Operando XAFS studies of homogeneous and heterogeneous catalysts in liquid-phase reactions

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Motivation

• Why operando?
  ✓ Capture catalyst structure during reaction
  ✓ Elucidate the active or resting state of the catalyst
  ✓ Evolve and test proposed reaction pathways
  ✓ Direct comparison to DFT and DFT-molecular dynamics methods.
  ✓ Potential for dramatic new insights

• Why XAFS?
  ✓ Oxidation state of catalyst
  ✓ Full coordination structure about the transition-metal
  ✓ Readily applied to broad range of catalyst systems
  ✓ Readily applied under *broad range* operando conditions.
  ✓ Measure kinetics/mechanism of catalyst formation

**Operando means:**
  ✓ At the reaction temperature (Up to 500 °C)
  ✓ At the reaction pressure (Up to 1 kbar)
  ✓ Using homogeneous or heterogeneous catalysts
  ✓ While collecting kinetic data
  ✓ *While converting the reactants to products*
XAFS of Catalysts

- Detailed local structure about catalyst
  - Distances to ±0.005 Å
  - Coordination numbers (±15%)
  - Disorder, Debye-Waller factor
  - Angular correlation of nearby atoms (multiple scattering)
  - Chemical identity of neighboring atoms
  - Good sensitivity (~ 1 mM)
  - Measure the cluster/nanoparticle size

- Ab initio scattering theory
  - FEFF9

The XAFS process

Interference of incoming and outgoing photoelectron wave in the vicinity of the central atom produces XAFS
## Operando XAFS of diverse chemical systems

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Characterization of homogeneous \( \text{Mn}^{2+}-\text{Br}^- \) Catalyst

Supercritical Water Process -- \( \text{MnBr}_2 \) ion-pairs are the catalyst.

- Yield appears to be nearly equal to the world’s most efficient oxidation
- Eliminates \( \sim30-40\% \) capital investment to remove / manage 4-carboxybenzaldehyde (side product)
- All state of the art catalysts use cobalt. This uses 10 X cheaper manganese
- What is the structure of the active catalyst species? What is the mechanism of this reaction?

Oxidation

\[
\begin{align*}
\text{CH}_3 &\rightarrow \text{O}_2 \\
\text{O} &\rightarrow \text{Mn}^{2+} \\
\text{CH}_3 &\rightarrow \text{OH} \\
\text{OH} &\rightarrow \text{H}_2\text{O}
\end{align*}
\]

400°C
300 bar
H₂O


Direct sample injection system

Pressure cell

Water @ 400°C
600 bar

“Inert” alloy, Pt:Ir, Ti, etc.

single crystal or polycrystalline diamond window

Pathlength spacer

solution in

X-ray Beam

solution out

High-pressure sample delivery
Diamond-window transmission XAFS cell for low-Z ions

Cell used to study low-Z ions: Cl\(^-\), K\(^+\), Ca\(^{2+}\)

Cell Design (supercritical water)

- **500°C, 600 bar**
- **Beam size: 50-100 microns diameter,** obtained using K-B mirrors
- **Incident flux: \( \sim 10^9 \) photons/sec**
- **Window: \([110]\) diamond**
  - 10 microns thick
- **Pathlength: 50-250 microns**
- **Lowest Energy: 2750 eV.**

• First XAFS studies of low-Z elements in supercritical conditions

• Dramatic changes in the first shell structure
  ✓ Loss of over half the waters of hydration
  ✓ Contact ion pairing with approximately 2 chloride counter ions.
  ✓ Direct measure of the Ca-Cl interaction with bond distances and disorder.

