Ambient-Pressure NEXAFS and XPS at CSX2 Beamline: Soft X-rays for the *In-situ* Study of Catalytic Processes

Chemistry Dept

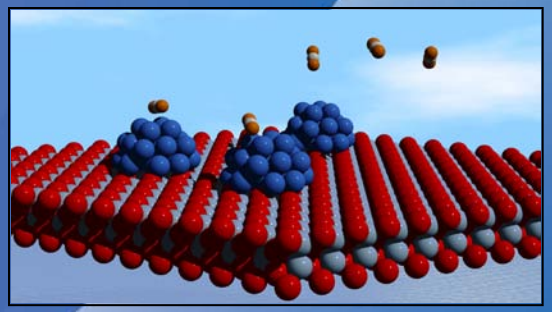
Sanjaya Senanayake
Dario Stacchiola
Jingguang Chen (SCC)
Jose Rodriguez (SCC)

CFN

Peter Sutter
Samuel Tenney
Anibal Boscoboinik

Photon Sciences

Cecilia Sanchez Hanke
Dario Arena



BROOKHAVEN NATIONAL LABORATORY

a passion for discovery

U.S. DEPARTMENT OF ENERGY | Office of Science

djs@bnl.gov

Goals

Instrumentation: Build and use end-stations for soft X-ray ambient-pressure AP-XPS and AP-NEXAFS at NSLS-II CSX2 beamline:
pressure range up to 1 atm.

Science case

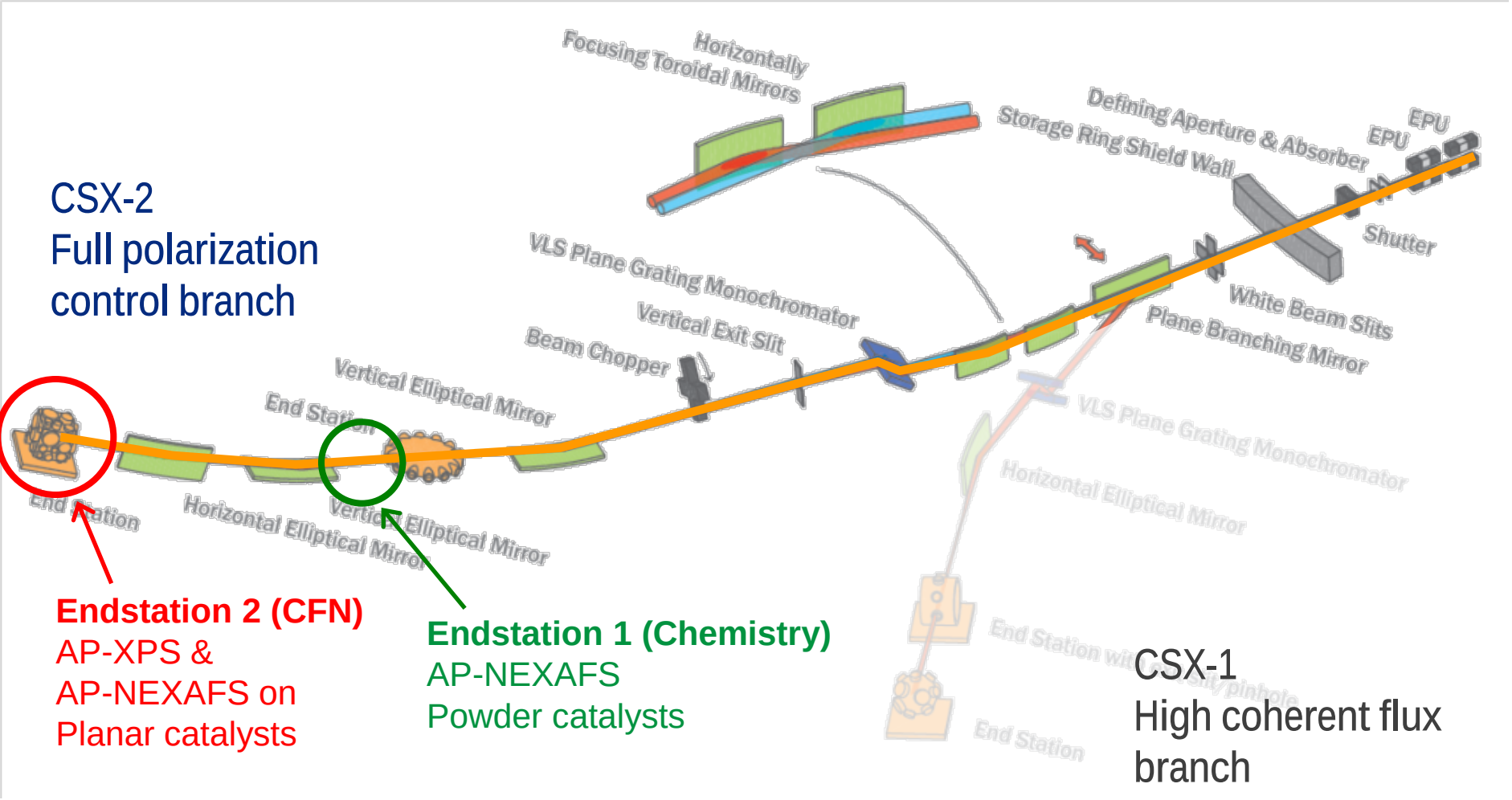
Catalysis: Study *in-situ* the water-gas shift (WGS) on (Au,Cu)/CeO_x/TiO_2

$$H_2O + CO \rightarrow CO_2 + H_2$$

Surface chemistry: Study in-situ the processes of CO_2 capture on solid sorbents.

