An efficient approach towards predictive kinetic models

W. Hauptmann, M. Votsmeier, J. Gieshoff, D. G. Vlachos, A. Drochner, H. Vogel
Introduction
- Literature Mechanisms -


An efficient approach towards predictive kinetic models
Modeling Process
- Process Steps -

- Experiments
- Model Development
- Simulation
- Model Analysis
- Optimization

Predictive Model
An efficient approach towards predictive kinetic models
Experiments
- Test Bench -

An efficient approach towards predictive kinetic models
Experiments
- Inverse Hysteresis -

\[ \varphi_0(\text{NO}) = 430 \text{ vol.-ppm}; \varphi_0(\text{O}_2) = 6 \text{ vol.-%}; \text{balance N}_2; \ \beta = \pm 5 \text{ K min}^{-1}; \]

An efficient approach towards predictive kinetic models
Model Development

Experiments

Model Development

Simulation

Model Analysis

Optimization

Predictive Model
Model Development
- Mechanism -


An efficient approach towards predictive kinetic models
An efficient approach towards predictive kinetic models

- Collision Theory
  - Adsorption
    - Sticking Coefficient
  - Transition State Theory
    - Desorption
      - Bimolecular Surface Reaction
        - A = $10^{16} \text{ s}^{-1}$
          (DoF$_{\text{Transition State}} >$ DoF$_{\text{Adsorbates}}$
        - A = $10^{11} \text{ s}^{-1}$
          (Mobile adsorbates without rotation)

Model Development
- Activation Energy -

Surface reaction (AB → A + B):
- Activation energy (forward reaction):
  \[ E_{a_f} = x_{AB,TS} \left( \Delta H_{\text{Surf}} + \frac{Q_A Q_{B(C)}}{Q_A + Q_{B(C)}} \right) \]
- \( \Delta H_{\text{Surf}} \):
  - Dissociation
    \[ \Delta H_{\text{Surf}} = Q_{AB} + D_{AB} - Q_A - Q_B \]
  - Bimolecular reaction
    \[ \Delta H_{\text{Surf}} = Q_C + Q_{AB} + D_{AB} - D_{BC} - Q_A - Q_{BC} \]
- Activation energy (back reaction):
  \[ E_{a_b} = E_{a_f} - \Delta H_{\text{Surf}} \]

Adsorption:
- \( E_a = 0.0 \text{ kJ mol}^{-1} \)

Desorption:
- \( E_a = \text{Heat of adsorption} \)


An efficient approach towards predictive kinetic models
An efficient approach towards predictive kinetic models
Simulation
- Initial Mechanism -

\[ \phi_0(\text{NO}) = 430 \text{ vol.-ppm}; \phi_0(\text{O}_2) = 6 \text{ vol.-\%}; \text{balance N}_2; \beta = \pm 5 \text{ K min}^{-1}; \]
Modeling Process
- Process Steps -

Experiments

Model Development

Simulation

Model Analysis

Optimization

Predictive Model
Model Analysis
- Sensitivity Analysis -

**Objective:**
- Identification of relevant parameters and/or reactions.
Model Analysis
- Sensitivity Analysis -

Objective:
- Identification of relevant parameters and/or reactions.

Procedure:
- Iterative variation of each parameter value.
- Calculation of normalized sensitivity coefficients (NSC).

Calculation:
\[ SC_{i,r} = \frac{\partial Res_i}{\partial Para_r} \]
\[ NSC_{i,r} = \frac{Para_r}{Res_i} \frac{\partial Res_i}{\partial Para_r} \]
Model Analysis
- Sensitivity Analysis -

**Objective:**
- Identification of relevant parameters and/or reactions.

**Procedure:**
- Iterative variation of each parameter value.
- Calculation of normalized sensitivity coefficients (NSC).

**Calculation:**
\[ SC_{i,r} = \frac{\partial Res_i}{\partial Para_r} \]
\[ NSC_{i,r} = \frac{Para_r}{Res_i} \cdot \frac{\partial Res_i}{\partial Para_r} \]

**Interpretation:**
- NSC-value corresponds to parameter impact.
- Sign (+/-) shows proportionality.

An efficient approach towards predictive kinetic models
Model Analysis
- Result -

\[
\begin{align*}
Pt-NO + Pt-O & \rightarrow Pt-NO_2 + Pt \\
Pt-NO_2 & \rightarrow NO_2 + Pt \\
NO_2 + Pt & \rightarrow Pt-NO_2 \\
Pt-NO & \rightarrow NO + Pt \\
NO + Pt & \rightarrow Pt-NO \\
2 Pt-O & \rightarrow O_2 + 2 Pt \\
O_2 + 2 Pt & \rightarrow 2 Pt-O
\end{align*}
\]

\[A' = \frac{A_{\text{Original}}}{10}\]
\[Ea' = Ea_{\text{Original}} + 20 \text{ kJ mol}^{-1}\]
\[Ea' = Ea_{\text{Original}} + 30 \text{ kJ mol}^{-1}\]
Optimization
Optimization
- Iterative Process -

