
Implementation of a beamline for fast XAFS/XRD experiments

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Outline

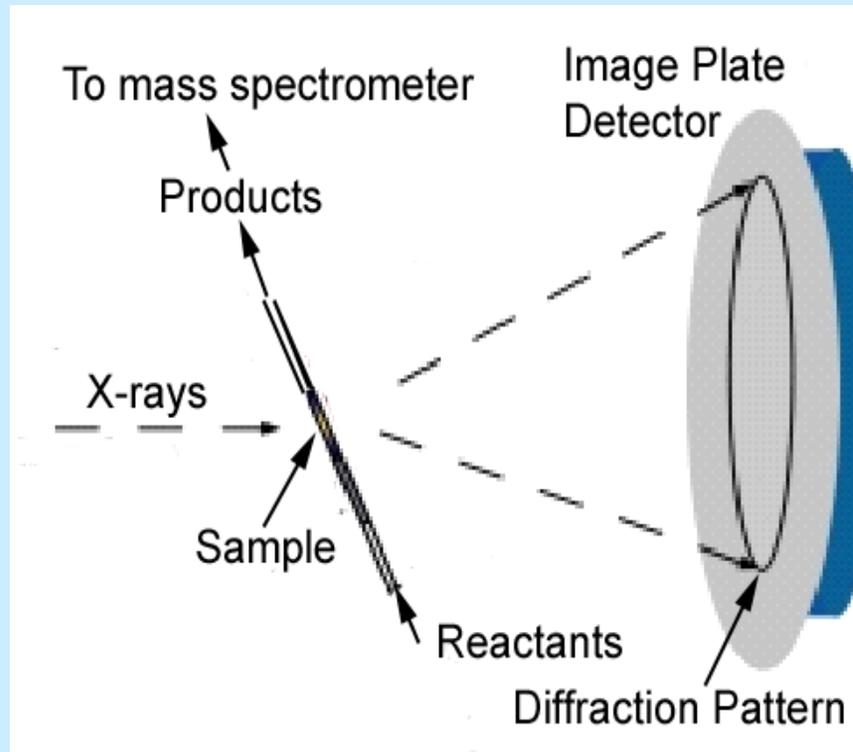
- ***In-situ* time-resolved X-ray diffraction at NSLS**
- **Quick XAFS at NSLS**
- **Need for simultaneous XRD and XAFS**
- **Projected XRD/XAFS beamline at NSLS-II**

2002 BESAC workshop *Opportunities in Catalysis in the 21st Century*: “**The Grand Challenge for catalysis science In the 21st century is to understand how to design catalyst structures to control catalytic activity and selectivity.**”

To meet this challenge, techniques for the characterization of catalysts *in-situ*, as they evolve in time, are necessary.

In situ Time-resolved X-ray Diffraction:

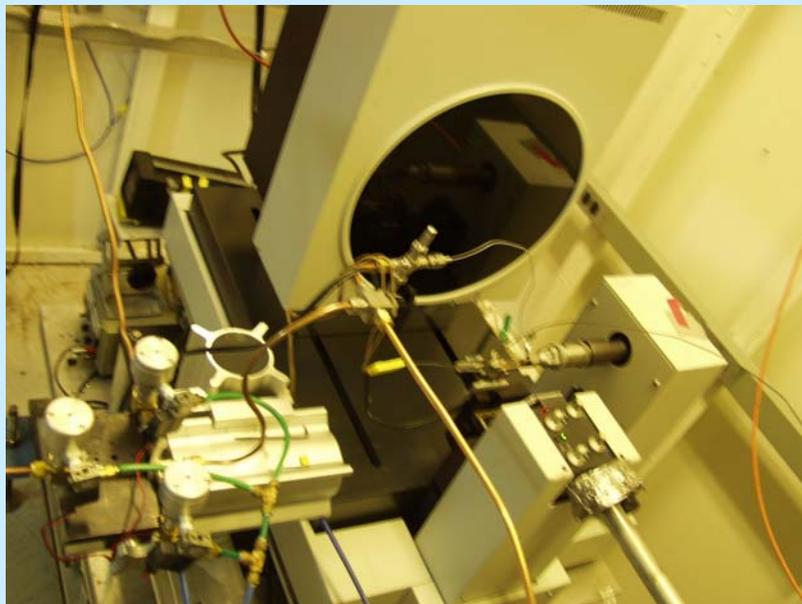
Experiments at BNL have shown that it is feasible to conduct subminute, time-resolved XRD experiments ($-190\text{ C} < T < 900\text{ C}$; $P < 45\text{ atm}$)



