UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Pt-Ga catalyst formation studied with *in situ* XAS using Fourier and wavelet transformed analysis.

M. Filez, H. Poelman, E. Redekop, V.V. Galvita, C. Detavernier, G.B. Marin

Laboratory for Chemical Technology, Ghent University

http://www.lct.UGent.be

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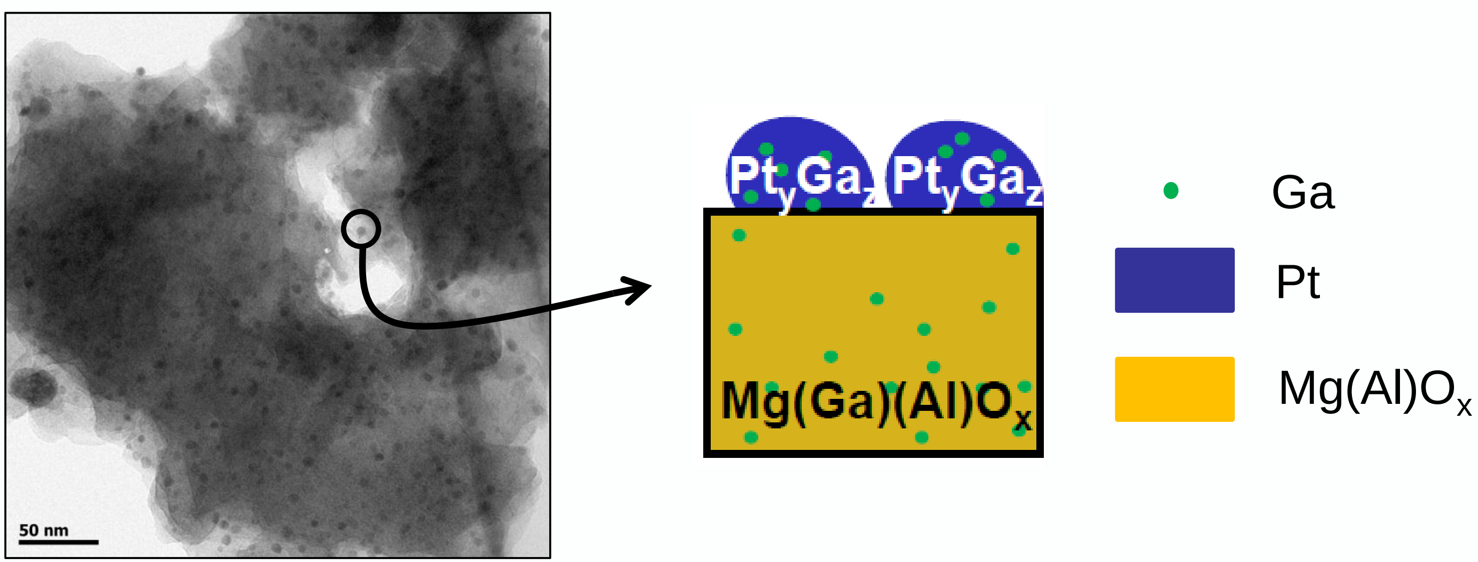
ERIC

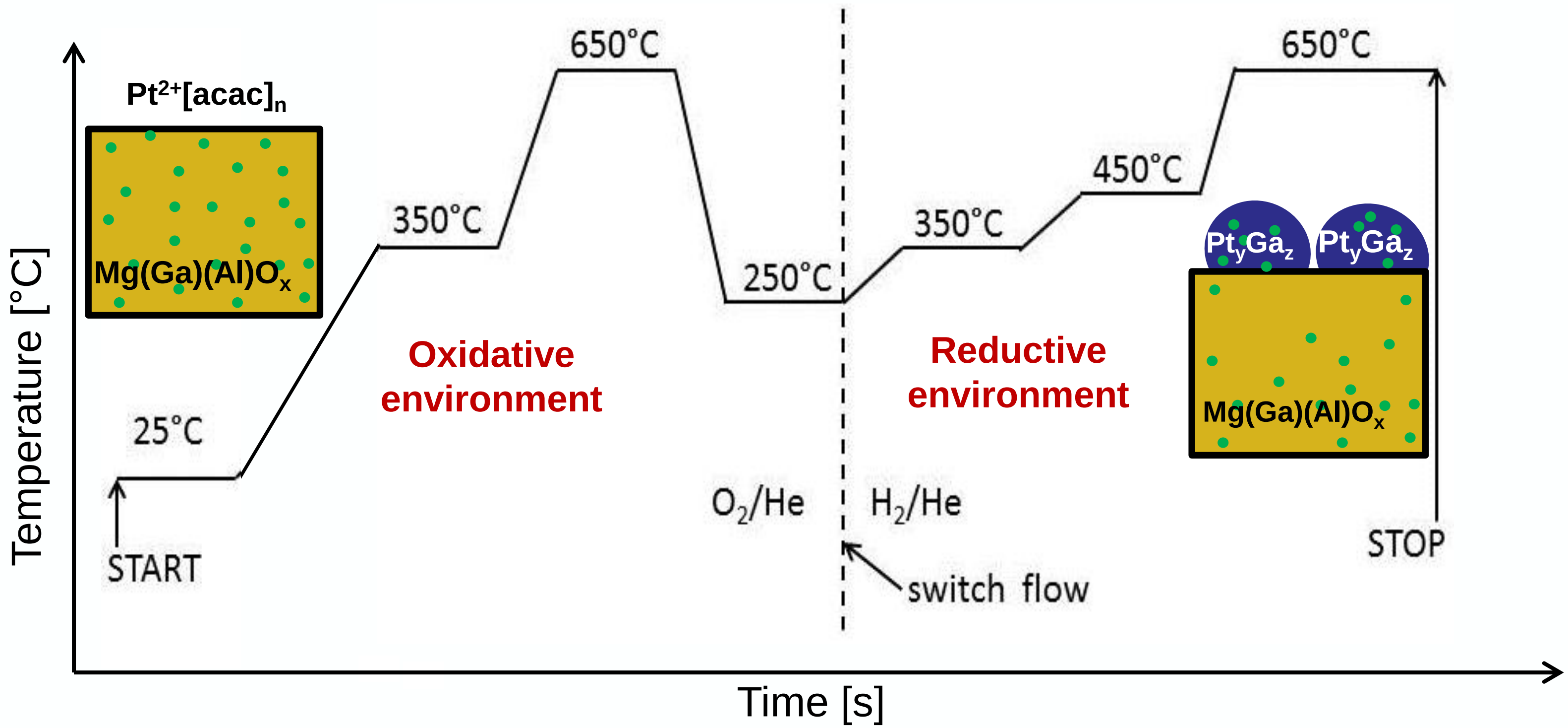
Introduction & Motivation

- 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)



