ADVANCED APPROACHES TO THE KINETIC STUDY OF CATALYTIC REACTIONS:

a) Transient methods;
b) Structured lab-scale reactors.
Outline (1/2)

1. Transient Response Methods applied to the kinetic analysis of the DeNOx-SCR reaction
   • Transient adsorption-desorption and reactivity study of the SCR reactants (NH$_3$, NO) over V/W/TiO$_2$ catalysts
   • Kinetic modeling and comparison with steady-state data
   • Role of WO$_3$, kinetic influence of H$_2$O
   • Application to dynamic modeling of SCR reactors
   • Extension of TRMs to the kinetic analysis of NOx storage in NOx traps (Pt/BaO/Al$_2$O$_3$ systems)
Outline (2/2)

2. Lab-scale structured reactors for kinetic measurements in catalytic combustion

✓ Design and operation of an **annular reactor** for the kinetic study of CH\textsubscript{4} catalytic combustion
  • Modeling
  • Minimizing the impact of transport limitations
  • Kinetic results over Pd/\(\gamma\)Al\textsubscript{2}O\textsubscript{3}

✓ Application of a **metallic plate-type reactor** to the kinetic study of CO catalytic oxidation
  • Use heat conduction to effectively remove the reaction heat
  • Experimental results over Pd/\(\gamma\)Al\textsubscript{2}O\textsubscript{3} coated Al slabs
  • Kinetic analysis
Debated Issues in SCR-DeNOx Catalysis over V$_2$O$_5$/WO$_3$/TiO$_2$ Systems

\[ 4 \text{ NO} + 4 \text{ NH}_3 + \text{ O}_2 \rightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O} \]

- ER vs. LH mechanism? Adsorption vs. active sites?
- Rate determining step? Steady-state rate expression:

\[ r_{\text{NO}} = k_{\text{NO}} C_{\text{NO}} \frac{K_{\text{NH}_3} C_{\text{NH}_3}}{1 + K_{\text{NH}_3} C_{\text{NH}_3}} \]

- Promoting role of WO$_3$?
- Inhibiting action of H$_2$O due to competitive adsorption with NH$_3$?
Transient Response Methods

- The reacting system is perturbed (e.g. by changes of the feed composition), and its transient response is recorded.
- The response (e.g. the outlet composition) reflects the characteristics of the elementary steps in the kinetic sequence of the reaction.
- The elementary steps do not proceed at the same rate.
SCR Transient Response Experiments

Approach

- Transient adsorption-desorption study of the individual SCR reactants (NH\textsubscript{3}, NO) over V/W/TiO\textsubscript{2}
  - NH\textsubscript{3}, NO adsorption onto model and commercial catalysts
  - NH\textsubscript{3} oxidation

- Transient reactivity study (NH\textsubscript{3} + NO)
  - stepwise and linear changes of NH\textsubscript{3} in NO continuous flow
  - stepwise and linear changes of NO in NH\textsubscript{3} continuous flow
Rigs for Transient Response Experiments at PoliMI
SCR Transient Response Experiments
Experimental Details

• Catalysts:
  – model \([V_2O_5(1.47\%)/TiO_2\) and \(V_2O_5(1.47\%)/WO_3(9\%)/TiO_2\)]
  – commercial \([V_2O_5(0.62\%)/WO_3(9\%)/TiO_2\)]

• Reactor:
  – \(W_{\text{cat}} = 0.12 - 0.16\) g; \(d_p = 100\) micron;
  – \(d_t = 0.6\) cm; \(L_b = 1\) cm

• Operating conditions:
  – \(Q = 120 - 280\) Ncm\(^3\)/min
  – \(GHSV = 45000 - 140000\) h\(^{-1}\)
  – \(C\) - ramp = 20 ppm/min
Transient Adsorption-desorption Study

