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

Definition of a methodology

D. Bazin
I. Introduction
   I-1. Nanometer scale metallic clusters.
   I-2. Structural parameters : N & R.

II. X-ray Absorption Spectroscopy
   II-1. K edge of 3d transition metals.
   II-2. L edge of 5d transition metals.
   II-3a. Monometallic clusters & II-3b Bimetallic clusters.
   II-4 Comparison between Xanes and Exafs.

III. Anomalous Wide Angle X-ray Scattering
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   III-2. Monometallic clusters
   III-3. Comparison between Xas and Awaxs
   III-4. Size distribution & morphology
   III-5. Bimetallic clusters.

IV. Anomalous Small Angle X-ray Scattering
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V. Generalities on Diffraction Anomalous Fine Structure
   V-1. Generalities
   V-2. First DAFS experimental results at the ESRF on metallic particles.

VI. Summary

VII. Future prospects
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

New trends in heterogeneous catalysis processes on metallic clusters from synchrotron radiation and theoretical studies

D. Bazin a,*, C. Mottet b, G. Tréglaia b, J. Lynch c

a LURE, Université Paris XI, Bât 209D, 91405 Orsay, France
b CRMC, Campus de Luminy, Case 918, 13288 Marseille Cedex 9, France
c Institut Français du Pétrole, BP 311, 92506 Rueil-Malmaison, France
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

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X-Ray Absorption Spectroscopy and Anomalous Wide Angle X-Ray Scattering:
Two Basic Tools in the Analysis of Heterogeneous Catalysts

D. Bazin\(^1\), J. Lynch\(^2\) and M. Ramos-Fernandez\(^2\)

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X-ray absorption spectroscopy under reaction conditions: suitability of different reaction cells for combined catalyst characterization and time-resolved studies

J.-D. Gruwaldt, M. Caravati, S. Hannemann and A. Baiker

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*Oil & Gas Science and Technology – Rev. IFP*, Vol. 58 (2003), No. 6, pp. 667-683
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*Phys. Chem. Chem. Phys.*, 2004, 6, 3037-3047

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D. Bazin et al., "*In situ* Xafs measurement of catalyst"

II.1 X-ray Absorption Spectroscopy

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

II.2 The associated formula

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

Structural terms
\[ f_j(k), \phi_j(k), \lambda, N_j, R_j, \sigma_j. \]
II.3 Nanometer scale metallic cluster & Xas

II.4a Some examples

1%wt Pt/oxide

Impregnation

Calcination

Reduction

- Xas studies of bimetallic Pt-Re(Rh)/Al₂O₃ catalysts in the first stages of preparation.
  - Bazin et al., J. of Cat. 110, 209 (1988).
- 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.
- 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.
  - Bazin et al., J. de Physique IV, 12-6, 379, (2002).
- Structure & size of bimetallic PtPd clusters in an hydrotreatment catalyst.
  - Bazin et al., Accepted in Oil & Gas Science and Technology - Rev. IFP

Reforming ...Pt, PtPd, PtRh, PtMo,PtSn,PtRe, PtIr, Fischer–Tropsch, Co, CoPt, CoPd, CoRu,
II.4b Some examples

**H₂**

\(T = 450°C\)

- Etat initial
- \(N(\text{PtO}) = 6\)
- \(R(\text{PtO}) = 2.04\)

\(\text{Pt} \quad \text{Pt} \quad \text{Pt} \quad \text{Pt} \quad \text{Pt}\)

\(\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{Pt}\)

**H₂**

\(T = 450°C\)

- \(N(\text{PtO}) = 0.4\)
- \(R(\text{PtO}) = 2.01\)

\(\text{Pt} \quad \text{Pt} \quad \text{Pt} \quad \text{Pt} \quad \text{Pt}\)

\(\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{Pt}\)

**1%H₂S/H₂**

\(T = 450°C\)

- \(N(\text{PtS}) = 2.8\)
- \(R(\text{PtS}) = 2.32\)

\(\text{S} \quad \text{Pt} \quad \text{S} \quad \text{Pt} \quad \text{S}\)

**H₂**

\(T = 450°C\)

- \(N(\text{PtS}) = 2.8\)
- \(R(\text{PtS}) = 2.30\)

\(\text{S} \quad \text{Pt} \quad \text{S} \quad \text{Pt} \quad \text{S}\)

**N(\text{PtO}) = 6.**

\(R(\text{PtO}) = 2.04\)

**N (\text{ReO}) = 4.1**

\(R(\text{ReO}) = 1.76\)

**N(\text{PtS}) = 2.0**

\(N(\text{PtMet}) = 4.2\)

**N(\text{ReS}) = 2.4**

\(N(\text{ReMet}) = 4.5\)

**N(\text{PtS}) = 1.0**

\(N(\text{PtMet}) = 4.0\)

**N(\text{ReS}) = 2.0**

\(N(\text{ReMet}) = 4.7\)
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.