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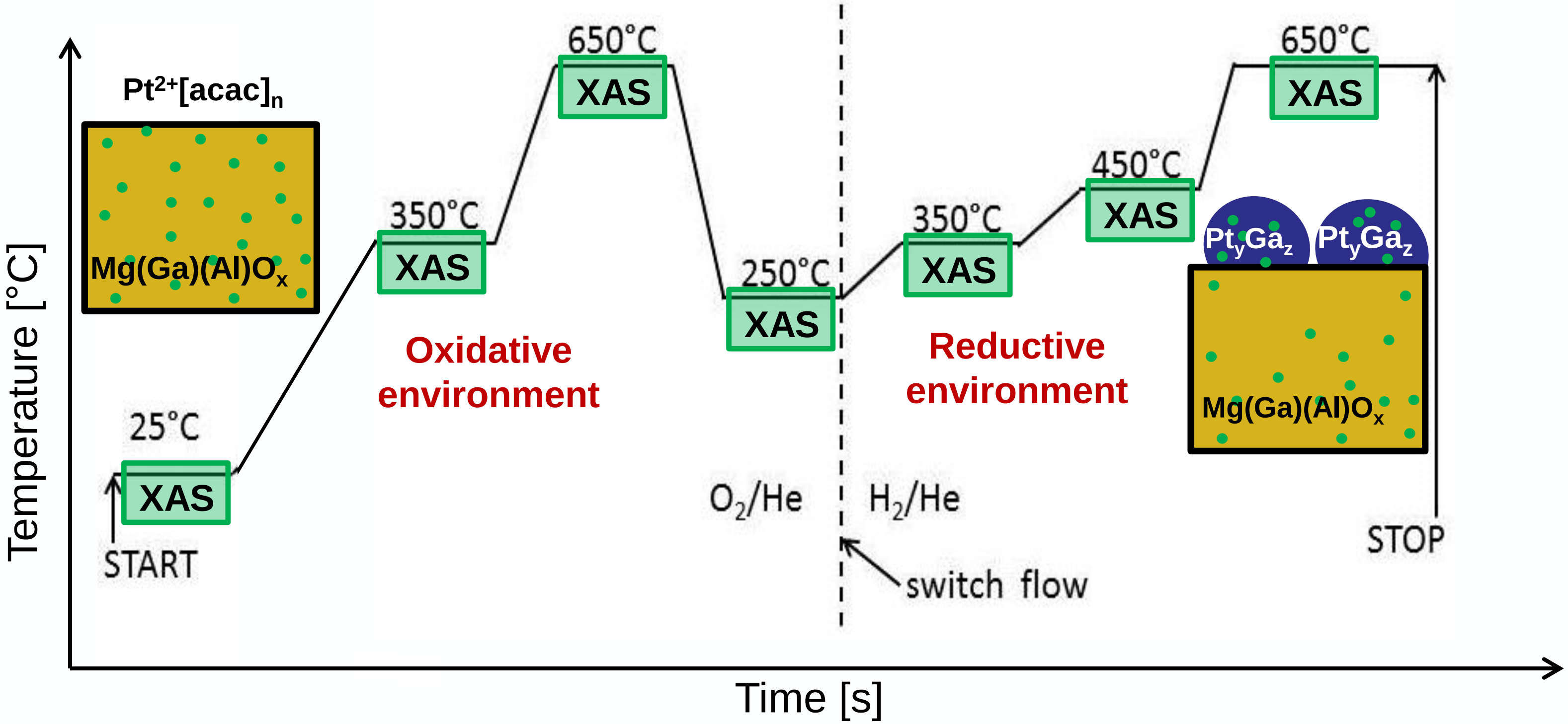
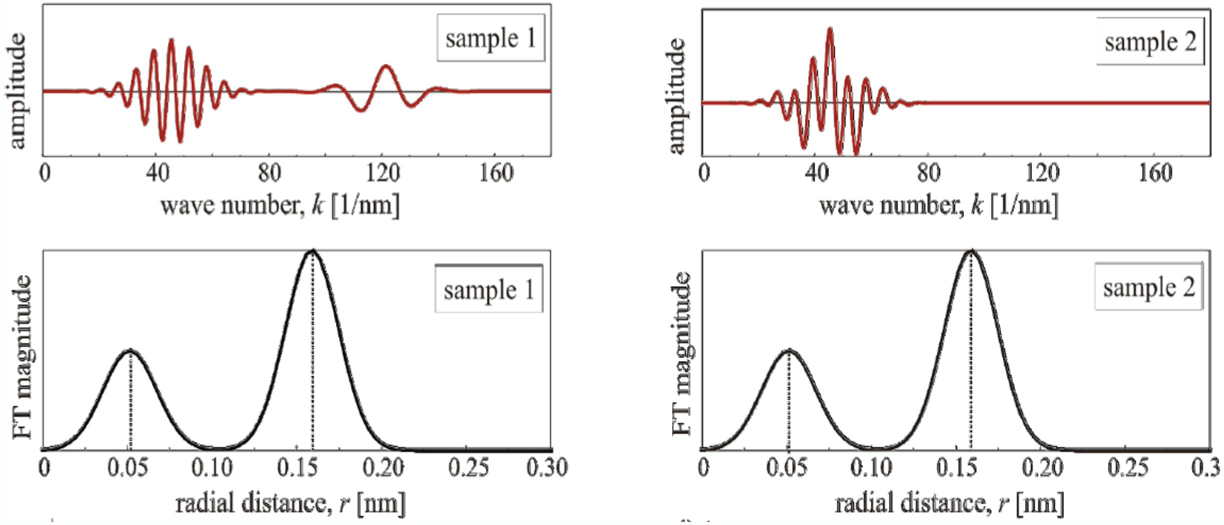


XAS wavelet transforms

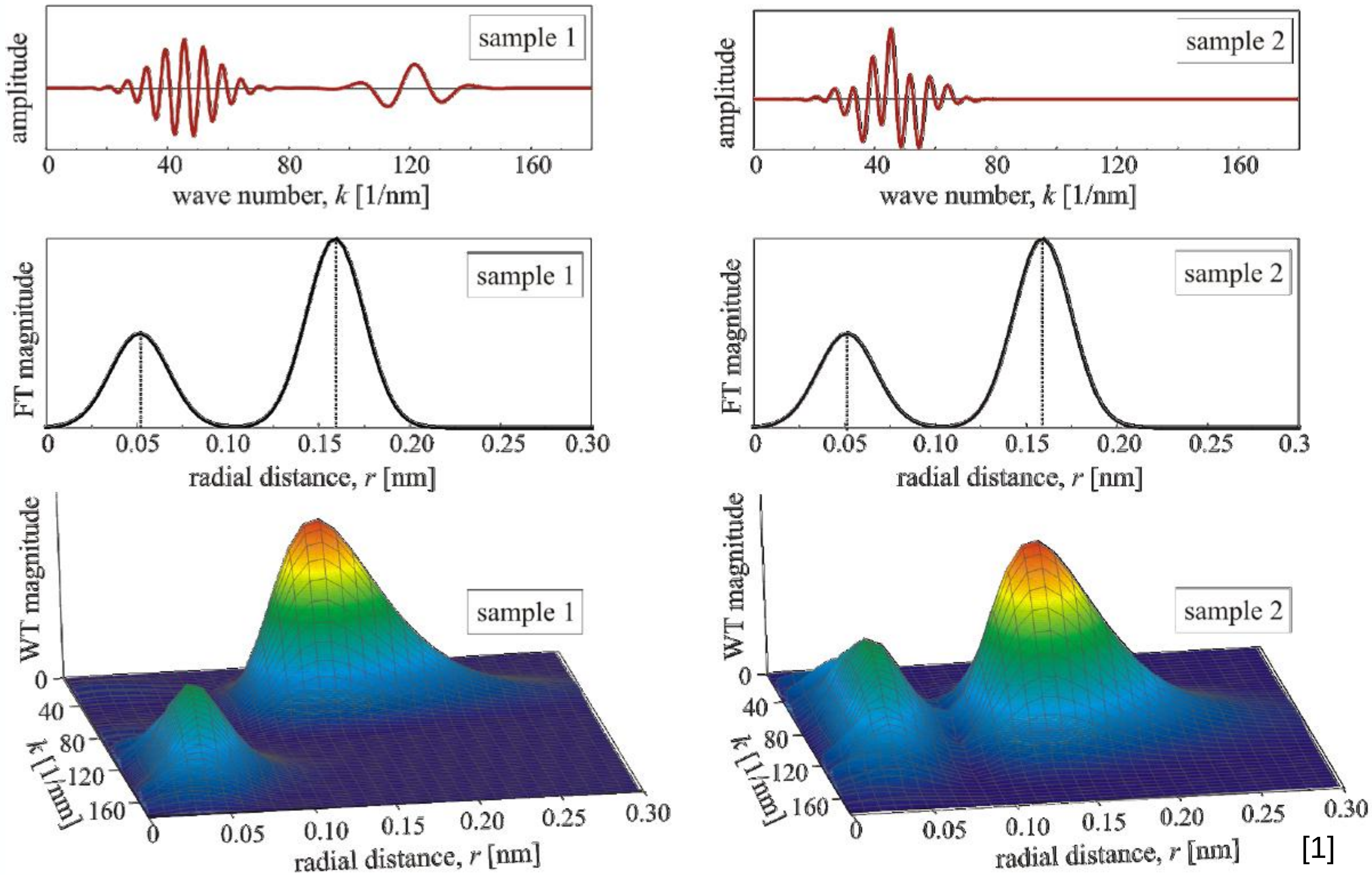
- Pt-Ga formation process:
  - variety of Pt neighbors (Pt-C, Pt-O, Pt-Ga, Pt-Pt)
  - Discrimination and localization of different atomic species necessary