**NH₃ Adsorption-desorption**

**Step change of the NH₃ inlet concentration**
in He + O₂ (1%); Model V₂O₅-WO₃/TiO₂ catalyst; T = 280°C

**Linear change of the NH₃ inlet concentration**
in He + O₂ (2%); Commercial V₂O₅-WO₃/TiO₂ catalyst; T = 300°C

---

EUROKIN 3, Billingham, June 2003 9
Transient Adsorption-desorption Study

$NH_3$ Adsorption-desorption – Effect of Temperature

Step change of $C^{°}NH_3$

Linear change of $C^{°}NH_3$
Transient Adsorption-desorption Study

**NO Adsorption-desorption**

- **a)** Step change of NO inlet concentration. Model ternary catalyst, $T = 280 \degree C$

- **b)** Linear change, commercial catalyst, $T = 300 \degree C$
Kinetic analysis of \( \text{NH}_3 \) Adsorption-desorption
1D Heterogeneous Isothermal PFR Model

- \( \text{NH}_3 \) mass balance, catalyst:
  \[
  \frac{\partial \theta_{\text{NH}_3}}{\partial \tau} = r_{\text{ad}} - r_{\text{des}} - r_{\text{ox}}
  \]

- \( \text{NH}_3 \) and \( \text{N}_2 \) mass balances, gas phase:
  \[
  \frac{\partial C_{\text{NH}_3}}{\partial \tau} = -v \cdot \frac{\partial C_{\text{NH}_3}}{\partial \zeta} - \Omega \cdot (r_{\text{ad}} - r_{\text{des}})
  \]
  \[
  \frac{\partial C_{\text{N}_2}}{\partial \tau} = -v \cdot \frac{\partial C_{\text{N}_2}}{\partial \zeta} + \Omega \cdot 0.5 \cdot r_{\text{ox}}
  \]

- Rate equations for \( \text{NH}_3 \) adsorption, desorption and oxidation:
  \[
  r_{\text{ads}} = k_{\text{ads}} C_{\text{NH}_3} \left(1 - \theta_{\text{NH}_3}\right)
  \]
  \[
  r_{\text{des}} = k_{\text{des}} \exp\left(-\frac{E_{\text{des}}}{RT} \left(1 - \alpha \theta_{\text{NH}_3}\right)\right) \cdot \theta_{\text{NH}_3}
  \]
  \[
  r_{\text{ox}} = k_{\text{ox}} \cdot \theta_{\text{NH}_3}
  \]
**Kinetic analysis of NH₃ Adsorption-desorption Data Fit**

**Step change of the NH₃ inlet concentration** in He + O₂.
Model V₂O₅-WO₃/TiO₂ catalyst
Kinetic parameters: \(k^o_a=0.487 \text{ m}^3/\text{mol s},\)
\(k^o_d=2.67 \times 10^5 \text{ 1/s},\)
\(E^o_d=22.9 \text{ kcal/mol},\)
\(\alpha=0.405, \Omega_{\text{NH}_3}=270 \text{ mol/m}^3\)

**Linear variation of the NH₃ inlet concentration** in He + O₂.
Commercial WO₃-V₂O₅/TiO₂ catalyst.
Kinetic parameters: \(k^o_a=33.87 \text{ m}^3/\text{mol s},\)
\(k^o_d=2.2 \times 10^6 \text{ 1/s},\)
\(E^o_d=23.0 \text{ kcal/mol},\)
\(\alpha=0.256, \Omega_{\text{NH}_3}=270 \text{ mol/m}^3\)
**Kinetic analysis of NH$_3$ Adsorption-desorption**

**NH$_3$ Oxidation**

Linear change of the NH$_3$ inlet concentration in He + O$_2$.