D. Bazin et al. J. de Physique C4-481, 6 (1996).
II.5a Xanes K edge of 3d transition metals: Morphology

Experimental data

2D-13Cu cluster ($R_{CuCu} = 2.55 \text{ Å}$)

3D-13Cu cluster ($R_{CuCu} = 2.55 \text{ Å}$)
II.5a Xanes K edge of 3d transition metals: Relaxation

Experimental data:

- 3D-13Cu RCuCu=2.60\(\text{Å}\)
- 3D-13Cu RCuCu=2.65\(\text{Å}\)
- 3D-13Cu RCuCu=2.70\(\text{Å}\)

Cu K edge absorption spectrum shown with energy (E) in eV.
II.5b Xanes L edge of 5d transition metals

- 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.

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. Gutar, T. Rosler, M. E. Jerri, and B. Bens

![Graph](image1.png)

**Figure 8.** Evolution of Cu K-edge XANES of CuO/ZnO at 320 K during oxygen addition to a methanol steam reforming feed (c(\(\text{H}_2\)) \~ 6 vol%, c(H\(_2\)O) \~ 15 vol%) in 25 ml/min He). Different Cu phases are indicated.

at the Cu K-edge was \~1.5. XANES spectra were measured in the Quick-EXAFS mode with a time resolution of 15 s/spectrum (8959–9100 eV).


In situ EXAFS study of Pd/Al\(_2\)O\(_3\) during aerobic oxidation of cinnamyl alcohol in an organic solvent

Jan-Dieter Grunwaldt, Csilla Kerestegi, Tamas Mallat, and Alfons Bailer

![Graph](image2.png)

**Figure 2.** In situ QEXAFS at Co K-edge of the sulfidation of a Co on alumina catalyst

In situ QEXAFS investigation at Co K-edge of the sulfidation of a CoMo/Al\(_2\)O\(_3\) hydrotreating catalyst

Christophe Geantet, Yvonne Sollos, Cécile Glosson, Nobuyuki Matsuyoshi, Michel Laerois, Olivier Proux, Olivier Ulrich, and Jean-Louis Lazard

**Catalysis Letters Vol. 73, No. 2-4, 2001**
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>
</tr>
</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.

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'.
II.5c Xanes L edge : Dynamical process

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

Sample B

\[
\begin{array}{ccc}
B & 0.97 & 1.0 & 1.2 \\
B' & 1.0 & 1.0 & 1.0 \\
B'' & 1.0 & 1.0 & 1.0 \\
\end{array}
\]

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'.

Sample B’

Sample B”
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.
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 \( \rho(r) \)
  \[ f_0(q) = 4\pi \int_0^{\infty} \rho(r)\sin(qr)/qr \, r^2 \, dr \]

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

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

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

D. Raoux in “Resonant anomalous X-ray scattering: Theory and applications”
III.1 Monometallic clusters.

![Graph showing intensity vs q(S⁻¹) for different Pt clusters, including peaks at 111, 200, 220, and 222.]

- N = 2869 Pt
- N = 3871 Pt
- N = 5083 Pt
- N = 6525 Pt
- N = 8217 Pt
- N = 10179 Pt

![Graph showing F.T. (a.u.) vs R(S) for different Pt clusters, including N = 55 Pt and N = 13 Pt.]

