In situ X-ray absorption study of CuO-CeO$_2$/Al$_2$O$_3$ catalysts in the total oxidation of propane.


Laboratory for Chemical Technology

http://www.lct.ugent.be
Overview

• Introduction

• Experimental & analysis procedure

• Operando XAS measurements
  - XAS measurements under oxidation, reduction and total oxidation conditions
  - Structure-activity relationship

• Conclusions
Introduction

- **Objective:**
  - To elucidate the several components and state of Cu in the CuO-CeO$_2$/Al$_2$O$_3$ catalyst during oxidation, reduction and total oxidation conditions by time-resolved operando XAS study under transient as well as steady state conditions
  - To obtain insight into the reaction mechanism

- **Method:**
  - XANES at Cu K edge
  - Mass spectrometry
  - Structure of the active phase (e.g., coordination, oxidation state)
  - Conversion, selectivity
Experimental setup

**Oven**

*Capillary made out of quartz (ID = 0.9 mm, OD = 1.0 mm)*

**Fixed bed reactor**

- quartz
- Cat.
- quartz

Gas flow

~5 mg cat. (particle size: 75-100 µm)
Experimental procedure

• Step response experiments performed, T= 573-723 K:
  ➢ Catalyst reduction and oxidation cycles: He |→ 10%O₂/He → He |→ 2%C₃H₈/He, constant flow rate = 1.5 \times 10^{-5} \text{ mol/s}

• Total oxidation experiments under steady state conditions
  ➢ Catalyst He |→ (1%C₃H₈+ 5% or 10%O₂)/He, space times = 38.3-127.7 kg s / mol
Analysis procedure

- **MS: 0.1s/amu**
  - amu’s followed: 4, 12, 14, 18, 28, 29, 32, 41, 44
  - gas phase compositions: He (internal standard), CO, C₃H₈, O₂, C₃H₆, CO₂

- **XANES: 0.1s/spectrum**
  - Raw data in pixels (of the camera) → **energy calibration** by comparing a Cu foil measured in pixels (taken at ID 24) to one measured in eV (taken at the energy scanning beamline BM26)
  - Determination of **edge position, background subtraction & normalization** of calibrated raw data
  - Solid phase compositions from **spectral de-convolution**:  
    - Standard spectra used: oxidized catalyst sample (Cu²⁺), reduced catalyst sample after treatment with propane (Cu⁰), Cu₂O reference sample (Cu¹⁺)
    - **Principal component analysis (PCA)** to find number of phases and assess suitability of standards for describing a given set of spectra
    - **Linear combination fitting (LCF)** to quantify the ratio of Cu²⁺/Cu¹⁺/Cu⁰
XANES results under reduction conditions

- XANES of the CuO-CeO$_2$/Al$_2$O$_3$: He$\rightarrow$ 2%C$_3$H$_8$/He step-response experiment at 723 K

→ Catalyst reduction: a two step process is found
LCF & MS analysis

- Catalyst reduction at 723 K
  1. PCA: 3 components
  2. LCF & MS analysis:

    → Mechanism of catalyst reduction:
      \[ \text{Cu}^{2+} \rightarrow \text{Cu}^{1+} \rightarrow \text{Cu}^0 \]

    → No CO$_2$ when the catalyst is fully reduced

    → The LCF analysis agrees with the MS results
XANES results under oxidation conditions

- XANES of the CuO-CeO$_2$/Al$_2$O$_3$: He$\rightarrow$ 10%O$_2$/He step-response experiment at 723 K

$\rightarrow$ Catalyst reduction is reversible with reoxidation
LCF analysis Cu phase change vs time

- Catalyst reduction and oxidation cycles: LCF analysis

Conversion of CuO-phase of CuO-CeO$_2$/Al$_2$O$_3$ catalyst during reduction with 2%C$_3$H$_8$/He

Conversion of Cu-phase of CuO-CeO$_2$/Al$_2$O$_3$ catalyst during re-oxidation with 10% O$_2$/He

\[ X_{CuO} = 1 - e^{-\frac{t}{\tau}} \]

\[ X_{Cu} = 1 - e^{-\frac{t}{\tau}} \]

\[ \tau_{\text{red}} \] (s) | 782.7 | 229.6 | 88.3 | 37.2
\[ \tau_{\text{ox}} \] (s) | 5.7   | 1.0   | 0.5   | 0.5

\[ \rightarrow \text{re-oxidation of catalyst occurs faster than its reduction at all } T \]
\[ \rightarrow \text{both processes speed up with } T \]
• Catalyst reduction and oxidation cycles: LCF analysis

