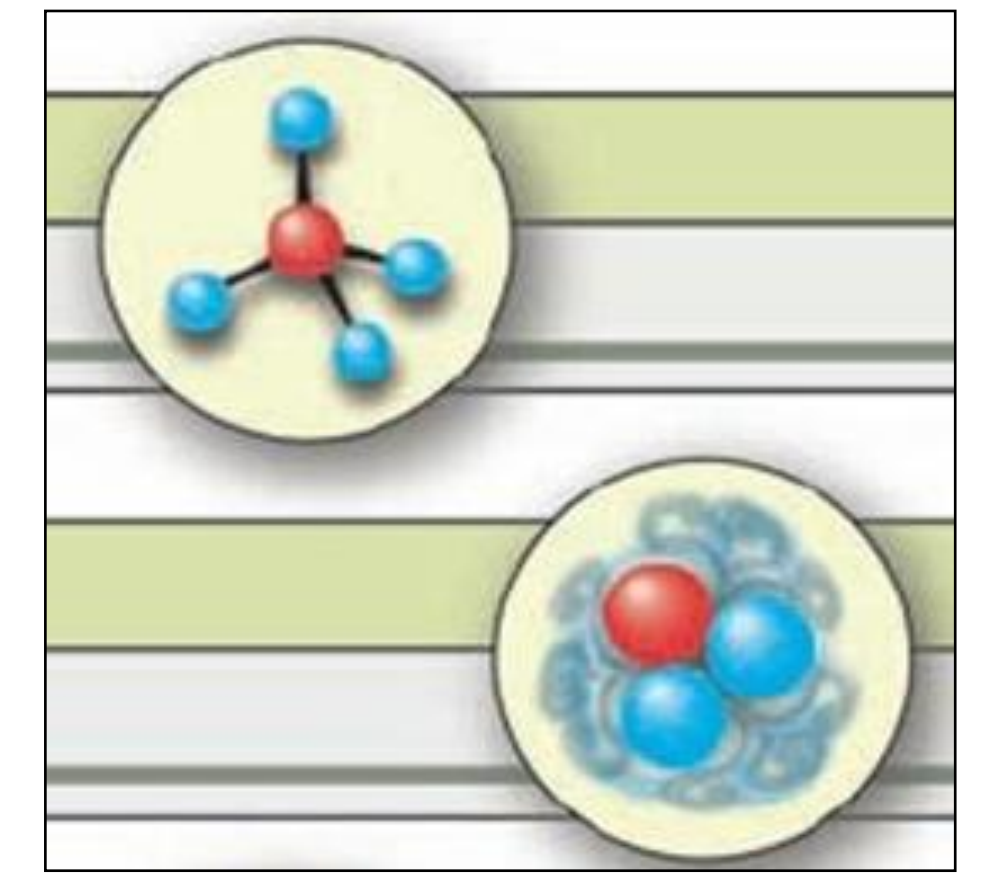


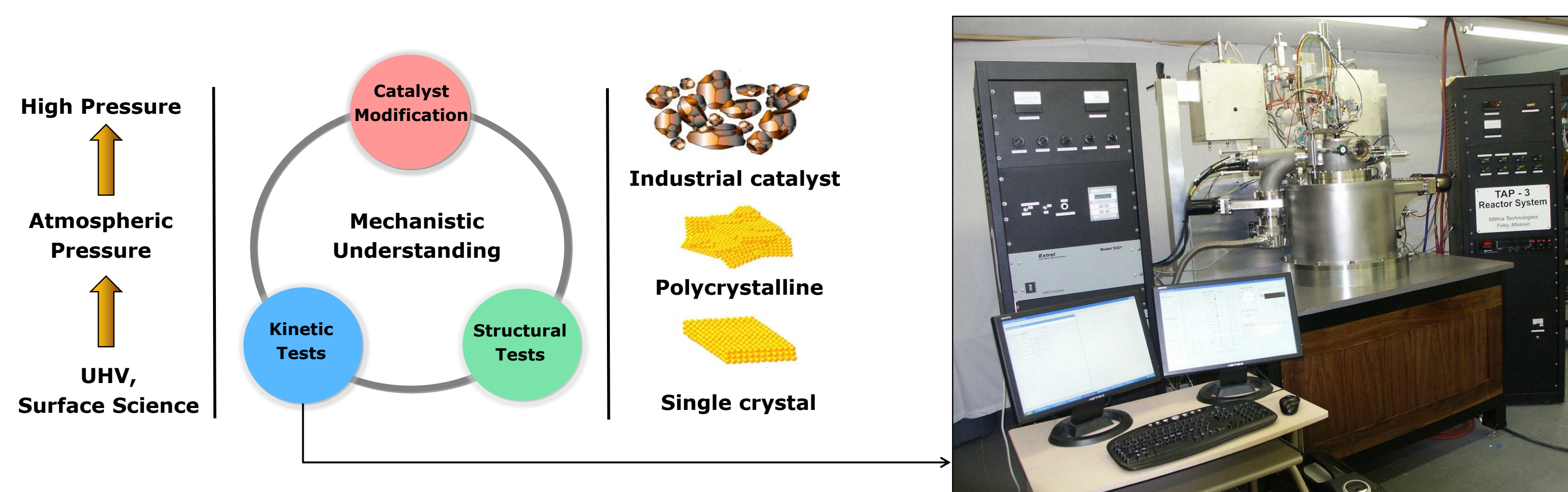
Non-Steady-State Catalyst Characterization with Thin Zone TAP experiments.