- 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

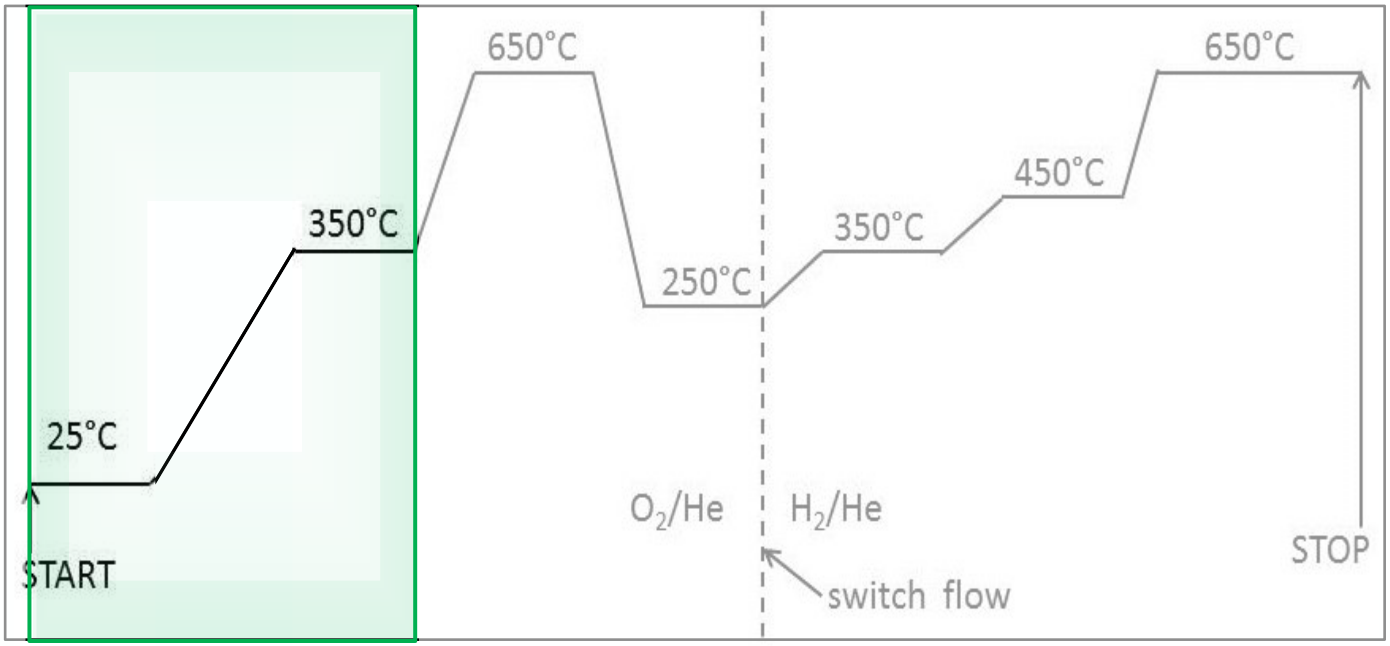


→ simultaneous R and k space resolution[1,2]: appoint k-space backscattering region to each R-space peak

[1] C. Antoniak, *Beilstein J. Nanotechnol.* **2011,** *2,* 237–251

[2] Muñoz M., Argoul P. and Farges F. (2003) American Mineralogist vol. 88, pp. 694-700

Results: Region 1



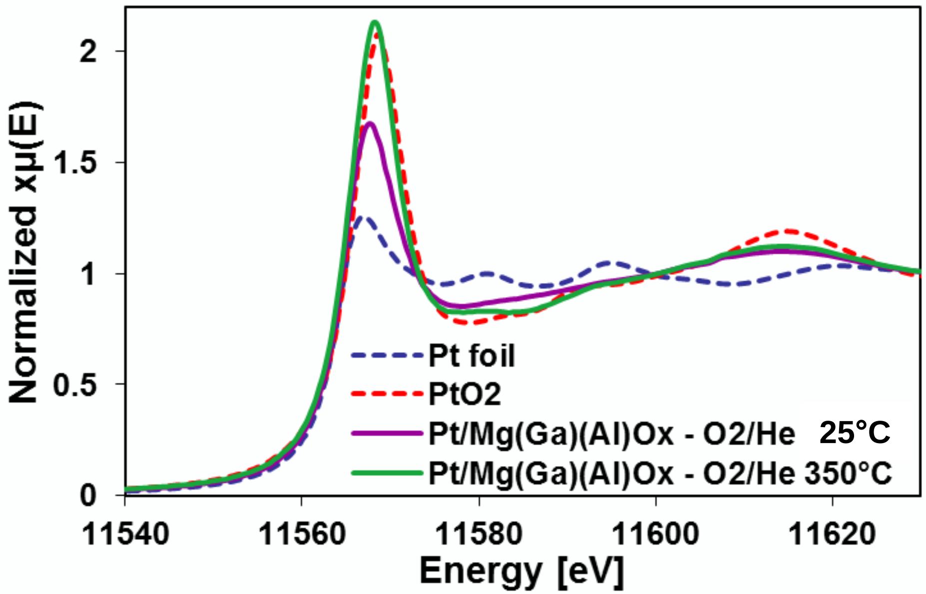
Region 1: 25°C – 350°C in O_2/He

Region 2: 350°C – 650°C – 250°C in O_2/He

Region 3: 250°C – 350°C – 450°C in H_2/He

Region 4: 450°C – 650°C in H_2/He

25°C – 350°C in O_2/He

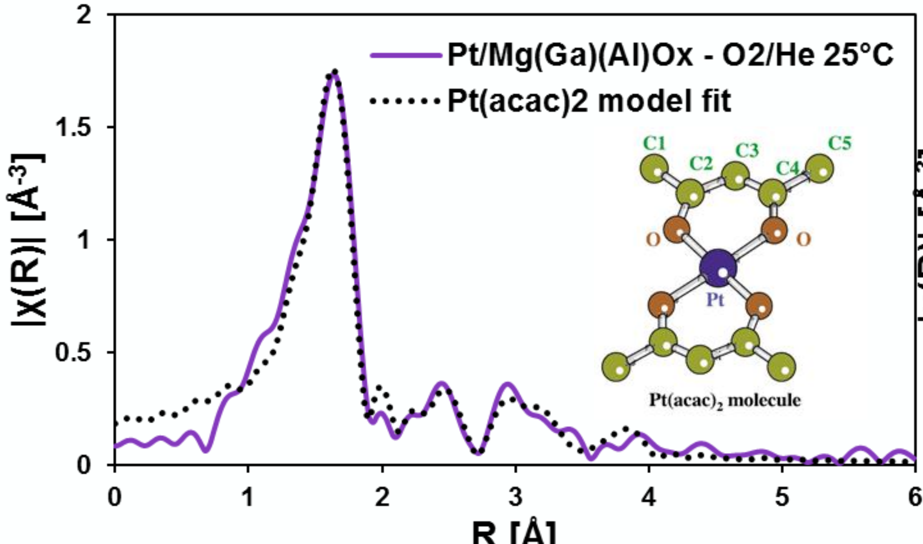


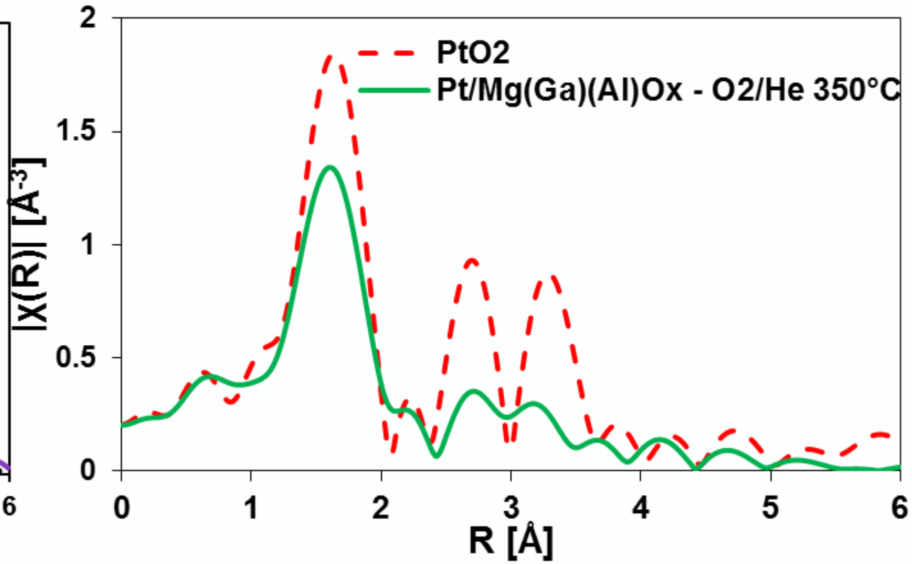
XANES

- WL at 25°C = II+ = $Pt^{2+}[acac]_2$
- Oxidation to 350°C: $Pt^{4+}O_2$-like XANES

