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Chemical Sciences and Engineering

Establishing the relationship between structure and function at different length and time scales under reaction conditions

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Office of Science
U.S. DEPARTMENT OF ENERGY

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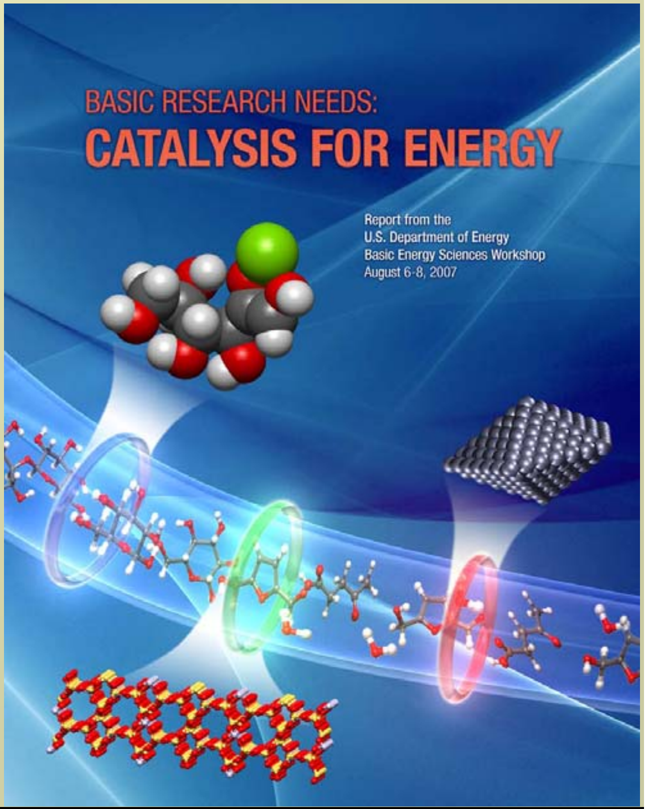
Impact of Field

- Heterogeneous Catalysis
  - Production of fuels and chemicals
  - Critical to future, secure energy solutions
  - Essential for environmental protection
- Fuel Cells
  - Efficient electro-chemical power
- Solution Chemistry
  - Solubility/transport of heavy metals
  - Solid-liquid interfacial partitioning

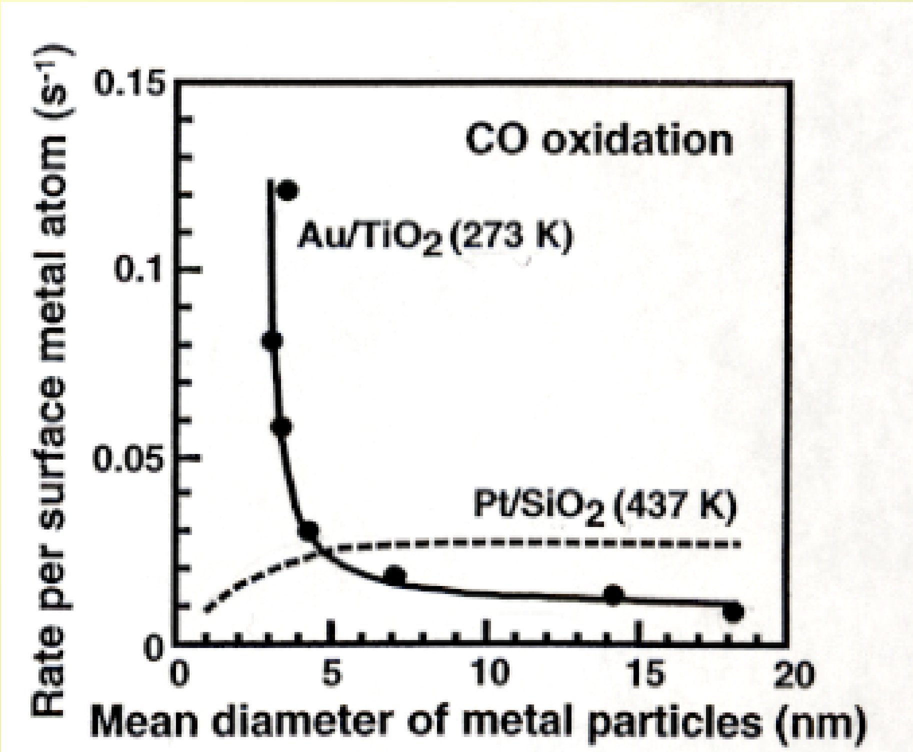


Today's Key Techniques

- **Essential to characterize materials under realistic reaction conditions**
  - **Reactive gases (Hydrocarbons, H_2, CO, O_2, NO_x, H_2S, etc.)**
  - **High Temperature (>800°C)**
  - **High pressure (1-100 bar)**
  - **Gas and liquid phase**
  - **Corrosive environments**
- **Spectroscopy (EXAFS, XANES)**
- **Diffraction (XRD/PDF)**
- **Scattering (SAXS)**

Catalysis of Au Nanoparticles

- **Historically, these are very low activity catalysts**
- **Au foil does not chemisorb H_2, CO or O_2**
- **Highly active for low temperature CO oxidation**

