Powder Diffraction and Catalysis at NSLS and NSLS-II

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Beam Line X7B

Catalysis and NSLS II

Synchrotron radiation facilities provide unique and powerful tools for characterizing the temporal and spatial evolution of **working catalysts**. The properties of catalysts can be studied using a wide range of x-ray techniques, such as **x-ray powder** and/or single-crystal diffraction, small-angle x-ray scattering, and many x-ray spectroscopy methods. The high brightness and flux of NSLS-II light is for these techniques to be applied with the high spatial, energy, and time resolution necessary to fully characterize these complex catalytic systems.

Reason for talk

- Promote *in situ* powder diffraction studies of Catalysts at new beam line.
  - Sample studies at NSLS-I
  - Sample studies from other synchrotrons
  - Proposed studies for NSLS II
- Sample cells and sample positioning questions

Overall Approach

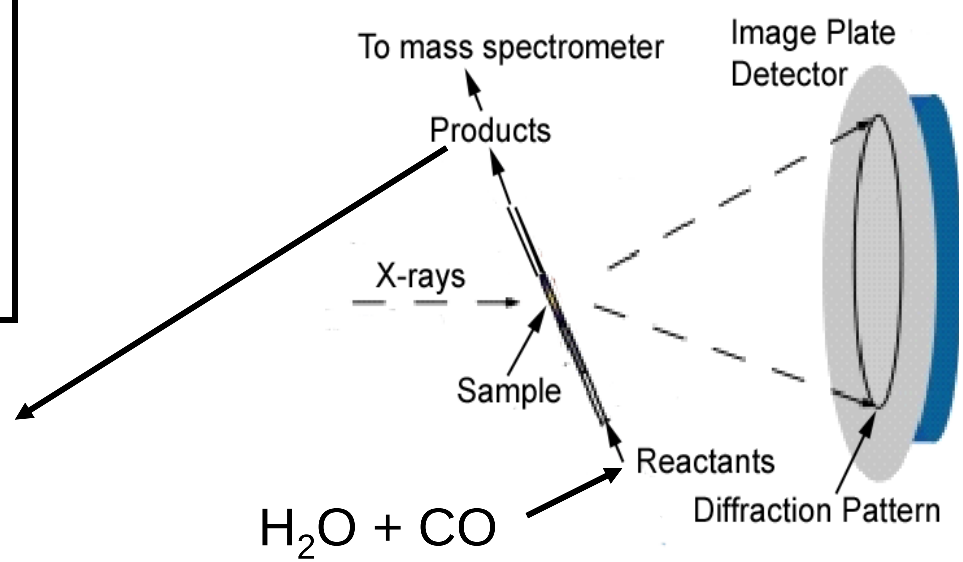
- Observe structure of active catalysts under "operando" conditions
- Observe structure changes during catalyst synthesis
- Methods
  - Powder diffraction
    - Crystalline (Profile refinement)
    - Amorphous (Pair Distribution Function)
  - Extended X-ray absorption fine structure

