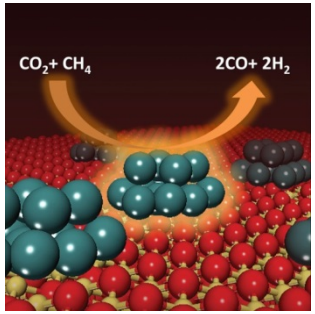


José A. Rodriguez

DOE Distinguished Scientist Project:
New Tools for Mechanistic Transient Studies in Catalysis

Chemistry Division
Brookhaven National Laboratory

BROOKHAVEN NATIONAL LABORATORY

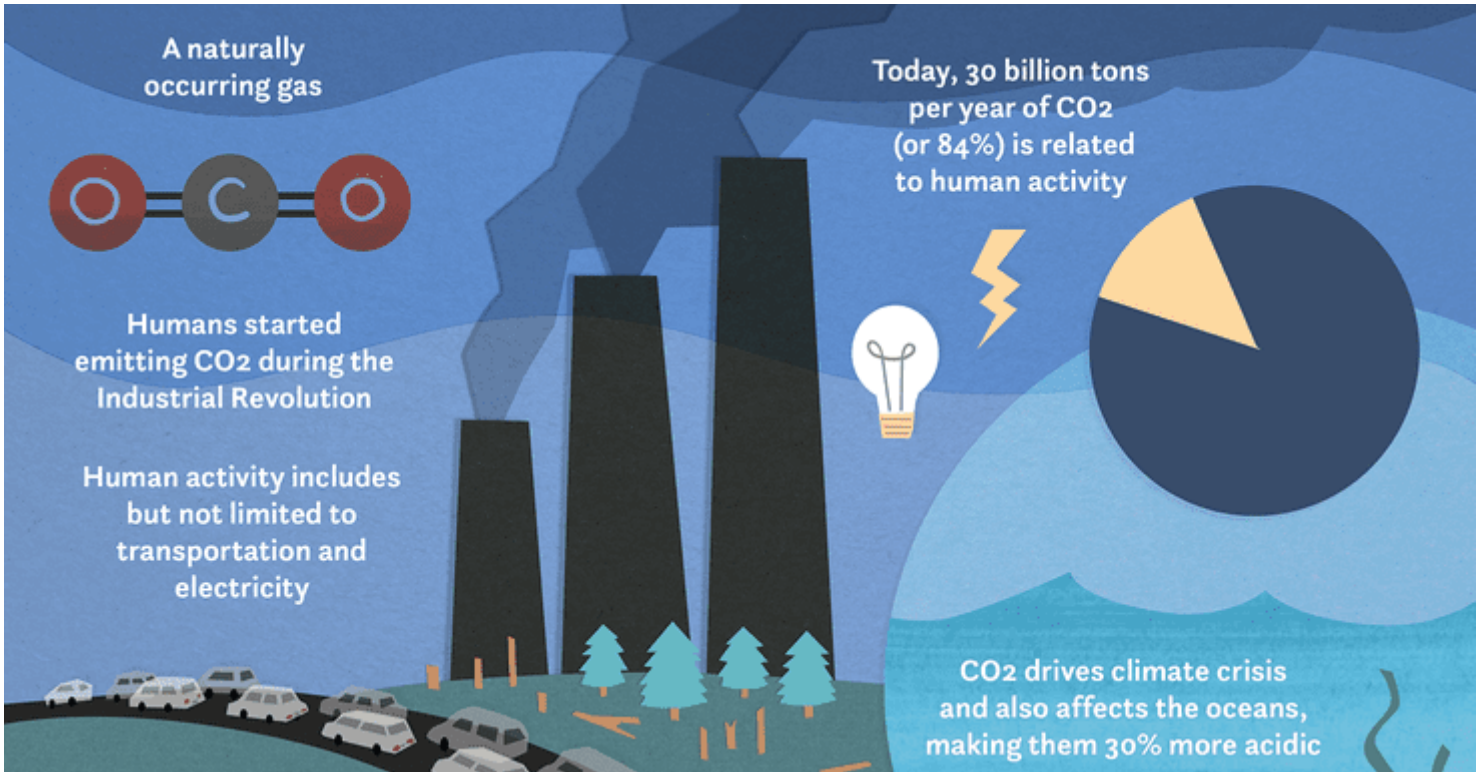
Outline

- **Fundamental studies on the conversion of CO_2 to methanol**

- **Development of techniques and strategies for the *in-situ* characterization of catalysts**

Both topics are at the core of this DOE Distinguished Scientist project.