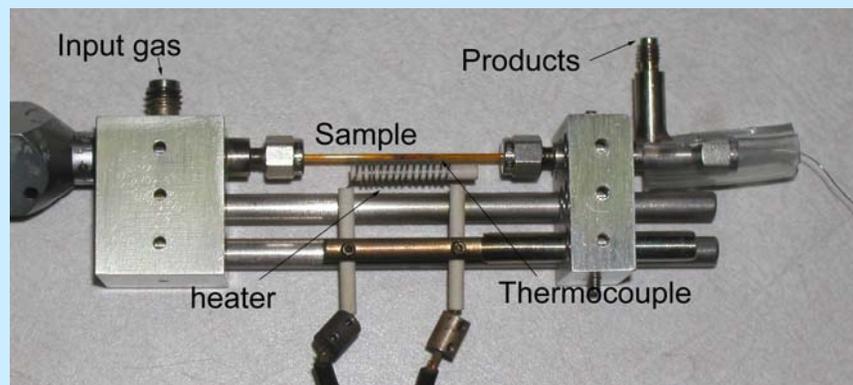
Norby and Hanson, Catal. Today 39 (1998) 301

Rodriguez and Hanson, Ciencia, 14 (2006) 177

Tools for *In situ* Time-resolved XRD:



Set up, image plate detector

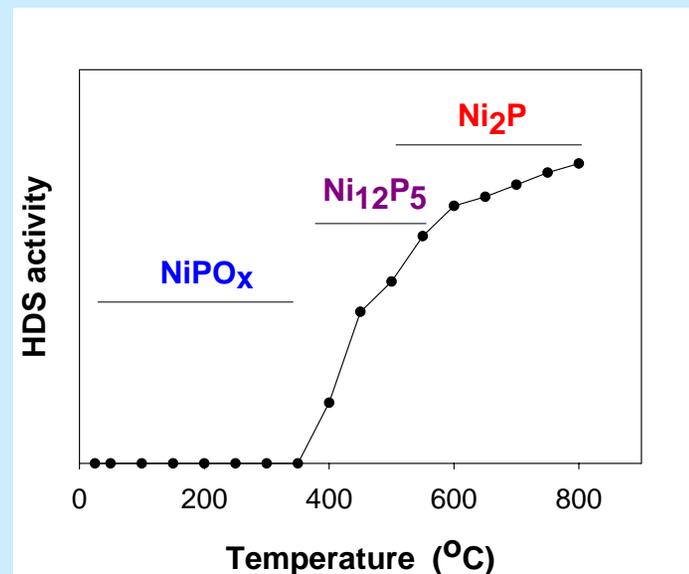
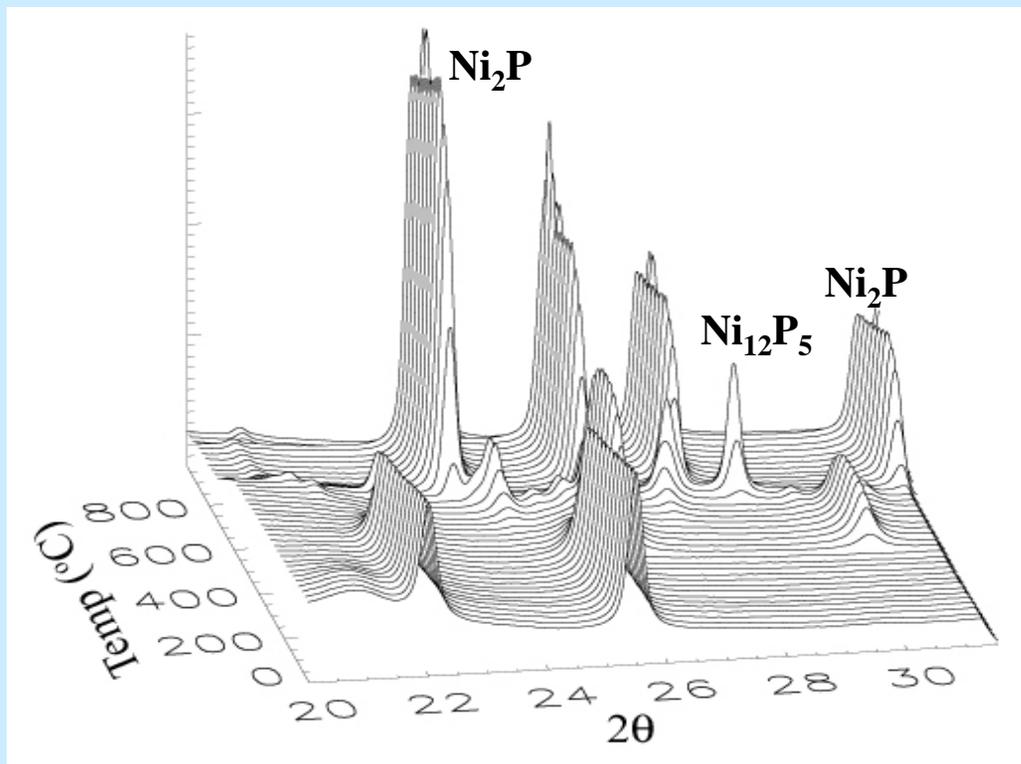


flow micro-reactor

This important advance results from combining the high intensity of synchrotron radiation with new parallel data-collection devices. Using time-resolved XRD, one can get information about:

- **Kinetics of crystallization of nanoparticles and bulk solids**
- **Crystallite size as a function of time/temperature**
- **Real-time crystal structure refinement**
- **Identify crystalline or amorphous intermediates during phase transitions occurring in nanoparticles or bulk solids**
- **Phase identification and composition of catalysts under reaction conditions**

Synthesis of a $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst: Time-resolved XRD studies



A nickel phosphate precursor is reduced in a flow of hydrogen/thiophene

Water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) on CuO/CeO_2

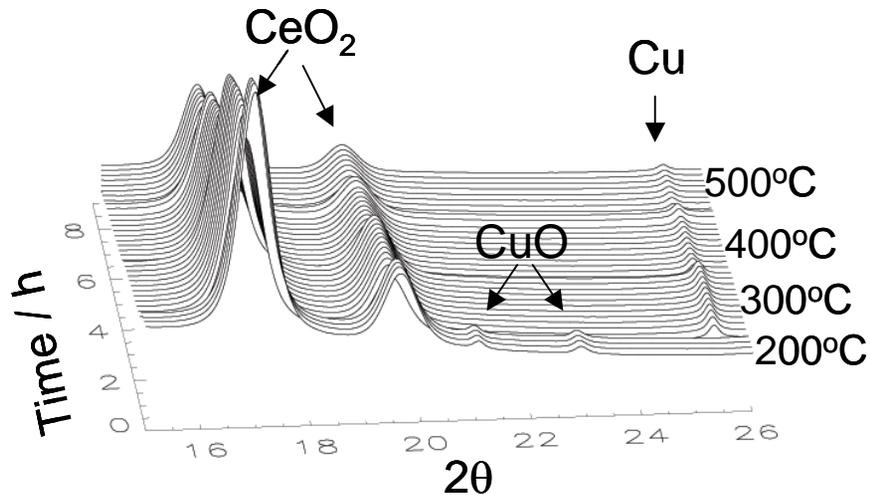


Figure 1. TR-XRD patterns for 5%CuO/CeO₂ during the WGS reaction. ($\lambda=0.921\text{\AA}$)

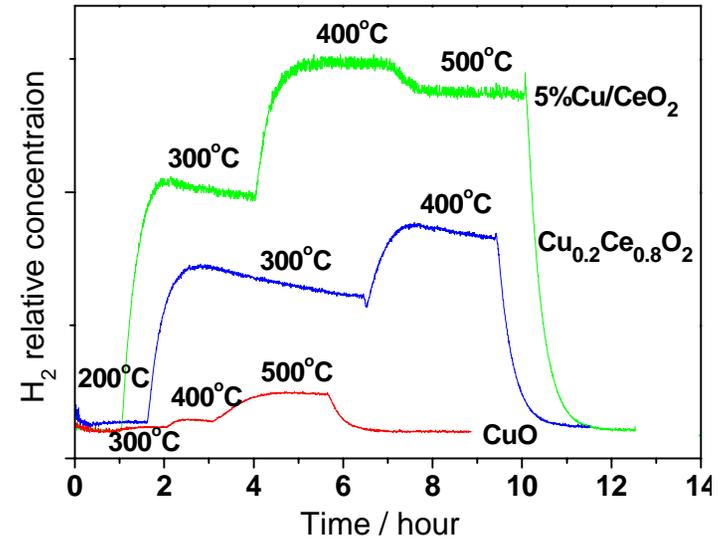


Figure 2. Relative H₂ concentrations in the products.

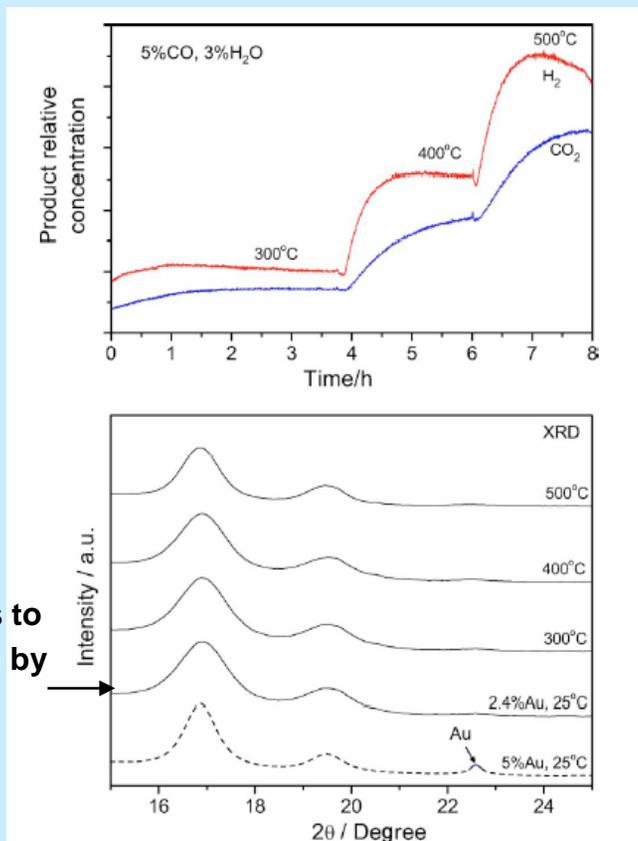
metallic Cu is the active phase

Many materials constructed at the nanoscale lack the translational symmetry and long-range order of perfect crystals. This poses a real challenge to the usual techniques for structure characterization. A combination of techniques may be necessary to establish the structure and morphology of nano materials:

- X-ray diffraction**
- X-ray absorption fine structure**
- Electron microscopy, scanning tunneling microscopy**
- Raman and infrared spectroscopy**
- Pair distribution function measurements**
- etc**

The diffraction patterns of nano materials may show only a few Bragg peaks, if any, and a pronounced diffuse component.

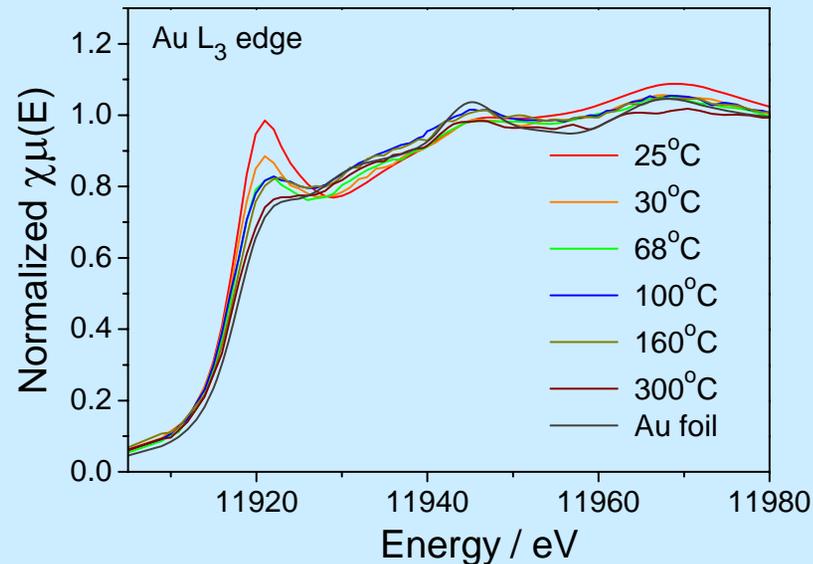
AuO_x-CeO₂ under WGS conditions



Au nanoparticles to small to be seen by XRD !!
Size < 2 nm

FIG. 1. Top panel: Relative amounts of H₂ and CO₂ formed during the WGS reaction on a 2.4 wt % Au–Ce(10 at. % Gd)O_x catalyst. A mixture of 5% CO and 3% H₂O in He (total flow ~10 ml/min) was passed over the catalyst at 300, 400, or 500 °C. Bottom panel: x-ray diffraction patterns collected *in situ* during the WGS on the 2.4 wt % Au–Ce(10 at. % Gd)O_x catalyst. For comparison, we are also including the XRD pattern for a fresh catalyst with 5 wt % Au, dashed trace.