Polarization control: Identify surface species and reaction intermediates taking advantage of the unique polarization-switching capabilities of the CSX2 beamline.

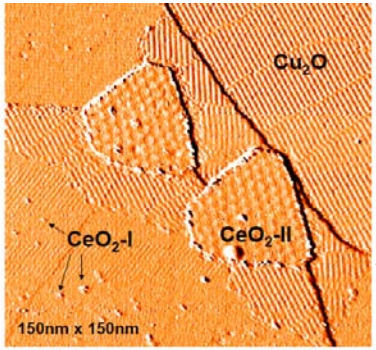
CSX2 beamline real-space layout



AP-XPS & AP-NEXAFS at NSLS-II

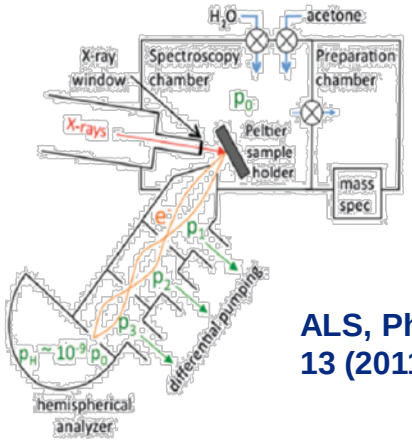
AP-STM: CeO_x/CuO

Model catalysts



Endstation 2

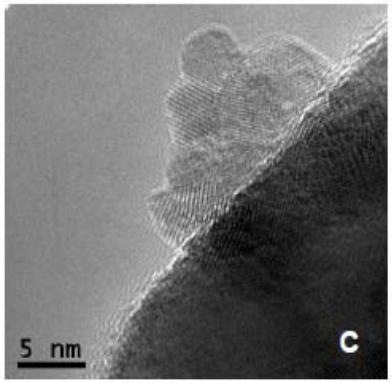
AP-XPS
AP-NEXAFS
model catalysts



ALS, Phys. Chem. Chem. Phys. 13 (2011) 19988

Powder catalysts

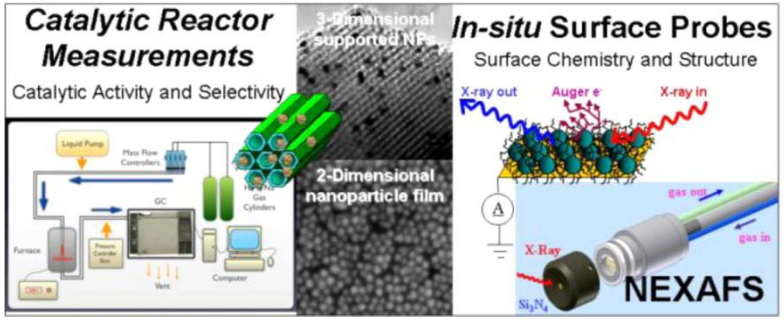
E-TEM: CeO_x/CuO



Endstation 1

AP-NEXAFS
powders

