Numerical and experimental aspects of Temporal Analysis of Products: a tool for understanding and designing heterogeneous catalysts

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Overview

• Introduction

• Case: total oxidation of volatile organic components

• Mathematical analysis

• Statistical analysis

• Best practices

• Conclusions
Steady-state versus transient

A ⇌ B ⇌ C ⇌ D

steady-state experiment

only rate-determining step manifested

Relaxation methods in heterogeneous catalysis

Pulse or step in carrier gas flow

Pulse response – TAP
No carrier gas flow

Temporal Analysis of Product (TAP) Pulse Response Experiment

Exit flow ($F_A$)

- Inert
- Reactant
- Product

0.0 time (s) 0.5

Microreactor
Reactant mixture
Catalyst
Vacuum ($10^{-8}$ torr)
Mass spectrometer

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Types of experiments

**Single pulse experiment**

- Knudsen diffusion regime
- No change in the state of the catalyst

Size ~ $10^{13}$ molecules

**Multi pulse experiment**

- Molecular diffusion regime
- Deliberate change in the state of the catalyst

Size > $10^{14}$ molecules/pulse

**Alternating pulse experiment**

- Two pulses of different gases
- By varying the time delay of the pulses, lifetime of active surface species can be determined
Two pulses of different gases
By varying the time delay of the pulses, lifetime of active surface species can be determined
Temporal Resolution of TAP

Pulse response

If reactant pulses small enough: Knudsen diffusion
Temporal Analysis of Products (TAP) setup

TAP-1
1988

TAP-2
1997

TAP-3E
2014


Main chamber
Mass spectrometer chamber
Diffusion pump
Set of pneumatic cylinders:
- Vacuum/Pressure experiments (By slide valve)
- Heating system
Manifold, Reactor Extractor
Main gate valve
The TAP-3E menu of experiments includes:

• Multireactors system (carousel). Reactor can be easily and rapidly removed from the system without venting the vacuum chambers. Easily switching between 6 reactors (in situ) within 1 minute.

• Vacuum pulse-responses. The four pulse valves can be triggered simultaneously or in a programmed alternating sequence

• Atmospheric pressure steady-state, step-transient, and SSITKA experiments, temperature programmed desorption (TPD), and temperature programmed reaction (TPR) experiments;

• Highly automated instrument that can be operated either locally or remotely via the Internet (with limited intervention on site for the initial experiment configuration)
Reactor extractor

Reactor carousel (6 reactors)

Reactor
Reactor carousel and reactor extractor
Manifold
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EXTREL QMS with conical aperture for increased signal-to-noise ratio
Experimental data and Knudsen model

Experimental (●) and simulated (─) responses

D = 1.75 x 10^{-3} m^2/s

Ar

D = 5.02 x 10^{-3} m^2/s

He

298 K

D vs sqrt T

D vs sqrt T

P^2 = 0.994

SQRT(T_{sp}), K^{0.5}
Intracrystalline diffusion

T = 298K

Ar

quartz (–)  H-ZSM 5 (–)
TAP-3: Atmospheric pressure experiments

The TAP-3E menu of experiments includes:

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TAP-3E: Atmospheric pressure experiments

Slide valve
(Atmospheric pressure experiments)

Reactor carousel
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Mars-van Krevelen (Redox) cycle

\[
\text{CuO-CeO}_2/\gamma-\text{Al}_2\text{O}_3
\]

re-oxidation

Reaction mechanism

Elementary steps + Active sites

\[ \text{C}_3\text{H}_8 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

- Elementary steps
- Active sites

- \( \text{Al}_2\text{O}_3 \)
- \( \text{CuO or CeO}_2 \)
- \( \text{O}^{*,s} \)
- \( \text{O}_\text{ads} \)
- \( \text{CO}_2 \)
- \( \text{O}_2 \)
- \( \text{C}_3\text{H}_8 \)
Kinetic modeling

\[ \text{C}_3\text{H}_8 \xrightarrow{\text{r}_5 = k_5 \text{C}_3\text{H}_8 \text{C}_\text{O}^*,\text{s}} \text{C}_3\text{H}_8\text{O}^*,\text{s} \]

\[ \text{C}_2\text{H}_4\text{O}^*,\text{s} \xrightarrow{\text{r}_6 = k_6 \text{C}_3\text{H}_8\text{O}^*,\text{s}} \text{CH}_3 \]

\[ \text{C}_2\text{H}_4\text{O}^*,\text{s} \xrightarrow{\text{r}_7 = k_7 \text{C}_3\text{H}_8 \text{C}_\text{O}^*,\text{s}} \text{C}_2\text{O}^*,\text{s} \]