FT EXAFS

- As prepared catalyst at RT: $Pt[acac]_2$
- Oxidation to 350°C: dispersed PtO_2

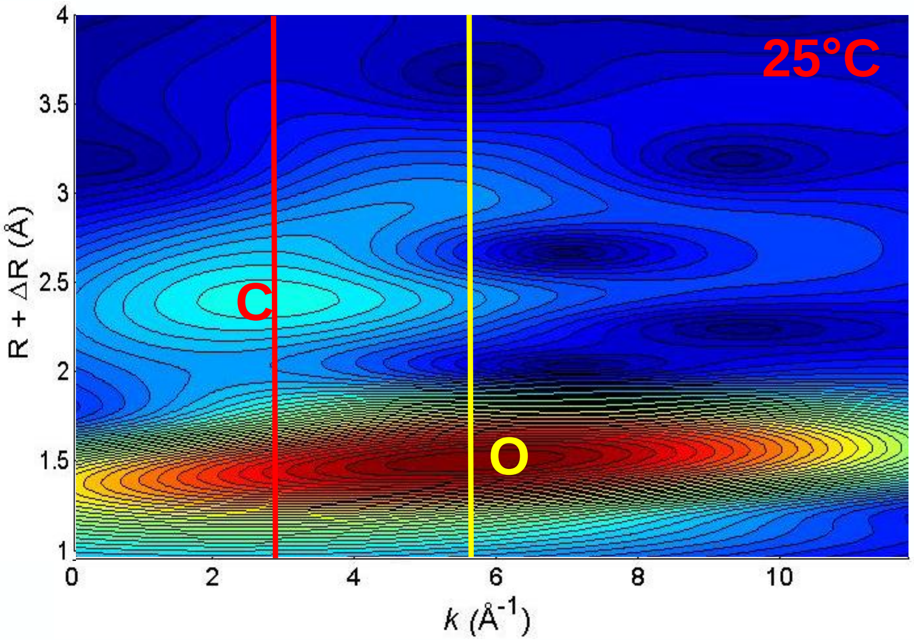


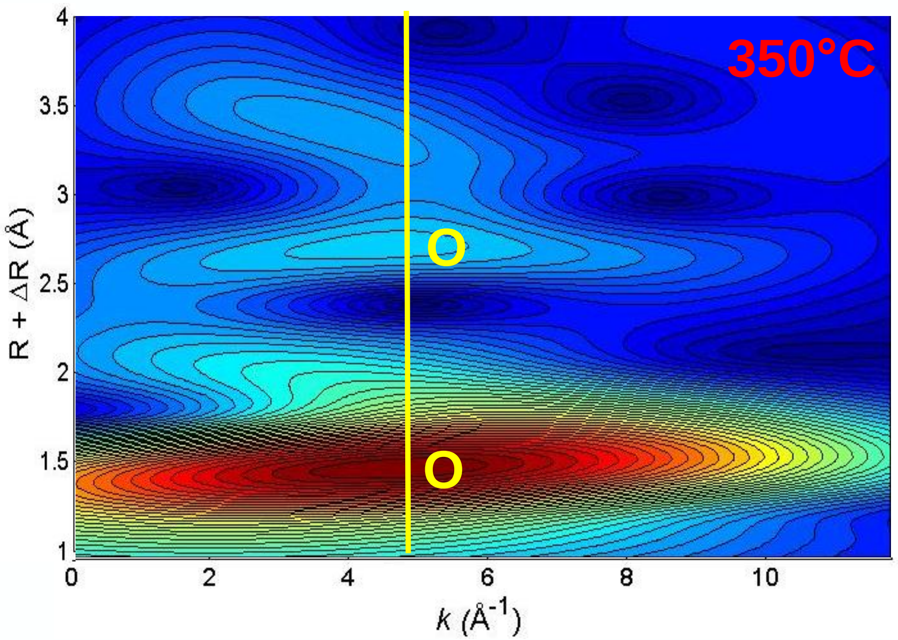


25°C – 350°C in O_2/He

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

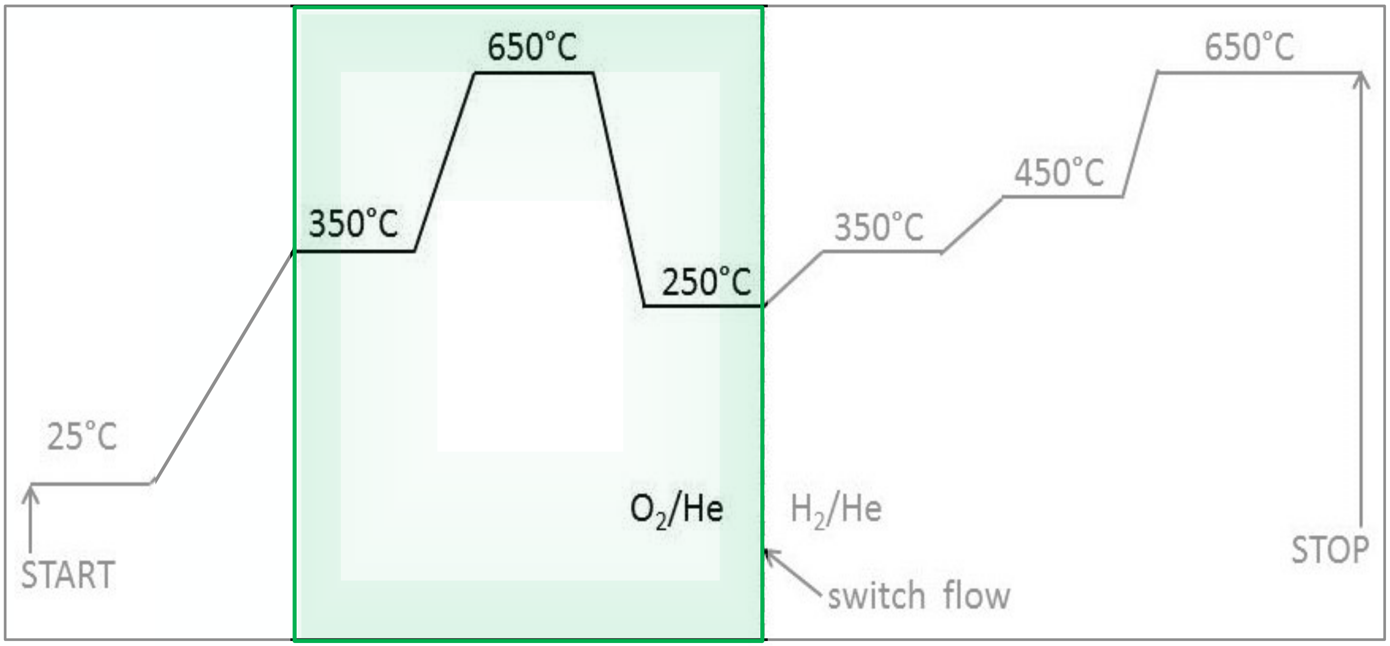




25°C – 350°C, O_2: Pt[acac]$_2$ decomposition + dispersed PtO_2 phase formation

[2] Software: Muñoz M., Argoul P. and Farges F. (2003) American Mineralogist vol. 88, pp. 694-700

Results: Region 2



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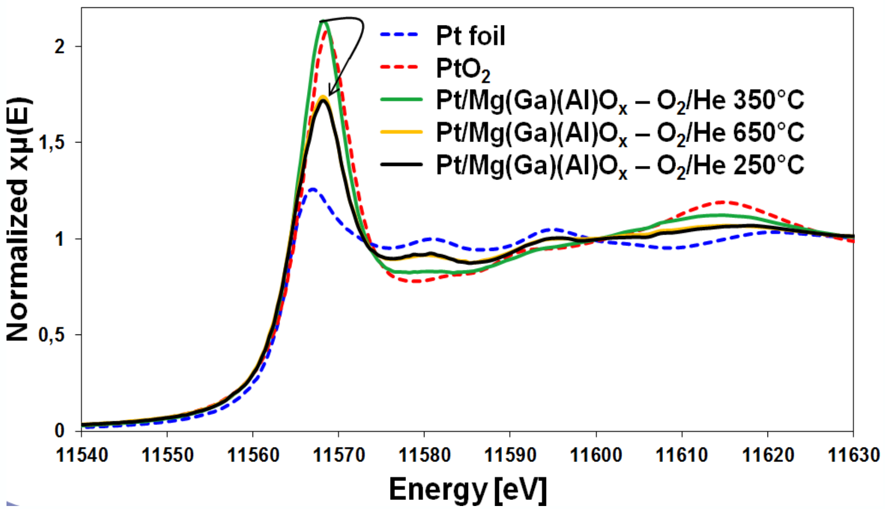
350°C – 650°C – 250°C in O_2/He