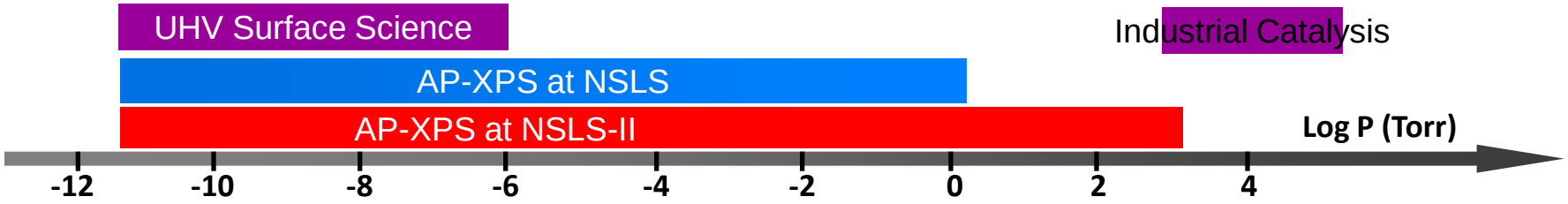
beam



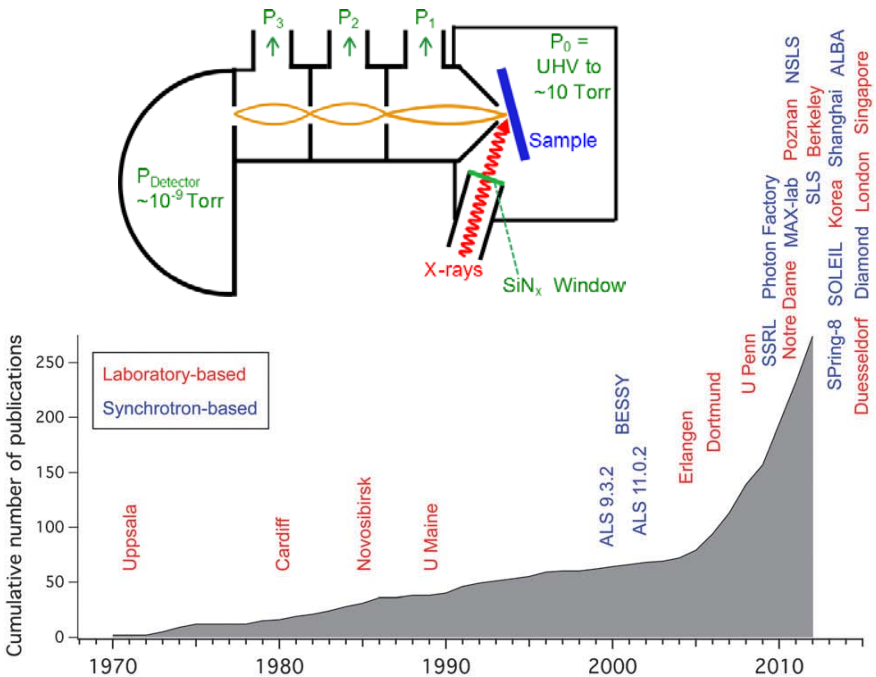
ALS, ACS Catal. 2 (2012) 2250

AP-XPS – Powerful Method with High User Demand

Ambient pressure XPS: chemically sensitive spectroscopy at elevated pressures



International growth – Opportunity for leading-edge performance at NSLS II



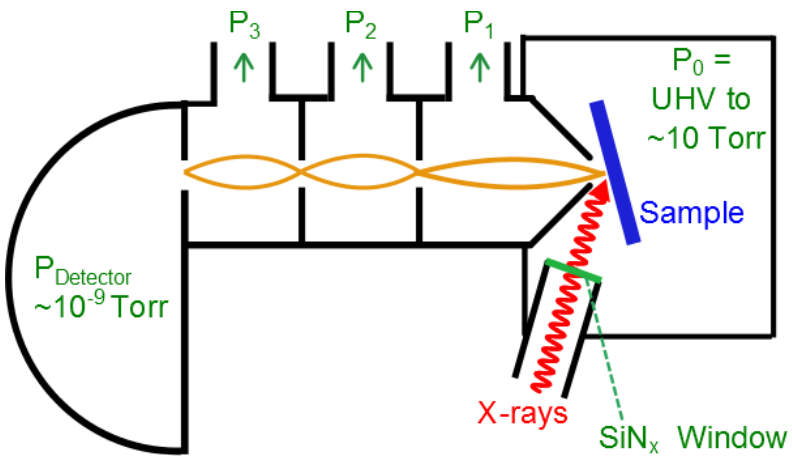
Chem. Soc. Rev., 2013, ***42, 5833--5857***

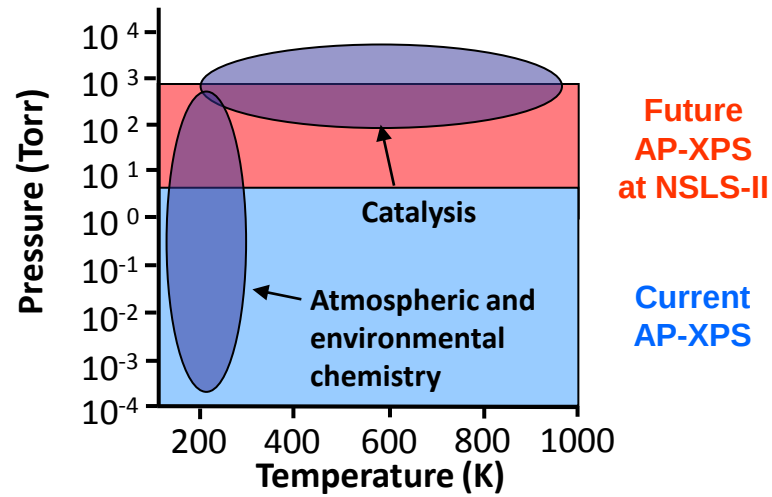
ALS Beamline 11.0.2: consistently most oversubscribed beamline for time at the ALS - Berkeley
Current cycle: Only 9% of requested beamtime allocated