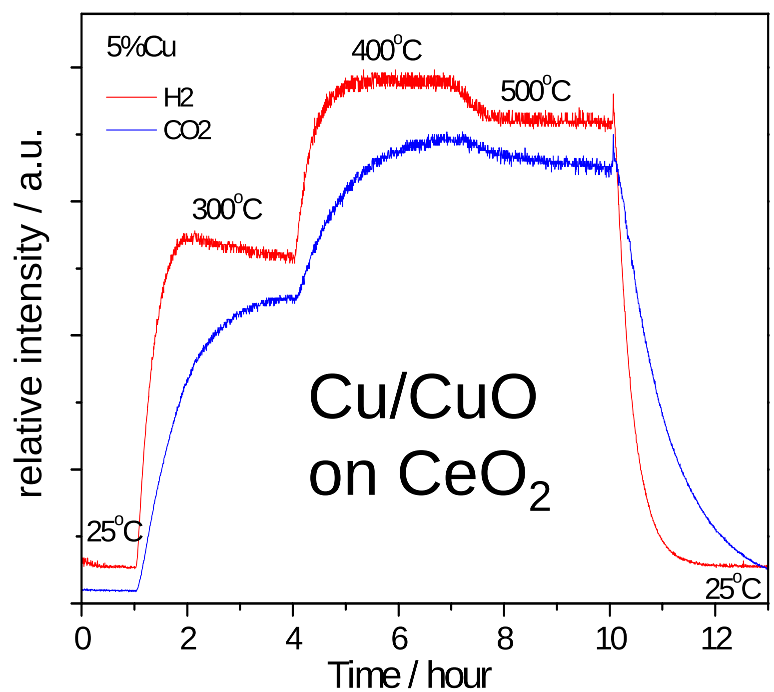
In situ Time-resolved XRD Schematic

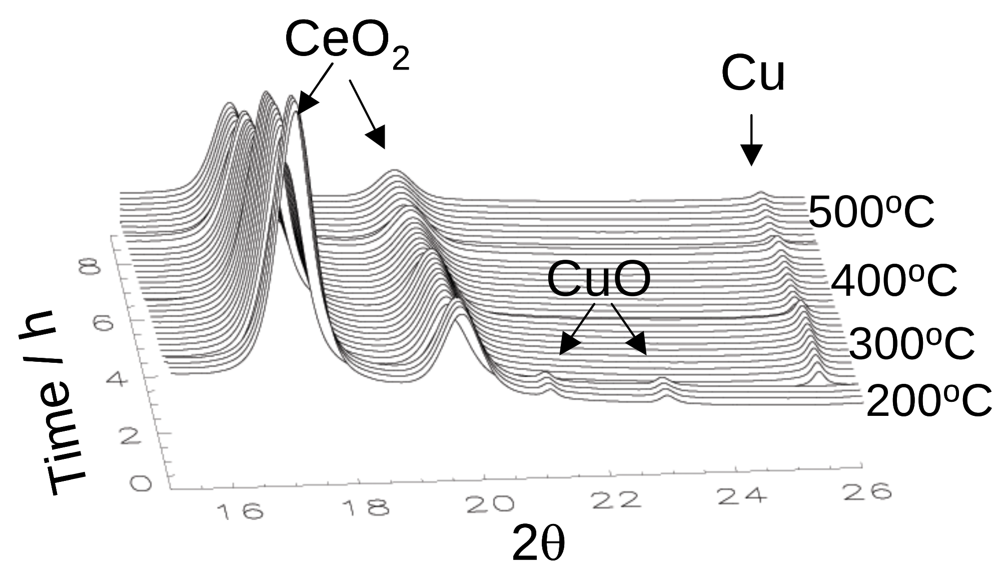
$CO + H_2O \rightarrow H_2 + CO_2$

Reactants Products

Water Gas Shift Reaction

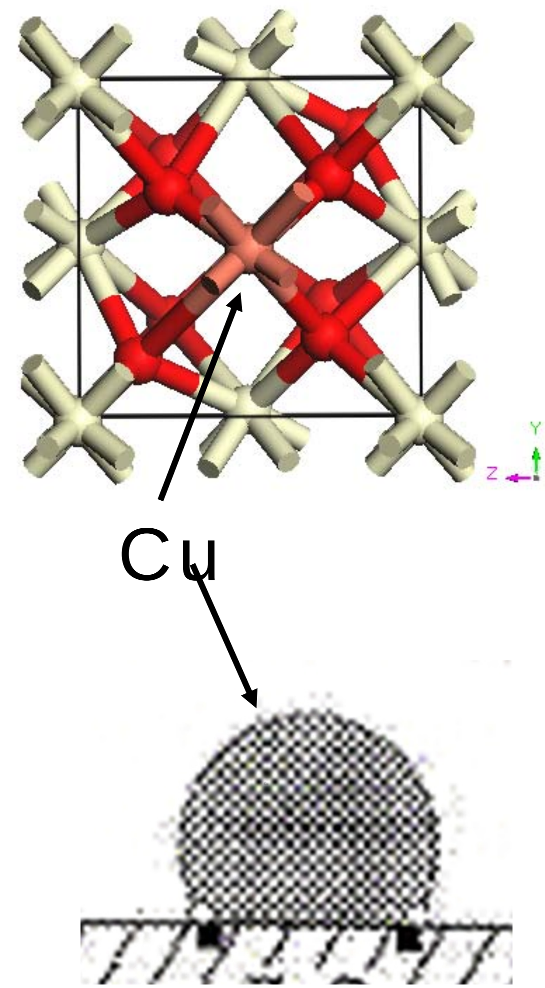






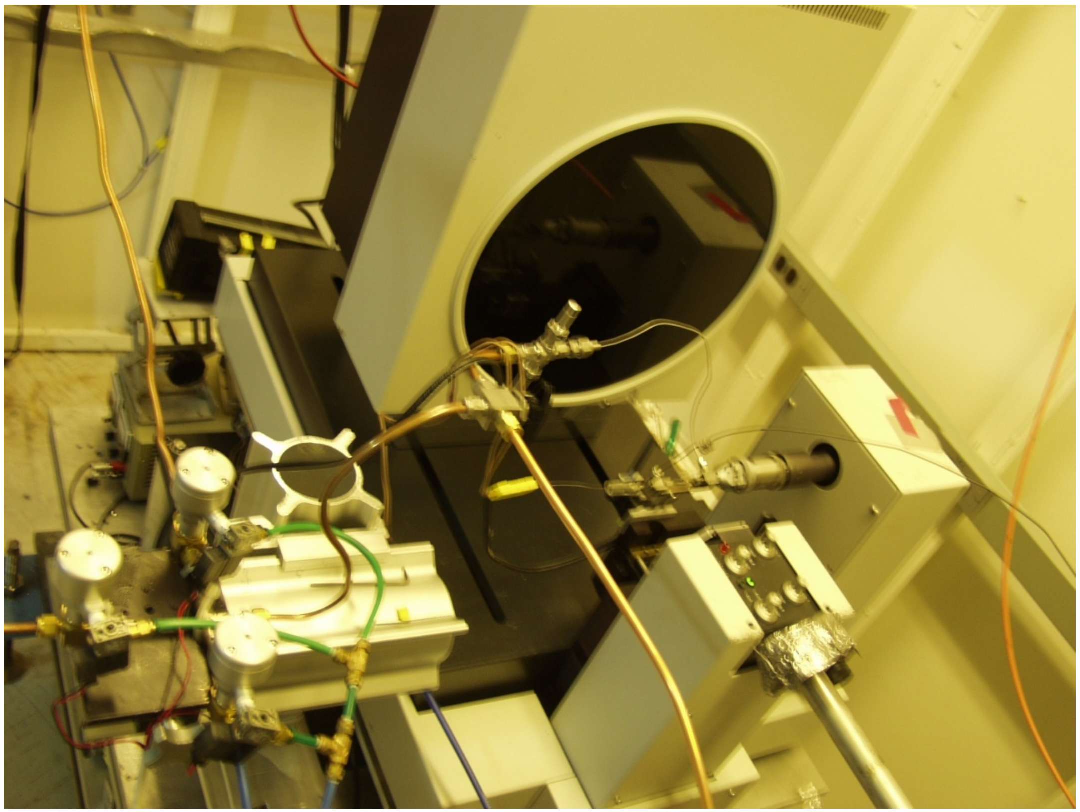
New Low Temperature WGS Catalysts

- Cu/CeO_2:
  - doped: Cu on Ce sites (Cu migrates in and out of ceria structure)
  - impregnated: Cu/CuO on the CeO_2 surface
- Issues to understand mechanism
  - Oxidation state of the Cu during WGS
  - Location of metal on/in metal oxide
  - Vacancies in CeO_2