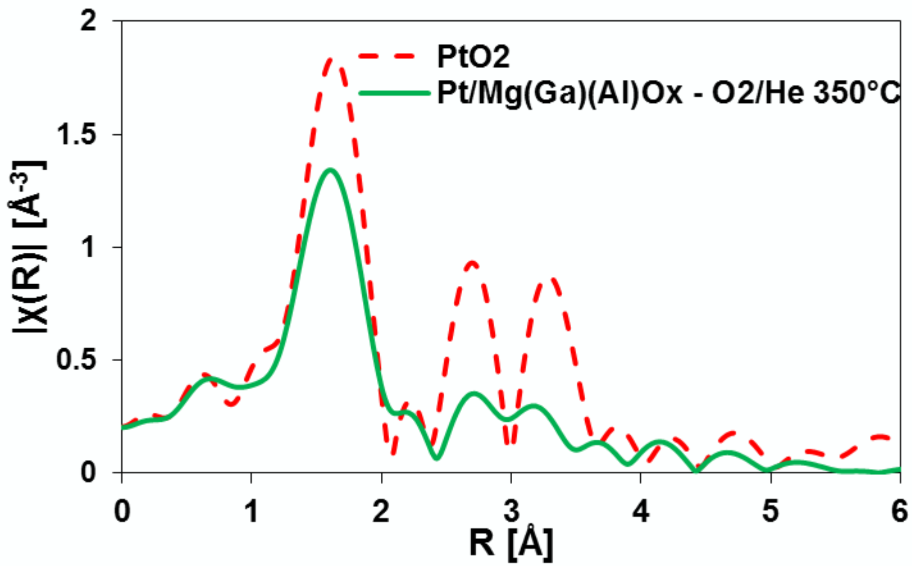


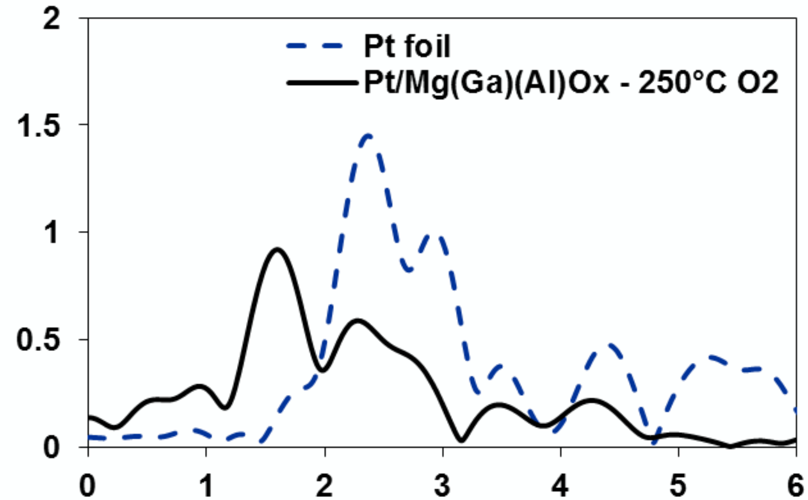
XANES

- 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 PtO_2

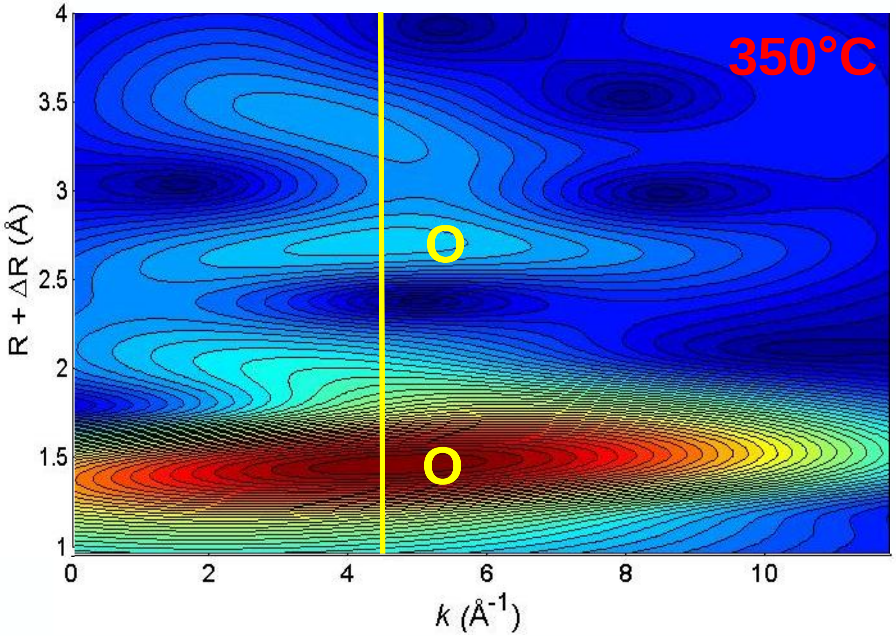


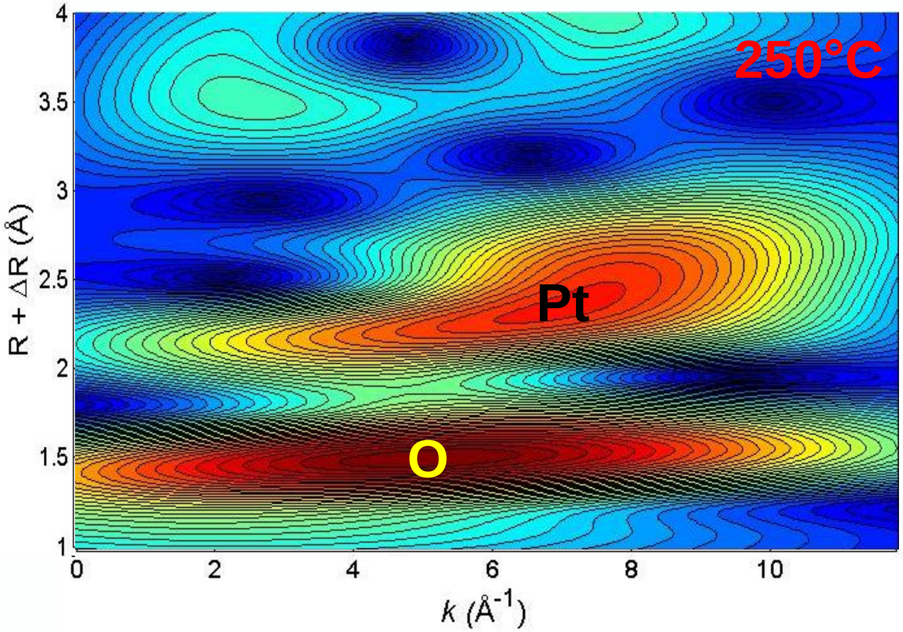


350°C – 650°C – 250°C in O_2/He

WT EXAFS

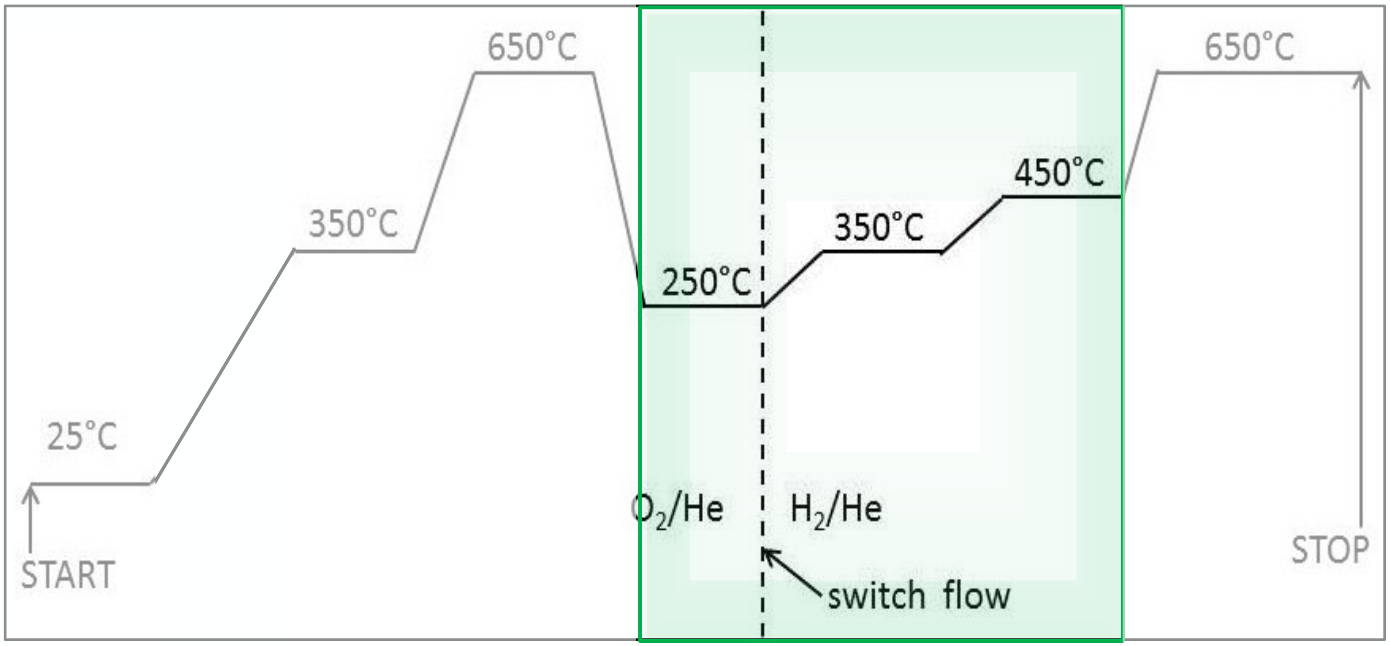
- O backscatterer (350°C) → oxidation 650°C → Pt backscatterer (250°C) after oxidation