• Important for understanding geochemical and biochemical processes.
Mn$^{2+}$ and Br$^{-}$ Coordination Structure for a SCW Catalyst

**Summary**

- Complete structural characterization of first-shell "ligands" about Mn$^{2+}$ and Br$^{-}$
- Br• free radical process via charge transfer with Mn$^{2+}$/Mn$^{3+}$ in the contact ion pair

**Exciting new oxidation catalyst:**

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Importance:

- First-generation $\text{H}_2$ storage compound
- Amine-boranes are a class of compounds having high $\text{H}_2$-storage density
- Facile release of copious quantities $\text{H}_2$
- Need fundamental understanding of catalyst mechanism

Dehydrogenation

$$\text{Me}_2\text{NH} \quad -2 \text{H}_2 \quad \text{BH}_3 \quad \text{Rh} \quad N\text{Me}_2\text{BH}_2 \quad \text{BH}_2\text{NMe}_2$$

25°C
1 bar
toluene
Dehydrogenation

\[
\begin{align*}
2 \text{Me}_2\text{NH} \quad \text{BH}_3 & \quad \xrightarrow{\text{Rh}} \quad \text{NMe}_2 \quad \text{BH}_2 \\
& \quad \text{BH}_2 \quad \text{NMe}_2
\end{align*}
\]

25°C
1 bar
toluene

The Reaction

\[
\begin{align*}
2 \quad \text{Me}_2\text{NH} \quad \text{BH}_3 & \quad \xrightarrow{\text{Rh}} \quad 2 \quad \text{Me}_2\text{N} \quad \text{BH} \\
& \quad + \quad 2 \quad \text{H}_2 \quad \xrightarrow{\text{Toluene} \ 25 \text{ C}} \quad \text{NMe}_2 \quad \text{BH}_2 \\
& \quad \text{BH}_2 \quad \text{NMe}_2
\end{align*}
\]

The Catalyst

Precursor

[\text{Rh}(1,5\text{-cyclooctadiene})\text{Cl}]_2

✓ Reaction solution is black (common for nanoparticles)
✓ Forms black precipitate at completion
✓ Literature identifies 2 nm Rh(0) nanoparticles by \textit{ex-situ} TEM (Manners, et al, JACS, 2003, 125, 9424)
Dehydrogenation

$$2\text{Me}_2\text{NH} + \text{BH}_3 \rightarrow 2\text{NMe}_2 + \text{BH}_2 \text{Rh}$$

25°C
1 bar
toluene

In Situ Rh K-edge XAFS during catalysis

Energy (eV)

Dehydrogenation

\[ \text{Me}_2\text{NH} \xrightarrow{-2 \text{H}_2} \text{NMe}_2-\text{BH}_2 \]

\[ \text{BH}_2-\text{NMe}_2 \]

25°C
1 bar
toluene

Refined structure from operando XAFS

Aerobic reaction conditions

- In presence of O$_2$, Rh(0) metal is formed
- The BN ligand is oxidized and it no longer stabilizes the Rh cluster
- Sampling of the anaerobic catalyst for *ex situ* analysis would be difficult or impossible

---


4 other precursors shown to transform to Rh$_4$ clusters decorated with ligands in O$_2$ free reaction cells.
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Benzene Hydrogenation

The Reaction

\[
\text{C}_6\text{H}_6 + \text{H}_2 \xrightarrow{\text{Rh}} \text{C}_6\text{H}_{12} + \text{H}_2\text{O}
\]

100°C
50 bar \(\text{H}_2\)
2-propanol triethylamine

The Catalyst

Precursor

- Reaction solution is black (common for nanoparticles)
- Literature identifies Rh(0) nanoparticles
- Textbook model for hydrogenation
History of this reaction

- 1975 Maitlis proposes that $[\text{Cp}^*\text{RhCl}_2]^2_2$ hydrogenates benzene "homogeneously" i.e. no metallic particles.
- Controversy for next 30 years
  - Recent volumes state many "homogeneous" catalyzed reactions are actually catalyzed by small amounts of metallic nanoparticles
  - "Benzene hydrogenation is a telltale sign of heterogeneous catalysis"
- 2005 Finke shows benzene is hydrogenated by rhodium metal nanoparticles formed from $[\text{Cp}^*\text{RhCl}_2]^2_2$
  - Kinetics studies
  - *Ex situ TEM and Ex situ XPS*
  - Hg poisoning test
- In collaboration with Finke took another look using *operando* XAFS

Hydrogenation

100°C
50 bar H₂
IPA, Et₃N

Operando XAFS cell

H₂ delivery system

2-phase reaction
The precatalyst \([\text{RhCp}^*\text{Cl}_2]_2\) evolves primarily to a single new form of rhodium during the catalysis.

