Pt-Ga catalyst formation studied with \textit{in situ} XAS using Fourier and wavelet transformed analysis.

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Introduction & Motivation

- Supported Pt-Ga catalysts: alkane dehydrogenation
  - Improved selectivity and stability
  - Major improvements possible
  - Elucidate formation mechanisms: improve performance

- Novel catalyst formation process: intimate Pt-Ga contact
  - Ga in Mg(Al)O_x → Mg(Ga)(Al)O_x
  - Pt[acac]_2 on calcined Mg(Ga)(Al)O_x
  - Oxidation & reduction → Pt-Ga catalyst
Experiments

- Isothermal *in situ* XAS experiments @ DUBBLE, ESRF
  - Catalyst: Pt[acac]$_n$/Mg(Ga)(Al)O$_x$ (5 wt% Pt, 3.75 wt% Ga)
  - Capillary quartz tubular reactor (OD = 2 mm)
  - Pt L$_{III}$ edge (11564 eV, transmission)
Experiments

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XAS wavelet transforms

- Pt-Ga formation process:
  - variety of Pt neighbors (Pt-C, Pt-O, Pt-Ga, Pt-Pt)
  - Discrimination and localization of different atomic species necessary

- Fourier transformed (FT) signals
  - k-region of backscattering ~ atomic mass: C < O < Ga < Pt
  - 2 ≠ species, 2 ≠ locations vs 2 = species, 2 ≠ locations

→ invoke wavelet transformated (WT) XAS analysis
XAS wavelet transforms

$\rightarrow$ simultaneous R and k space resolution$^{[1,2]}$: appoint k-space backscattering region to each R-space peak

Results: Region 1

Region 1: 25°C – 350°C in O₂/He
Region 2: 350°C – 650°C – 250°C in O₂/He
Region 3: 250°C – 350°C – 450°C in H₂/He
Region 4: 450°C – 650°C in H₂/He
25°C – 350°C in O₂/He

XANES
- WL at 25°C = II+ = Pt²⁺[acac]₂
- Oxidation to 350°C: Pt⁴⁺O₂-like XANES

FT EXAFS
- As prepared catalyst at RT: Pt[acac]₂
- Oxidation to 350°C: dispersed PtO₂
25°C – 350°C in O₂/He

WT EXAFS
• R: radial distribution function around Pt
• k-space resolution for R-space peaks
• C backscatterer (25°C) → O backscatterer (350°C) during oxidation

25°C – 350°C, O₂: Pt[acac]₂ decomposition + dispersed PtO₂ phase formation

Results: Region 2

Region 1: 25°C – 350°C in O₂/He
Region 2: 350°C – 650°C – 250°C in O₂/He
Region 3: 250°C – 350°C – 450°C in H₂/He
Region 4: 450°C – 650°C in H₂/He
350°C – 650°C – 250°C in O₂/He

**XANES**
- Further oxidation up to 650°C: decrease oxidation state
- Cool down to 250°C: no effect

**FT EXAFS**
- Pt fcc metal structure + Pt-O shell: metal core + oxidized shell → sintering of dispersed PtO₂
WT EXAFS

- O backscatterer (350°C) → oxidation 650°C → Pt backscatterer (250°C) after oxidation

350°C – 650°C – 250°C in O₂/He

350°C – 650°C – 250°C, O₂: sintering dispersed PtO₂ → Pt⁰ cluster core with oxidized outer shell
Region 1: 25°C – 350°C in O₂/He
Region 2: 350°C – 650°C – 250°C in O₂/He
Region 3: 250°C – 350°C – 450°C in H₂/He
Region 4: 450°C – 650°C in H₂/He
250°C – 350°C – 450°C in H₂/He

**XANES**
- WL decrease
- Evolution to Pt metal

**FT EXAFS**
- Cluster structure remains stable
- Pt-O/Pt-Pt decreases: reduction

<table>
<thead>
<tr>
<th>Condition</th>
<th>Pt-O/Pt-Pt amplitude</th>
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<tbody>
<tr>
<td>O₂/He 250°C</td>
<td>1,44</td>
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<tr>
<td>H₂/He 350°C</td>
<td>1,01</td>
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<tr>
<td>H₂/He 450°C</td>
<td>0,76</td>
</tr>
</tbody>
</table>
WT EXAFS
• Decreased O intensity relative to Pt intensity upon heating in H₂/He

250°C – 450°C, H₂: gradual reduction of Pt clusters
Results: Region 4

Region 1: 25°C – 350°C in O₂/He
Region 2: 350°C – 650°C – 250°C in O₂/He
Region 3: 250°C – 350°C – 450°C in H₂/He
Region 4: 450°C – 650°C in H₂/He
XANES
- Shift of edge energy to higher energy
- WL intensity decreases.
  → alloying \(^{[3]}\) (confirmed by EDX)

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Pt$^2+$[acac]$_n$  Pt$^2+$[acac]$_n$  Pt$^2+$[acac]$_n$

25°C
Pt$^{2+}$[acac]$_n$ Pt$^{2+}$[acac]$_n$ Pt$^{2+}$[acac]$_n$

- Pt[acac]$_2$ decomposition
- Dispersed PtO$_2$ phase formation
Conclusions

- Pt[acac]₂ decomposition
- Dispersed PtO₂ phase formation

- PtO₂ sintering
- Pt cluster = metal core + oxidized shell
Conclusions

- Pt[acac]$_2$ decomposition
- Dispersed PtO$_2$ phase formation
- PtO$_2$ sintering
- Pt cluster = metal core + oxidized shell
- Reduction of outer shell
Conclusions

- Pt(acac)_2 decomposition
- Dispersed PtO_2 phase formation

- PtO_2 sintering
- Pt cluster = metal core + oxidized shell

- Reduction of outer shell

- Pt-Ga formation
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• XAS: X-ray Absorption Spectroscopy
• XANES: X-ray Absorption Near Edge Structure
• EXAFS: Extended X-ray Absorption Fine Structure
• FT: Fourier Transformation
• WT: Wavelet Transformation
• EDX: Energy Dispersive X-ray spectroscopy
• WL: White Line (first maximum at the absorption edge)
• fcc: face centered cubic structure
• absorber: atomic species absorbing X-ray fotons leading to the excitation their core-electrons.
• backscatterer: atomic species surrounding the absorber which scatter back the excited photo-electron to the absorber in the continuum.