AP-XPS at NSLS II CSX2 Beamline

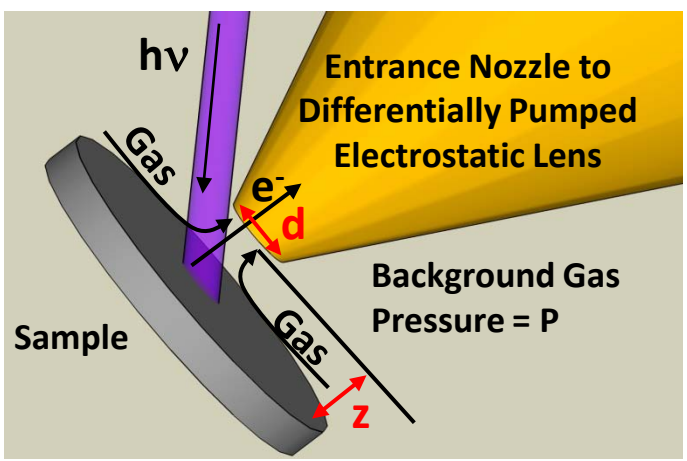
Towards Ambient Pressure XPS

Fundamental pressure limit: Elastic & inelastic e^- scattering in gas phase.





$$I_p = I_{vac} \cdot \exp\left(-z\sigma(E)P/kT\right) \quad z \approx d \quad P \propto \frac{1}{d}$$



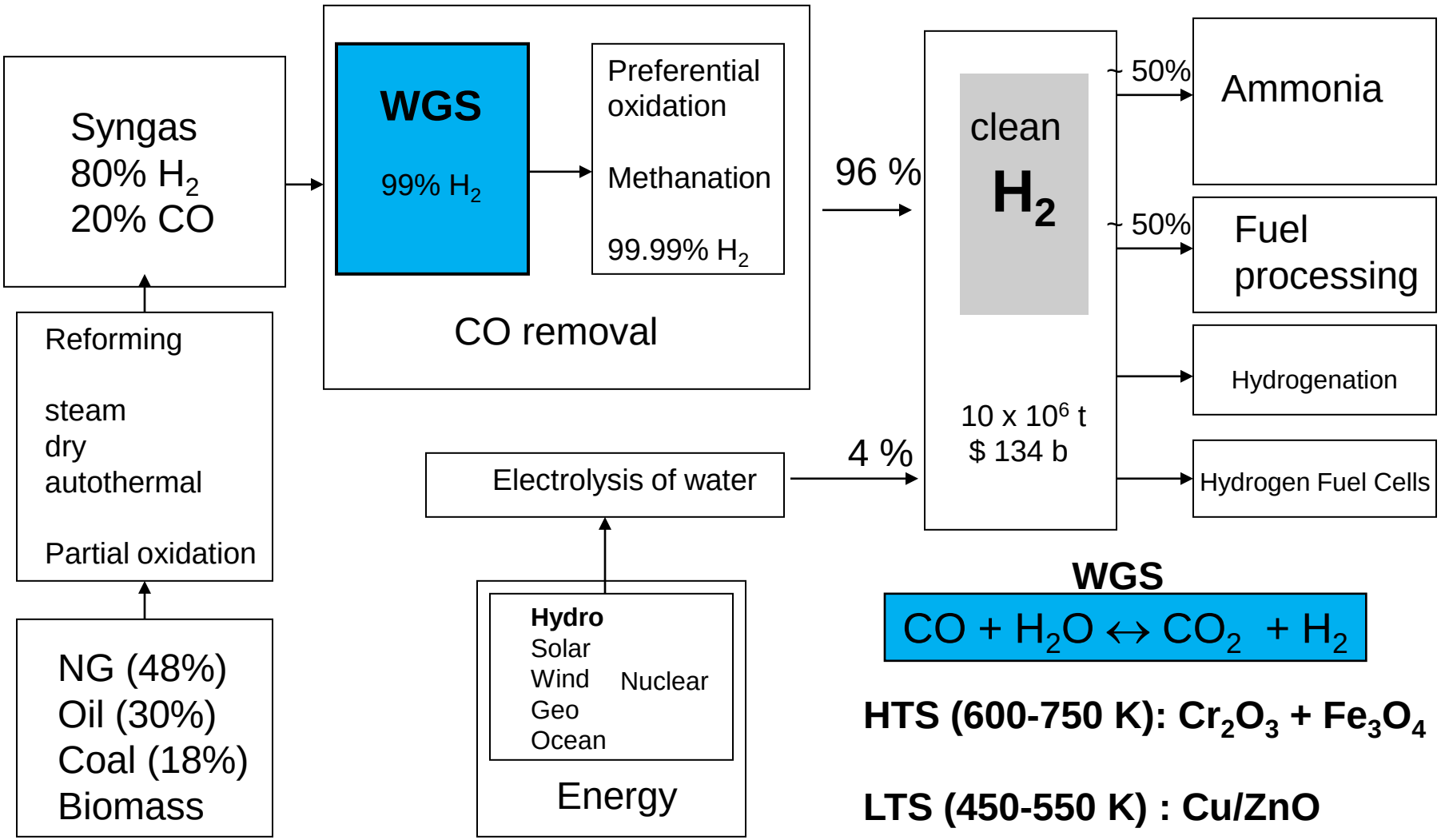
	d_{Nozzle}	spacing, z	P_{max}	Performance
Current config.	300 μm	300 μm	5 Torr	Current AP-XPS @ ALS, Berkeley
Plus two focusing mirrors	2 μm	2 μm	750 Torr	Atmospheric P