Commercial V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst

Kinetic parameters:

- $k_{ox}^o = 3.25 \times 10^6$ 1/s,
- $E_{ox}^o = 28.8$ kcal/mol
Transient NH$_3$ + NO Reactivity Study

NH$_3$ variations in constant NO flow

**NH$_3$ step change**
in He + O$_2$ (1% v/v)+NO (700 ppm)
Model WO$_3$-V$_2$O$_5$/TiO$_2$ catalyst
T=220°C, GHSV = 75000 h$^{-1}$

**NH$_3$ linear change**
in He + O$_2$ (2% v/v)+NO (750 ppm)
Commercial WO$_3$-V$_2$O$_5$/TiO$_2$ catalyst
T=300°C, GHSV = 140000 h$^{-1}$
Transient NH$_3$ + NO Reactivity Study

*NO variations in constant NH$_3$ flow*

NO step change
in He + O$_2$ (1\% v/v) + NH$_3$ (700ppm)
Model WO$_3$-V$_2$O$_5$/TiO$_2$ catalyst
T=220°C, GHSV = 45000 h$^{-1}$

NO linear change
in He + O$_2$ (2 \% v/v) + NH$_3$ (840 ppm)
Commercial WO$_3$-V$_2$O$_5$/TiO$_2$ catalyst
T=300°C, GHSV = 140000 h$^{-1}$
Transient Kinetic Analysis

*Dual-site “NH₃ Reservoir” Kinetics*

\[
\begin{align*}
(1) & \quad \text{NH}_3 + T & \xleftrightarrow{k_{\text{ads}}} & [\text{NH}_3^*]_T \\
 & & \xleftrightarrow{k_{\text{des}}} & \\
(2) & \quad [\text{NH}_3^*]_T + V & \xleftrightarrow{K_{VT}} & [\text{NH}_3^*]_V + T \\
(3) & \quad [\text{NH}_3^*]_V + \text{NO} & \xrightarrow{k_{\text{NO}}} & \text{N}_2 + \text{H}_2\text{O} + V \\
& & + \text{O}_2 & \\
\end{align*}
\]

\[
r_3 = k_{\text{NO}}C_{\text{NO}} \frac{K_{VT}q_{\text{NH}_3,T}}{1 + (K_{VT} - 1)q_{\text{NH}_3,T}}
\]
Transient Kinetic Analysis

NH₃ changes in continuous NO flow: Data Fit

NH₃ step change in He + O₂.
Model V₂O₅-WO₃/TiO₂ catalyst
Kinetic parameters: $k^\circ_{NO} = 9.2 \times 10^4$ 1/s, $E^\circ_{NO} = 14.2$ kcal/mol, $K_{VT} = 12.4$

NH₃ linear variation in He + O₂.
Commercial WO₃-V₂O₅/TiO₂ catalyst.
Kinetic parameters: $k^\circ_{NO} = 7.1 \times 10^6$ 1/s, $E^\circ_{NO} = 19.2$ kcal/mol, $K_{VT} = 68.0$
Transient Kinetic Analysis

NO changes in continuous NH₃ flow: Simulation

**NO step change**
in He + O₂ (1% v/v) + NH₃ (700ppm)
Model WO₃-V₂O₅/TiO₂ catalyst
T=220°C, GHSV = 75000 h⁻¹

**NO linear variation**
in He + O₂ (2% v/v) + NH₃ (840 ppm)
Commercial WO₃-V₂O₅/TiO₂ catalyst
T=300°C, GHSV = 140000 h⁻¹
Transient Kinetic Analysis

Rate determining step at steady-state

\[ \text{NH}_3 \rightleftharpoons \text{NH}_3^* \quad \text{N}_2 + \text{NO} \]

Surface reaction = r.d.s. if: \[ \Phi = \frac{r_{\text{ads}}}{r_{\text{NO}}} \gg 1 \]

<table>
<thead>
<tr>
<th>Values of $\Phi$ ($C_{\text{NO}}=500$ ppm)</th>
<th>$T = 300$ °C</th>
<th>$T = 340$ °C</th>
<th>$T = 380$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{NH}_3}=500$ ppm</td>
<td>37.3</td>
<td>17.0</td>
<td>8.23</td>
</tr>
<tr>
<td>$C_{\text{NH}_3}=400$ ppm</td>
<td>31.9</td>
<td>14.3</td>
<td>6.91</td>
</tr>
<tr>
<td>$C_{\text{NH}_3}=300$ ppm</td>
<td>25.9</td>
<td>11.5</td>
<td>5.50</td>
</tr>
</tbody>
</table>
Role of \( \text{WO}_3 \) in \( \text{NH}_3 \) adsorption-desorption