XAFS shows the formation of ligated \(\text{Rh}_4\) cluster
Hydrogenation

\[ \text{Hydrogenation} \quad \begin{array}{c}
\text{Benzene} \\
\rightarrow \\
\text{PPH}_3
\end{array} \]

100°C
50 bar H\(_2\)
IPA, Et\(_3\)N

Refined structure from operando XAFS

**Active Rh\(_4\) Complex**

**FEFF8 model fit**

**Rh precursor**

**Rh metal/foil**

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<tr>
<th>bond</th>
<th>N</th>
<th>r/Å</th>
<th>(\sigma^2/\text{Å}^2)</th>
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<tr>
<td>Rh-Rh</td>
<td>3.0±0.1</td>
<td>2.71±0.004</td>
<td>0.007±0.001</td>
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<tr>
<td>Rh-Cp*</td>
<td>0.6±0.1</td>
<td>2.22±0.012</td>
<td>0.005±0.002</td>
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<tr>
<td>Rh-Cl</td>
<td>1.3±0.5</td>
<td>2.32±0.031</td>
<td>0.013±0.009</td>
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<tr>
<td>Rh-Rh in metal</td>
<td>12</td>
<td>2.68±0.002</td>
<td>0.004±0.0005</td>
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Rh metal higher shells

FEFF8 : Fit Results

R, Å
Summary

• This reaction has never been studied by XAFS because of difficulty of working with H₂ pressurized systems
• A Rh₄ cluster is the catalytic species
  ✓ Rh-Rh bond lengths (2.71Å) and coordination numbers (3) consistent with Rh₄ cluster.
  ✓ No higher shell Rh-Rh atoms are present as would be necessary for nanoparticles.
  ✓ Rh₄ cluster with Cp*, benzene, IPA or chloride ligands
• Just as with the ammonia borane systems under aerobic conditions, O₂ oxidizes the ligands leading to metallic Rh (nanoparticles).
  ✓ Sampling of the anaerobic catalyst for ex situ analysis would be difficult or impossible
• Are there a series of Rh₄-6 clusters that are the active catalysts for both hydrogenation and dehydrogenation reactions?
• The true catalyst structure is only apparent under operando conditions

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Reaction pathway for phenol hydrodeoxygenation

\[
\text{OH} \xrightarrow{\text{Pd/C, H}_2} \text{O} \xrightarrow{\text{Pd/C, H}_2} \text{OH} \xrightarrow{\text{H}_3\text{PO}_4} \xrightarrow{\text{Pd/C, H}_2} \]

Step 1: Hydrogenation
(TOF): $6.2 \times 10^3$ h$^{-1}$

Step 2: Hydrogenation
Rate: $1.2 \times 10^4$ h$^{-1}$

Step 3: Dehydration
Rate: 15 h$^{-1}$

Step 4: Hydrogenation
Rate: $9 \times 10^6$ h$^{-1}$

- Importance:
  - Key step in a new lignocellulose conversion by Lercher et al. to diesel/jet fuels
  - Water is the inherent, “green” reaction solvent
  - In water, the pathways, rates and selectivities are dramatically different
  - Large literature base on Pd nanoparticle catalysis
    - Little is known about the effect of water
  - What is the role of water for Pd nanoparticle catalysis?
    - State of the Pd metal?
    - Surface species?
    - Does water mediate reactant and product binding?

Hydrodeoxygenation

200°C
50 bar H₂
H₂O

**XAFS Challenges:**
- High temperature, high pressure
- Liquid and gas (H₂) phase equilibrium
- Heterogeneous (Pd/C) catalyst

Operando XAFS cell

- Glassy-carbon window
- X-ray beam
- Porous cylinder to center catalyst in beam
- Stir bar

2-phase reaction
H₂

Heterogeneous

Pd nanoparticles on carbon

IV

HO

H₂

Pd/C

→

Glassy-
carbon

window

X-ray beam

Porous cylinder to center catalyst in beam

Stir bar

Hydrodeoxygenation (IV)

H₂

OH

26
**IV Hydrodeoxygenation**

200°C

50 bar H₂

H₂O

Reaction platform installed at the beamline

XAFS cell

XAFS spectrum @ 200°C

- Pd “metal” nanoparticle
- Pd hydride nanoparticle

High S/N with two 10 min scans

H₂ lecture bottle

H₂ reaction reservoir

High-temperature enclosure

X-ray beam

Stirrer
Hydrodeoxygenation

\[
\text{HO} \quad \overset{\text{H}_2}{\underset{\text{Pd/C}}{\longrightarrow}} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]

200°C
50 bar H\(_2\)
H\(_2\)O

Addition of phenol regenerates the “metal” from the hydride.