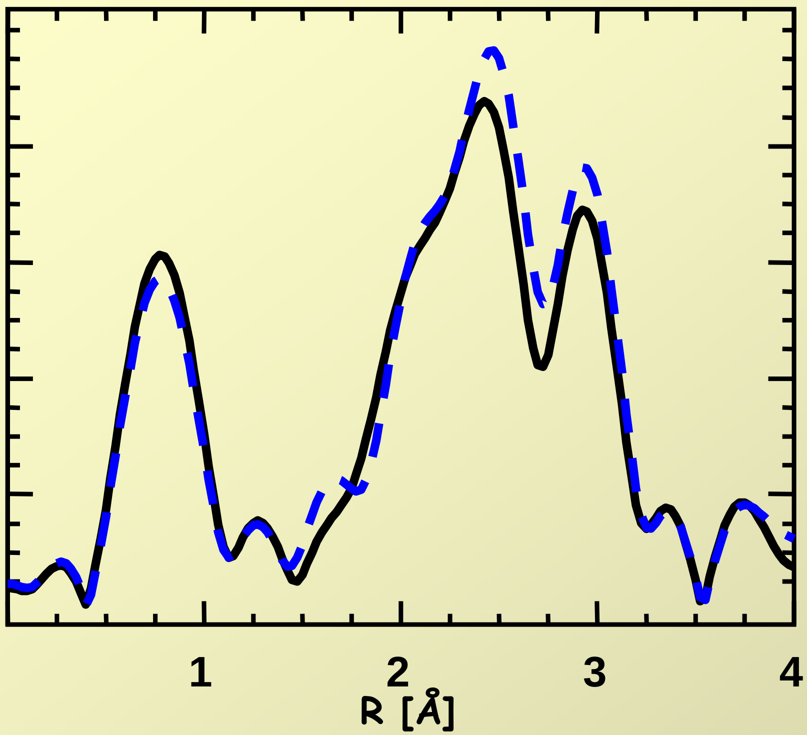


Additional reactions

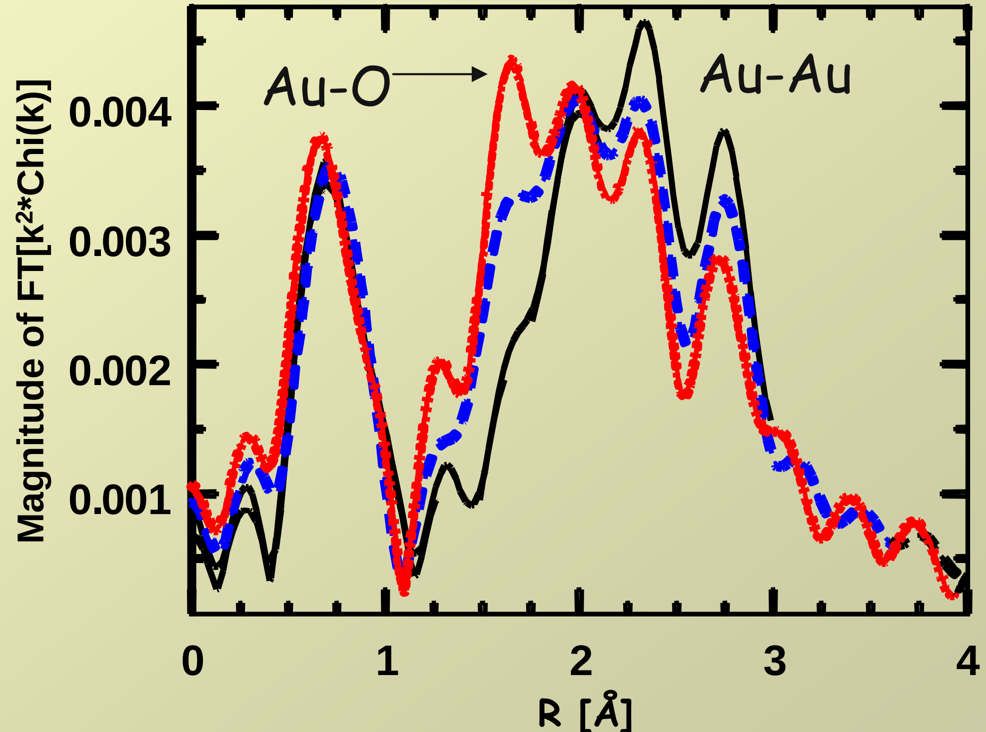
Selective CO(H2) oxidation
LT Water gas shift
DeNOx
Decomposition of halogen compounds
Selective hydrogenation
H_2O_2 synthesis from H_2 and O_2