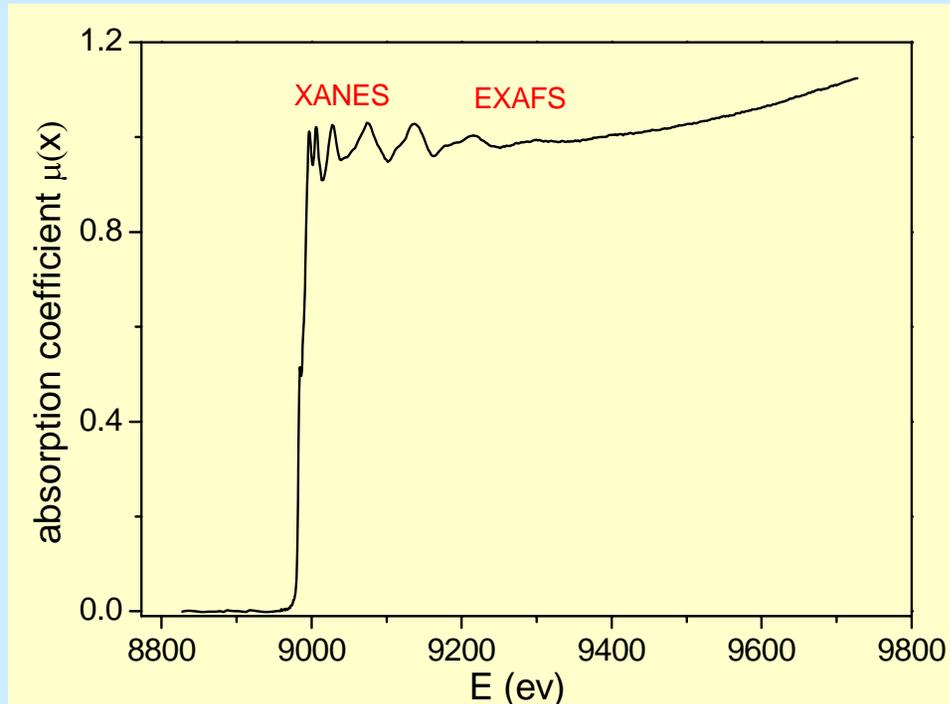
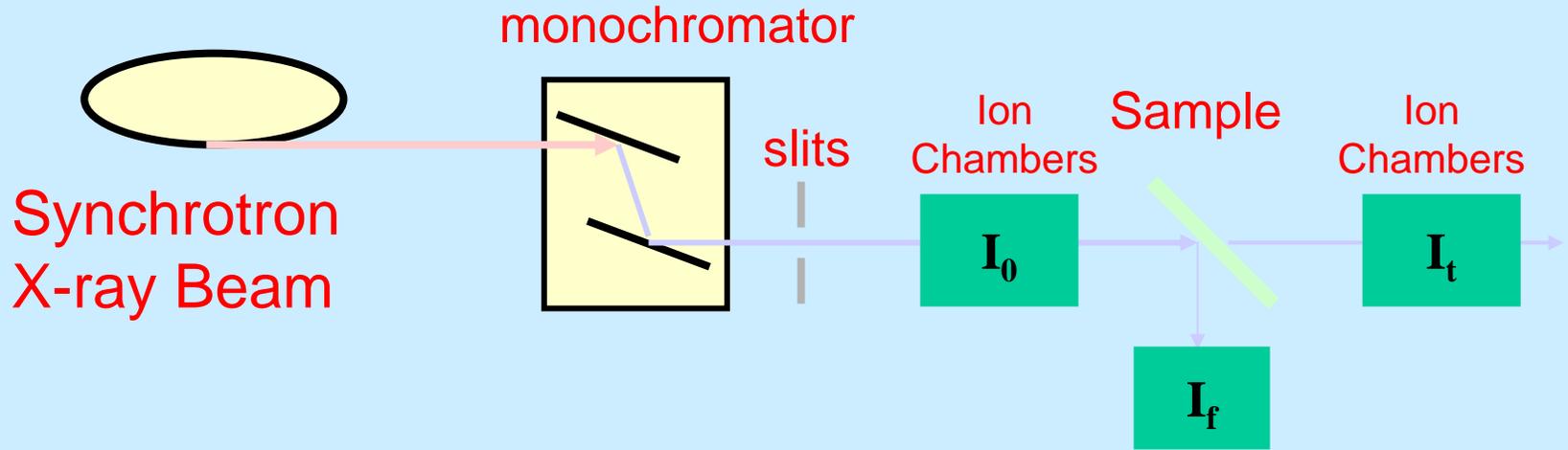
XRD useful only to study the ceria lattice in the catalyst