\( \text{NH}_3 \) step change in \( \text{He} + \text{O}_2 \) (1% v/v)
Model catalysts.
\( T=280^\circ \text{C}, \ GHSV = 75000 \ \text{h}^{-1} \)
Role of WO$_3$

*in* NH$_3$ + NO reactivity

NH$_3$ step change
in He + O$_2$ (1% v/v) + NO (700 ppm)
Model catalysts.
T=280°C, GHSV = 75000 h$^{-1}$
SCR Transient kinetic study: Conclusions

- NH₃ is strongly adsorbed onto V₂O₅/WO₃/TiO₂ catalysts, which work as “ammonia storage” systems
- NO is not appreciably adsorbed
- NH₃ adsorption-desorption rate was fitted by Temkin-type kinetics
- NO + NH₃ surface reaction rate was fitted according to dual-site “reservoir” kinetics
- The assumption of equilibrium NH₃ adsorption may be critical
- WO₃ does not affect NH₃ adsorption, but greatly promotes NO + NH₃ reactivity
- Inhibition by H₂O does not result from competitive adsorption with NH₃
Dynamic modeling of SCR-DeNOx monolith reactors

• Unsteady kinetics of DeNOx catalysis by Transient Response Methods (Lietti et al., AIChE J, 1996)
• Dynamic SCR monolith reactor model + validation (Tronconi et al., IEC Res., 1998)
• Inclusion of SO$_2$ oxidation (Tronconi et al., IEC Res., 1999)
Validation of the dynamic SCR monolith reactor model

- Experimental and simulated evolutions of the NO outlet concentration during SCR reactor start-up and shut-down, and following step variations of NO inlet concentration
  
Main literature references for transient SCR kinetics

L. Lietti, I. Nova, S. Camurri, E. Tronconi, P. Forzatti
“Study of the Dynamics of the SCR - DeNOx Reaction by the Transient Response Method”
AIChe J., 43, 2559-2570 (1997).

E. Tronconi, A. Cavanna, P. Forzatti
“Unsteady Analysis of NO Reduction over Selective Catalytic Reduction - De-NOx Monolith Catalysts”

E. Tronconi, C. Orsenigo, A. Cavanna, P. Forzatti
“Transient Kinetics of SO2 Oxidation over SCR-DeNOx Monolith Catalysts”

I. Nova, L. Lietti, E. Tronconi, P. Forzatti
"Transient response method applied to the kinetic analysis of the DeNOx-SCR reaction”
Applying TRMs to study the kinetics of NOx storage in NOx traps (Pt/BaO/Al₂O₃ systems)

**Elementary Steps**

- $\text{O}_2 + 2\text{Pt} \xrightleftarrows \frac{1}{2} 2\text{Pt-O}$
- $\text{NO} + \text{Pt} \xrightleftarrows \frac{3}{4} \text{Pt-NO}$
- $\text{NO}_2 + \text{Pt} \xrightleftarrows \frac{5}{6} \text{Pt-NO}_2$
- $\text{Pt-NO} + \text{Pt-O} \xrightleftarrows \frac{7}{8} \text{Pt-NO}_2 + \text{Pt}$
- $\text{NO}_2 + \text{S} \xrightarrow{9/10} \text{S-NO}_2$
- $\text{S-NO}_2 \xrightarrow{11/12} \text{S-O} + \text{NO}$
- $\text{NO}_2 + \text{S-O} \xrightarrow{13/14} \text{S-NO}_3$
- $\text{NO}_2 + \text{S-NO}_3 \xrightarrow{15/16} \text{Ba(NO}_3)_2$
- $2\text{S-O} \xrightarrow{17/18} 2\text{S} + \text{O}_2$
- $\text{Pt-NO}_2 + \text{S-NO}_3 \xrightarrow{19/20} \text{Ba(NO}_3)_2 + \text{Pt}$