EXAFS of Oxidized Au

3.2 wt % Au/SiO_2
CN =8.7, R =2.85 Å

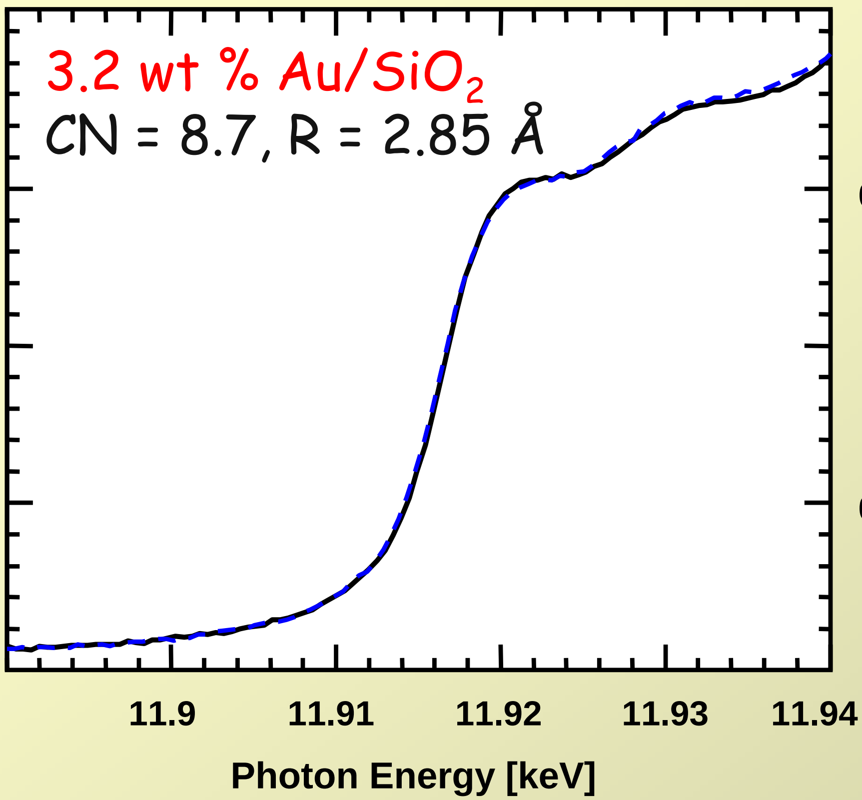


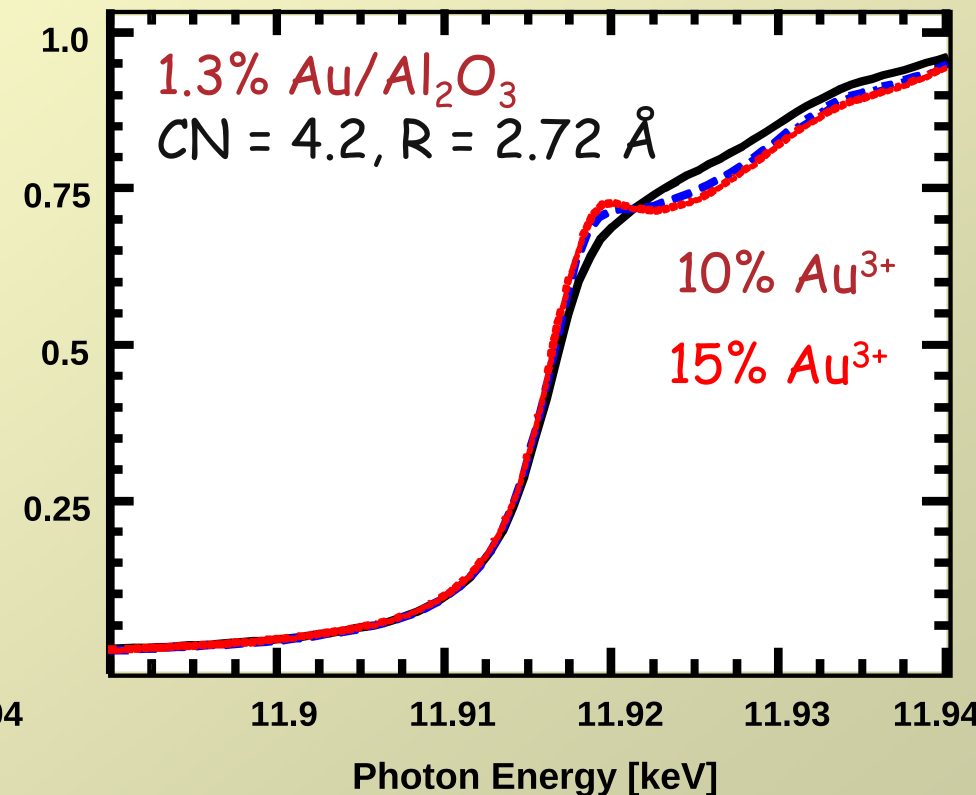
1.3% Au/Al_2O_3
CN = 4.2, R = 2.72 Å



Black: Reduced in H_2 at 250°C
Blue: Followed by air at RT
Red: Followed by air at 225°C