350°C – 650°C – 250°C, O_2: sintering dispersed PtO_2 → Pt^0 cluster core with oxidized outer shell

Results: Region 3



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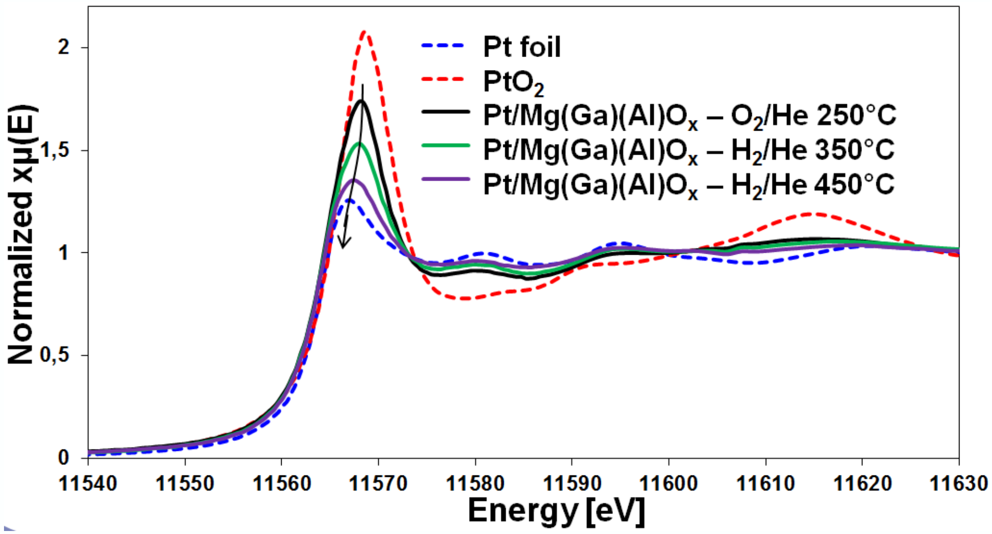
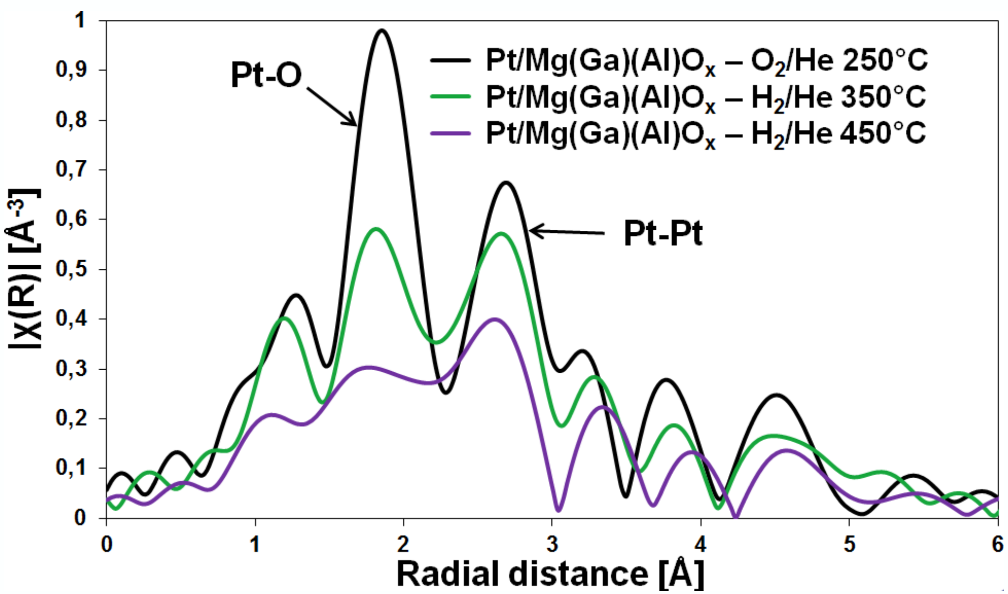
250°C – 350°C – 450°C in H_2/He





<u>XANES</u>

- WL decrease
- Evolution to Pt metal

<u>FT EXAFS</u>

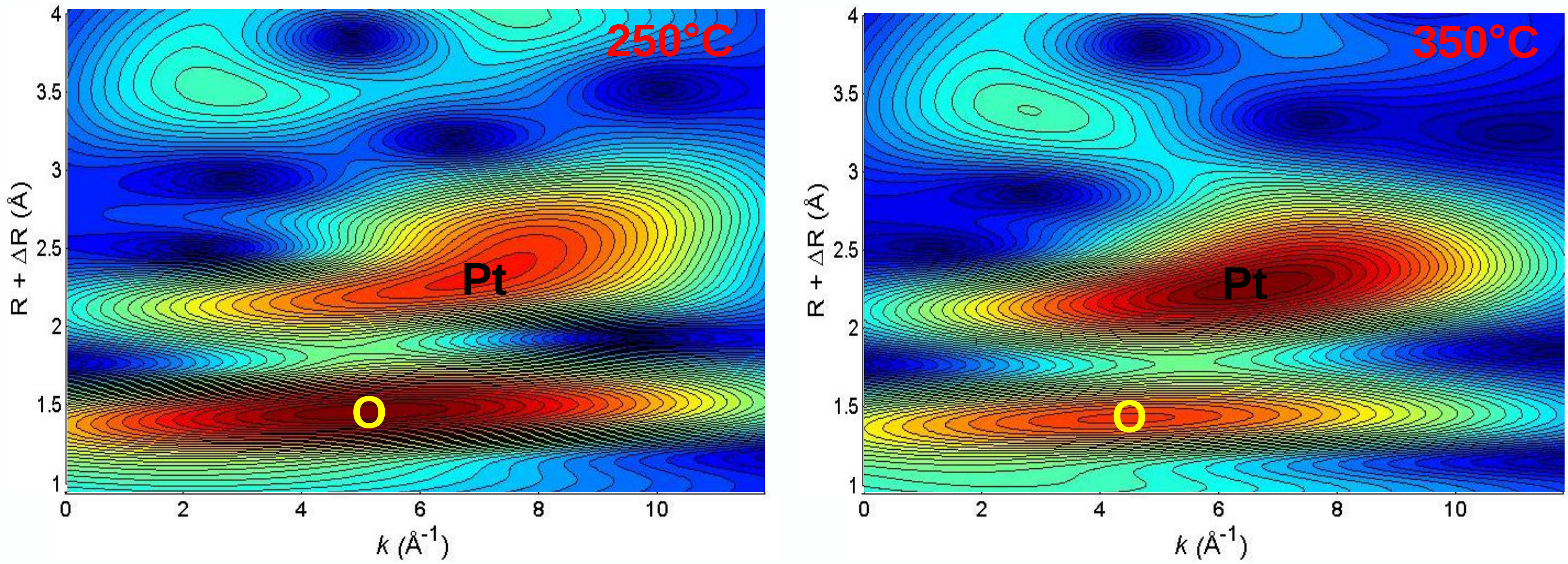
- Cluster structure remains stable
- Pt-O/Pt-Pt decreases: reduction