- **Reactions over Pt**
- **Reactions over BaO**
- **Spillover**

**Detailed kinetic scheme proposed by Olsson et al.,**


adapted and compared to our TRM data, covering a variety of combinations of:
- catalytic systems (binary, ternary)
- feed compositions (NO, NO₂, O₂)

in order to test its physico-chemical consistency
TRM - Experimental

Adsorption + TPD

- NO\textsubscript{x} storage phase
- Temperature programmed desorption

Feed mixtures

- NO\textsubscript{2} (1000 ppm)
- NO\textsubscript{2} (1000 ppm) + O\textsubscript{2} (3%)
- NO (1000 ppm)
- NO (1000 ppm) + O\textsubscript{2} (3%)

Catalytic systems

- Pt/Ba/Al\textsubscript{2}O\textsubscript{3}
- Ba/Al\textsubscript{2}O\textsubscript{3}
- Pt/Al\textsubscript{2}O\textsubscript{3}
Simulation of the experimental micro-reactor

Simulation of the experimental microreactor with a plug – flow non stationary heterogeneous model

- Bed density = 0.7 g/cc; Void fraction ~ 0.35
- Flow ~ 200 Ncc/min; catalyst mass ~ 0.12 g

Space Velocity: \( \sim 10^5 \text{ Ncc/g/h} \)

- Pt load=1%; Ba load=16.7%
- Pt and Ba dispersions: fitted by non linear regression

Active Pt e Ba moles

Hypothesis
- Neither internal nor external diffusional resistances
- No axial dispersion

\[
\begin{align*}
\varepsilon \frac{\partial C_i}{\partial t} &= - \varepsilon \frac{\partial C_i}{\partial x} + \frac{\Omega_{Pt}}{\tau} \sum_{j=1}^{NR_{Pt}} v_{ij} r_j + \frac{\Omega_{Ba}}{} \sum_{k=1}^{NR_{Ba}} v_{ik} r_k \\
\frac{\partial \theta_i}{\partial t} &= \sum_{j=1}^{NR} v_{ij} r_j \\
\theta_i &= \text{Pt, Ba species}
\end{align*}
\]
Feed mixture: \[ \text{NO}_2 \]  

System: \[ \text{Ba/Al}_2\text{O}_3 \]

\[ 3\text{NO}_2 + \text{BaO} \rightarrow \text{Ba(NO}_3\text{)}_2 + \text{NO} \]

- S-\text{NO}_2 (NITRITES) decomposition = RDS toward NITRATES formation

\[ \text{NO}_2 \rightarrow \text{NO} \]

Overall stoicheometry

3\text{NO}_2 + \text{BaO} → \text{Ba(NO}_3\text{)}_2 + \text{NO}

Disproportionation

EUROKIN 3, Billingham, June 2003
According to the model Pt catalyses these reactions:

- \( \text{NO}_2 \rightarrow \text{NO} + \frac{1}{2}\text{O}_2 \) : higher outlet concentrations of NO

- Spillover reaction, in competition with the formation of nitrates via gas – phase
Transient kinetics of NOx storage: Conclusions

The kinetic model has been tested in a wide experimental range of:
- feed mixtures
- catalytic systems

Its predictions are useful in identifying the roles of catalyst components and of reacting species:

**Role of gas – phase species**
- NO\(_2\) is the key species for NOx storage
- O\(_2\) has a role in the presence of Pt, feeding NO or NO\(_2\), involving a dead time both for NO and NO\(_2\)

**Role of surface species**
- Main Barium species: S-NO\(_2\) (nitrites) and Ba(NO\(_3\))\(_2\) (nitrates)
- The storage involves a *two - step disproportionation, with a* nitrites to nitrates *slow evolution* for all the experiments where storage takes place (IR data seem to suggest a different kinetic of evolution of nitrites to nitrates)
- Pt sites oxidize NO ⇔ NO\(_2\)
2. Lab-scale structured reactors for kinetic measurements in catalytic combustion

2.1 Structured Annular Reactor for investigation of High Temperature Kinetics of CH$_4$ Combustion over very active PdO-based Catalysts

