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

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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/SiO₂ 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 \((10^{14} \text{ molecules})\) and narrow \((150 \mu \text{s})\) 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)

Kinetic parameters for assumed mechanism

F_{inlet} \rightarrow \text{Model fitting} \rightarrow \text{Kinetic parameters for assumed mechanism} \rightarrow F_{exit}(t)
Model fitting vs. the Y-Procedure

Model fitting (regression)

Kinetic parameters for assumed mechanism

Connectivity features of pseudo-monomolecular reaction networks

R. Roelant et. al, 2011 (Fourier analysis)
Model fitting vs. the Y-Procedure

Model fitting (regression)
R. Roelant et. al, 2011 (Fourier analysis)

Kinetic parameters for assumed mechanism

Connectivity features of pseudo-monomolecular reaction networks

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

$C_g(t)$ and $R(t)$

G. S. Yablonsky et. al, 2007

(Fourier analysis)
Model fitting vs. the Y-Procedure

Model fitting (regression)

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

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Connectivity features of pseudo-monomolecular reaction networks

Kinetic parameters for assumed mechanism

C_g(t) and R(t)

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

G. S. Yablonsky et. al, 2007
(Fourier analysis)
Systematic strategy

A. For a given catalyst state:

1. Reconstruct gas concentrations and reaction rates

2. Evaluate surface uptakes based on gas rates

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

B. Repeat for evolving catalyst states
Concept

Surface Uptakes
Communication between gas and surface phases

Molecular adsorption: \[ Z + A = ZA \]

Dissociative adsorption: \[ 2Z + A = 2ZA \]

Product release: \[ ZA = Z + B \]
Communication between gas and surface phases

1. Molecular adsorption:  \[ Z + A = ZA \]
   Dissociative adsorption:  \[ 2Z + A = 2ZA \]
   Product release:  \[ ZA = Z + B \]

2. Impact reaction steps:  \[ ZA + B = Z + AB \]
Communication between gas and surface phases

1. Molecular adsorption:  
   \[ Z + A = ZA \]

2. Dissociative adsorption:  
   \[ 2Z + A = 2ZA \]

3. Product release:  
   \[ ZA = Z + B \]

Impact reaction steps:

4. \[ ZA + B = Z + AB \]

‘Hidden’ surface steps:

5. \[ ZA + ZB = Z + ZC \]

6. \[ ZA = ZC \]

7. \[ ZA + Z = Z_2A \]
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:

\[
C_s(t) = C_{s,\text{init}} + \int_0^t \sum_i \nu_i I_i^+(t') dt' - \int_0^t \sum_i \nu_i I_i^-(t') dt' = C_{s,\text{init}} + \int_0^t \sum_g \nu_g R_g(t') dt'
\]

Uptake  Release  Gas Rates
Concept

Kinetic coherency
Kinetic (de)coherency

**Kinetic coherency** – Every combination of elementary steps leads to synchronization of certain kinetic characteristics
Kinetic (de)coherency

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

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

\[ \text{O}_2 + 2Z \xrightarrow{k_1} 2ZO \]

\[ \text{CO} + Z \xrightarrow{k_{+2}} \text{ZCO} \xleftarrow{k_2} \text{ZCO} \]

\[ \text{ZO} + \text{CO} \xrightarrow{k_3} Z + \text{CO}_2 \]

\[ \text{ZO} + \text{ZCO} \xrightarrow{k_4} 2Z + \text{CO}_2 \]
Prototypical mechanism: CO oxidation

Impact mechanism or Eley-Rideal (ER)

$O_2 + 2Z \xrightleftharpoons[k_1]{k_2} 2ZO$

$CO + Z \xrightarrow{k_3} ZCO$

$ZO + CO \xrightarrow{k_4} Z + CO_2$

$ZO + ZCO \xrightarrow{k_4} ZZ + CO_2$

- oxygen atom
- carbon atom
Prototypical mechanism: CO oxidation

Adsorption mechanism or Langmuir-Hinshelwood (LH)

\[
\begin{align*}
O_2 + 2Z & \xrightarrow{k_1} 2ZO \\
CO + Z & \xleftrightarrow{k_{+2}, k_2} ZCO \\
ZO + CO & \xrightarrow{k_3} Z + CO_2 \\
ZO + ZCO & \xrightarrow{k_4} 2Z + CO_2
\end{align*}
\]

- oxygen atom
- carbon atom
Prototypical mechanism: CO oxidation

ER + buffer CO adsorption

\[ \text{O}_2 + 2Z \xrightarrow{k_1} 2ZO \]

\[ \text{CO} + Z \xrightarrow{k_2} \text{ZCO} \]

\[ ZO + CO \xrightarrow{k_3} Z + \text{CO}_2 \]

\[ ZO + ZCO \xrightarrow{k_4} ZZ + \text{CO}_2 \]
Prototypical mechanism: CO oxidation

Combined mechanism or ER + LH

\[ O_2 + 2Z \xrightarrow{k_1} 2ZO \]

\[ CO + Z \xrightarrow{k_{+2}} ZCO \quad \xleftarrow{k_2} ZCO \]

\[ ZO + CO \xrightarrow{k_3} Z + CO_2 \]

\[ ZO + ZCO \xrightarrow{k_4} 2Z + CO_2 \]
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

\[ ZO + CO \rightarrow Z + CO_2 \]

CO and CO\(_2\) rates are identical
Numerical example: CO oxidation

CO pulse over fully oxidized surface

\[
CO + Z \rightleftharpoons ZCO \\
ZO + ZCO \rightarrow 2Z + CO_2
\]

CO and CO\(_2\) rates are different
Numerical example: CO oxidation
CO pulse over fully oxidized surface

\[ \text{Eley-Rideal} \]
\[ \text{Langmuir-Hinshelwood} \]

\[ ZO + CO \rightarrow Z + CO_2 \]
\[ CO + Z \rightleftharpoons ZCO \]
\[ ZO + ZCO \rightarrow 2Z + CO_2 \]

Y-Procedure facilitates mechanism discrimination

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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

X. Zheng et al., 2010
Case study: CO oxidation on Au/SiO$_2$

Experiment

1. Pretreatment with O$_2$ flow

2. Evacuation to TAP cond.

3. Titration with CO pulses

X. Zheng et al., 2010
Case study: CO oxidation on Au/SiO₂

1. Pretreatment with O₂ flow
   \[ \text{O}_2 \]

2. Evacuation to TAP cond.

3. Titration with CO pulses
   \[ \text{CO} \]

X. Zheng et al., 2010
Case study: CO oxidation on Au/SiO$_2$

**Experiment**

1. Pretreatment with O$_2$ flow
2. Evacuation to TAP cond.
3. Titration with CO pulses

**Global analysis**

- Total titrated oxygen
- Pretreatment pressure

**Mechanistic hypothesis**

X. Zheng et al., 2010

Oxygen
flow pretr.

TAP: CO titr.

Two kinetically distinct “reservoirs” exchanging oxygen
Case study: CO oxidation on Au/SiO₂

Intra-pulse analysis (Y-Procedure)
Case study: CO oxidation on Au/SiO$_2$

Intra-pulse analysis (Y-Procedure)
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)

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.

Oxygen on the surface active for CO oxidation

Oxygen stored in the subsurface layer
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.
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