AP-XPS for Catalysis & Surface Chemistry

Example I: Water-gas-shift catalysis

Stacchiola, Senanayake, Rodriguez, Chem Dept
ALS 9.2

Need for clean hydrogen : Water Gas Shift (WGS) Reaction



WGS

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

HTS (600-750 K): $Cr_2O_3 + Fe_3O_4$

LTS (450-550 K) : Cu/ZnO

AP-XPS for Catalysis & Surface Chemistry

Example I: Water-gas-shift catalysis

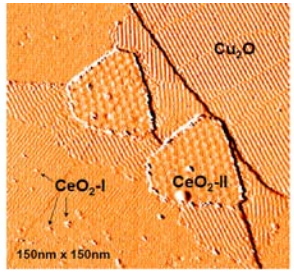
Stacchiola, Senanayake, Rodriguez, Chem Dept
ALS 9.2

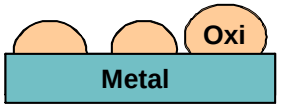
WGS

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Angew. Chemie Int. Ed **2013** DOI 10.1002/anie.201210077

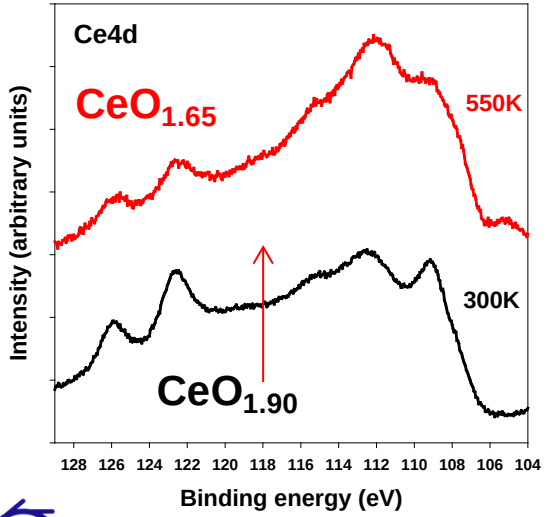
CeO_x / Cu(111)

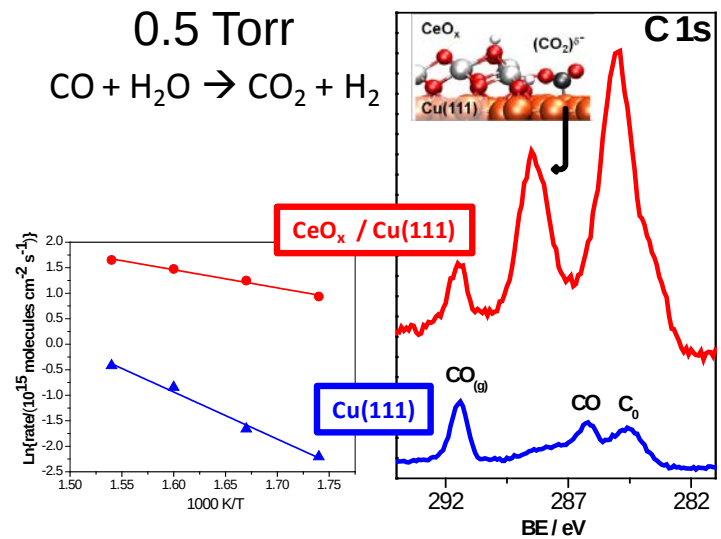




Inverse

State of catalyst under reaction conditions





Activity of ceria/metal catalysts, and
Ambient Pressure XPS under *in-situ* conditions

ALS ADVANCED LIGHT SOURCE Beamline 9.3.2 Zhi Liu

Example II: Solid-state CO_2 capture

S. Tenney, P. Sutter, CFN, NSLS X1A

Conventional liquid-phase CO_2 capture

$$CO_2(aq) \xrightarrow{H_2O} H_2CO_3 \xrightarrow{MEA} HCO_3^- + AH^+$$

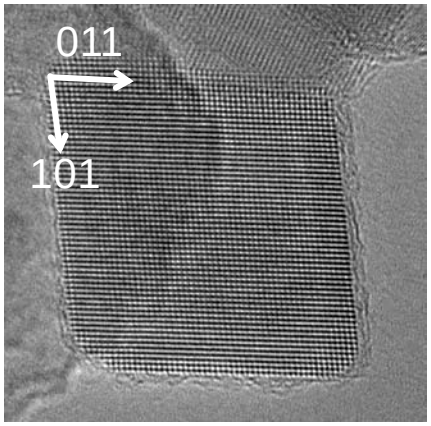
$$CO_2(aq) + MEA \rightarrow {}^-OOCHNC_2H_4OH + AH^+$$

A = monoetanolamine [MEA] = $H_2NC_2H_4OH$

Issues:

- Energy intensive CO_2 removal.
- MEA solution corrosive.
- NO_x/SO_x poison solution.