Condition	Pt-O/Pt-Pt amplitude
O_2/He 250°C	1,44
H_2/He 350°C	1,01
H_2/He 450°C	0,76

250°C – 350°C – 450°C in H_2/He

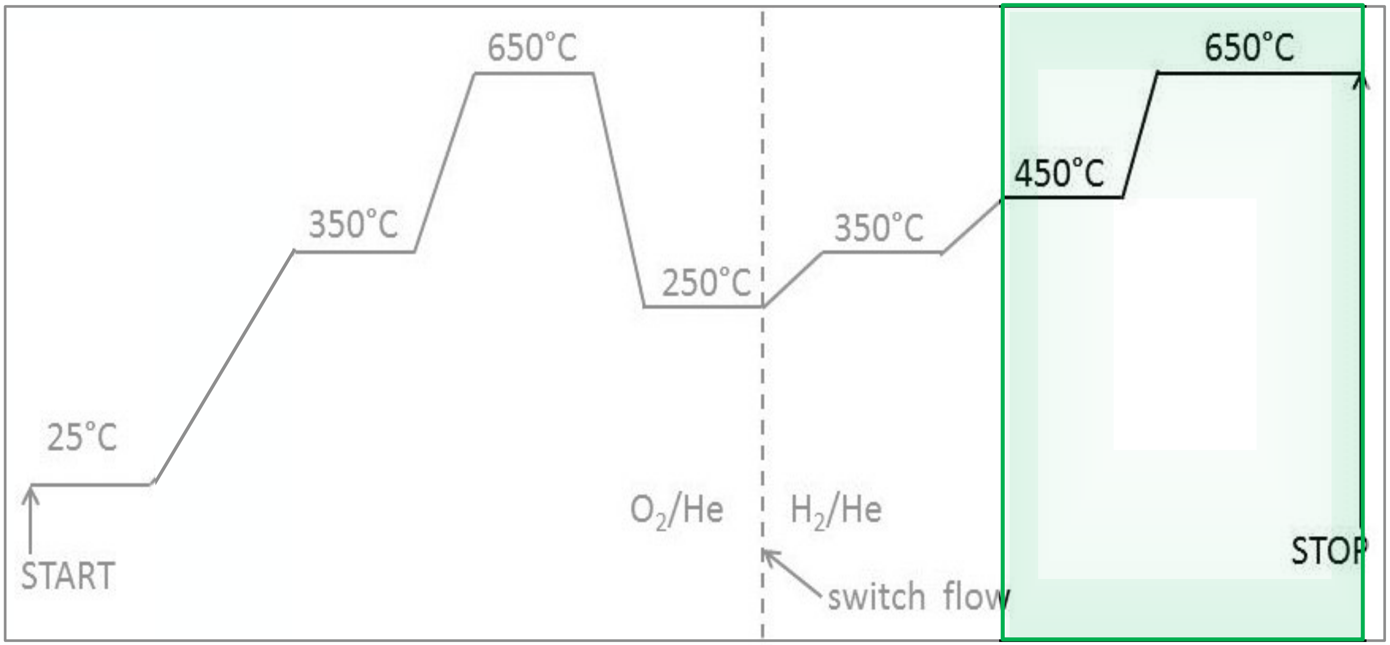
<u>WT EXAFS</u>

- Decreased O intensity relative to Pt intensity upon heating in H_2/He



250°C – 450°C, H_2: gradual reduction of Pt clusters

Results: Region 4



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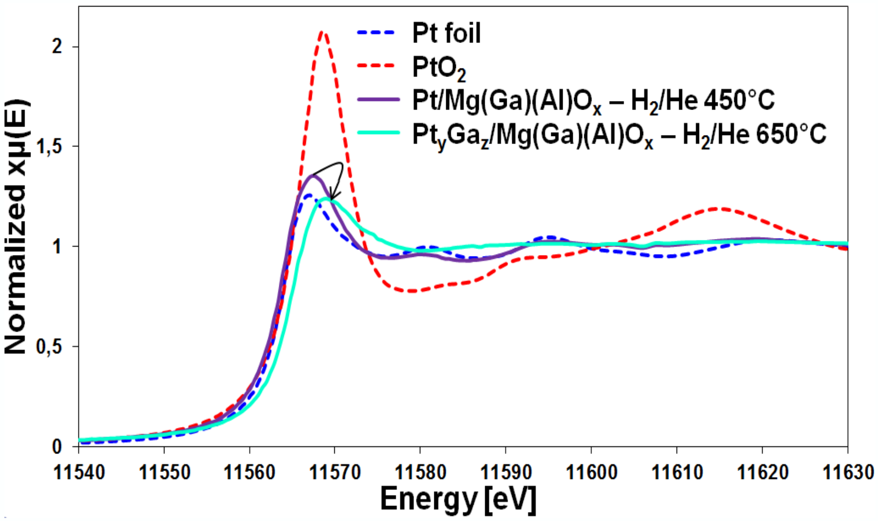
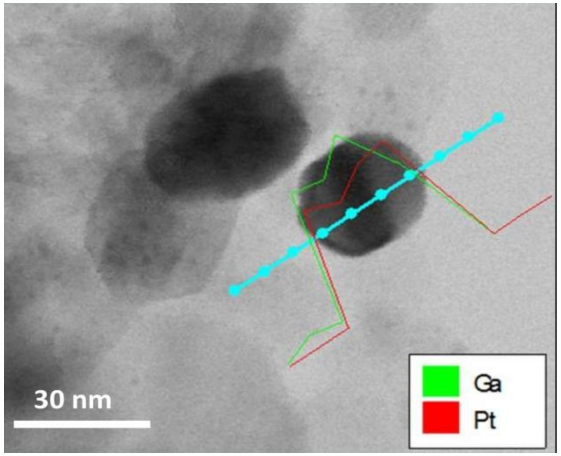
Region 4: 450°C – 650°C in H_2/He

450 – 650°C in H_2/He





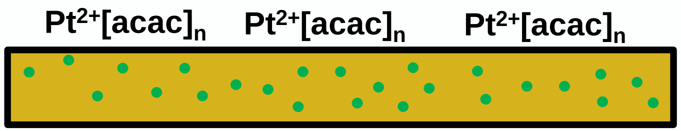
<u>XANES</u>

- Shift of edge energy to higher energy
- WL intensity decreases.

→ alloying [3] (confirmed by EDX)

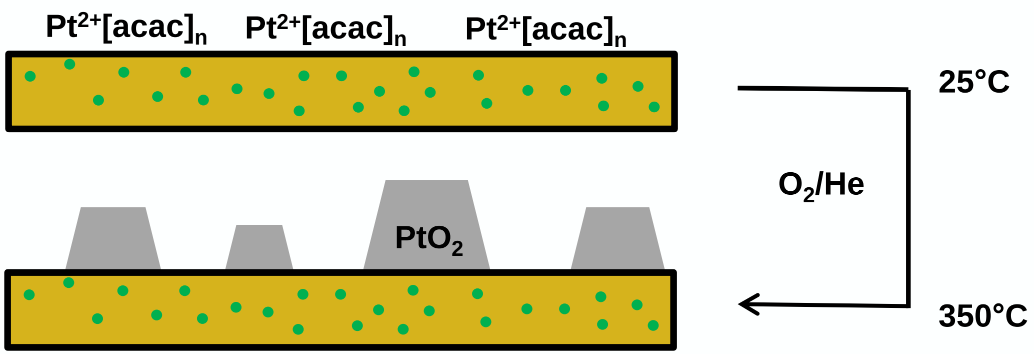
[3] R. Giedigkeit et al., http://hasyweb.desy.de/science/annual_reports/2002_report/part1/contrib/41/6974.pdf