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Unraveling Catalytic Complexity Kinetic Testing with Thin Zone TAP reactor

- Relating small changes of intrinsic kinetic properties to changes of catalyst composition helps better understand **multiscale catalytic phenomena** which can improve rational catalyst design.
- Transient measurements of intrinsic kinetics are needed to discriminate mechanistic models of catalytic reactions and to identify needed scale up parameters.
- TAP-3 reactor system is capable of, [1]:
 - Measuring kinetics of both, model and industrial catalysts;
 - Switching between Knudsen diffusion regime and atmospheric pressure.

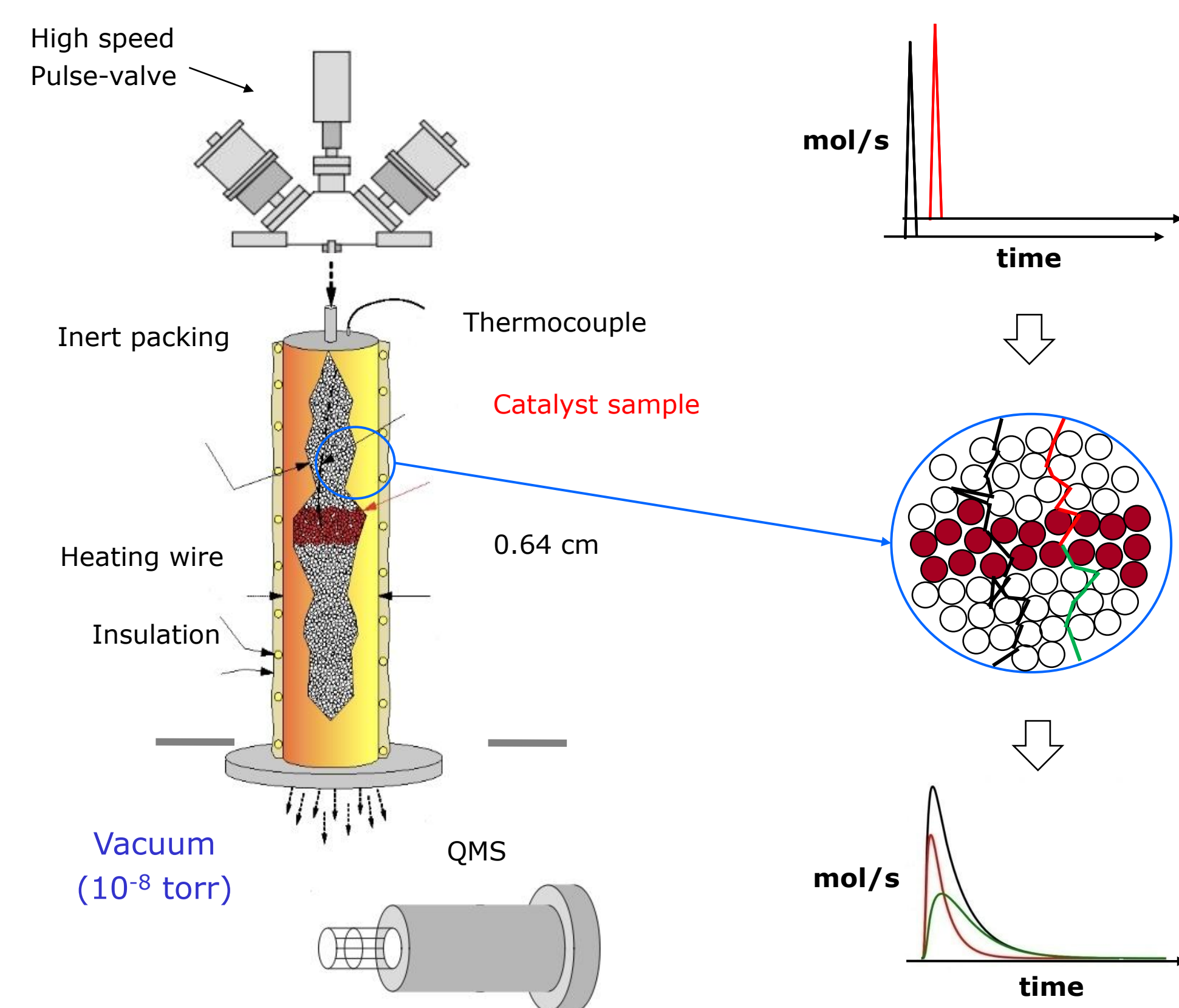


Requirements for catalyst characterization:

- Well defined transport to decouple intrinsic kinetics
- Control over catalyst changes during measurement