- Design of the annular reactor by mathematical modeling
- Experimental performances of the annular reactor
- Kinetics of CH$_4$ combustion over PdO/ZrO$_2$ (10% w/w of Pd) catalyst
Kinetic measurements in catalytic combustion

• Demanding task
  – Wide temperature ranges are relevant to practical applications (e.g. 350-850°C for G.T.);
  – Extremely fast reactions in the high-T range which are typically affected by diffusion limitation
  – Onset of temperature gradients associated with highly exothermic combustion reactions (high fuel concentration)
  – Industrial applications typically require structured monolith catalysts
Annular flow microreactor

- High GHSV with minimum pressure drop
- Partial conversion at high reaction rate (high T)
- Well defined geometry (and flow pattern) ⇒ assessment and control of diffusional effects
- Effective dissipation of the heat of reaction (radiation)

Annular microreactor: Modeling Assumptions

- Steady state
- Fully developed laminar flow
- 1D lumped description of the gas phase
- 2D description of the catalyst phase
- Isothermal conditions
- Negligible pressure drop
- Planar geometry of the catalyst layer ($r_i/\delta_w > 50$)
Governing equations

Gas phase mass balance of f-species

\[
\frac{\partial C_{f,g}}{\partial z} - \left( D_{m,f} + D_{ea,f} \right) \frac{\partial^2 C_{f,g}}{\partial z^2} = \frac{4}{d_h} \left[ \frac{(r_i + \delta_w)}{r_0 + (r_i + \delta_w)} \right] K_{g,f} \left( C_{f,w} - C_{f,g} \right)
\]

Catalyst phase mass balance of f-species

\[
D_{e,f} \frac{\partial^2 C_{f,w}}{\partial n^2} + \nu_f R_{f,w} = 0
\]

Boundary condition

\[ u \left( C_{f,g} - C_{f,g}^0 \right) = \left( D_{m,f} + D_{ea,f} \right) \frac{\partial C_{f,g}}{\partial z} \quad \text{inlet condition (at } z=0) \]

\[ \frac{\partial C_{f,g}}{\partial z} = 0 \quad \text{outlet condition (at } z=L) \]

\[ D_{e,f} \frac{\partial C_{f,w}}{\partial n} = K_{g,f} \left( C_{f,g} - C_{f,w} \right) \quad \text{at catalyst surface (} n=\delta_w) \]

\[ \frac{\partial C_{f,w}}{\partial n} = 0 \quad \text{at catalyst/} \alpha\text{-A}_2\text{O}_3 \text{ interface (} n=0) \]
Reactor design

Design parameters:
Catalyst layer thickness ($\delta_w$), annular chamber height ($\delta_a$)

Catalyst and reactor efficiencies (design targets)

$$\eta_{int}^{aw} = \frac{\int_{0}^{\delta_w} \int_{0}^{\delta_w} R_w(z, n) ln 0 R_w(z, \delta_w) \delta_w \, \text{d}z / L}{\int_{0}^{\delta_w} R_w(z, \delta_w) \delta_w \, \text{d}z / L}$$ internal catalyst efficiency

$$\eta_{glob} = \frac{K_{r, eff}}{K_r}$$ global reactor efficiency

$K_{r, eff}$ has been calculated using the following simple model:

$$\frac{dC_{f,g}}{dz} + \left( \frac{r_i + \delta_w}{r_i - (r_i + \delta_w)} \right)^2 R_{f,w}^{eff} = 0$$ Mass balance of f-species

$$C_{f,g} = C_{f,g}^{in}$$ inlet condition

Kinetics

$$R_w = \frac{K_r C_{CH_4,w}}{1 + K_{H_2,O} C_{H_2,O,w}}$$
Overall reactor efficiency

Overall effectiveness factor

\[ \delta_A = 0.2 \text{ mm} \]

\[ \delta_A = 0.6 \text{ mm} \]
Experimental

• Reactor geometry
  – Structured support: dense $\alpha$-Al$_2$O$_3$ tube
  – $r_i$=3.25 mm  $r_o$=3.5 mm  $L_{tot}$=80 mm  $L_{catalyst}$=10 mm