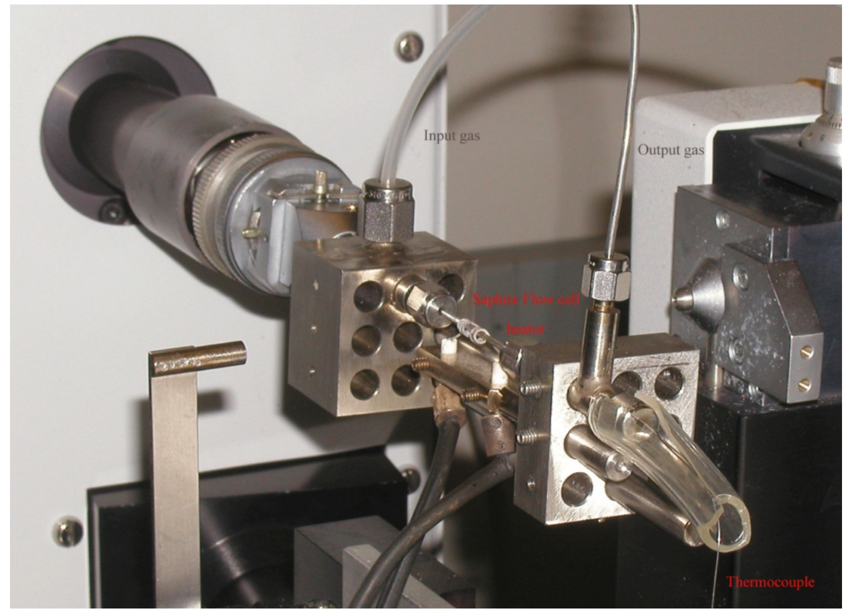


CeO_2

X7B *In Situ* Diffraction Apparatus



Mar345 Image Plate detector
and flow controls

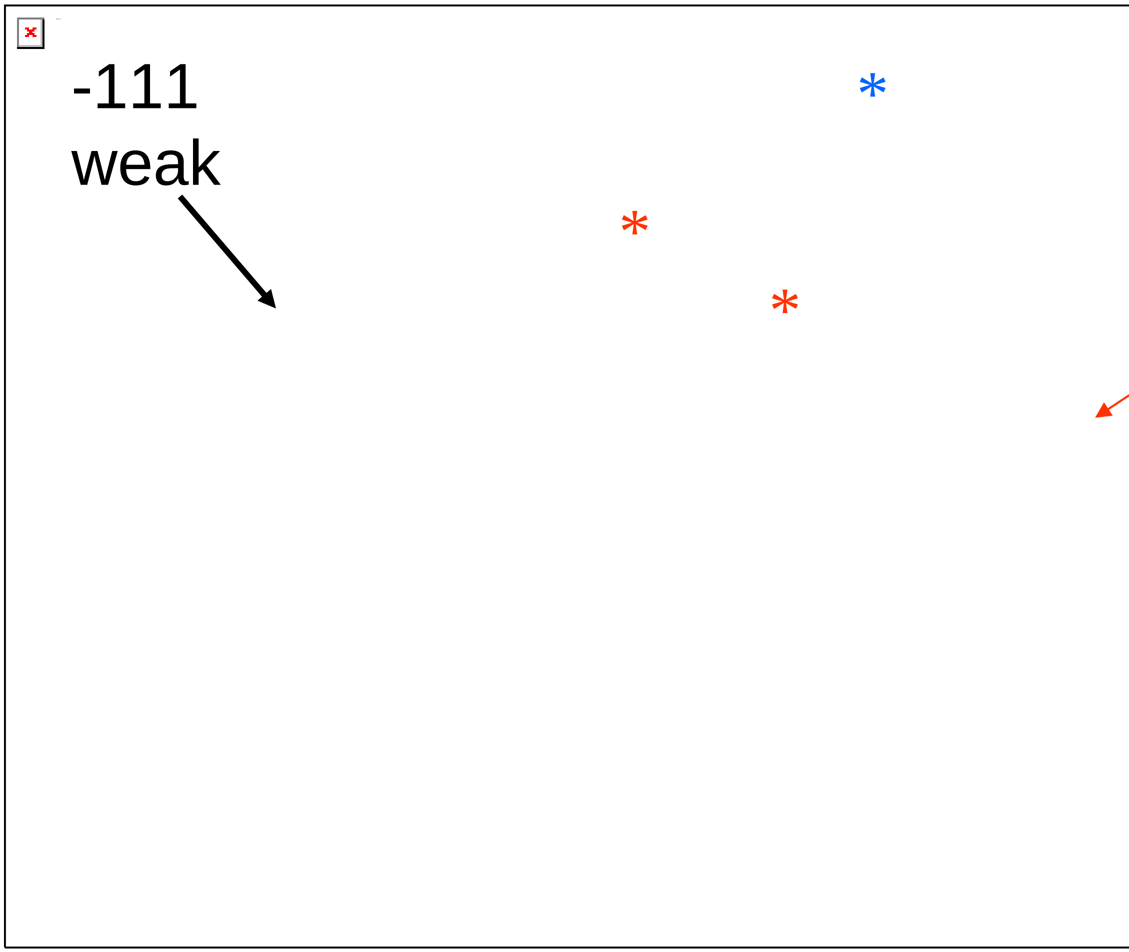


Flow Cell with heater
and TC
(T<1000C, P<45Atm)