**Catalyst state during the reaction sequence**

- **As-received Pd/C nanoparticles**
  
  \(T = 25^\circ\text{C}\)
  \(t = 0\) min

- **Pd “metal” nanoparticles**
  
  \(T = 200^\circ\text{C}\)
  \(t = 3\) min

- **Pd hydride nanoparticles**
  
  \(T = 200^\circ\text{C}\)
  \(t = 200\) min

- **Add reactants**

- **End of reaction**

- **Add phenol**

- **Pd hydride nanoparticles**
  
  \(T = 200^\circ\text{C}\)
  \(t = 210\) min

- 2.7 nm

- ✓ Addition of phenol regenerates the “metal” from the hydride.
Metal hydride nanoparticle structure is virtually identical between pure H₂ and H₂O solvation environments (~50% surface/50% core Pd sites).

No evidence of a specific water interaction with hydrided metal surface.

Interactions are diffuse. Suggest that the hydride surface is mostly hydrophobic.

The role of water

- Hydrodeoxygenation

IV

200°C
50 bar H₂

Pd/H₂O region

2.7 nm Pd nanoparticles in pure H₂

2.7 nm Pd nanoparticles in H₂O

0.5
1

R (Å)

Pd-Pd

Pd-H₂O region

Pd-Pd 2nd

Pd-Pd 3rd

Pd-Pd 4th

200°C
50 bar H₂

DFT-MD water on Pd(111)

Phenol binds to surface

Water diffusely interacts

Surface hydride may further weaken interaction

Courtesy Donghai Mei/ PNNL
2.7 nm Pd
5% Pd/C
5 wt% Phenol/H₂O
0.5 wt% H₃PO₄/H₂O
50 bar @ 200 °C

Near the end of the reaction there is a rapid phase transition to Pd-hydride nanoparticles.
The process is reversible with addition of more phenol.
Important insights to the mechanism of the hydrogenation step.

Spectra recorded at 2 m intervals.
We establish the chemical state of Pd nanoparticles in water and follow evolution of the Pd hydride formation.

Pd hydride nanoparticle structure is virtually identical in pure H$_2$ and liquid H$_2$O environments.

No evidence for the particles interacting with water, with phenol, cyclohexanone, or cyclohexanol at 200 °C.

Equilibrium between Pd metallic and Pd hydride forms provides key insights into the reaction mechanism.

The true catalyst structure is only apparent under operando conditions.

Guidelines for *operando* XAFS

- Design XAFS cell specifically for the chemistry
  - ✓ Use the beamtime most efficiently
- Do your homework beforehand
  - ✓ Optimize for transmission (if possible),
  - ✓ Optimize edge heights/pathlengths
  - ✓ Test chemistry in cell before arriving
- Review plan with beamline scientist
- Bring all (!) the chemistry to the beamline
  - ✓ Utilize the beamline labs
- Preplan detailed experiment list
  - ✓ Evaluate results “real time”
  - ✓ Amend as necessary during run
- Bring enough manpower.

vitreous carbon window for operation at 200 °C, 50 bar
Overall Summary

• The XAFS method can be applied to almost any reacting chemical system
  ✓ Extremes of temperature and pressure
  ✓ Multi-phase systems
  ✓ Homogeneous and heterogeneous systems

• Operando XAFS is required to help establish the active state of the catalytic species
  ✓ Combination of XAFS and DFT-MD provides powerful method to establish details of the reaction mechanism
  ✓ XAFS combined with other methods such as analysis of reaction kinetics, NMR, or mass spectrometry can shed valuable light on catalytic mechanisms.

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