- Spatial uniformity of the sample to assign measured kinetics to a particular state of the catalyst

TAP-3 reactor system provides:

- Knudsen diffusion (gas interacts only with solid)
- State Defining, State Altering, Multipulse
- Thin Zone configuration maintains uniformity for conversions up to 80%, [2]



Short pulse
(10^{13} molecules)
Inert + Reagent

Knudsen diffusion
+ Reaction

Exit flux recorded
by QMS

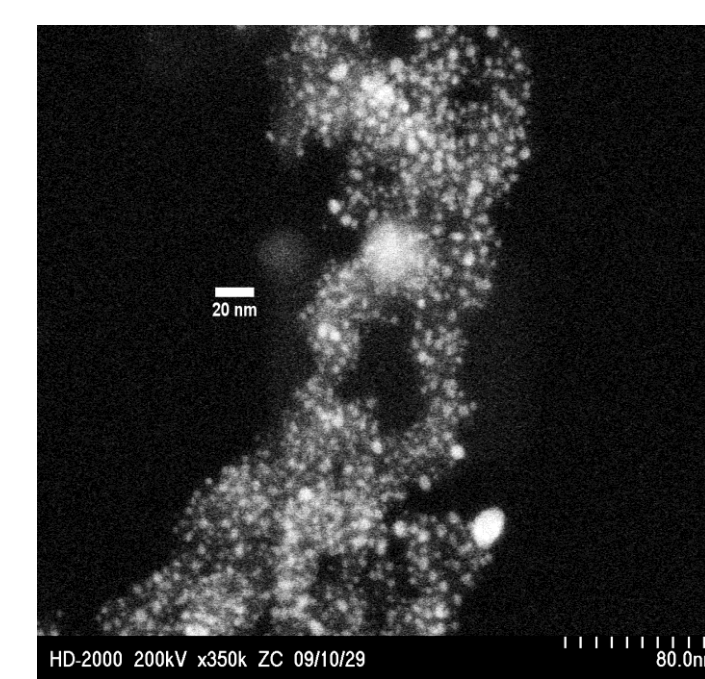
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- [5] - G. S. Yablonsky, D. Constaes, S. O. Shekhtman, J. T. Gleaves, The Y-Procedure: How to extract the chemical transformation rate from reaction-diffusion data with no assumption on the kinetic model, *Chem. Eng. Sci.*, **62** (2007) 6754

Application for Green Chemistry Gold Nanoparticles Supported on Silica, [3]