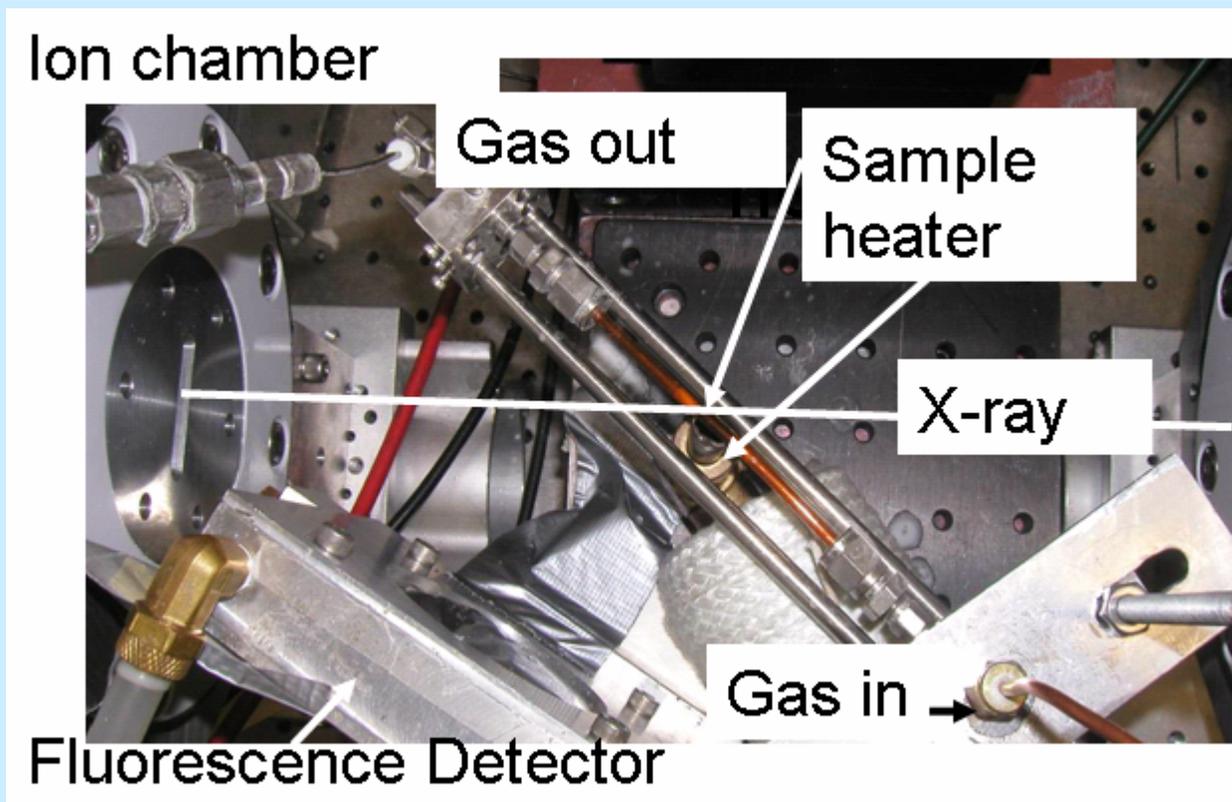
XAFS: Au can be detected

You need a combination of XRD and XAFS to study structure and electronic properties.

X-ray Absorption Fine Structure

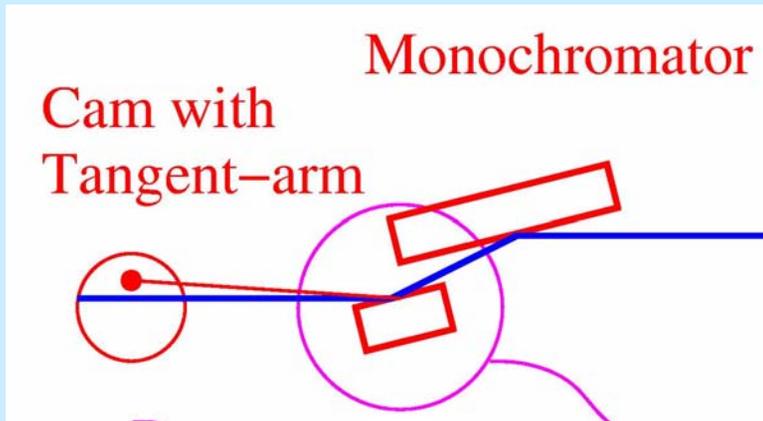


***In-situ* plug flow cell at NSLS X18: Top view**



Synchrotron Catalysis Consortium:

Quick EXAFS at NSLS X18B



- Adjustable Cam drives oscillation of monochromator
- Rapid readout of motor encoder and detectors (2000pts/sec)

