Comparison between XAS (Xanes-Exafs), AWAXS, ASAXS and DAFS applied to nanometer scale supported metallic clusters.
Definition of a methodology

D. Bazin
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VI. Summary
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I.1 Nanometer scale metallic clusters

**Monometallic clusters**

- **Morphology:** Icosahedra are preferred to cubooctahedra,
- **Relaxation:** Large compressions of the central atom are observed for the icos geometries (6%) while small core compressions are found for the fcc geometries (1%)

**Bimetallic clusters**

- Distribution of the metals inside the cluster: statistical distribution or core/shell distribution

Interaction between the cluster and the support
I.2 Structural parameters N & R

**Monometallic cluster**

Coordinations \((N_1,N_2,N_3,N_4)\) --> Size & Morphology
Interatomic distances --> Compression/dilatation

**Bimetallic cluster**

Coordination \((N_{AA}, N_{AB}, N_{BA}, N_{BB})\) --> Segregation

**Very high reactivity** --> *In situ* methods to preserve the physico chemistry integrity of the metallic cluster

- In-situ spectroscopy of catalysts
I.3 L’outil d’investigation : une source de rayons X

100000 km/s --> 1000km/s

Brillance Nb de photons/cône

**Tube** : $10^7$ \quad \Rightarrow \quad **Synchrotron** : $10^{20}$

la fluorescence X (identifier les éléments) ou la diffraction X (identifier les phases)

Temps d’acquisition, Cartographie, Sensibilité

la spectroscopie d’absorption X.

Spéciation
1.4 R.S. à travers le monde & Recherche finalisée

**Denmark:**
ISA (Aarhus).

**France:**
ESRF (Grenoble),
Soleil (Orsay).

**Germany:**
ANKA (Karlsruhe),
BESSY (Berlin),
DELTA (Dortmund),
ELSA (Bonn),
HASYLAB (Hamburg).

**Italy:**
Elettra (Trieste).

**Spain:**
LLS (Barcelona).

**Sweden:**
MAX (Lund).

**Switzerland:**
SLS (PSI) (Villigen).

**U.K.:**
Diamond (Didcot),
SRS (Daresbury).

**Brazil:**
LNLS (Campinas SP).

**Canada:**
CLS (Saskatoon).

**USA:**
ALS (Berkeley CA),
APS (Argonne IL),
CAMD (Baton Rouge LA),
DFELL (Durham NC),
CHESS (Ithaca NY),
SLS (Upton NY), SRC (Madison WI),
SSRL (Stanford, CA),
SURF II (Gaithersburg MD).

**China (PR):**
BSRF (Beijing).

**India:**
INDUS (Indore).

**Japan:**
Nano-Hana (Ichihara),
Photon Factory (Tsukuba),
SPring-8 (Nishi Harima).

**Russia:**
SSRC (BINP) (Novosibirsk).

**South Korea:**
Pohang Acc. Lab (Pohang).

**Taiwan:**
SRRC (Hsinchu).

**Australia:**
Australian Syn. (Melbourne).
II.1 X-ray Absorption Spectroscopy

\[ \mu_x(E) = \log(\frac{I_0}{I_1}) \]

II.2 The associated formula

\[ \chi(k) = \sum_{j} \frac{N_j}{R_j^2} f_j(k) \exp\left(-\frac{R_j}{\lambda}\right) \exp\left(-2\sigma_j^2 k^2\right) \sin(2kR_j + \phi_j(k)) \]

Electronic terms
\[ f_j(k), \phi_j(k), \lambda \]

Structural terms
\[ N_j, R_j, \sigma_j \]
II.3 Nanometer scale metallic cluster & Xas

II.4a Some examples

**1%wt Pt/oxide**

- Xas studies of bimetallic Pt-Re(Rh)/Al₂O₃ catalysts in the first stages of preparation.
- Bimetallic reforming catalysts: Xas of the particle growing process during the reduction.
- *In situ* high temperature and high pressure Exafs studies of Pt/Al₂O₃ catalysts: Part I.
- *In situ* high temperature and high pressure Exafs studies of Pt/Al₂O₃ catalysts: Part II.
  N. S. Guyot-Sionnest et al., Cat. Let 8, 297 (1991).
- Investigation of dispersion and localisation of Pt species in mazzite using Exafs.
- *In situ* study by Xas of the sulfuration of industrial catalysts: the Pt & PtRe/Al₂O₃ system.
- Xas of electronic state correlations during the reduction of the bimetallic PtRe/Al₂O₃ system.
- Influence of the H₂S/H₂ ratio and the temperature on the local order of Pd atoms in the case of a highly dispersed multimetallic catalyst: Pd-Ni-Mo/Al₂O₃.
  D. Bazin et al., J. of Physique IV, 12-6, 379, (2002).
- Structure & size of bimetallic PtPd clusters in an hydrotreatment catalyst.
  D. Bazin et al., Accepted in Oil & Gas Science and Technology - Rev. IFP
II.4b Experimental set up