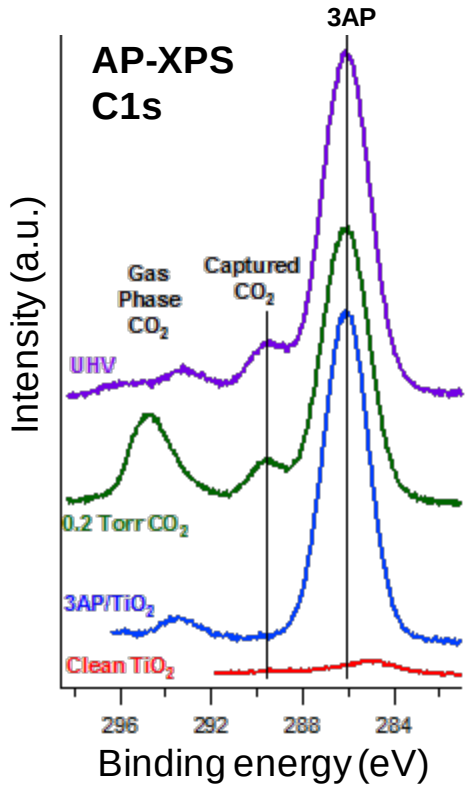
Oxide-supported amines



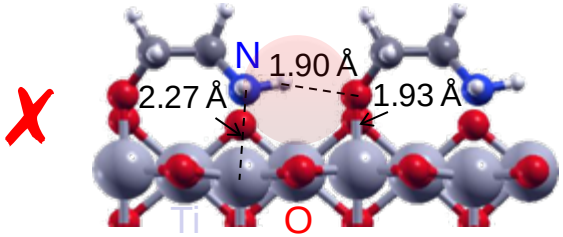
Questions:

- Capture mechanism
- Influence of support
- Effect of 'poisons', NO_x,SO_x
- Capture & release kinetics

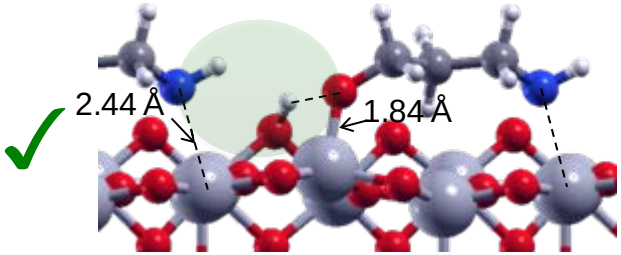
AP-XPS on model systems: Amines on $TiO_2(110)$



MEA/TiO_2(110)



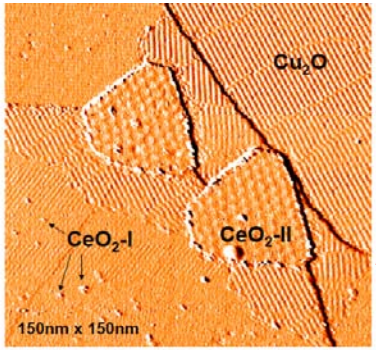
3AP/TiO_2(110)



