant drops within each pulse
as well as from one pulse to the next

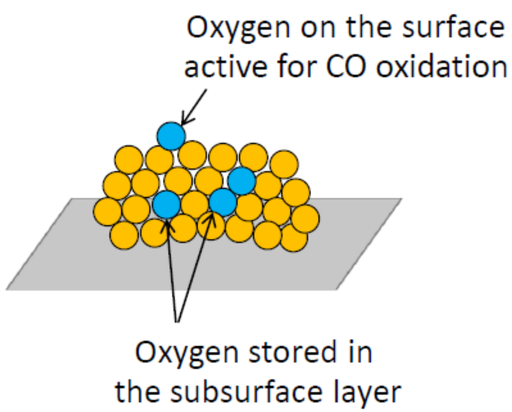


Apparent impact mechanism

$$R_{CO_2}(t) / C_{CO}(t) = k\, C_{ZO}(t)$$

Case study: CO oxidation on Au/SiO_2

Intra-pulse analysis (sub-second time scale)



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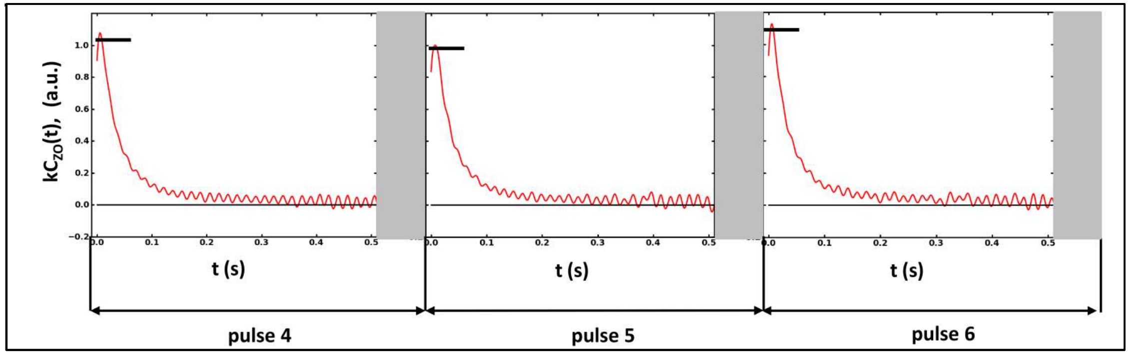

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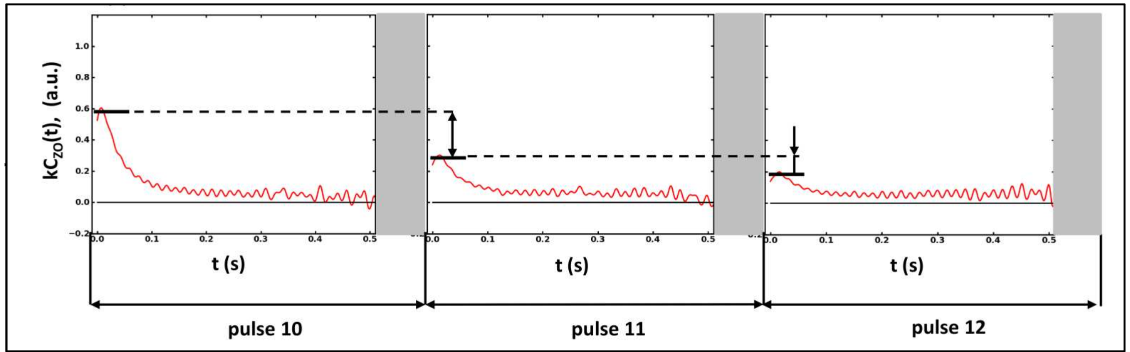

Conclusions

- Developed **novel systematic approach** to mechanism discrimination based on the transient kinetic analysis via the Y-Procedure.

- Case study suggest the existence of at least **two states of oxygen** on the Au/SiO_2 catalyst, only one of which is directly involved in CO oxidation under TAP conditions.

Acknowledgements

Prof. G. B. Marin

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Colleagues at various places

Q&A