- N = 55 Pt
- N = 13 Pt

Intensity (a.u.)
Nanotube (111) & Nanotube (001)

Intensity vs. $2\pi/d$ for various nanotube configurations.
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.
III.3 Size distribution & Morphology

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, $R = 0.067, B = 1.1 (10^{-2} \text{ nm}^2)$; (b) only cuboctahedra, $R = 0.252, B = 2.4 (10^{-2} \text{ nm}^2)$; (c) only decahedra, $R = 0.085, B = 1.2 (10^{-2} \text{ nm}^2)$; (d) only hcp clusters, $R = 0.094, B = 1.5 (10^{-2} \text{ nm}^2)$. 
III.4a Awaxs-Bimetallic Modeling

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

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

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

\[ f'(E) = 2/\pi \int_0^\infty e^{f''(e)}/(e^2-E^2) \, de \]

Théorème optique

\[ f''(q,E) = E \sigma(E)/2hcre \]

---

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

$\text{AB}_2\text{O}_4$ - $\text{CoFe}_2\text{O}_4$ - decomposition of $\text{N}_2\text{O}$

$\text{Zn/Al}_2\text{O}_3 \rightarrow \text{ZnAl}_2\text{O}_4/\text{Al}_2\text{O}_3$ : Atomic comp. Zn 2%
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

\[ I(q) = \sum_{i} \sum_{j} f(q) f(q) \sin(qR_{ij}) / qR_{ij} \]
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

Zn$^{2+}$
Structure spinelle

ZnAl$_2$O$_4$ :
ZnO N=4. , R=1.95Å

Figure 2. Modulus of the FT of the experimental data of the ZnAl$_2$O$_4$
point (line) compared to the numerical simulation (dashed) including single (diamond) and multiple scattering contributions (circles).
Données structurales extraites de l’affinement 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>
</tr>
</thead>
<tbody>
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<td>Zn-O</td>
<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>
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<tr>
<td>Zn-O</td>
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<td>Zn-Al-O</td>
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<td>3.62</td>
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<td>12</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>
III.5f Zn K and L edge


Influence of cation vacancies on the K and L\textsubscript{III} Zn edges of spinel related compounds

D. BAZIN, R. REVEL, A. M. FLANK
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

Soft X-ray absorption spectroscopy at the cutting edge for nanomaterials used in heterogeneous catalysis: the state of the art

D. Bazin$^a$, and J. Rehr$^b$

$^a$ LURE, Université Paris XI, Bât 209D, 91405 Orsay, France
$^b$ Department of Physics, University of Washington, Seattle, WA 98195-1900, USA
An \textit{in situ} study using Anomalous Wide Angle X-ray Scattering and X-ray Absorption Spectroscopy of the binary metal oxide catalytic system \textit{SnO}_2-\textit{ZnAl}_2\textit{O}_4 supported on alumina.

R. Revel\textsuperscript{1}, D. Bazin\textsuperscript{1}, B. Bouchet-Fabre, A. Seigneurin\textsuperscript{2}, Y. Kihn\textsuperscript{3}

\textsuperscript{1}LURE, Université Paris XI, Bât 209D, Orsay, 91405, France.
\textsuperscript{2}Rhodia, Centre de Recherches d’Aubervilliers, 52 rue de la Haie Coq, 93308 Aubervilliers Cedex, France.
\textsuperscript{3}CEMES-CNRS, BP 4347, 31055 Toulouse Cedex 04, France
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 \textit{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.
V. Diffraction Anomalous Fine Structure (Dafs)

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

- Debye equation
  \[ I(q) = \Sigma \Sigma f(q)f(q)\sin(qR_{ij})/qR_{ij} \]
V. Diffraction Anomalous Fine Structure (Dafs)

Complex atomic factor

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

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>
</tr>
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<tr>
<td>Network</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Size</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Size distribution</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Morphology</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

### Bimetallic cluster

<table>
<thead>
<tr>
<th></th>
<th>Xas</th>
<th>Awaxs</th>
<th>Asaxs</th>
</tr>
</thead>
<tbody>
<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.

• Comparison between Xas & AwaXs applied to monometallic clusters. D. Bazin, D. Sayers, Jpn J. Appl. Phys. 32-2, 249, 1993.


• New opportunities to understand heterogeneous catalysis processes through S.R. studies and theoretical calculations of density of states: The case of nanometer scale bimetallic particles D. Bazin, C. Mottet, G. Treglia, Applied Catalysis A (1-2), 47-54, 2000.
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.

Solid State Physics and Synchrotron Radiation Techniques to Understand Heterogeneous Catalysis
D. C. Bazin*
Nanotechnology in Catalysis Volumes 1 and 2 Series: Nanostructure Science and Technology
Bing Zhou; Hermans, Sophie; Somorjai, Gabor A. (Eds.) 2004