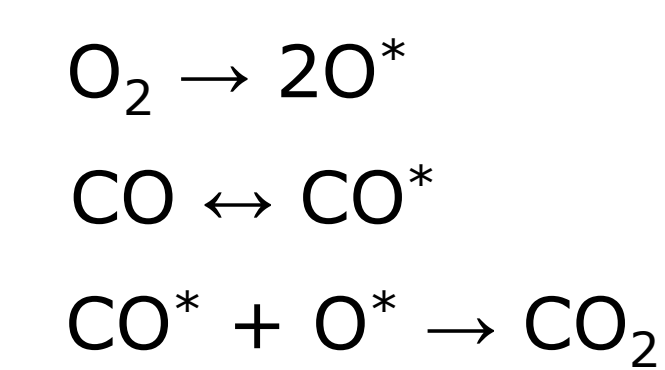
- Supported gold nano particles are potential candidates for new, more selective oxidation processes.
- The nature of catalytic activity and selectivity greatly depends on the preparation protocol and is still not fully understood.
- Non-reducible support (SiO₂) allows measuring intrinsic catalytic properties of gold nanoparticles.

Au/SiO₂



Magnetron Sputtering, [4]
(11 wt. %, ~3.2 nm)

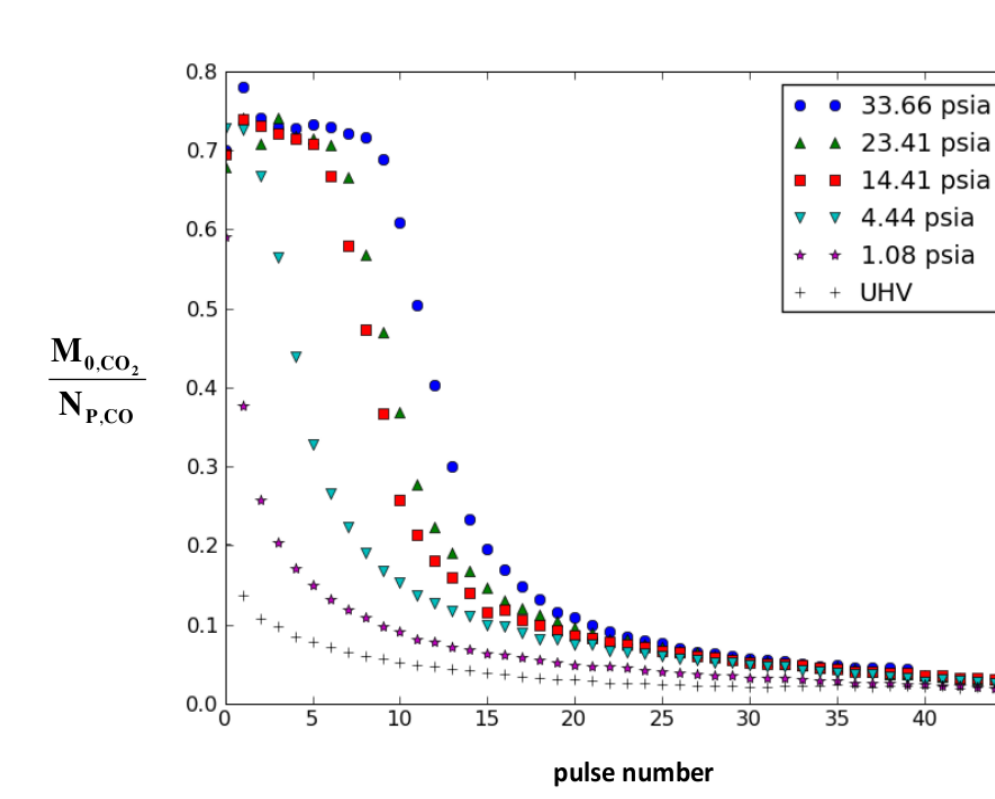
Model reaction - CO oxidation:



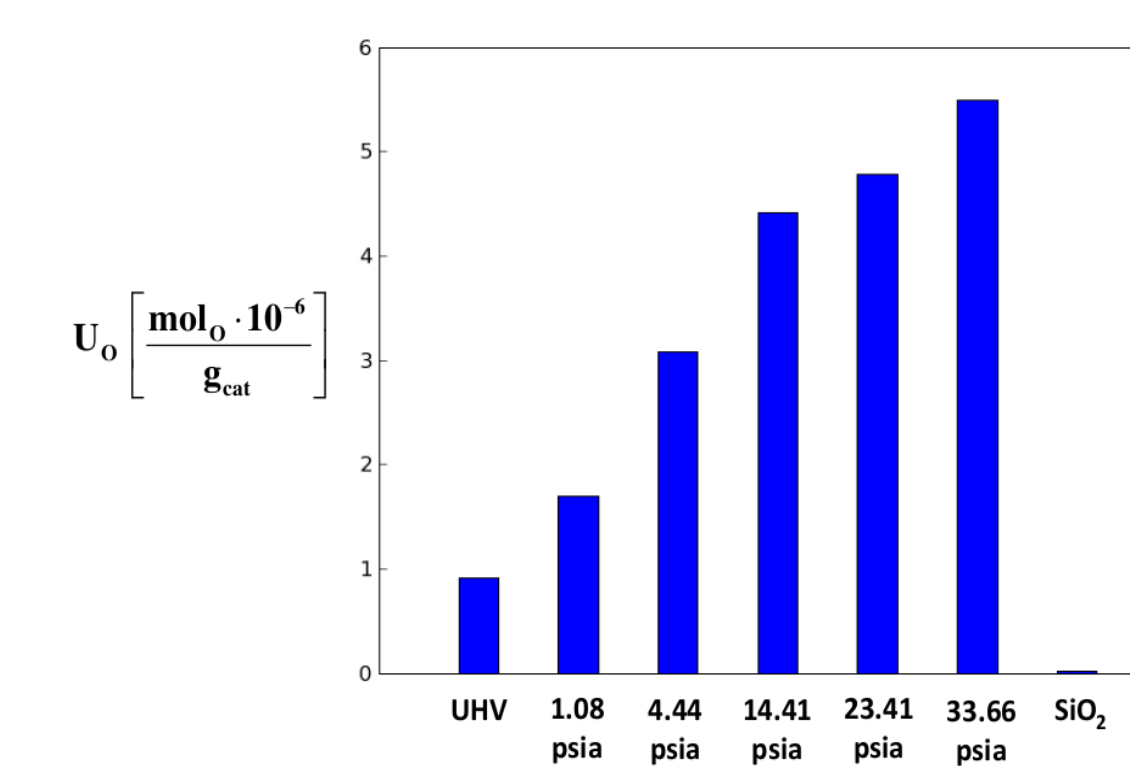
Experimental approach:

- Catalyst pretreatment with oxygen at elevated pressures
- Titration of the oxidized catalyst with CO under TAP conditions

Experimental Results:



CO titration curves for different pretreatment pressures



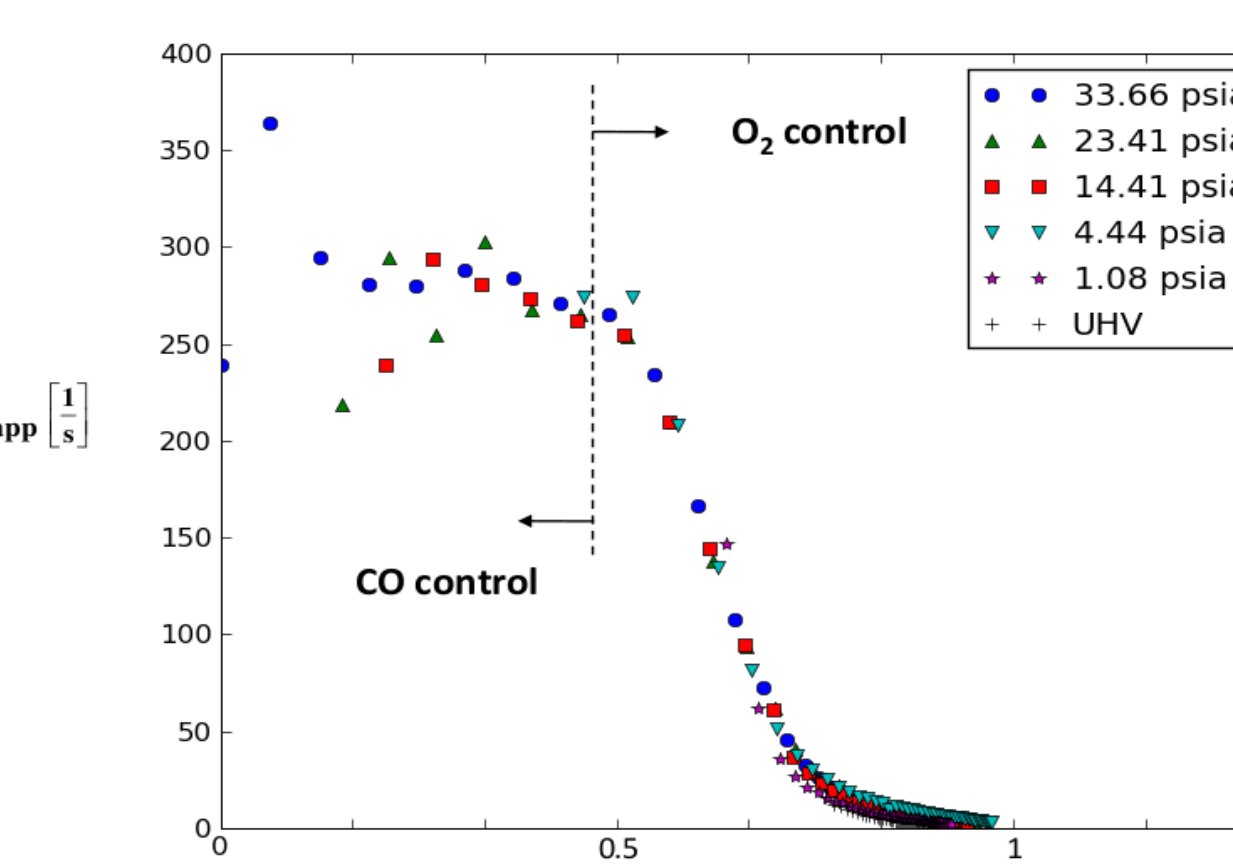
Integral amount of titrated oxygen

Kinetic Analysis via Moments:

$$\text{CO conversion: } X_{\text{CO}} = 1 - \frac{M_{\text{O,CO}}}{N_{\text{p,CO}}}$$

$$\text{Apparent kinetic constant: } k_{\text{app}} = \frac{X_{\text{CO}}}{1 - X_{\text{CO}}} \frac{1}{\tau_{\text{res}}} \quad k_{\text{app}} [1]$$