Reactivity of Au Particles to O_2





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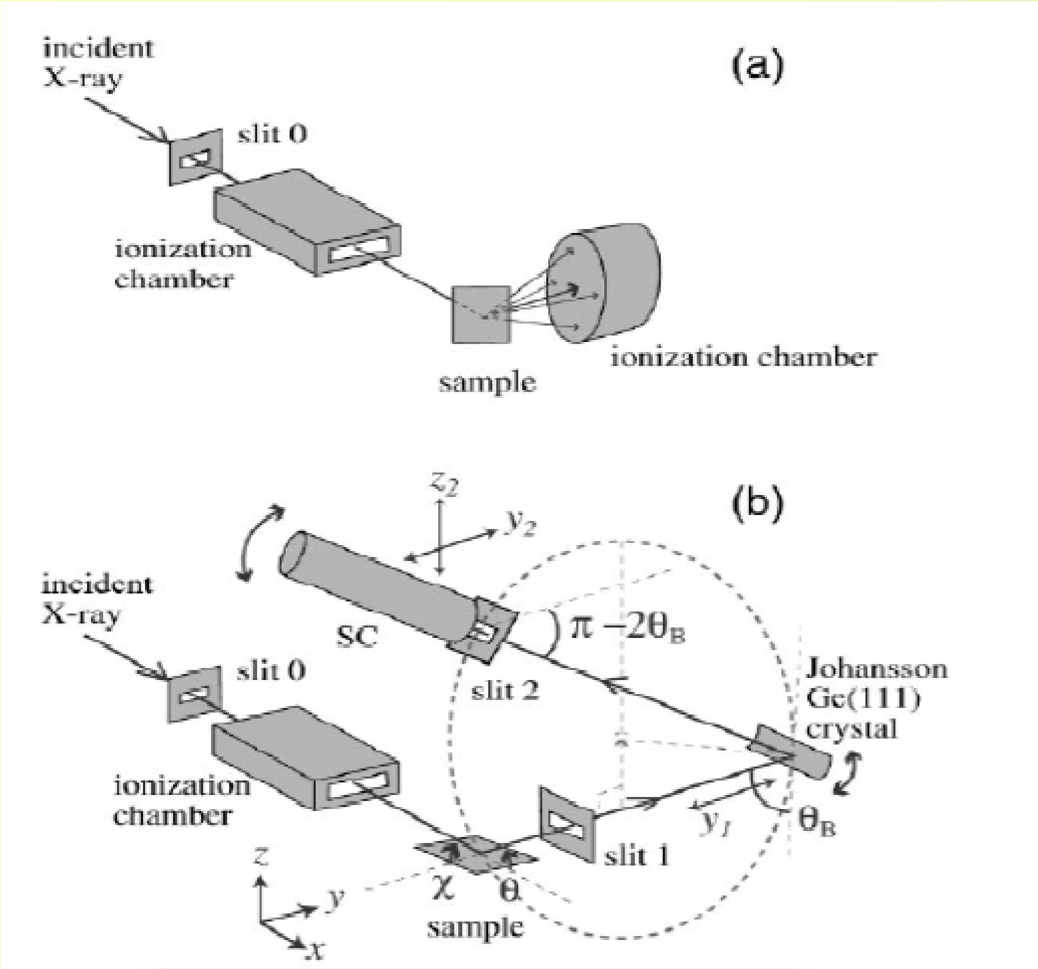
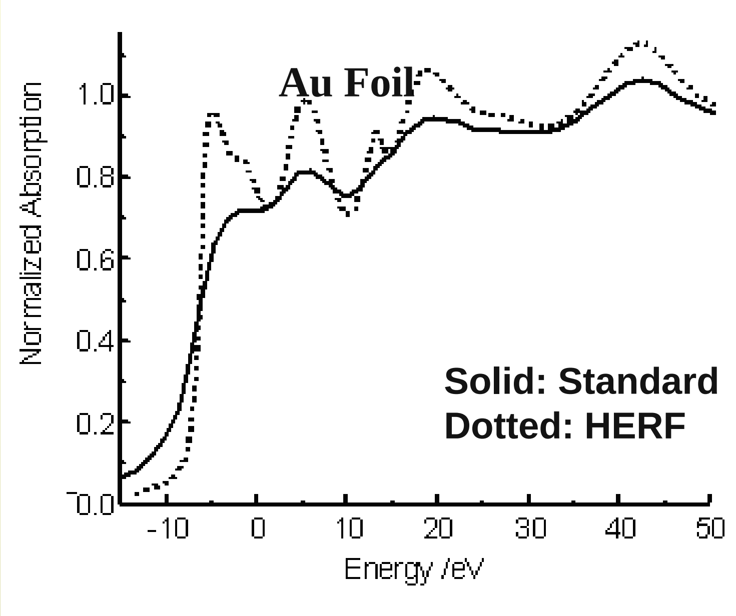
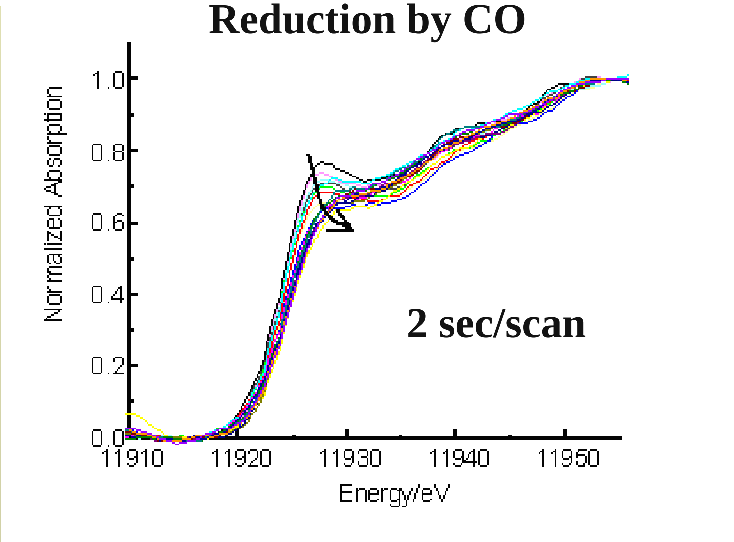
Miller, et al.