Rates of elementary steps

Kinetic model

Optimal description of experimental data
Propane responses

Calculated

Experimental

Flow rate [10^{-8} mol s^{-1}]

Time [s]
Toluene: Oxygen labeling experiment

- Only 10% of water formed contained $\text{H}_2^{18}\text{O}$
- Mainly lattice oxygen participates in reaction

Unmesh Menon et al., J. Catal. 283 (2011) 1
Toluene: Oxygen labeling experiment

- $^{18}\text{O}$ in CO$_2$ more than in H$_2$O but still mainly $^{16}\text{O}$ in CO$_2$
- Di-Oxygen is mainly required for re-oxidation of the reduced surface metal centers

$\square + ^{18}\text{O}_2 \leftrightarrow ^{18}\text{O}_L + ^{18}\text{O}_s$

$^{18}\text{O}_s + \square \leftrightarrow ^{18}\text{O}_L$

$\square + ^{16}\text{O}_L^b \leftrightarrow ^{16}\text{O}_L + \square^b$

One pulse experiment

C$_7$H$_8$/$^{18}$O$_2$/Ar

$^{16}$O$_2$ pretreated catalyst

T=823 K

Unmesh Menon et al., J. Catal. 283 (2011) 1
Toluene: Carbon labeling experiment

 Activation of C-C bonds

\[ \text{\(^{12}\text{C}_6\text{H}_5^{13}\text{CH}_3} \rightarrow \text{^{12}\text{CO}_2} \quad \text{^{13}\text{CO}_2} \]  

\[ \text{Abstraction of methyl carbon atom followed by destruction of aromatic ring} \]

\[ \text{\(^{13}\text{CO}_2 \text{ is formed before } \text{^{12}\text{CO}_2} \} \]

Unmesh Menon et al., J. Catal. 283 (2011) 1
Toluene: Hydrogen labeling experiment

Peaks of H$_2$O, HDO, D$_2$O very close to each other

Simultaneous abstraction of hydrogen from methyl and aromatic ring or scrambling of hydroxyl groups on the surface

Unmesh Menon et al., J. Catal. 283 (2011) 1
Total oxidation mechanism: summary

Unmesh Menon et al., J. Catal. 283 (2011) 1
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TAP, designed for simple math

- Knudsen diffusion: constant diffusivity
- Tiny inlet pulse: essentially linear kinetics
- Long cylinder: 1D model suffices
- Linear equations in each zone

\[
\varepsilon \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - K_{cc} C + K_{c0} \Theta \\
\frac{\partial \Theta}{\partial t} = K_{\Theta C} C - K_{\Theta \Theta} \Theta
\]
Laplace transform

- Laplace transform: \( \mathcal{L}F(s) = \int_{0}^{+\infty} e^{-st} F(t) \, dt \)
- Derivatives to algebra: \( \mathcal{L}F'(s) = s\mathcal{L}F(s) - F(0) \)
- Initial conditions \( C = 0 \) and \( \Theta = 0 \)
- Determine coverages from equation:
  \[ \mathcal{L}\Theta = (s + K_{\Theta\Theta})^{-1} K_{\Theta C} \mathcal{L}C \]
- Transformed equations in each zone:
  \[ \varepsilon \, s \mathcal{L}C = D \frac{\partial^2 \mathcal{L}C}{\partial x^2} - K(s) \mathcal{L}C, \text{ i.e.} \]
  \[ \frac{\partial \mathcal{L}C}{\partial x} = -D^{-1} \mathcal{L}F \text{ and } \frac{\partial \mathcal{L}F}{\partial x} = -(\varepsilon \, s + K(s)) \mathcal{L}C \]

• In 2D or 3D, additional terms in Laplacian
• Simple math, separation of variables is possible.
• Transversally nonuniform components exhibit diffusional decay (pseudo-reaction \( k = D\lambda / r^2 \))
• At current aspect ratios, justifiably negligible: extinct in less than 1/15\(^{th}\) of peak time
Other boundary conditions