1. Model
2. Initial Guess
3. DoE
4. Fit Polynomial
5. Minimize Objective Function
6. Reference Data
8. Use last Initial Guess. Reduce Size of Design.
9. Yes: Res< \text{SC}
10. No: Res> \text{SC}

An efficient approach towards predictive kinetic models

Clean air is our business
Optimization
- Optimization Results -

\[ X_{\text{NO}} \]

\( T / ^\circ \text{C} \)

- Heating

\( X_{\text{NO}} \) Experiment Run 1

- Simulation Run 1

\( X_{\text{NO}, \text{eq}} \)

\[ \varphi_0(\text{NO}) = 430 \text{ vol.-ppm}; \varphi_0(\text{O}_2) = 6 \text{ vol.-%}; \text{balance N}_2 \]


An efficient approach towards predictive kinetic models

Clean air is our business
Optimization
- Model Assessment -

\[ \phi_0(\text{NO}) = 280 \text{ vol.-ppm}; \quad \phi_0(\text{O}_2) = 6 \text{ vol.-\%}; \quad \text{balance } \text{N}_2 \]


An efficient approach towards predictive kinetic models

Clean air is our business
Optimization
- Model Assessment Light-Off/Light-Out-

Mechanism can't describe inverse hysteresis

\[ \varphi_0(\text{NO}) = 430 \text{ vol.-ppm; } \varphi_0(\text{O}_2) = 6 \text{ vol.-\%}; \text{ balance N}_2 \]
An efficient approach towards predictive kinetic models
Model Elaboration
- Implementation of Catalyst Deactivation -

| R1  | O₂ + 2 Pt | → | 2 Pt-O |
| R2  | 2 Pt-O    | → | O₂ + 2 Pt |
| R3  | NO + Pt  | → | Pt-NO |
| R4  | Pt-NO    | → | NO + Pt |
| R5  | NO₂ + Pt | → | Pt-NO₂ |
| R6  | Pt-NO₂   | → | NO₂ + Pt |
| R7  | Pt-NO + Pt-O | → | Pt-NO₂ + Pt |
| R8  | Pt-NO₂ + Pt | → | Pt-NO + Pt-O |
| R9  | Pt-NO₂   | → | PtOx + NO |
| R10 | PtOx + NO | → | Pt-NO₂ |

Model Elaboration
- Model Performance -

\[ X_{\text{NO}} \text{ Experiment Run1} \]
\[ X_{\text{NO}} \text{ Experiment Run2} \]
\[ X_{\text{NO}} \text{ Simulation Run1} \]
\[ X_{\text{NO}} \text{ Simulation Run2} \]
\[ X_{\text{NO}, \text{eq}} \]

\( \varphi_{0}(\text{NO}) = 430 \text{ vol.-ppm}; \varphi_{0}(\text{O}_2) = 6 \text{ vol.-%}; \text{balance N}_2 \)

Model Elaboration
- Model Assessment -

\[ \varphi_0(\text{NO}) = 280 \text{ vol.-ppm}; \varphi_0(\text{O}_2) = 6 \text{ vol.-%}; \text{balance N}_2 \]


An efficient approach towards predictive kinetic models
Model Elaboration
- Model Assessment II -

\[ \phi_0(\text{NO}) = 430 \text{ vol.-ppm}; \phi_0(\text{O}_2) = 6 \text{ vol.-\%}; \text{balance N}_2 \]


An efficient approach towards predictive kinetic models
Summary

**Model Development:** Applied theories are appropriate to parameterize kinetic models.

**Simulation:** Low temperature activity of the initial mechanism is too high.

**Model Analysis:** Sensitivity analysis and Shainin analysis are able to determine the active parameters.

**Optimization:** Iterative process is appropriate for parameter estimation.

**Predictive Model:** Model without catalyst deactivation is able to describe the light-off-behavior. Model including catalyst deactivation is able to describe the light-off/light-out behavior.

Experiments: The NO oxidation on Pt shows an inverse hysteresis.

An efficient approach towards predictive kinetic models
Special thanks go to

- Alfons Drochner
- Herbert Vogel
- Martin Votsmeier
- Jürgen Gieshoff
- Dion Vlachos
Thank you for your kind attention!