Negative impact of CO_2 on the environment



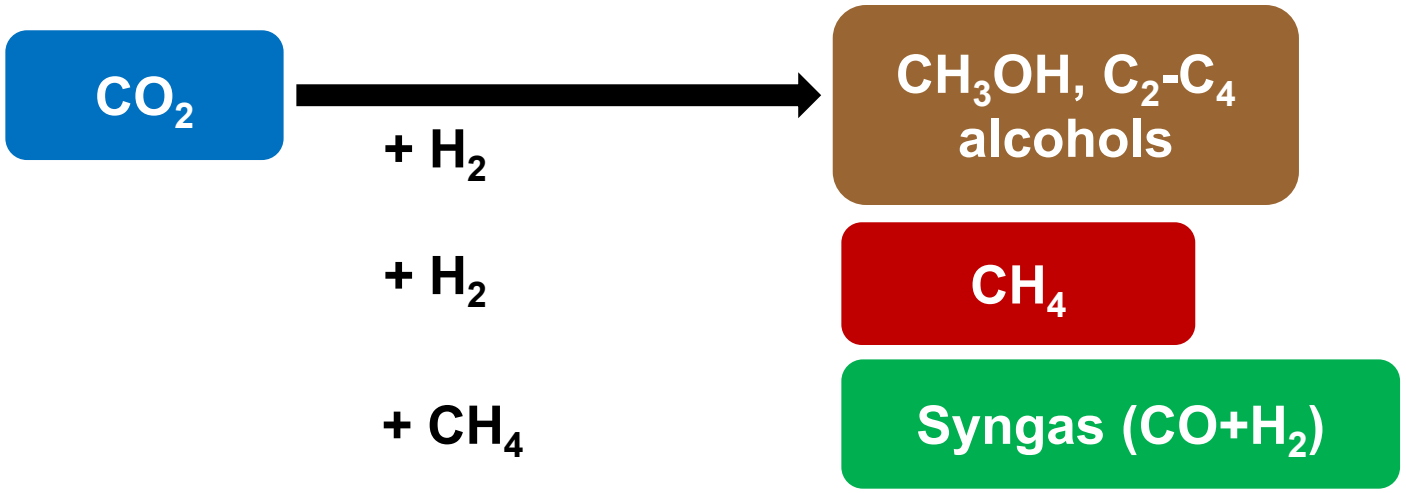
https://www.treehugger.com/co-why-is-carbon-dioxide-bad-4864246

Guidelines Department of Energy:

"..will develop innovative technologies to generate novel, marketable products using carbon dioxide (CO_2) or coal as a feedstock, potentially offering significant advantages over traditional products..

..test technologies that can use CO_2—from coal-based power systems or other industrial sources—as the primary feedstock to reduce emissions and create valuable products."

The Catalysis Group at Brookhaven is working on:

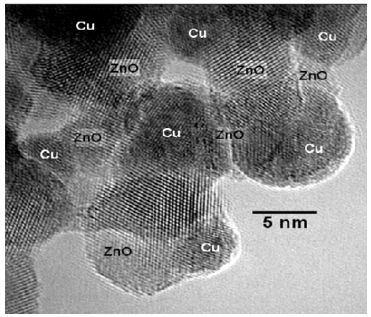


CO_2 to methanol

The synthesis of methanol through the hydrogenation of CO_2 is an attractive route for the production of clean fuels.

Cu/ZnO is a typical industrial catalysts

high pressure (40 atm)
high temperature (250 C)



TEM Cu/ZnO

More efficient catalysts are needed

We need to characterize this system under high pressures and temperature

Major issues are the identification of the catalyst active phase, the activation of CO_2, and the mechanism for methanol synthesis.

- J.J. Spivey and A. Egbebi, *Chem. Soc. Rev.* 2007, *36*, 1514.