- Inlet can have premixing chamber.
- Outlet condition can be $F_{\text{out}} = \nu C_{\text{out}}$ finite $\nu$
- Order 1 effect similar to zone length uncertainty
- Order 2 effect similar to tiny time shift
- Justifiably neglected in current reactor setups


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Fourier transform

- Fourier transform: \((\mathcal{F}F)(\omega) = \int_{-\infty}^{+\infty} e^{-i\omega t} F(t) \, dt\)
- System is empty for past eternity \(t < 0\)
  
  So \(\int_{-\infty}^{+\infty} = \int_{0}^{+\infty}\) and hence \(\mathcal{F}F^{\text{out}}(\omega) = \mathcal{L}F^{\text{out}}(i\omega)\)

- Inversion, from Fourier back to time:
  
  \((\mathcal{F}^{-1} f)(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t} f(\omega) \, d\omega\)

- Example response one-zone inert:
Noise

Signal (mV)

Di-oxygen pulse response

Modulus (mV)

Sample time (ms)

Frequency (Hz)

No meaningful information
Thin-zone TAP-reactor: Uniformity

- For **not-too-fast reactions**, narrow zone ($\Delta L_{\text{cat}}/L < 1/20$) minimizes spatial concentration and temperature non-uniformities.

- Observed kinetics can be related to a **uniform catalyst composition**.

- A Fourier-domain algorithm (**the Y-Procedure**) can be used to translate exit flow rates into otherwise non-observable gas concentrations $C_{TZg}$ and rates $R_{TZ}$ within the uniform catalytic zone.

- The Y-Procedure is **kinetically “model-free”**, i.e. it does not require a priori assumptions about the mechanism and kinetic model of catalytic reactions.

$C_{\text{inlet}} = C_{\text{outlet}} = C_{TZg}^{TZg}$

$F_{\text{inlet}} - F_{\text{outlet}} = S_{\text{cat}} R_{TZ}^{TZ}(C_{g}, C_{s})$
Thin-zone TAP-reactor: Info on intermediates

Information flow:

\[
F_{\text{exit}}(t) \Rightarrow C_g(t) + R(t) \Rightarrow C_S(t)
\]

- Exit flux
- Gas concentration
- Reaction rate
- Surface concentration

Kinetically 'model free'

Coverage, Uptake, Release

\[
C_S(t) = C_{S,\text{init}} + \int_0^t \sum_i \nu_i r_i^+(t') dt' - \int_0^t \sum_i \nu_i r_i^-(t') dt'
\]

Thin-zone TAP-reactor: use of Y-procedure

Simulation results: CO oxidation via different mechanisms

\[ \text{O}_2 + 2\text{CO} \rightarrow 2\text{CO}_2 \]

Possible elementary steps:

1. \( \text{O}_2 + 2* \rightarrow 2\text{O}^* \)
2. \( \text{CO} + * \leftrightarrow \text{CO}^* \)
3. \( \text{CO} + \text{O}^* \rightarrow * + \text{CO}_2 \)
4. \( \text{CO}^* + \text{O}^* \rightarrow 2* + \text{CO}_2 \)

Possible mechanisms (combinations of steps):

- Eley-Rideal (ER): steps 1 and 3
- Langmuir-Hinshelwood (LH): steps 1, 2, and 4
- ER + LH: steps 1 - 4
- ER + CO ads.: steps 1, 2, and 3

Analysis of rate-concentration dependencies allows for model discrimination

\[ \text{ER, ER+CO ads.} \quad \text{LH, ER+LH} \]

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Experimental data: time series

mole flow (mol/s)

1.5e-08
1e-08
5e-09
0

0 0.1 0.2 0.3 0.4

time (s)

pulse response
average pulse response
Conditions for maximum-likelihood estimates

- The independent variables contain no experimental errors
- The model is adequate
- The mean experimental error is zero
- All errors are normally distributed
- The errors are homoskedastic
- The errors are uncorrelated
Heteroskedasticity of TAP noise

More noise near peak than in tail
Autocorrelation of TAP noise

\[ F \]

\[ t \]

\[ \varepsilon_1 \]

\[ \varepsilon_2 \]

Autocorrelation of TAP-noise
Second-order statistical regression

- G(aussian)
- H(omoskedastic)
- U(ncorrelated)

Average experimental time series → NLSQ → Model-calculated time series → Linear transform → Transformed average experimental time series