•Typical times for

•Foils

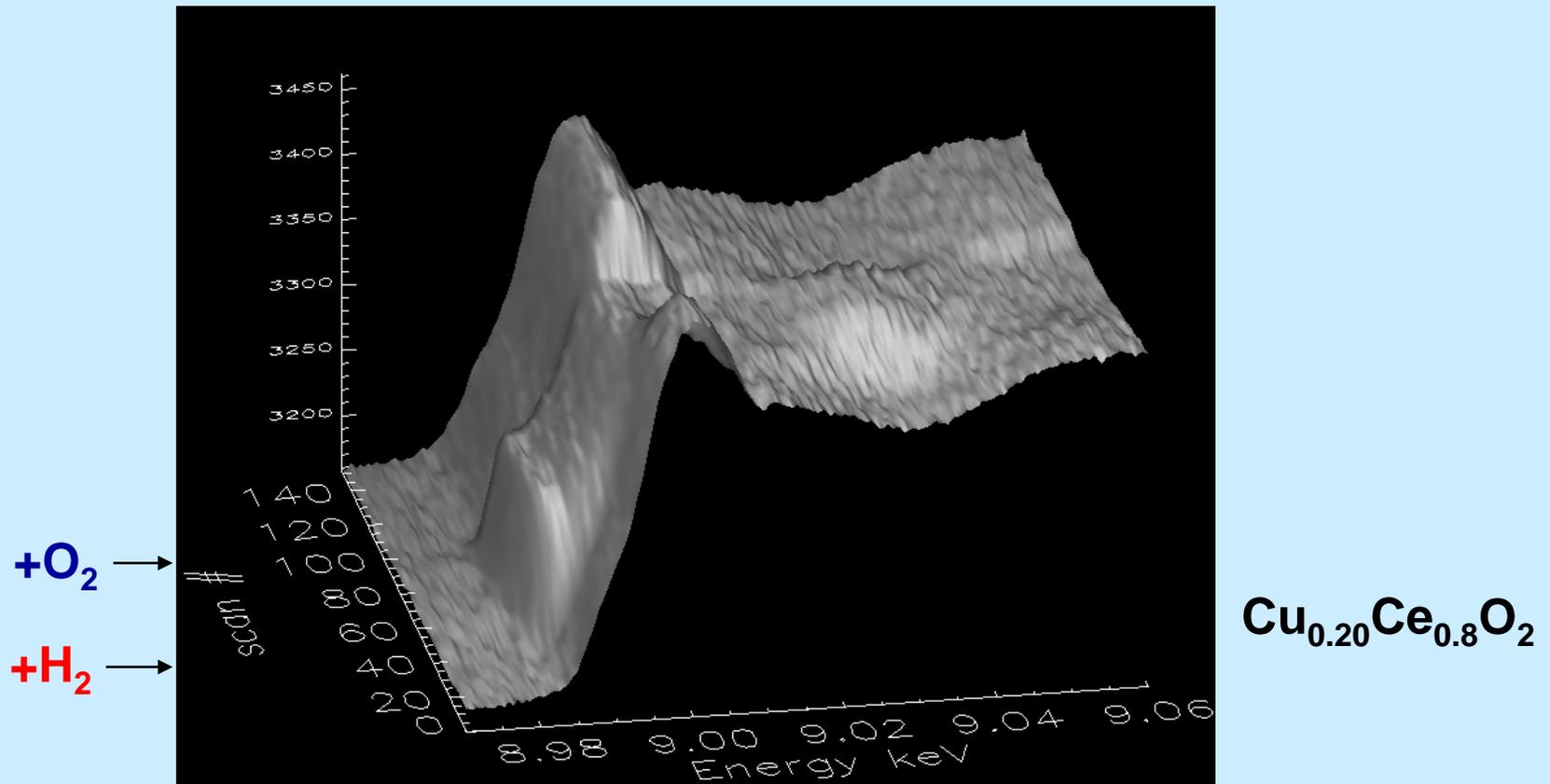
- XANES 1 sec
- EXAFS 3 sec

•Dilute samples

- XANES 5 sec
- EXAFS 15 sec

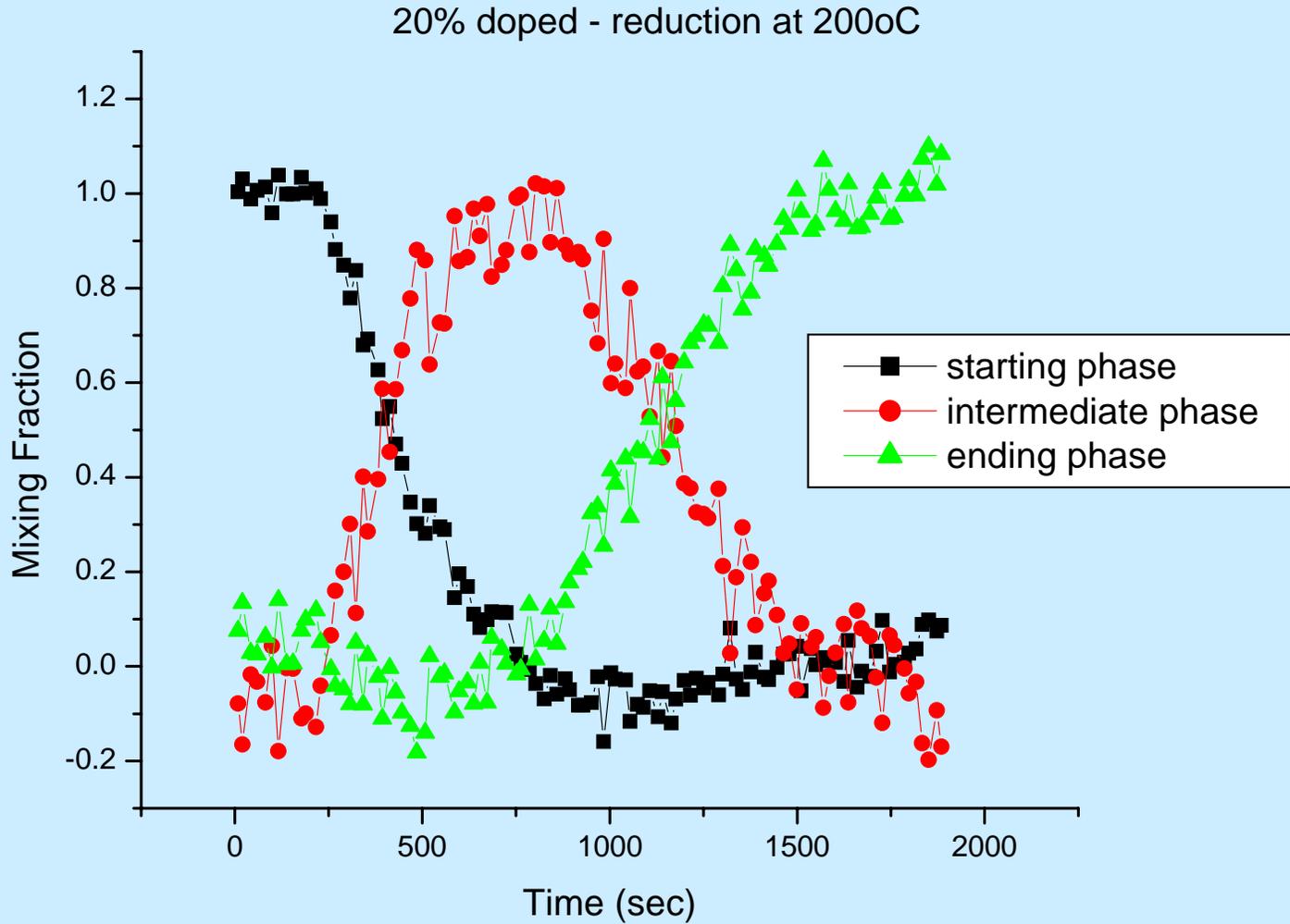
Limitation beam intensity and sample concentration