Figure 1: Partial view of the sample holder
1, 2: Boron nitride sample holder and cover plate
3: Carbon foil for gas leakage
4, 5: Stainless steel mounting block and cover plate

Figure 2: General view of the sample holder

X-ray beam
Catalyst
Water cooling
Quick disconnect for gas flow
Sample holder
Thermocouple
Gas output
Gas input

QuickTimeª et un décompressor Photo - JPEG sont requis pour visualiser cette image.
II.4c Some examples

**Pt/Al$_2$O$_3$**

- $N_{PtO}=6$
- $N_{PtPt}=4.5$

$H_2$

$T=450°C$

- $N_{PtO}=0.4$
- $N_{PtPt}=4.5$

$1%H_2S/H_2$

$T=450°C$

- $N_{PtS}=2.8$

$H_2$

$T=450°C$

- $N_{PtS}=2.8$
- $N_{PtPt}=1.5$

**PtRe/Al$_2$O$_3$**

- $N_{PtO}=6.0$
- $N_{ReO}=4.1$

- $N_{PtO}=0.3$
- $N_{PtMet}=3.9$

- $N_{ReO}=0.9$
- $N_{ReMet}=3.7$

- $N_{PtS}=2.0$
- $N_{PtMet}=4.2$

- $N_{PtS}=2.4$
- $N_{ReS}=2.4$
- $N_{ReMet}=4.5$

- $N_{PtS}=1.0$
- $N_{PtMet}=4.0$

- $N_{PtS}=2.0$
- $N_{ReS}=2.0$
- $N_{ReMet}=4.7$
In the case of a cluster, it is essential to consider each kind of atom since the signal coming from the surface and the central atom are definitely not the same. A 13 Cu environment is not enough to produce the resonance C.

- For nanometer scale materials, it is definitely not possible to simulate their Xanes part for K edge with a linear combination of the Xanes of well crystallised reference compounds.
From an experimental point of view, the $L_{III}$ white line is at the centre of electronic charge transfer between either the nanometer scale metallic particle and the support or between the two metals which are present inside the cluster.

Ab initio calculation of DOS regarding Pt clusters show that the DOS of clusters is clearly different from the DOS of the Pt bulk.

Two physical phenomenon can affect the intensity of the white line: the size of the cluster which can be considered as an intrinsic effect and a possible charge transfer which can be considered as an extrinsic effect.

Averaged D.O.S. of $13\,\text{Pt}$, $55\,\text{Pt}$, $147\,\text{Pt}$, $309\,\text{Pt}$, $923\,\text{Pt}$ cuboctahedra.

II.5c Dynamical processes

**Journal of Catalysis** 203, 133–149 (2001)

Redox Behavior of Copper Oxide/Zinc Oxide Catalysts in the Steam Reforming of Methanol Studied by in Situ X-Ray Diffraction and Absorption Spectroscopy

M. M. Gunes, T. Rossler, J. E. Jeronimo, and B. Brenis

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In situ EXAFS study of Pd/Al₂O₃ during aerobic oxidation of cinnamyl alcohol in an organic solvent

Jan-Dierk Grunwaldt, Csilla Keresszegi, Tamas Makkat, and Alfons Bailer

---

![Graph](https://via.placeholder.com/150)

**Figure 8.** Evolution of Cu K-edge XANES of CuO/ZnO at 523 K during oxygen addition to a methanol steam reforming feed (c(H₂O) ~ 6 vol%, c(H₂) ~ 15 vol% in 25 ml/min He). Different Cu phases are indicated.