AP-NEXAFS at NSLS-II

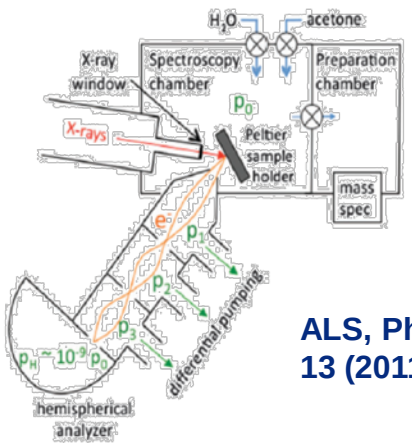
AP-STM: CeO_x/CuO

Model catalysts



Endstation 2

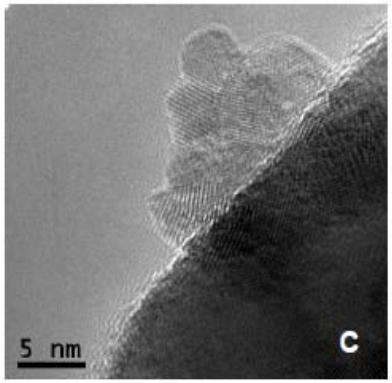
AP-XPS
AP-NEXAFS
model catalysts



ALS, Phys. Chem. Chem. Phys. 13 (2011) 19988

Powder catalysts

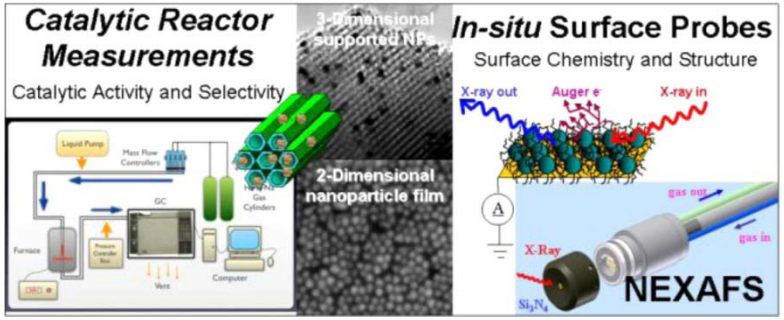
E-TEM: CeO_x/CuO



Endstation 1

AP-NEXAFS
powders

beam



ALS, ACS Catal. 2 (2012) 2250

AP-NEXAFS at NSLS-II

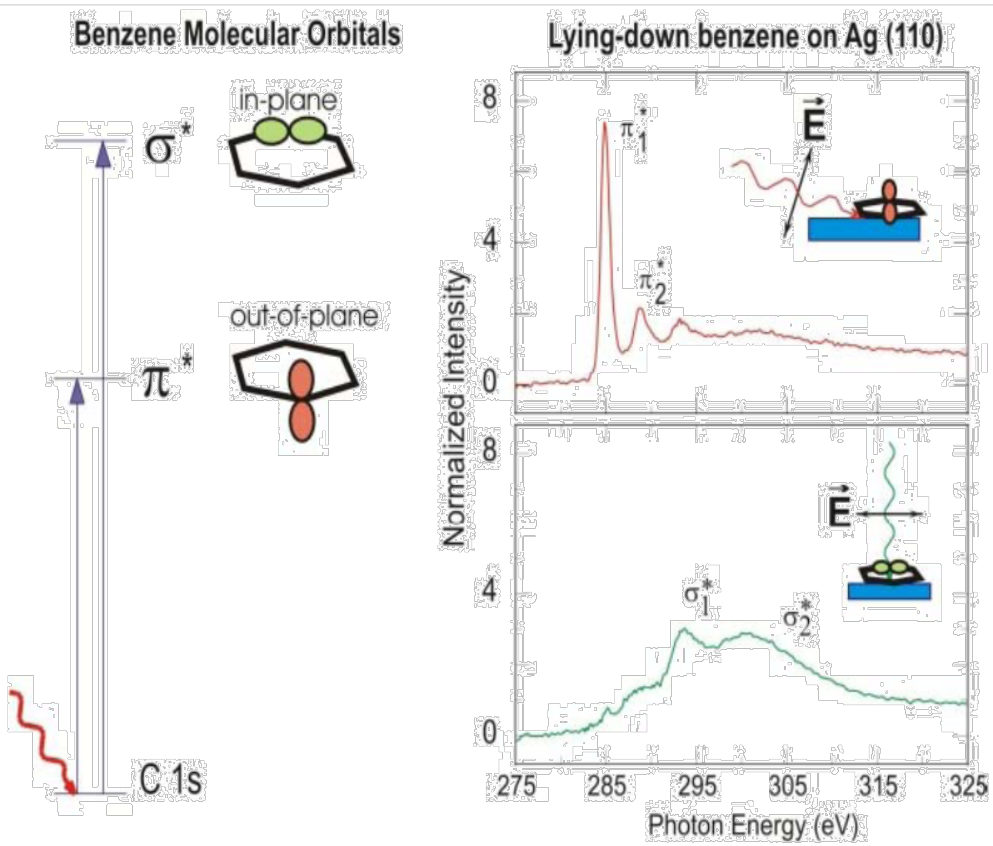


Fig. 4. Polarization dependent NEXAFS spectra of benzene chemisorbed on Ag(110), illustrating the capability to determine molecular orientations.

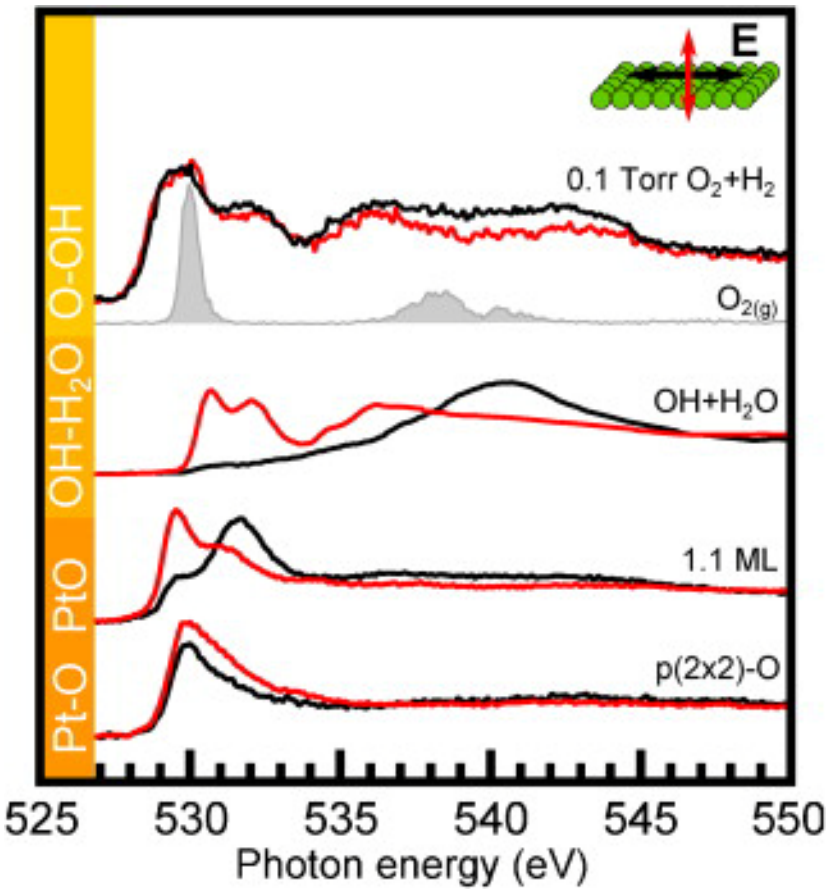
Experiments of AP-NEXAFS on model catalysts