J. Catal., 240, 222-234 (2006)

High Energy Resolution Fluorescence (HERF) XANES (ESRF)





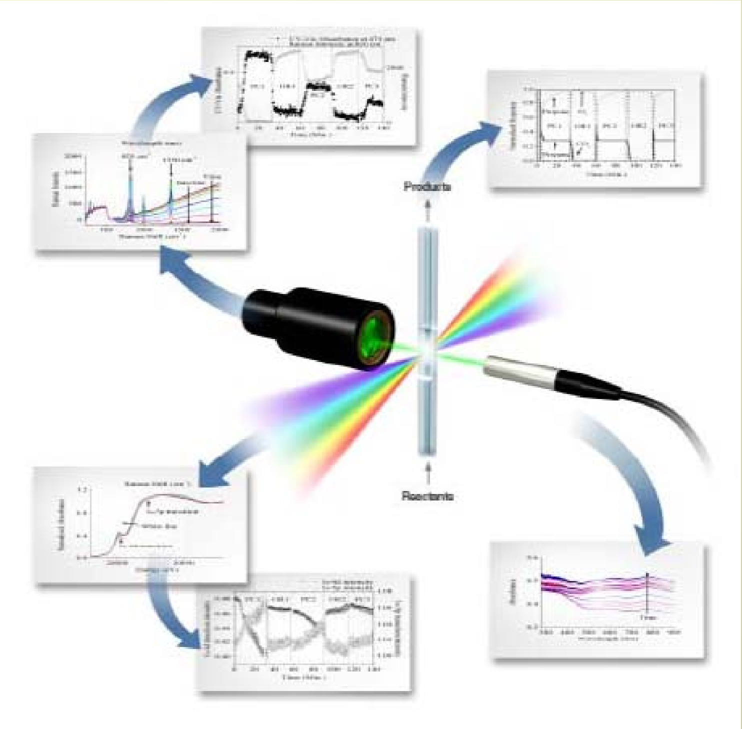


van Bokhoven (ETH), et al.

Angw. Chem. Int. Ed., 45, 4651 (2006)

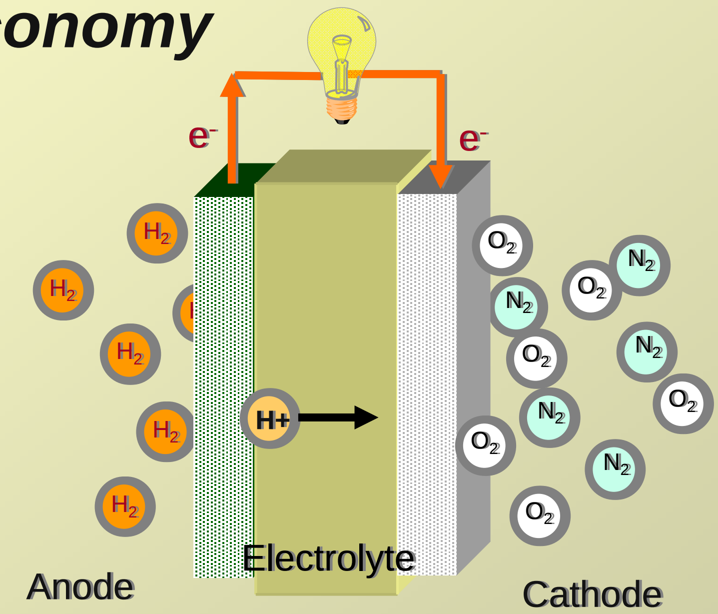
Desirable New in situ *Capabilities*

- Combined techniques: metals and adsorbates
  - Synchrotron (EXAFS, XRD, PDF, SAXS)
  - Non-synchrotron (kinetics, IR, Raman, UV-Vis, etc.)
- Higher signal to noise
  - Fast acquisition (1 μsec) XAFS
  - Fast kinetics
  - Lower concentrations
  - Unprecedented structural detail
- High-energy-resolution fluorescence XANES
- Surface selective structural methods
- More detailed electronic information, e.g., energy and occupancy of d-orbitals

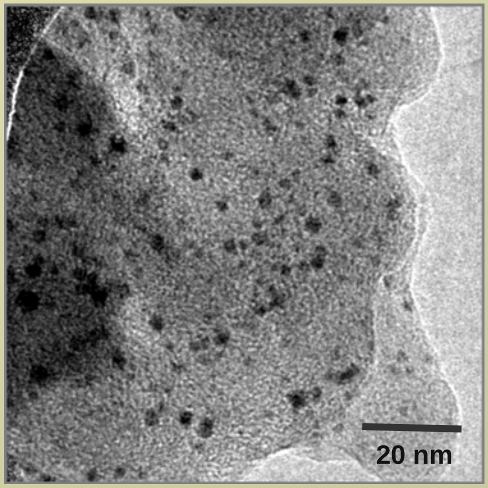


Combined Laser Raman, UV-Vis, EXAFS and Kinetics (B. Weckhuysen, Utrecht)

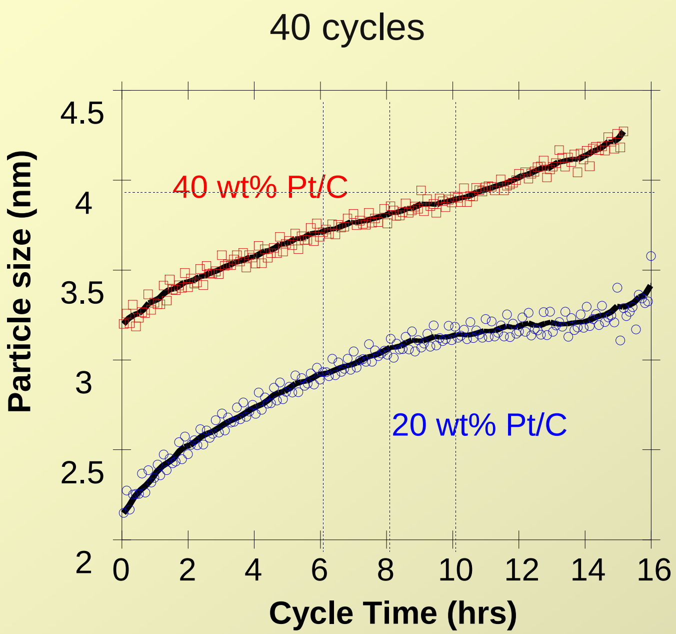
Electro-catalysts for the Hydrogen Economy