Clausen, Norby, Chupas

Example of Catalyst Preparation

•Pre-treat $NiMoO_4$ in He at 500ºC

•Flow $CO/H_2O/He$



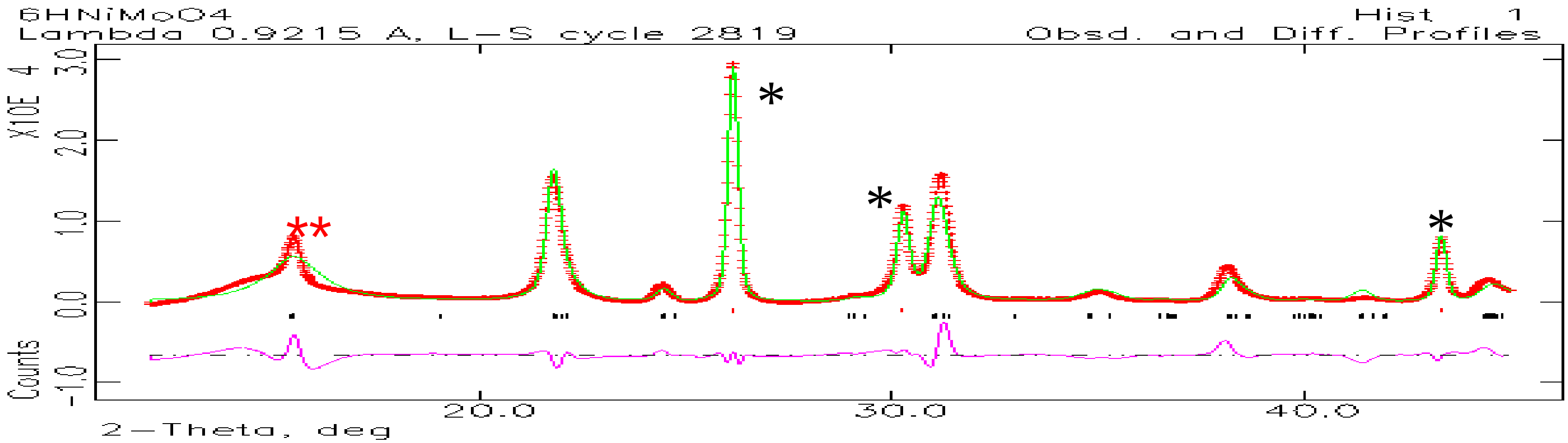
Catalysts I

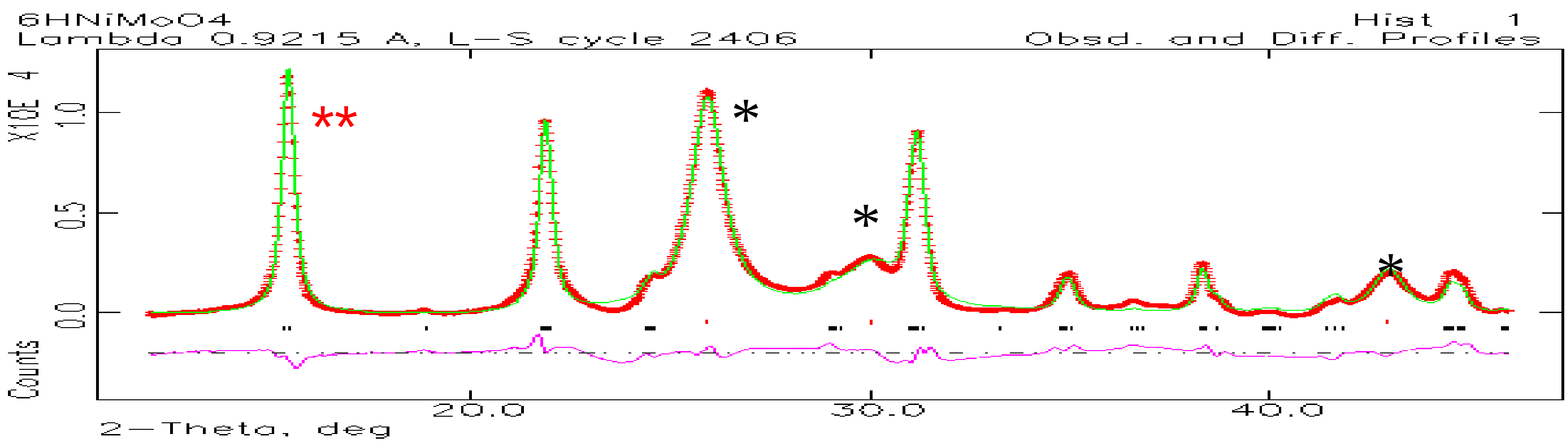
* Ni