- Activation energies for reduction & oxidation of CuO-CeO$_2$/Al$_2$O$_3$

\[ y = -8.3822x + 7.984 \]
\[ R^2 = 0.9997 \]

\[ y = -6.635x + 10.183 \]
\[ R^2 = 0.8661 \]

\[ E_a = 70.0 \text{ kJ/mol} \]

\[ E_a = 55.2 \text{ kJ/mol} \]

\[ \rightarrow \text{Catalyst reduction requires a higher } E_a \text{ than catalyst oxidation} \]

\[ \rightarrow \text{Therefore, during hydrocarbon oxidation over the metal oxide catalyst, a reaction that can occur via the following mechanism:} \]

\[ \begin{align*}
\text{O}_2 & \quad \text{HC} \\
\text{M-O-M-O-M} & \quad \text{M-O-M} \\
\text{HCO} & \quad \text{O}_2 \\
\end{align*} \]

\[ \text{the first step (i.e. catalyst reduction) will be rate-determining} \]
Total oxidation MS results

- MS: Total oxidation reaction under steady state conditions

- \( \gamma = \frac{y_{\text{O}_2(0)}}{y_{\text{C}_3\text{H}_8(0)}} = 5 \)
- \( \text{CO}_2 \): main product
- \( \text{CO} \): not observed
- \( \text{C}_3\text{H}_6 \): very small traces (ca. 100 ppm) within experimental error

→ Apparent activation energy from MS analysis agrees with the apparent activation energy from the LCF analysis for catalyst reduction (rate-determining step)
XANES under total oxidation conditions

- XANES of the CuO-CeO$_2$/Al$_2$O$_3$: He $\rightarrow$ \{1\%C$_3$H$_8$-5\%O$_2$\}/He step-response experiment at 723 K

$\rightarrow$ no changes in the spectra and same spectra as fresh catalyst (in-set spectra)

$\rightarrow$ catalyst remains oxidized under total oxidation reaction conditions
Catalyst structure from XANES data

- **Theoretical XANES calculations:**
  - FDMNES
  - Muffin-tin approximation
  - Models used: crystal structure of Cu, Cu$_2$O, CuO
  - Cluster size of 8.3 Å
  - Convolution parameters obtained from the best fit with the references

- Variance:

  \[
  \sigma^2 = 100 \frac{\int (\chi_{\text{model}}(E) - \chi_{\text{exp}}(E))^2 dE}{\int (\chi_{\text{exp}}(E))^2 dE}
  \]
XANES: structure of the active phase

CuO-CeO$_2$/Al$_2$O$_3$ under steady-state reductive and oxidative conditions

Structure of active phase of catalyst modeled using the fcc Cu structure or the monoclinic CuO structure as input

→ Good agreement between theory and experiment (variance < 1%)
1. Reduced catalyst

<table>
<thead>
<tr>
<th>Bond distance (Å)</th>
<th>Crystal structure</th>
<th>XANES fit values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu reference foil</td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>2.56</td>
<td>2.64</td>
</tr>
</tbody>
</table>

- Reduced catalyst same structure as metallic copper

2. Oxidized catalyst

<table>
<thead>
<tr>
<th>Bond distance (Å)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CuO reference sample</td>
</tr>
<tr>
<td>Cu-O</td>
<td>1.95 - 1.96</td>
<td>2.01 - 2.02</td>
</tr>
</tbody>
</table>

- Oxidized catalyst CuO-like structure with larger Cu-O distances compared to reference
  - Weaker Cu-O bonds
Conclusions

• The copper phase of the catalyst remains oxidized during total oxidation reaction conditions.

• Based on the PCA and LCF results, three components are present during reduction and re-oxidation cycles (i.e. Cu(+2), Cu(+1) and Cu(0)) and a two-step mechanism is found.

• The solid phase analysis of LCF under reduction conditions and gas analysis of MS have shown similar $E_a$, which indicates that the rate determination step for the reaction mechanism is reduction step.

• These results are in good agreement with the rate determining step of the Mars-van-Krevelen reaction mechanism.

• Theoretical spectra have been successfully fitted to experimental XANES of the CuO-CeO$_2$-Al$_2$O$_3$ catalyst.
Acknowledgement

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Thank you very much for your kind attention