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**In situ QEXAFS investigation at Co K-edge of the sulfidation of a CoMo/Al₂O₃ hydrotreating catalyst**

Christophe Geantet, Yvon Le Soléo, Cédric Guillon, Nobuyuki Matsumura, Michel Laureix, Olivier Prévot, Olivier Ulrich, and Jean-Louis Lazennec

**Catalysis Letters** Vol. 73, No. 2-4, 2001
II.5c Xanes L edge : Dynamical process

Pt-Re/Al₂O₃

Preparation data (%wt)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pt</th>
<th>Re</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.97</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>A'</td>
<td>1.0</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>B</td>
<td>0.97</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>B'</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>B''</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Water controls the migration of the Re oxide phase, we distinguish:

- **Hydrated calcined samples** (samples A, A') which were reduced after a three month exposure to air, implying that they have been largely rehydrated.

- **Dehydrated calcined samples** (samples B, B', B'') which were reduced after a new drying operation of 15 hours at 100°C. For samples B' and B'', an in situ drying at 150°C (120 min for sample B' and 360 min for sample B'') was carried out immediately before reduction.
II.5c Xanes L edge : Dynamical process

Samples with water : mobility of the Re oxide species

Preparation data (%wt)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pt</th>
<th>Re</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.97</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>A'</td>
<td>1.0</td>
<td>0.5</td>
<td>1.0</td>
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</tbody>
</table>

Sample A

Fig. 4: Evolution of the white line intensities of the two metals (platinum and rhenium) during the reduction of the hydrated sample A.

Fig. 6: Evolution of the white line intensities of the two metals (platinum and rhenium) during the reduction of the hydrated sample A'.

Sample A’
II.5c Xanes L edge : Dynamical process

Samples without water : Re oxide species “fixed on the support”

**Sample B**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt, L_{III} edge</th>
<th>Re, L_{II} edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.97</td>
<td>1.0</td>
</tr>
<tr>
<td>B'</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>B''</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**Sample B'**

**Sample B”**

Fig. 8. Evolution of the white line intensities of the two metals (platinum and rhenium) during the reduction of the dehydrated sample B.

Fig. 9. Evolution of the white line intensities of the two metals (platinum and rhenium) during the reduction of the dehydrated sample B'.

Fig. 10. Evolution of the white line intensities of the two metals (platinum and rhenium) during the reduction of the dehydrated sample B". 
II.5c Xanes L edge: Dynamical process

PtRe bimetallic clusters

Considering the results obtained on the sample A, we can assume that the first regime is linked to the building of the Pt/Re alloy, the atomic ratio being equal to 1.

Monometallic clusters
One of the limitations is the fact that Xas is insensitive to polydispersity. It is clear that the results given by mixing clusters which have 13 & 1415 atoms are similar to the coordination number associated with a cluster of 147 atoms.
II.6b Bimetallic clusters: repartition of the two metals

Bimetallic system

These relations are no longer valid when monometallic clusters coexist with bimetallic ones. N_{AB} decreases as N_{Mono} increases. The distribution of the two metals inside the cluster given by the different coordination is simply false.
These two figures show that Xas (Xanes) and (Exafs) are well adapted to metallic cluster containing a few atoms.

Xanes as well as Exafs is very sensitive to the size of the particle.
III.1 Anomalous Wide Angle X-ray Scattering

- **Complex atomic factor**
  \[ f(q,E) = f_0(q) + f'(E) + i f''(E) \]

- **Relation between** \( f_0(q) \) **& the density** \( \rho(r) \)
  \[ f_0(q)=4\pi\int_0^\infty \rho(r)\sin(qr)/qr \; r^2dr \]

- **Kramers-Kronig relation**
  \[ f'(E)=\frac{2}{\pi P}\int_0^\infty \frac{ef''(e)}{(e^2-E^2)} \; de \]

- **Optical theorem**
  \[ f''(q,E) = E \; \sigma(E)/2hc \]

- **Debye equation**
  \[ I(q)=\Sigma_i \Sigma_j f_i(q)f_j(q)\sin(qR_{ij})/qR_{ij} \]

---


III.1 Monometallic clusters.

![Graph showing intensity vs. 2π/d(Å⁻¹) for different Pt clusters with labels for N=2057, N=1415, N=923, N=561, N=309, N=147, N=55, and N=13.]

- N=2057
- N=1415
- N=923
- N=561
- N=309
- N=147
- N=55
- N=13

The graph on the right shows intensity vs. 2π/d(Å⁻¹) with intensity labeled in arbitrary units (a.u.).