* MoO_2

$NiMoO_4$

-111 does not form when the other MoO_2 peaks form

Ni/MoO_2 catalysts with different activity





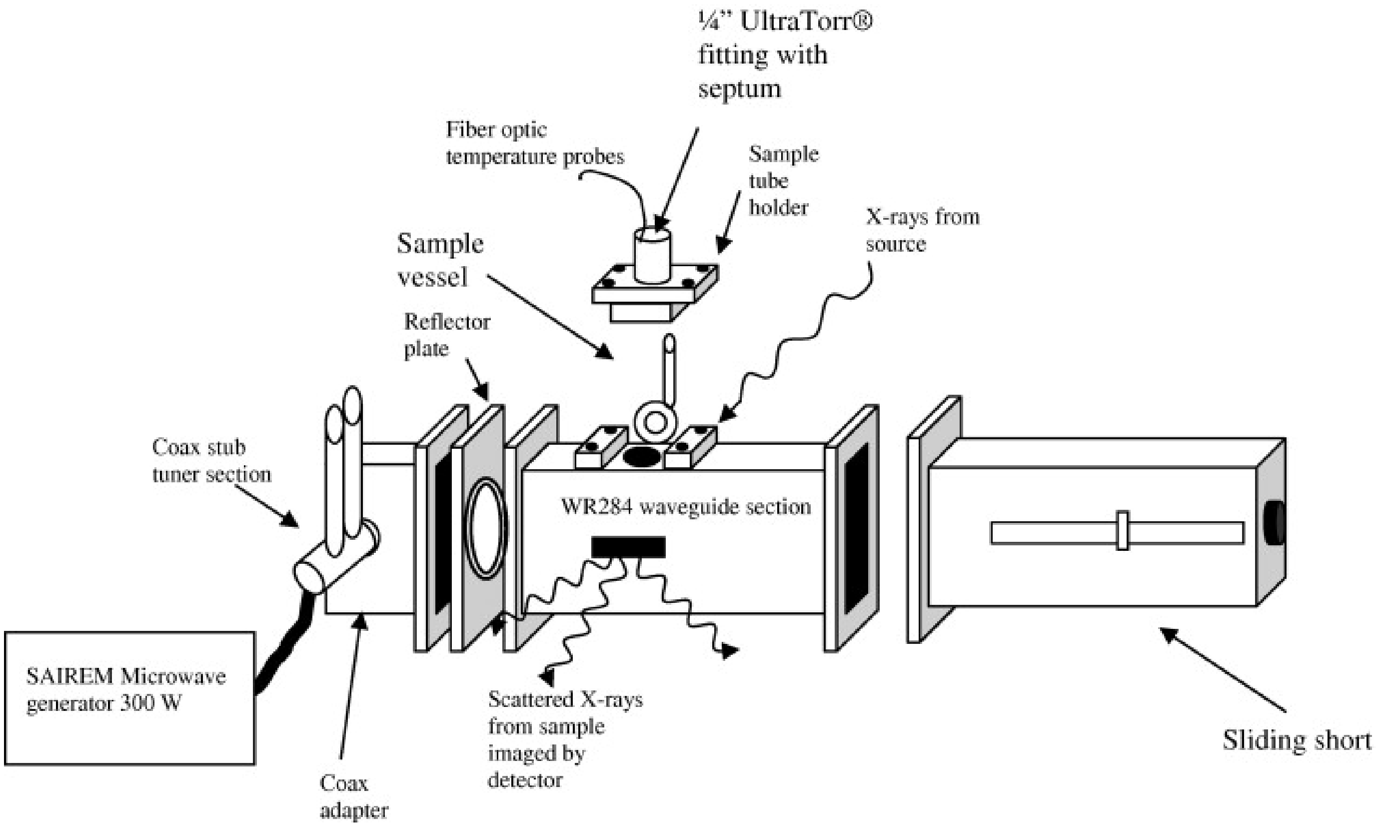
* Ni

**MoO_2 –111 peak

Stacking faults in MoO_2

Particle size in Ni

Microwave cell developed by Conner (UMass) at X10



G Tompsett, B Panzarella, W Conner, S Bennett, K Jones, In Situ SAXS and WAXS of Zeolite Microwave Synthesis, *Nucl. Instrum. Meth. B*, **261**: 863-866 (2007)