Conclusions



25°C

Conclusions



- $Pt[acac]_2$ decomposition
- Dispersed PtO_2 phase formation

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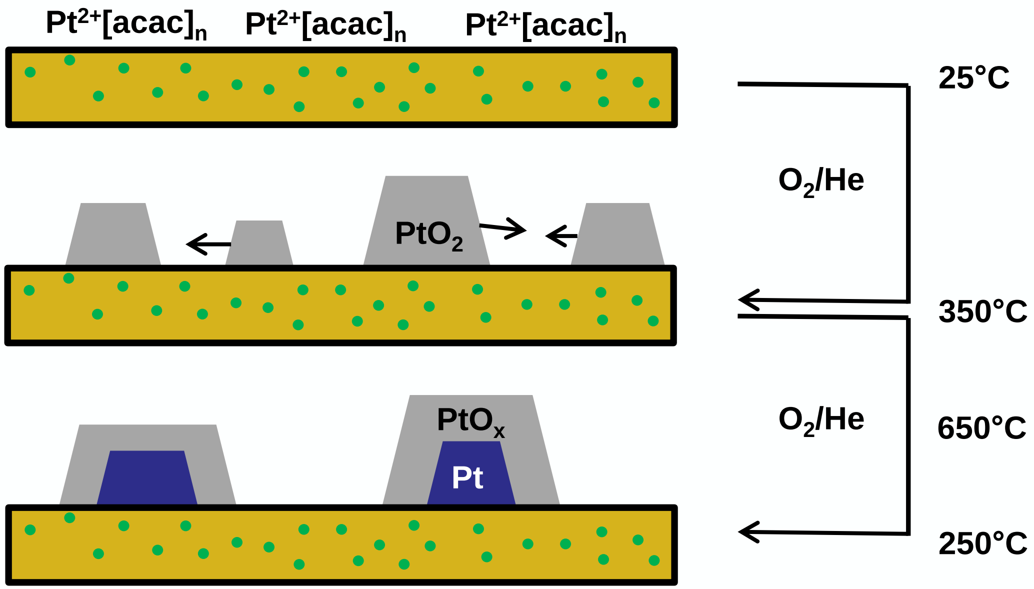

- Pt[acac]$_2$ decomposition
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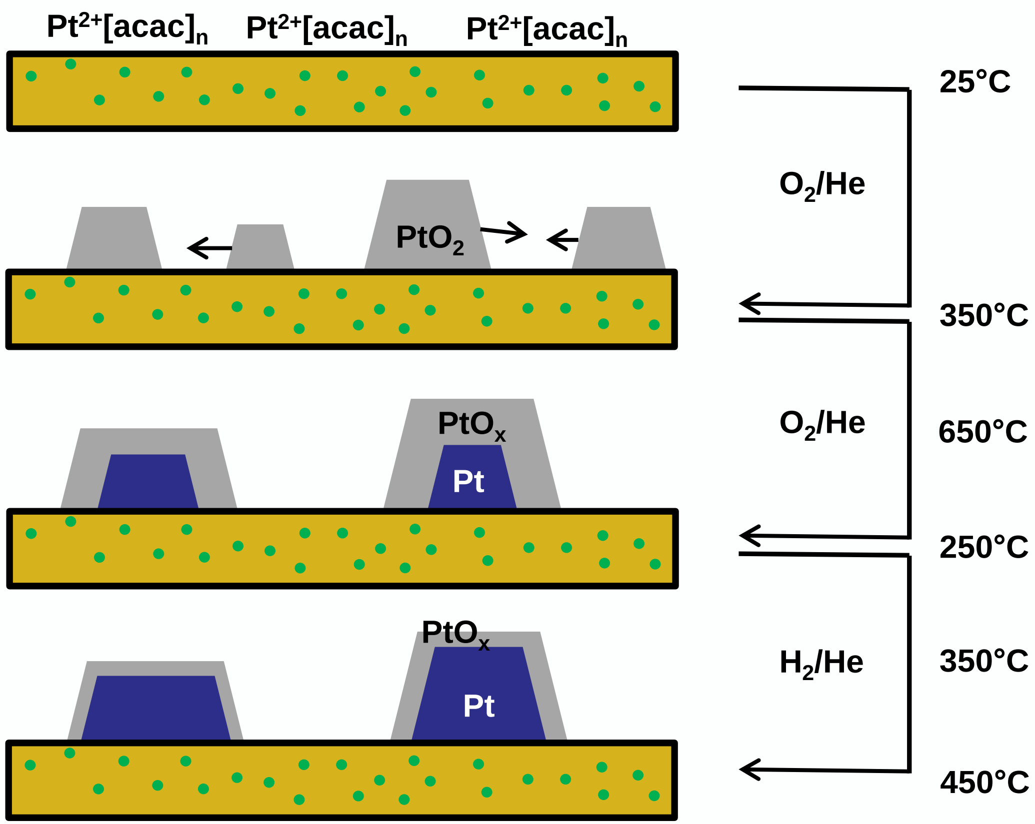

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- Reduction of outer shell

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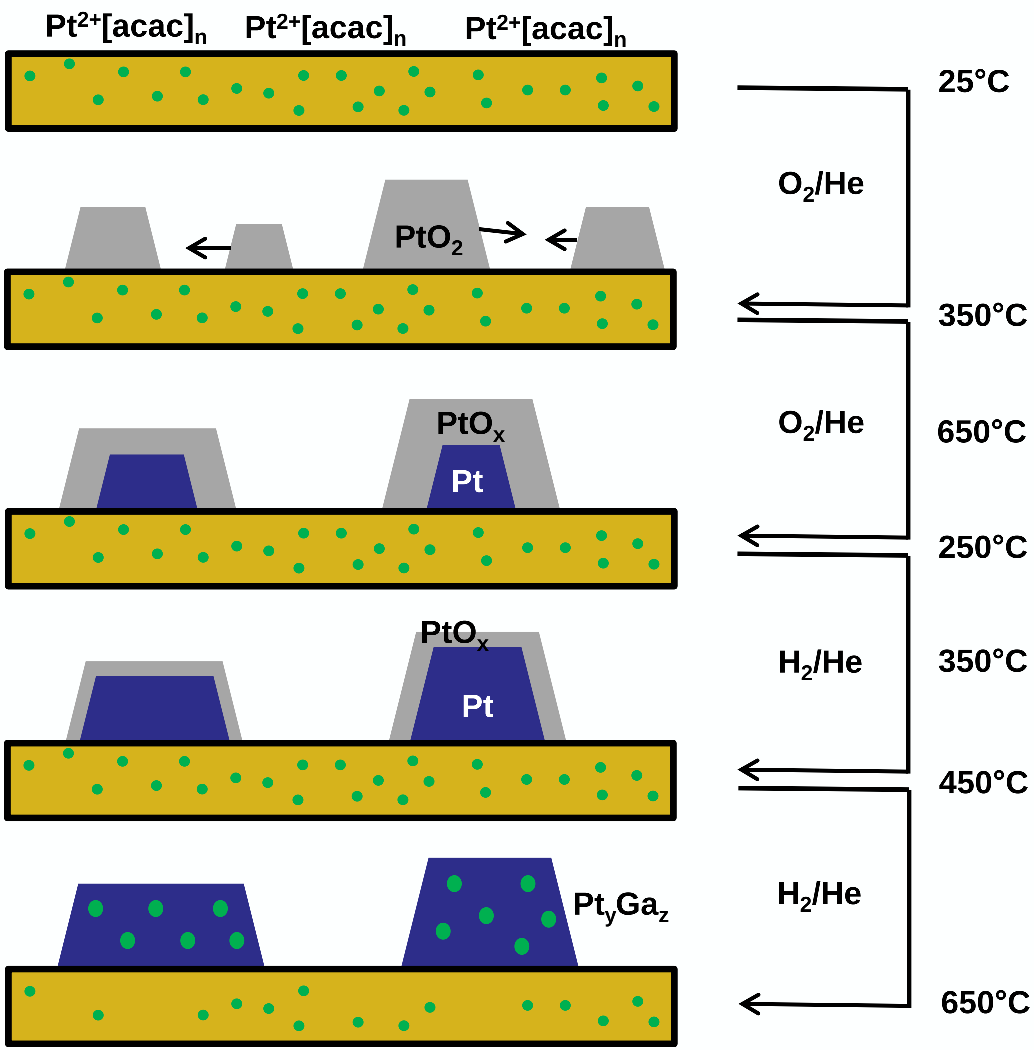

- $Pt[acac]_2$ decomposition
- Dispersed PtO_2 phase formation

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

- Reduction of outer shell

- Pt-Ga formation

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- Marie Curie IIF Fellowship of the European Commission.

Glossary

- 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.