- N=55 Pt
- N=13 Pt

The intensity peaks for N=55 Pt and N=13 Pt are indicated in the graph.
Nanotube (111) & Nanotube (001)

Nanotube (111) N=45
Nanotube (111) N=69
Nanotube (111) N=95
Nanotube (111) N=121
Nanotube (111) N=235
Nanotube (111) N=335

Nanotube (001) N=31
Nanotube (001) N=95
Nanotube (001) N=147
Nanotube (001) N=191
Nanotube (001) N=243
III.2 Comparison between Xas & Awaxs

- Awaxs is better than Xas for the determination of the local order after the first shell.
- The low k range of the absorption spectrum is dominated by multiple scattering which lead to a loss of information in the high R range.
- If X-ray scattering factors have similar k dependence whatever the atomic number Z and this is true for wide as well as for small angle scattering, it is not the case of the Xas. Amplitude as well as phase scattering change significantly with Z for the latter and thus the chemical sensitivity of Xas is much higher.
Figure 5. Comparison of the experimental diffraction curve of sample 1 (including angular-dependent corrections) and simulated diffraction curves in the WAXS range (room temperature) and the corresponding mass fractions of the clusters: (a) only icosahedra, $R = 0.067$, $B = 1.1 \times 10^{-2}$ nm$^2$; (b) only cuboctahedra, $R = 0.252$, $B = 2.4 \times 10^{-2}$ nm$^2$; (c) only decahedra, $R = 0.085$, $B = 1.2 \times 10^{-2}$ nm$^2$; (d) only hcp clusters, $R = 0.094$, $B = 1.5 \times 10^{-2}$ nm$^2$. 

III.4a Awaaxs-Bimetallic Modeling

**For cluster A** (Pt155-Mo154), we consider a statistical distribution of Pt and Mo.

Equation de Debye
\[ I(q) = \sum_i \sum_j f_i(q) f_j(q) \sin(qR_{ij})/qR_{ij} \]

Facteur de diff. atom. : \( f(q, E) = f_0(q) + f'(E) + i f''(E) \)

Relation entre \( f_0(q) \) & la densité électronique \( \rho(r) \)
\[ f_0(q) = 4\pi \int_0^\infty \rho(r) \sin(qr)/qr \ r^2 \ dr \]

Relation de Kramers-Kronig
\[ f'(E) = 2/\pi \int_0^\infty e f''(e)/(e^2-E^2) \ de \]
\[ f''(q,E) = E \sigma(E)/2hcre \]

**For cluster B** (Pt147-Mo162), Pt atoms are in the core and Mo atoms are at the surface.

III.4b Awaxs-Bimetallic Results

**For cluster A** (Pt155-Mo154), we consider a statistical distribution of Pt and Mo. The WPSFs at the Pt and Mo edges are basically the same. The only difference is in the amplitude due to the fact that the atomic scattering factor is larger for Mo than for Pt.

For cluster B (Pt147-Mo162), Pt atoms are in the core and Mo atoms are at the surface.

The splitting between the 111 and 200 peaks is less well defined for the WPSFs at the Pt edge than at the Mo edge.
III.5 The case of metal oxide

**AB\textsubscript{2}O\textsubscript{4} - CoFe\textsubscript{2}O\textsubscript{4} - decomposition of N\textsubscript{2}O**

**Zn/Al\textsubscript{2}O\textsubscript{3} -> ZnAl\textsubscript{2}O\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} : Atomic comp. Zn 2%**

![Graph and image with peaks and labels indicating structural characteristics for Zn]
III.5a AWAXS at the Zn K edge

- Complex atomic factor
  \[ f(q,E) = f_0(q) + f'(E) + i f''(E) \]
  \[ E = 9660.\text{eV} \]
  \[ E = 9200.\text{eV} \]

\[ I(9660.) = I(\text{ZnAlO}) + I(\text{Al}_2\text{O}_3) \]
\[ I(9200.) = I(\text{ZnAlO}) + I(\text{Al}_2\text{O}_3) \]
\[ \Delta I = \Delta I(\text{ZnAlO}) \]

- Debye equation
  \[ I(q) = \sum \sum f_i(q)f_j(q)\sin(qR_{ij})/qR_{ij} \]
III.5c Numerical simulation

Simulations basées sur une substitution sur les sites tétrahédriques : \((\text{Zn}_{1-x}\text{Al}_x)\text{T}_d (\text{Al}_2)\text{O}_h \text{O}_4\)
III.5d Xas at the Zn K edge

$\log (I/I_0)$ vs. E (eV)