Reduction/re-oxidation of Cu doped ceria at 200°C

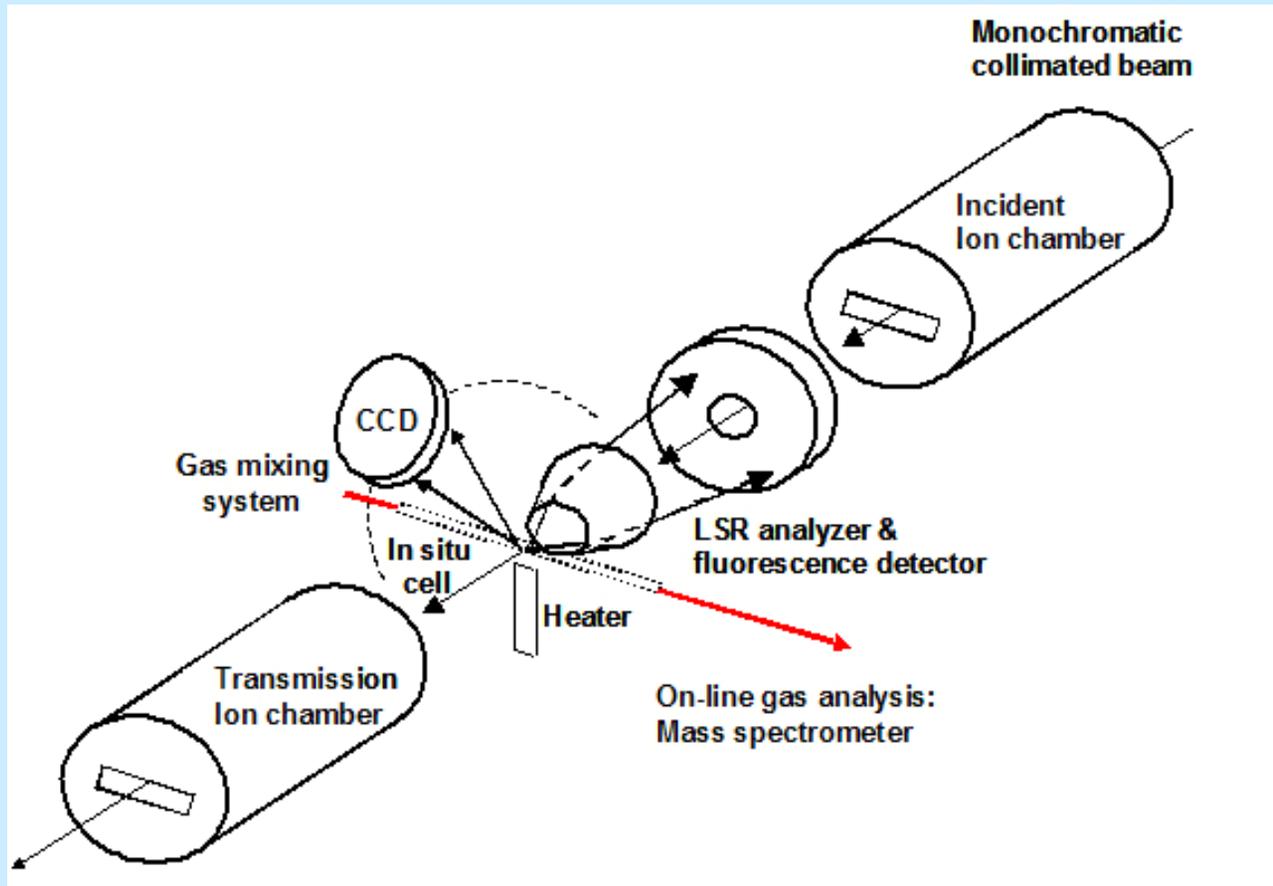


Cu K-edge of sample

PCA 3-component fit to reduction of doped ceria at 200°C



Projected XRD/XAFS beamline at NSLS-II



The instrumentation will take full advantage of the high intensity and brightness of the NSLS-II

It will have fast XRD (3ms time resolution) and fast XAFS (< 1s time resolution). Ability to study metal loadings as diluted as < 0.1 % with quick XAFS.

Our proposed set-up will be the **best combination of XRD/XAFS in the world. Superior in sensitivity and fast readout time to those existing in HASYLAB/DESY (Hamburg) and SRS (Daresbury).**