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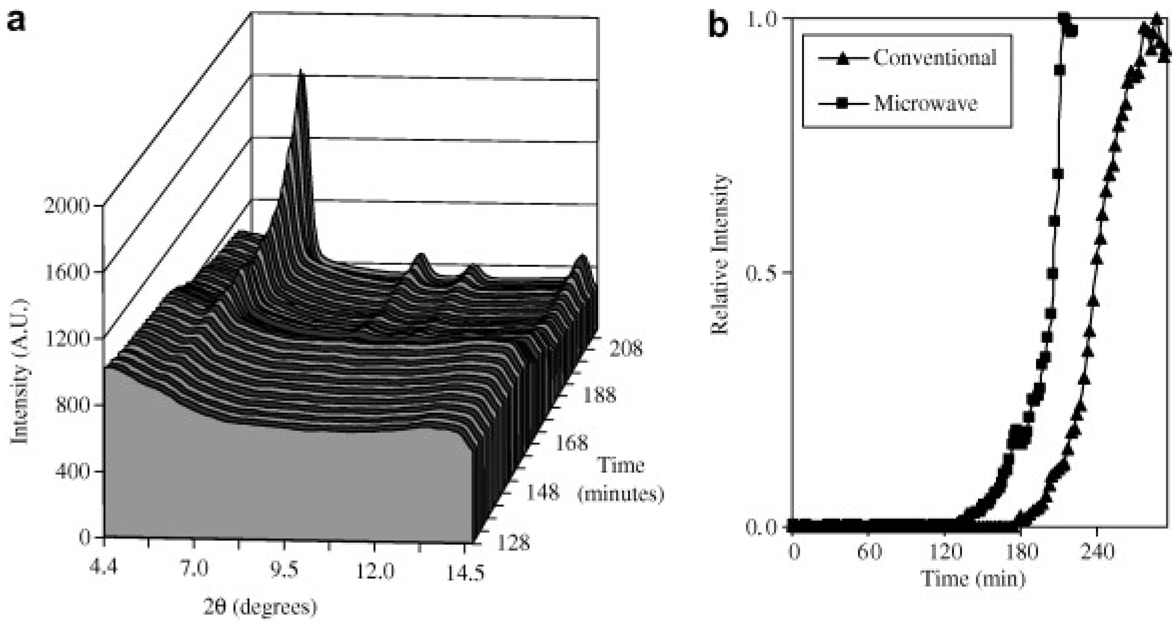

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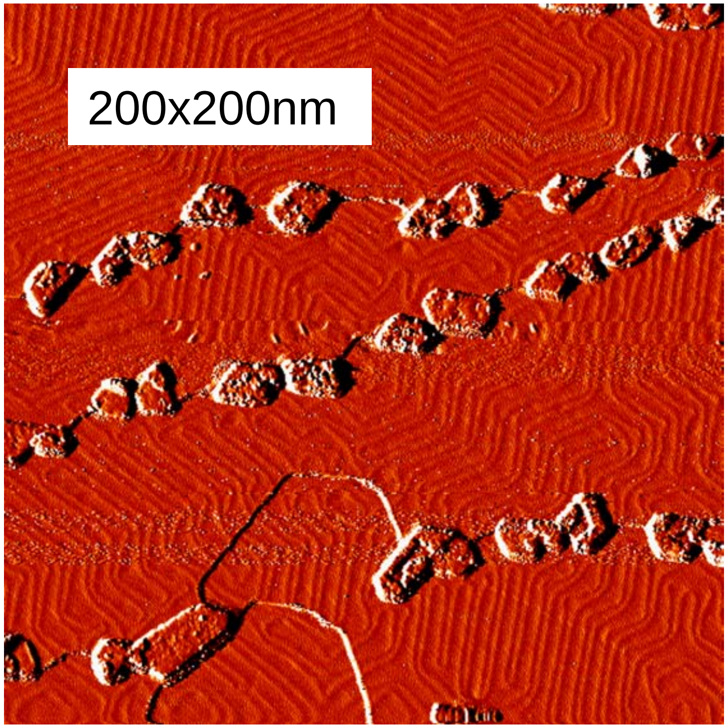
Diffraction studies by catalysis groups at other synchrotrons

- Ressler @ DESY
  - Methanol reforming
  - Propane oxidation
- Sankar and Thomas @Daresbury
  - Zeolite synthesis
  - Redox studies

In Situ Diffraction from supported nano particles

Challenge for NSLS II

Inverse Catalyst:
Ceria on Gold



J. A. Rodriguez et al. Science **318** 1757-1760 (2007)

Problems

1. Manipulate nano particles into 20nm beam
2. Preferred orientation
3. In situ cell to control/monitor reaction