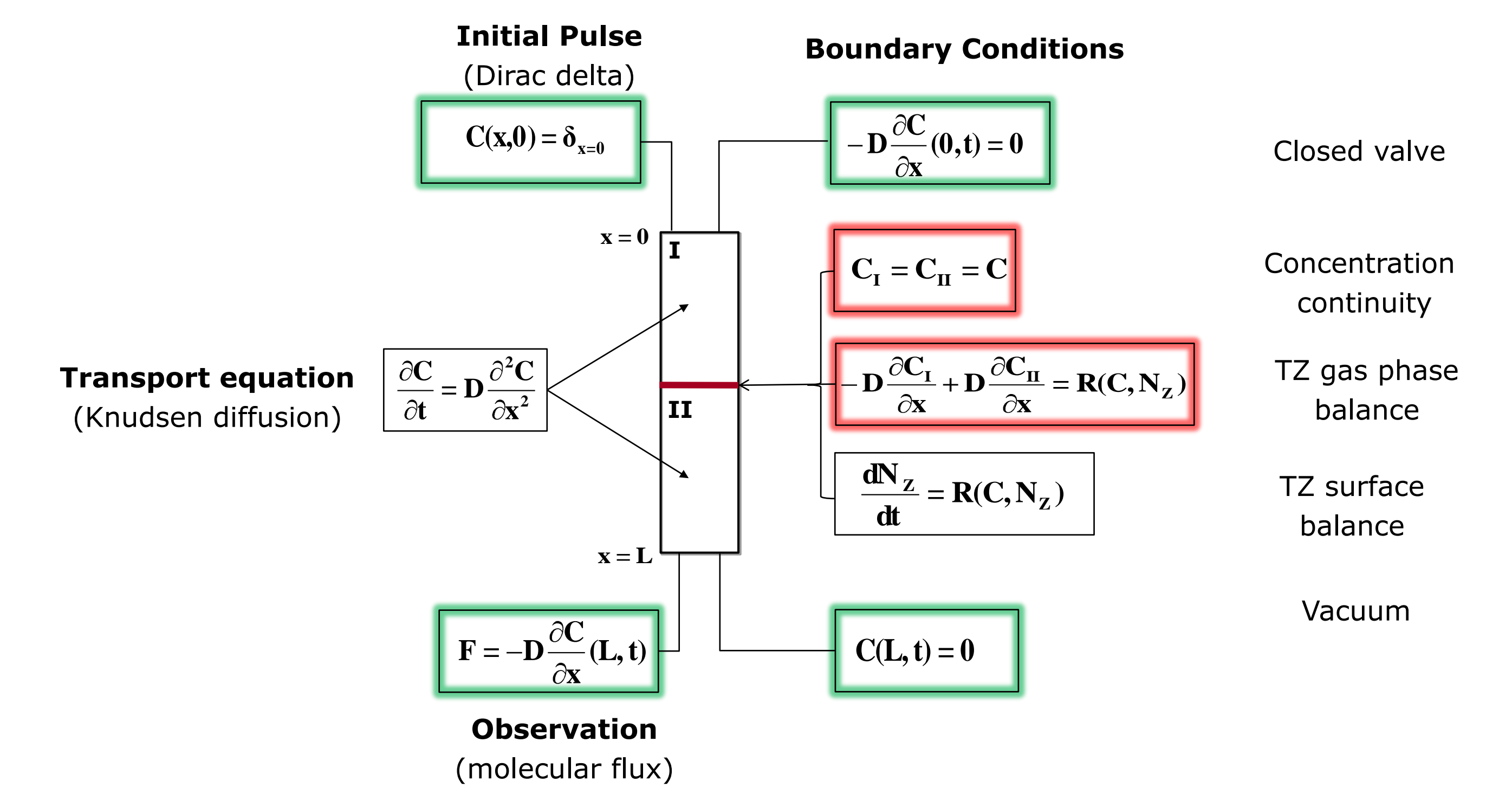
$$\text{Reduction degree: } \text{RD} = \frac{U_{\text{O}}}{U_{\text{O}}^{\text{max}}}$$



- Dependency of the apparent kinetic constant on the reduction degree, i.e. CO controlled plateau region followed by O₂ controlled decay region, reveals the presence of an oxygen reservoir created on the catalyst during the high pressure pretreatment
- Reservoir capacity is determined by the pretreatment pressure

Major Accomplishments 'Model-free' reconstruction of the Non-Steady-State Reaction Rates, Gas and Surface Concentrations

I. Mathematical model of the Thin Zone TAP reactor is posed as an inverse problem:

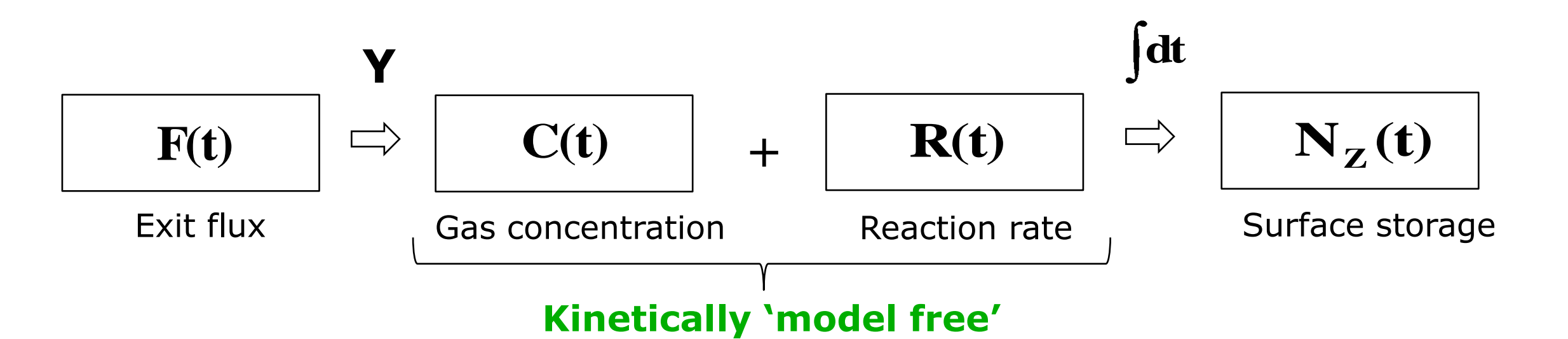


Solution of the Inverse Diffusion Problem:

Laplace/Fourier solution of the inverse diffusion problem relates gas concentration and molecular flux on one side of the inert zone to those on the other side, [5]:

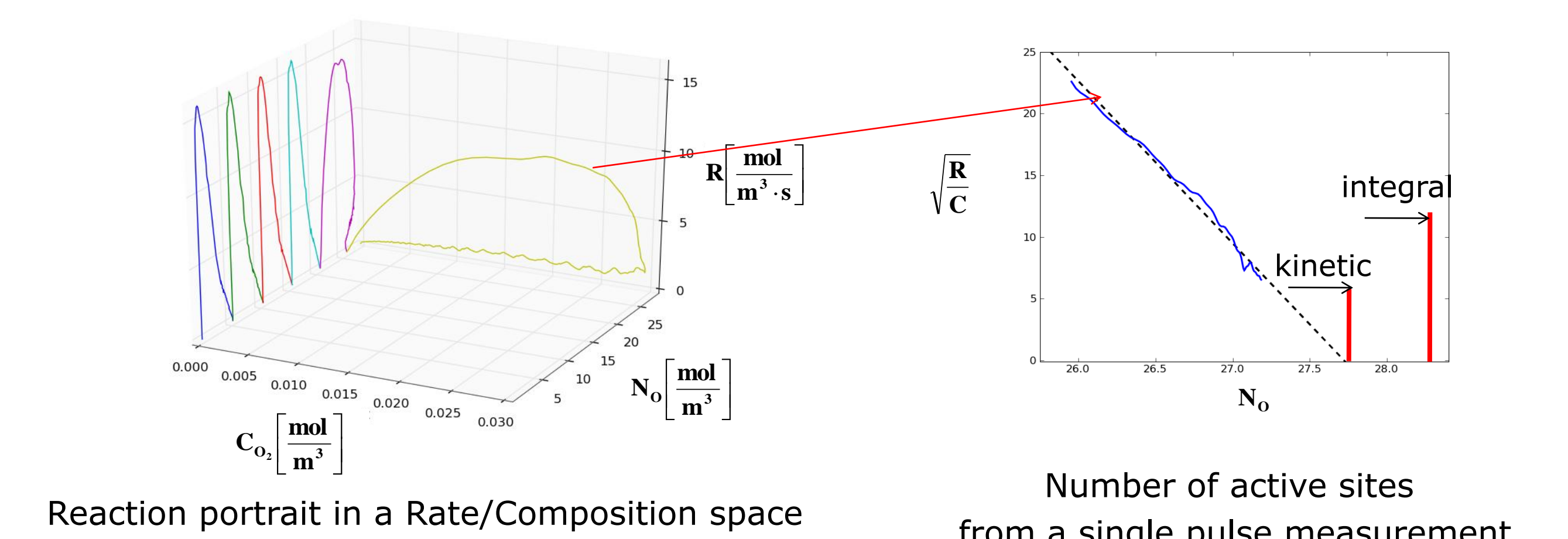
$$\begin{bmatrix} \exists C_{\text{TZ}} \\ \exists R_{\text{TZ}} \end{bmatrix} = \Psi(D, l, \epsilon) \begin{bmatrix} \exists C_{\text{exit}} \\ \exists F_{\text{exit}} \end{bmatrix}$$

Transient kinetics in the catalyst zone can be reconstructed with no *a priori* assumptions about the mechanism and the rate form:



II. Experimental applications of the Y-Procedure:

$$\text{Oxygen uptake on Pd: } R_{\text{O}_2} = k(N_{\text{Z,tot}} - N_{\text{OZ}})^2 C_{\text{O}_2}$$



Reaction portrait in a Rate/Composition space

$$\text{CO adsorption on Pd: } R_{\text{CO}} = k^+(N_{\text{Z,tot}} - N_{\text{ZCO}})C_{\text{CO}} - k^-N_{\text{ZCO}}$$