Scientists have been working on the conversion of CO_2 to methanol for more than a century

Indiana University
PhD studies 1985-1988

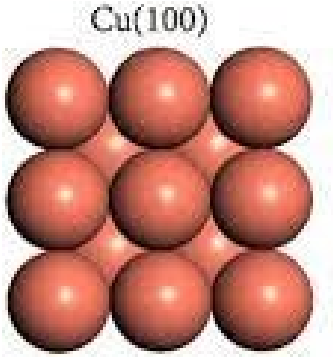
J.A. Rodriguez worked with Prof C. T. Campbell on fundamental studies on the adsorption of CO_2 on:

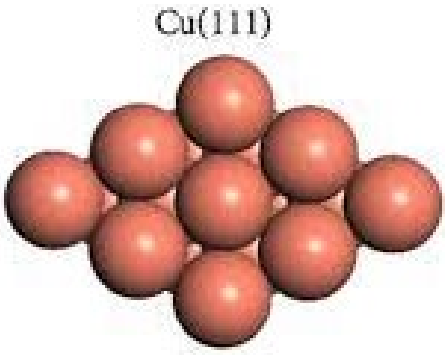
- **Cu(111), Cu(100)**
- **Cs/Cu(100)**

- **Rodriguez, Clendening and Campbell, J. Phys. Chem. 93 (1989) 5238**
- **Nakamura, Rodriguez and Campbell, J. Phys.: Condensed Matter, 1 (1989) SB149**

Major findings of the studies for CO_2 adsorption on Cu(100), Cu(111) and Cs/Cu(100) in 1980's were:

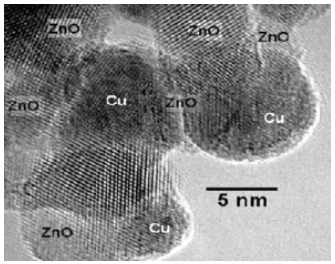
- **The dissociative sticking probability of CO_2 on pure copper is extremely low (< 10^{-6})**
- **Cs helps to bind and dissociate CO_2 and leads to a new surface chemistry**





Challenges:

- **Materials gap**



TEM Cu/ZnO

- **Pressure and characterization gap**

Process takes place at high pressures (> 20 atm)

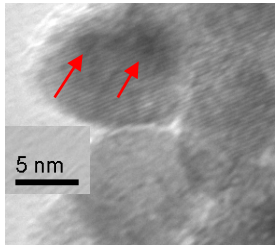
Catalysis Group at BNL : Clean Fuels and Green Chemistry

Reducing environmental pollution by:

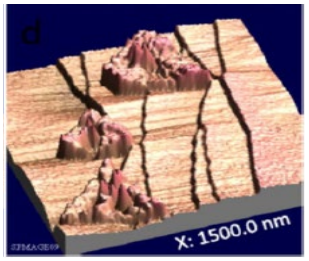
(i) Synthesis of methanol by CO_2 hydrogenation

(ii) Conversion of CO_2 and CH_4 to high value chemicals

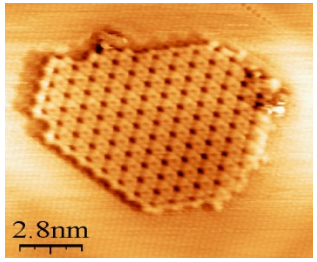
We work with powders and well-defined interfaces of metals with oxides, carbides, sulfides and phosphides.



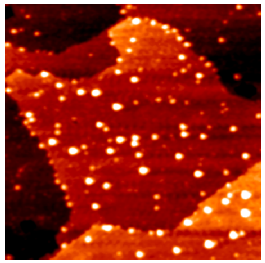
TEM: Au-CeO_2 powder



STM: ZnO on Cu(111)



STM: RuS_2 on Au(111)



STM: Cu on TiO_2(110)

The phenomena responsible for the catalytic properties are studied using several techniques (STM, TPD, XPS, FT-IRAS, XRD, PDF, XAFS) and catalytic testing.

- active phase?
- size effects?
- role of structural and electronic effects?
- reaction mechanism?

Science, 2017, *355*, 1296; *J. Am. Chem. Soc.* 2021, *143*, 13130; *Science,* 2020, *368. 513*

Synchrotron studies at NSLS-II: Catalysis Focused End-stations

Intense and tunable radiation enables

X-ray tools for catalyst characterization

Imaging, spectroscopy, scattering multimodal:

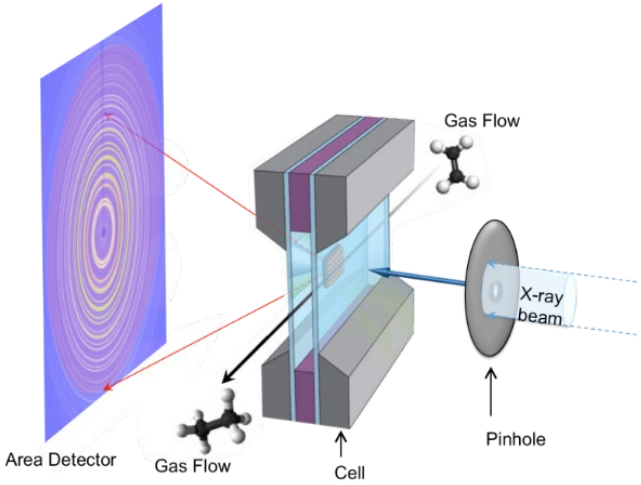
Structural, electronic and chemical properties of catalysts under reaction conditions