• Active catalyst layer
  Precursor powders
  – PdO/ZrO$_2$ (10% w/w of Pd) dry impregnation with Pd(NO$_3$)$_2$ solution
  Washcoat deposition (critical step)
  – Dipping the support in a slurry prepared by ball milling precursor powders in a HNO$_3$ aqueous solution
  $\delta_w$=15 $\mu$m (6 mg) by SEM and weight measurements ($T_c$=800°C)

• Investigated ranges of operating variables
  – T=400-550°C; GHSV=10$^6$ cm$^3$/gh (@STP)
  – CH$_4$=0.8-3.0%; H$_2$O=0-3.5%; CO$_2$=0-2.7%; O$_2$=10-20%
Effect of carrier gas

- Negligible diffusional limitations
- Partial conversion has been obtained up to 550°C
Thermal behaviour-1

CH₄ combustion experiments

Effective dissipation of reaction heat results in an almost isothermal catalyst layer
Thermal behaviour-2

CO-H₂ combustion tests (CO=4%, H₂=4%)

Mechanisms of heat dispersion:
radiation at high T (more effective) convection at low T.
Effects of reactant concentrations

0\textsuperscript{th} order in $O_2$ concentration
(lean conditions)
Effects of product concentrations

Power law Kinetics: \[ r = k_r C_{CH4} C_{H2O}^{\beta} C_{CO2}^{\gamma} \]

\[ E_{act} = 108 \text{ kJ/mol}; \quad \beta = -0.32; \quad \gamma = -0.25 \]
Role of the support on $\text{H}_2\text{O}$ and $\text{CO}_2$ inhibition

PdO/ZrO$_2$

PdO/Al$_2$O$_3$

GHSV=$10^6$ cm$^3$/gh

CO$_2$ inhibition was not observed up to 10% CO$_2$ over PdO/Al$_2$O$_3$. 
CH$_4$ combustion in annular reactor - Conclusions

- A specifically designed annular reactor has allowed to investigate the kinetics of CH$_4$ combustion over PdO/ZrO$_2$ (10% Pd w/w) in a 400-550$^\circ$C T-range with:
  - minimum impact of diffusional limitations ($\delta_w=15\mu$m)
  - nearly isothermal conditions (radiation)

- The results of the kinetic study indicated that under the investigated conditions both H$_2$O and CO$_2$ similarly inhibit the reaction rate up to 550$^\circ$C.

- Indications on a primary role of the support on the extent of both such inhibition effects have been found
2. Lab-scale structured reactors for kinetic measurements in catalytic combustion

2.2 Metallic Structured Catalysts with High Thermal Conductivity for the kinetic investigation of strongly exothermic G/S reactions

– Investigate experimentally the thermal behavior of structured metallic catalysts in the presence of a strongly exothermic G/S reaction (CO oxidation)

– Demonstrate the influence of catalyst design parameters
  • support material and geometry
  • coating formulation

– Develop an engineering analysis of the experimental results
  • kinetics
  • thermal resistances
Structured catalysts
in non-adiabatic g/s reactors

- Potential advantages:
  - reduced pressure drop
  - easy scale-up
  - favourable heat transfer properties due to heat conduction in the connected matrix
Preparation of structured test catalysts - 1

• Supports consisting of four slabs assembled to form 3 parallel rectangular channels
• Catalyst \((L = 200 \text{ mm})\) loaded into a rectangular \((50\times30 \text{ mm})\) reactor tube in an oven with air recirculation
• Five 1/16” tubings glued on the slabs to act as thermowells
• Front view:
Preparation of structured test catalysts - 2

• Three samples with supports made of
  – Aluminium: \( k_{\text{sol}} = 200 \text{ W/(m K)}, s = 0.5 \text{ mm} \)
    Sample A
  – AISI 304: \( k_{\text{sol}} = 20 \text{ W/(m K)}, s = 0.5 \text{ mm} \)
    Sample B
  – AISI 304: \( k_{\text{sol}} = 20 \text{ W/(m K)}, s = 0.2 \text{ mm} \)
    Sample C