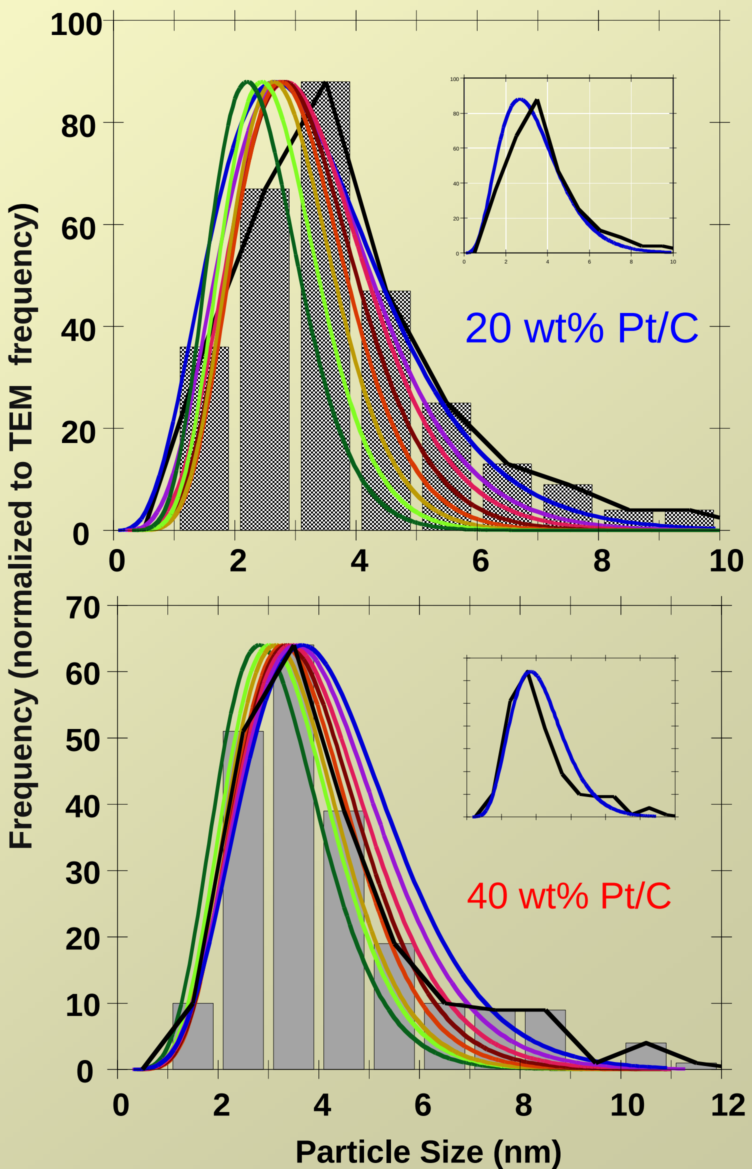


- **Hydrogen Fuel Cells are an efficient, new energy source for automotive power**
- **Current state-of-the-art fuel cell electrocatalysts are nanoparticles of Pt or Pt alloys but have:**
  - **Have insufficient catalytic activity**
  - **Composed of expensive metals**
  - **Lose of performance with time**
- **Significant improvements can only be made through a fundamental understanding of:**
  - **Identification of the active site and reaction intermediates**
  - **Understanding the structural changes that occur during degradation**