$ZnAl_2O_4 :$
ZnO $N=4,$ $R=1.95\,\text{Å}$

$Zn^{2+}$
Structure spinelle

$ZnAl_2O_4$
III.5e Quantitative results

Données structurales extraites de l’affinément de Zn/Al$_2$O$_3$
comparées à celles du modèle ZnAl$_2$O$_4$

<table>
<thead>
<tr>
<th>Chemins</th>
<th>N</th>
<th>N</th>
<th>R(Å)</th>
<th>R(Å)</th>
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<td>4</td>
<td>4</td>
<td>1.95</td>
<td>1.95</td>
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<tr>
<td>Zn-Al</td>
<td>10.9</td>
<td>12</td>
<td>3.34</td>
<td>3.36</td>
</tr>
<tr>
<td>Zn-O</td>
<td>10.9</td>
<td>12</td>
<td>3.38</td>
<td>3.40</td>
</tr>
<tr>
<td><strong>Zn-Zn</strong></td>
<td><strong>0.9</strong></td>
<td><strong>4</strong></td>
<td><strong>3.49</strong></td>
<td><strong>3.50</strong></td>
</tr>
<tr>
<td>Zn-Al-O</td>
<td>23.9</td>
<td>24</td>
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<td>3.62</td>
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<tr>
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<td>6.6</td>
<td>12</td>
<td>4.27</td>
<td>4.27</td>
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<tr>
<td>Zn-Al-O</td>
<td>14.3</td>
<td>24</td>
<td>4.35</td>
<td>4.36</td>
</tr>
</tbody>
</table>

T.F. (u.a)  
R (Å)
III.5f Zn K and L edge

Zn, K edge

- ZnAl$_2$O$_4$
- Sample 1
- Sample 2

Absorption (a.u.)

E(eV)

9650 9660 9670 9680 9690 9700

Zn, L$_{\text{III}}$ edge

- ZnAl$_2$O$_4$
- Sample 1
- Sample 2

Absorption (a.u.)

E(eV)

1020 1025 1030 1035 1040 1045 1050
**III.5f Zn K and L edge**

**Different structural hypothesis**

1. Multiple scattering processes of the photoelectron
2. Dimension of the ZnAl$_2$O$_4$
3. Influence of Zn vacancies
4. Influence of oxygen vacancies
III.5f Structural proposition
For fcc clusters, we can observe different modulations after the (0,0,0) peak and thus information regarding the crystallographic network as well as on the size on the particles is available through *ab initio* calculations.

Nevertheless, we have to point out that physical parameters such the interatomic distance modify the position of these modulations.

Also if other kinds of morphology like hemicuboctahedron are considered, no modulations exist.

- **Complex atomic factor**

\[
    f_{site}(q,E) = f_0(q) + f'_\text{site}(E) + i f''\text{site}(E)
\]

- **Debye equation**

\[
    I(q) = \sum_\text{i} \sum_\text{j} f(q) f(q) \sin(qR_{ij}) / qR_{ij}
\]
V. Diffraction Anomalous Fine Structure (Dafs)

**Complex atomic factor**

\[
f_{\text{site}}(q,E) = f_0(q) + f'_{\text{site}}(E) + if''_{\text{site}}(E)
\]

The Debye equation is then used to get the diffraction diagram and finally by plotting the maximum of the intensity versus the photon energy it is easy to build the Dafs spectrum.

This approach has been extended to clusters of Pt containing 13 and 55 atoms. It is clear that the Exafs oscillations are bigger than the Dafs ones.
First DAFS experimental results @ ESRF on NSMC

### Monometallic cluster

<table>
<thead>
<tr>
<th></th>
<th>Xas</th>
<th>Awaxs</th>
<th>Asaxs</th>
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<tbody>
<tr>
<td>Network</td>
<td>-</td>
<td>+</td>
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<td>+</td>
<td>+</td>
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<tr>
<td>Size distribution</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Morphology</td>
<td>-</td>
<td>+</td>
<td>+</td>
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### Bimetallic cluster

<table>
<thead>
<tr>
<th>Distribution of the metals inside the cluster</th>
<th>Xas</th>
<th>Awaxs</th>
<th>Asaxs</th>
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<tr>
<td>Distribution of the metals inside the cluster</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
II.5 N.S.M.C. & R.S.


VII. Conclusion - Future Prospects

- Characterisation technics related to synchrotron radiation like Xas, Awaxs, Asaxs are in situ chemical tools.
- Follow the evolution of catalysts during the activation process.

Structural Characterization @ the atomic scale

Catalytic Activity

In-Situ Spectroscopy of CATALYSTS

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