• Washcoated by deposition of 3% Pd/\( \gamma \)-Al\(_2\)O\(_3\) (19% w/w) dissolved in sodium silicate

• Sample D (Al, \( s=0.5 \text{ mm} \)) precoated with a pseudo-bohemite primer, dipped into a 3% Pd/\( \gamma \)-Al\(_2\)O\(_3\) silica-free slurry and flash-dried at 280 °C
CO oxidation runs: Kinetic study

- Investigated ranges, Sample A:
  \[ \begin{align*}
  Y^\circ_{CO} &= 0.02 - 0.09 \\
  Y^\circ_{O_2} &= 0.05 - 0.20 \\
  T &= 150 - 250 \degree C
  \end{align*} \]

- Isothermal conditions, no diffusional limitations

- Negative CO reaction order

- Rate expression [moles/m²/s]:
  \[ r_{CO} = \frac{k_1 p_{CO}^{1/2} p_{O_2}^{1/2}}{(1 + k_2 p_{CO})^2} \]
CO oxidation runs: Thermal behavior - 1

- **Al support (sample A):** influence of $T_{oven}$:

![Graph showing temperature vs. distance from inlet for different $T_{oven}$ values.]

- $T_{oven} = 256°C$: CO conv = 100%
- $T_{oven} = 216°C$: CO conv = 100%
- $T_{oven} = 196°C$: CO conv = 50.2%
- $T_{oven} = 176°C$: CO conv = 12.3%
CO oxidation runs: Thermal behavior - 2

- Comparison of Al and Steel supports (s = 0.5 mm):
  Al: $k_{\text{sol}} = 200 \text{ W/(m K)}$ vs. Steel: $k_{\text{sol}} = 20 \text{ W/(m K)}$
CO oxidation runs: Thermal behavior - 3

- Influences of support material and slab thickness:

![Graph](image-url)

- Steel, s=0.2 mm
- Steel, s=0.5 mm
- Aluminium, s=0.5 mm

Q = 1000 cc/min, Y°C0 = 0.05, Toven = 216°C
CO oxidation runs: Thermal behavior - 4

• Comparison of lab-scale reactors:

\[
\text{Heat Load} = \chi_{\text{CO}} Q \Gamma_{\text{CO}}^o \Delta H \, [\text{W}]
\]

- Aluminium, sample A
- Steel, sample B
- Annular reactor
- Packed bed
Catalytic activity of Sample D vs. Powders in CO oxidation

data are CO$_2$ productivities (g CO$_2$/g$_{cat}$/h)
Engineering analysis: Data fit

- Regression results on T-profiles, Sample A:

\[ Q = 1000 \text{ cc/min}, Y^{\circ} \text{CO} = 0.05 \]

\[ \text{Temperature, } ^{\circ} \text{C} \]

Axial distance, cm

<== Influence of T\text{oven}:

1D heterogeneous reactor model;

\underline{kinetics} from independent isothermal study;

model adaptive parameters are thermal resistances only.
High Conductivity Structured Catalysts: Conclusive remarks

- Heat conduction in the supports of structured metallic catalysts can be exploited to remove effectively the heat of reaction.

- Thermal conductivity and thickness of the support material are critical → catalyst design.

- In the case of highly conductive supports (Al),
  - isothermal runs are possible over wide ranges of operating conditions
  - heat transfer resistances at the catalyst/reactor interface become controlling.

- Results are of interest in view of applications to lab-scale microreactors for kinetic studies
Structured catalysts for catalytic combustion kinetics: main literature references

G. Groppi, E. Tronconi
"Continuous versus discrete models of nonadiabatic monolith catalysts",

G. Groppi, E. Tronconi, P. Forzatti
“Mathematical models for catalytic combustors”

E. Tronconi, G. Groppi
"A study on the thermal behavior of structured plate-type catalysts with metallic supports for
gas/solid exothermic reactions"

G. Groppi, W. Ibashi, E. Tronconi, P. Forzatti
“Structured reactors for kinetic measurements under severe conditions in catalytic combustion over palladium supported systems”