SAXS studies shows Pt particle growth with cycling

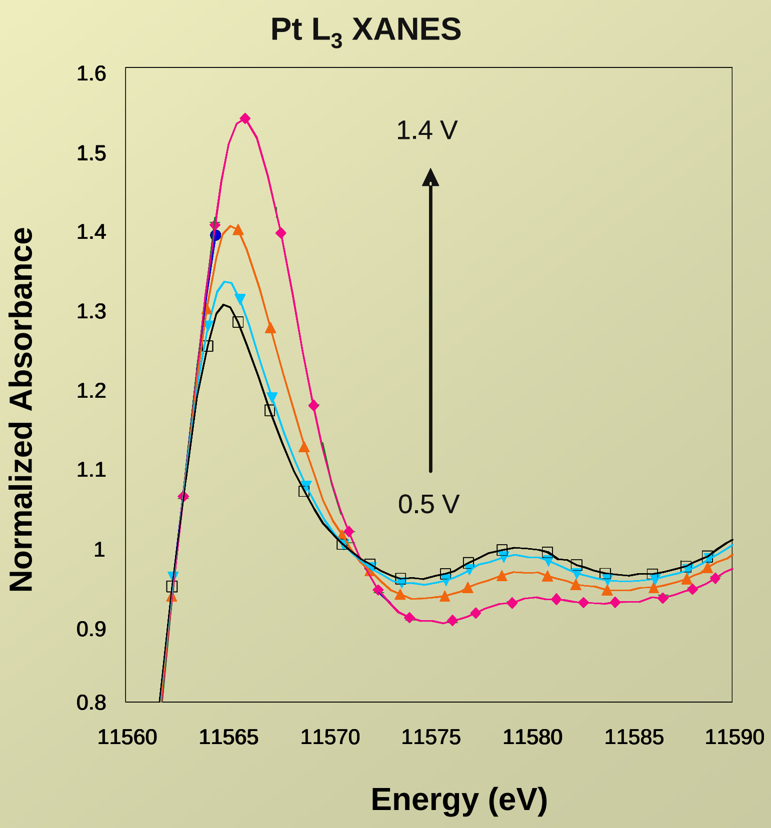




M.C. Smith et al., *J. Am. Chem. Soc.*, 2008

Needs for understanding Pt catalyst degradation

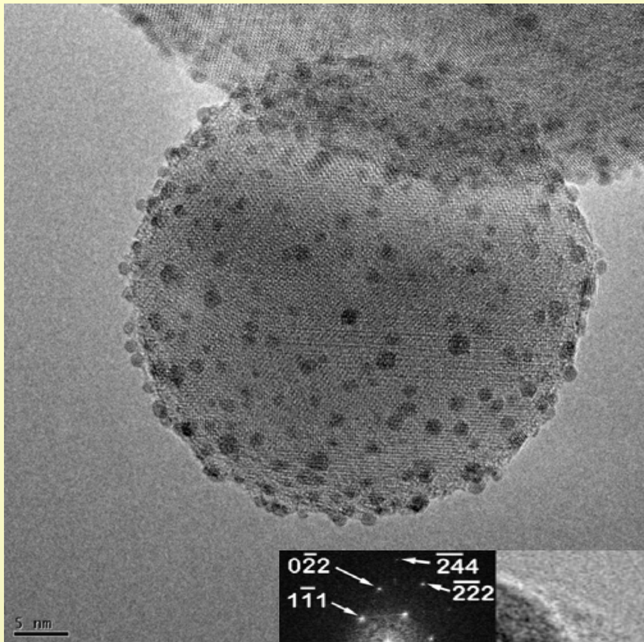
- Determine the structure of the **surface and sub-surface atomic** layers as a function of potential and relationship to dissolution
- Structural determination at **microsecond time-resolution** during operation
- Determine the structure of the soluble Pt species at **ppb** levels

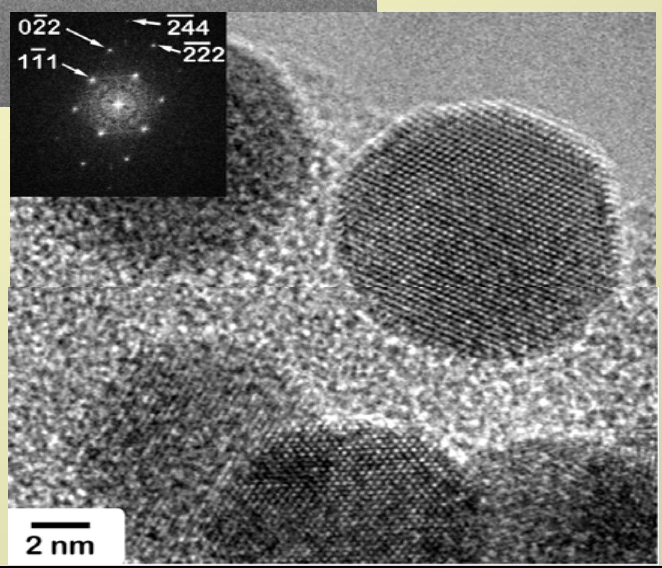


Advanced characterization of Fuel Cells

- Simultaneous **spatio-temporal resolved** (μm and μ-sec) structural, electronic, and particle size characterization for a wide range of metals (Cr-Cu, 6-9 keV, to Pd, 24 keV)
- Resolution of binding of oxygen and oxygenated intermediates on surface sites of 2-6 nm bimetallic nanoparticles
- EXAFS on high-Z element K-edges (e.g., Pt at 78.4 KeV)
  - Deeper penetration through thick layers of low-Z materials
  - Longer exposure times due to **less damage**
  - More accurate determination of metal **oxidation state**
- Oxidation state and structure of the metal species in aqueous electrolyte at **<10 ppb**

Imaging and Diffraction of Pt Nano-particles In Situ, Atomic Resolution TEM (Purdue)