Principal Component Analysis and rescaling

Projection on the Principal Component Axes

Rescaling of the principal component axes
Estimation of diffusion coefficient

Second Order Statistical Regression (SOSR): realistic confidence intervals

$D_e (m^2/s)$

with DKLT
without DKLT
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The Ten Commandments:

I. Thou shalt verify Knudsen
II. Correct thy baseline
III. Waste nor scrimp collection time
IV. Beware spectrally localized noise
V. Be neither finicky nor coarse in sampling
Regression of TAP-Data: Best Practices

The Ten Commandments (cont’d):

VI. Count thy replicates
VII. Thy pulse size will stray
VIII. Thy kinetics be linear: pulse modestly
IX. Rightfully regress
X. Spare thy fancy weaving the network
I. Knudsen diffusion regime

\[ D_j = \frac{4\pi r \varepsilon}{3 \tau} \sqrt{\frac{2RT}{\pi M_j}} \]

\[ D_j = D_{ref} \sqrt{\frac{T}{T_{ref}}} \sqrt{\frac{M_{ref}}{M_j}} \]
IV. Spectrally localized noise
V. Do not sample too much

\[ \rho(\Delta t) = \exp\left(-\frac{\Delta t}{\theta}\right) \quad \text{Gauss-Markov stochastic process} \]
VIII. Ensure state-defining conditions

Catalyst State

\[ \text{Rate} = \sum k_a (...) C_g + \sum k_j (...) \theta_j \]

Rate Coefficients that include catalyst state

in the catalyst zones

\[ \varepsilon_{\text{cat}} \frac{\partial C_g}{\partial t} = D_{\text{cat}} \frac{\partial^2 C_g}{\partial x^2} - k_a C_g + \sum k_j \theta_j \]

in the inert zones

\[ \varepsilon_{\text{in}} \frac{\partial C_g}{\partial t} = D_{\text{in}} \frac{\partial^2 C_g}{\partial x^2} \]
 IX. Second-Order Statistical Regression

noise needs to be
\- whitened
\- rendered homoskedastic
X. Parcimonious network selection

- Bode analysis helps bound network complexity
- In line with the experimental window on reality

Example:

\[ |H_{2,1}(2\pi i\nu)| \]

\[ \arg(H_{2,1}(2\pi i\nu)) \]

\[ \nu \text{ (Hz)} \]

\[ \begin{align*}
A_1 & \quad k_1 \quad A_3 \quad k_2 \quad 2A_2 \\
& \quad k_3 \quad A_4 \\
& \quad k_4 \quad A_5 \\
k_1 &= 550 \text{ Hz} \\
k_2 &= 5 \text{ Hz} \\
k_3 &= 50 \text{ Hz} \\
k_4 &= 1.5 \text{ Hz} \\
k_5 &= 1 \text{ Hz}
\end{align*} \]
Purpose

• Solve the direct problem: calculate TAP pulse responses from a general 1D reactor model
• Solve inverse problems: regress TAP experimental data and estimate various physical and kinetic parameters

Features

• Regresses the raw pulse responses (in volts) directly
• Regression
  • NLSQ (classical non-linear least square regression)
  • SOSR (second order statistical regression)
• Uses the Levenberg-Marquardt method for optimization
• Integration can be performed in
  • time domain
  • frequency domain (Fourier transformation, for linear kinetics)
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TAP offers a unique mix of opportunities:

• data acquisition near millisecond resolution
• insignificant perturbation of catalyst state
• robust math modeling
• both intuitive qualitative interpretation and advanced model-free analysis techniques
• challenges for catalytic, engineering and mathematical research
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For a linear, time-invariant system.....

**Transfer function** $H(2\pi iv)$ is a mathematical representation in terms of temporal frequency $v$ of the relation between the input $X(2\pi iv)$ and output $Y(2\pi iv)$ with zero initial conditions and zero-point equilibrium such that $Y(2\pi iv)=H(2\pi iv)\cdot X(2\pi iv)$

**Bode plot** is a graph of the transfer function versus frequency, typically plotted with a log-frequency axis. Often it is a combination of magnitude plot $|H(2\pi iv)|$ and phase plot $\arg(H(2\pi iv))$.

**Poles** of the transfer function show up on Bode plots as breakpoints at which the slope decreases.

**Zeros** of the transfer function show up on Bode plots as breakpoints at which the slope increases.