TAP-study on the total oxidation of propane over a CuO-CeO$_2$/γ-Al$_2$O$_3$ catalyst

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VOCs = Volatile Organic Compounds → important air pollutants

Total catalytic oxidation

\[ C_3H_8 + 5 O_2 \rightarrow 3 CO_2 + 4 H_2O \]

1. Which species are responsible for converting propane to \( CO_2 \)?

2. What is the role of the different metal oxide phases?
1. Introduction
2. Experimental set-up, conditions and catalysts
3. Results
   • Role and nature of active oxygen species
   • Oxygen mobility
   • Role of metal oxides
4. Conclusions
Three types of TAP pulse experiments

- **Single-pulse**
  - State-defining
  - Inlet: Frequency peaks over time
  - Outlet: Frequency peaks over time
  - Response: Frequency decreases over time

- **Multi-pulse**
  - State-altering
  - Inlet: Frequency peaks over time
  - Outlet: Frequency peaks over time
  - Response: Frequency peaks over time

- **Alternating pulse**
  - Inlet: Frequency peaks over time
  - Outlet: Frequency peaks over time
  - Response: Frequency decreases over time
Experimental conditions

C$_3$H$_8$ / Kr
O$_2$ / Ar
CO$_2$ / Ar
C$^{18}$O$_2$ / Ar

523 K < T < 923 K
50 mg

Upper limit for the total number of exchangeable O atoms

<table>
<thead>
<tr>
<th>O atoms related to</th>
<th>CuO and/or CeO$_2$ (10$^{19}$)</th>
<th>Al$_2$O$_3$ (10$^{19}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO-CeO$_2$/γ-Al$_2$O$_3$</td>
<td>7</td>
<td>70</td>
</tr>
<tr>
<td>CeO$_2$/γ-Al$_2$O$_3$</td>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td>CuO/θ-Al$_2$O$_3$</td>
<td>5</td>
<td>70</td>
</tr>
</tbody>
</table>

Pre-treatment of catalyst sample
→ heating to reaction temperature (5K/min)
→ multi-pulses of O$_2$ until constant level of oxygen response
Participation of lattice oxygen at surface

At 623 K, the diffusion of quartz only shows a certain conversion. When oxygen is introduced, there is a higher interaction, indicated by a peak in the normalized responses. The pure C3H8 sample shows a different behavior compared to the C3H8 + O2 mixture.
Participation of adsorbed oxygen species

\[ \text{C}_3\text{H}_8 \text{ conversion [\%]} \]

\[ \frac{\text{mol O consumed}}{\text{mol O in CuO and CeO}_2} \text{ [-]} \]

623 K

Diagram showing the conversion of \( \text{C}_3\text{H}_8 \) with varying \( \frac{\text{mol O consumed}}{\text{mol O in CuO and CeO}_2} \). The graph compares pure \( \text{C}_3\text{H}_8 \) (green triangles) and \( \text{C}_3\text{H}_8 + \text{O}_2 \) (blue dots).
Life time of adsorbed oxygen species

$673 \, K$, delay $= 0.5 \, s$

Flow rate $[10^{-8} \, \text{mol/s}]$

$O_2$, propane, CO$_2$

$V. \, Balcaen$, 6WCOC, Lille, France, July 5-10, 2009
Fast diffusion of oxygen species

$873 \, K$

![Graph showing the concentration of different isotopes at the reactor outlet versus $mol^{18}O$ consumed / $mol^{16}O$ in $Al_2O_3$]
Participation of lattice oxygen from bulk without introducing any gas at 923 K.

Graph showing conversion of $C_3H_8$ over mol O consumed / mol O in CuO and CeO$_2$.
CO₂ as oxidant

$623 \text{ K}$

$\text{C}_3\text{H}_8$ conversion [%]

$\text{mol O consumed} / \text{mol O in CuO and CeO}_2$ [-]

- **pure C₃H₈**
- **C₃H₈ + O₂**
- **C₃H₈ + CO₂**

V. Balcaen, 6WCOC, Lille, France, July 5-10, 2009
O produced from CO₂

Graph showing the mole of products at the reactor outlet in units of 10⁻⁵ mol as a function of the mole of O replenished divided by the mole of O in CuO + CeO₂. The graph includes lines for CO₂, in, CO₂, out, and CO.
Location of active species

CuO-CeO₂/γ-Al₂O₃ CeO₂/γ-Al₂O₃ CuO/θ-Al₂O₃
γ-Al₂O₃ θ-Al₂O₃

Normalized C₃H₈ flow rate [mol, out s⁻¹ mol⁻¹, in⁻¹]

Time [s]

623 K

Ar
7%
34%
29%
CO2 adsorption on alumina

CuO-CeO$_2$/γ-Al$_2$O$_3$  CeO$_2$/γ-Al$_2$O$_3$  CuO/θ-Al$_2$O$_3$
γ-Al$_2$O$_3$  θ-Al$_2$O$_3$

623 K

Normalized CO$_2$ flow rate [mol, out s$^{-1}$ mol$_{in}$ $^{-1}$]

Time [s]

$M_0$, CO$_2$  $< M_0$, Ar  \hline
Irreversible adsorption
Conclusions

• Four origins of active oxygen species, participating in total oxidation reaction
  1. Lattice oxygen at surface
  2. Lattice oxygen in bulk
  3. Surface oxygen produced from gas-phase $O_2$
  4. Lattice oxygen produced from gas-phase $CO_2$

• Location of these active oxygen species
  1. CuO and CeO$_2$ → active phases → contain active O species
  2. γ-Al$_2$O$_3$ → carrier → can produce active O species based on CO$_2$
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Thank you for your attention!

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