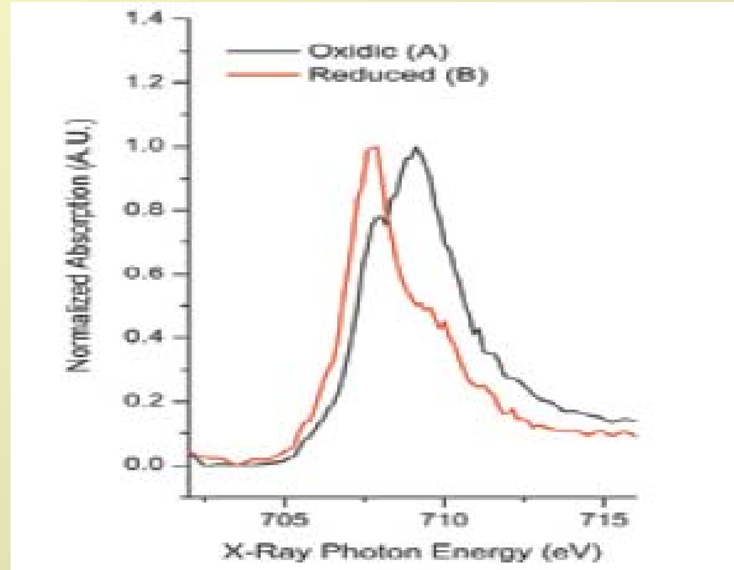




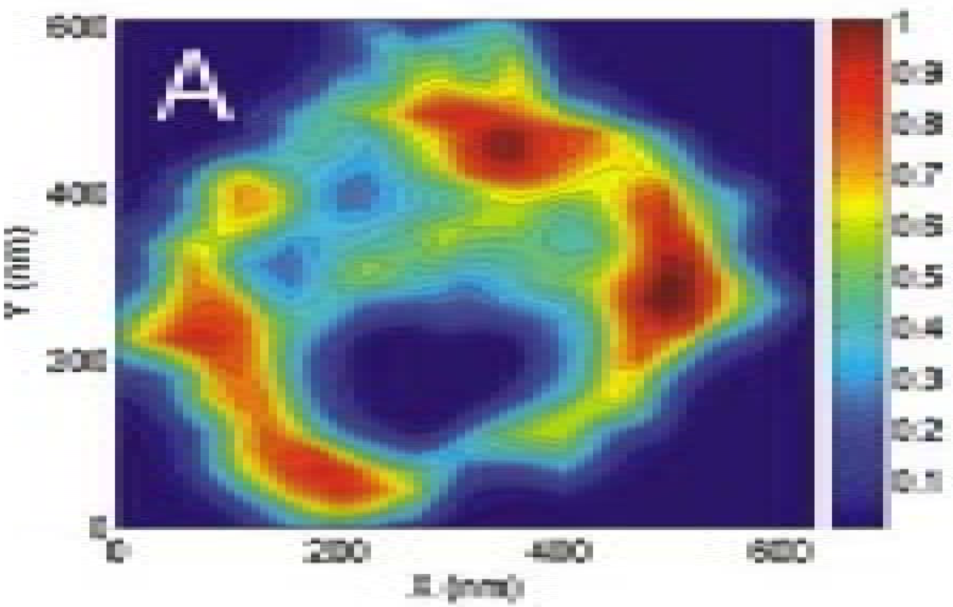
- X-ray imaging on Pt Nano-particles
  - Morphology and changes with reaction conditions
  - Inter-atomic distances
  - Novel bimetallic structures
  - Surface structures
  - Oxidation states
- Diffraction of Nano-particles?
  - Mixed phases
  - Alloy structure
  - Novel bimetallic structures
  - Structural changes under reaction conditions

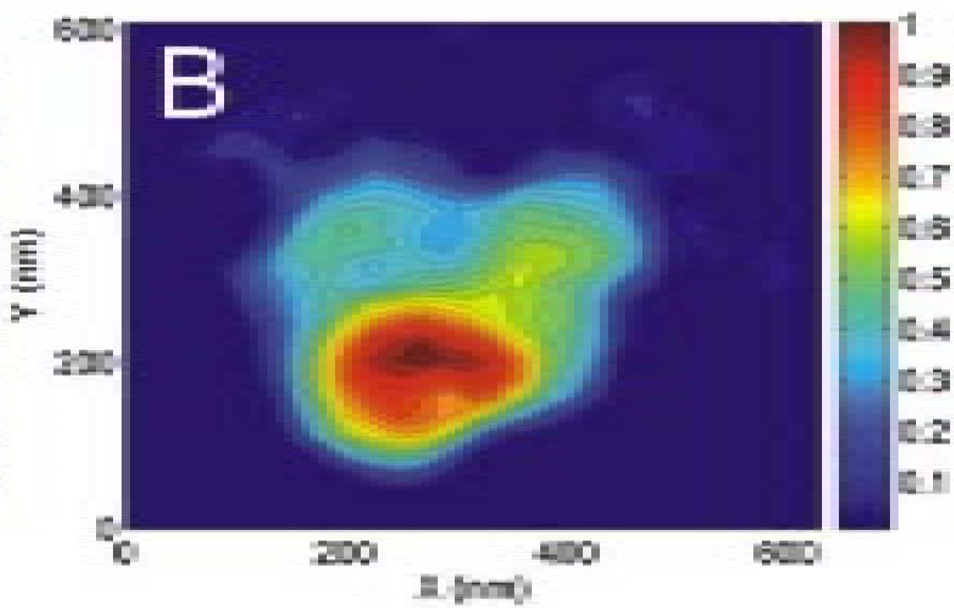
In-situ reduction of Fe_2O_3 Single Particle (BESSY)

In-Situ Micro-reactor:
1 bar, **750K**
Reduction +
Fischer-Tropsch
(CO+H2)



Frank de Groot
Utrecht U, Netherlands





Imaging Needs for Catalysis

- **Analysis under reaction conditions**
- **Atomic resolution**
- **Elemental composition**
- **Chemical information (oxidation states, DOS)**
- **Structural identification and quantification of multiple phases and complex (novel) structures**
- **Time resolved analysis, i.e., dynamic imaging**

Closing Thoughts: Chemical Sciences and Engineering

- **Energy demands are expected to double in the next 25 years**
- **New energy solutions are driven by new materials with novel properties**
- **Future materials will need to have rates several orders of magnitude higher than existing materials**
- **Future chemical reactions will need significantly higher selectivity**
  - **Higher yields**
  - **Fewer, less costly separations**
- **These advances will result from deeper understanding of the structural and electronic properties of the active site and how these interact with the reactants**
- **Synchrotron methods will be critical to the success of this future**