<u>Unique tool:</u>

Cross-section and features in the AP-NEXAFS will change with polarization of light

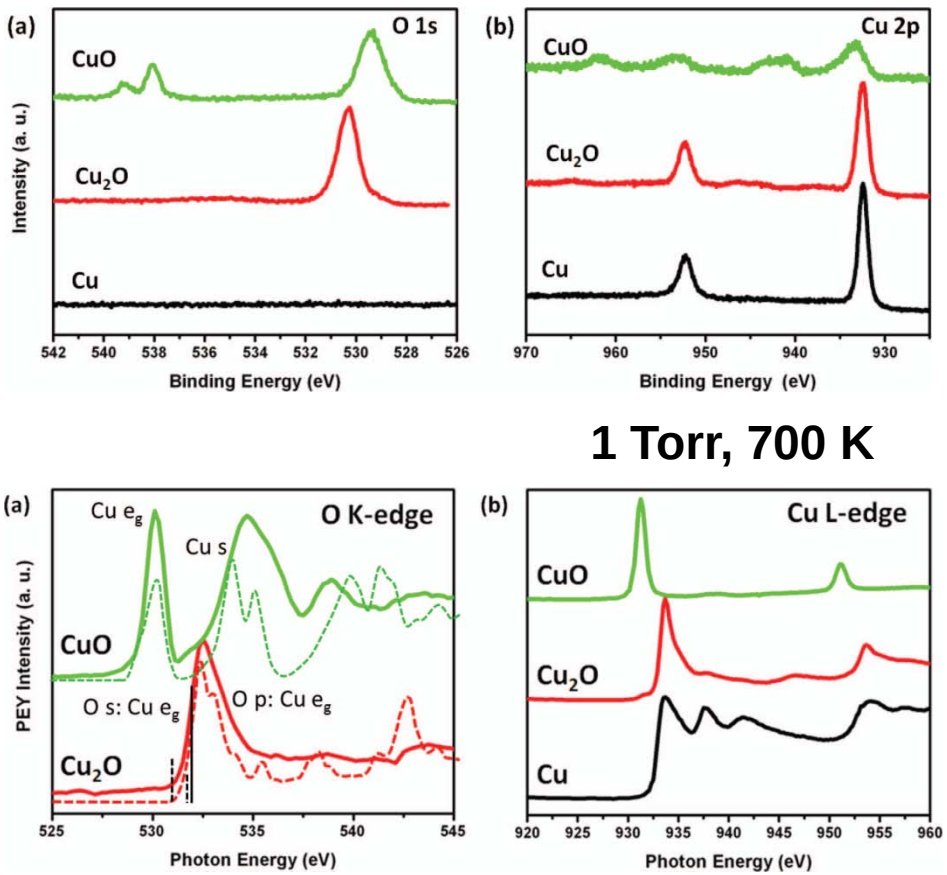
AP-NEXAFS at NSLS-II

SSRL



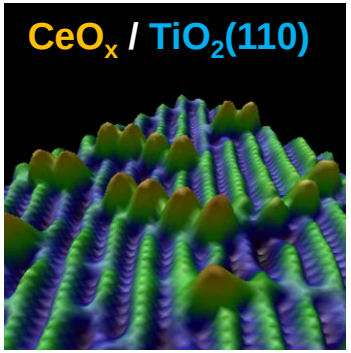
S. Kaya et al. / Catalysis Today 205 **(2013)** 101–105

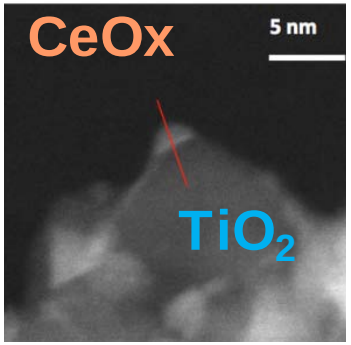
ALS



JCP 138, 024704 **(2013)**

Ambient-Pressure NEXAFS and XPS at CSX Beamline: Soft X-rays for the *In-situ* Study of Catalytic Processes





Objectives:

First light experiments:

- *In-situ* Study of the WGS on (Au,Cu)/CeO_x/TiO_2 Planar and Powder catalysts

- Study the mechanism for capture of CO_2 on solids

- We will be testing the linear polarization devices of the beamline

Development of instrumentation:

-Unique facilities for studying reaction mechanisms at the surface of planar and powder catalysts. These will benefit users at CFN and Synchrotron Catalysis Consortium (SCC)

-The combination of the linearly polarized light with AP-NEXAFS is unique. Will be the first to achieve Atmospheric pressures in AP-XPS