Multi-technique approach

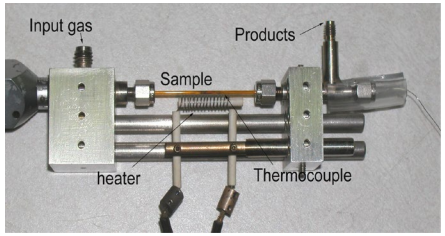
In-situ AP-XPS, XAFS
XRD, PDF

The BNL Catalysis Group is a pioneer in the development of synchrotron-based techniques and methodologies for the in-situ characterization of catalysts

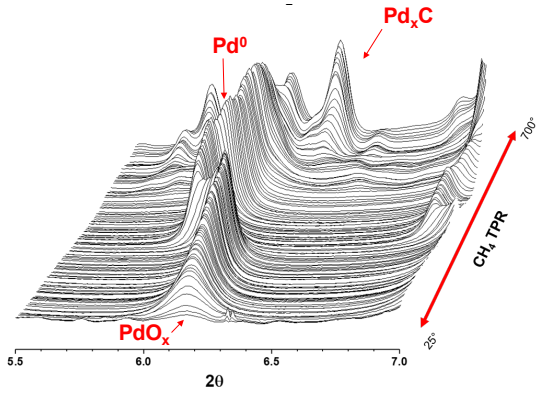
- In-situ Time-resolved X-ray Diffraction



Diffraction pattern can be obtained in 15-30 seconds



In a micro-reactor the catalyst can be exposed to different pressures and temperatures



Evolution of active phase as a function of pressure and temperature

1990s

P Norby and J Hanson: Studies on zeolite synthesis and inorganic materials

2002-2012

J Hanson and J Rodriguez: In-situ characterization of C1 catalysts

Moving beyond in-situ Time-resolved X-ray Diffraction

* Integration with other techniques

- **XRD/PDF and XRD/EXAFS**
  crystalline and amorphous active phases

- **XRD/XANES**
  structural and electronic properties (chemical state) of the active phase

- **XRD/IR and XRD/Raman**
  structural properties of the catalyst and the surface chemistry of the process.

* Multi-technique approach to obtain a full picture

- Palomino et al, J. of Synchrotron Radiation News, 30 (2017) 30.
- Frenkel, Rodriguez and Chen, ACS Catal. 2 (2012) 2269

Two approaches in the in-situ study of catalysts:

Steady-state methods

- **measure overall performance**
- **give integrated picture of reaction system**

Transient methods

- **give information on individual steps and reaction mechanism**
- **operate in millisecond time regime**

Two approaches in the in-situ study of catalysts:

Steady-state methods

current approach

- **measure overall performance**
- **give integrated picture of reaction system**

Transient methods

future approach

- **give information on individual steps and reaction mechanism**
- **operate in millisecond time regime**

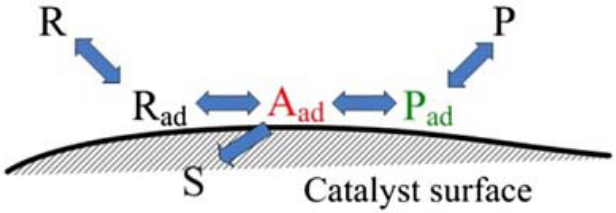
Key: High intensity of the beam in NSLS II allows to perform fast (10^{-3} –1 s) experiments with XRD, PDF and XAFS and match the response time of IR spectroscopy

DOE Distinguished Scientist Project:

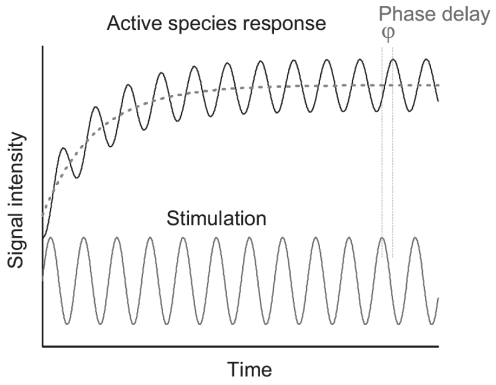
New Tools for Mechanistic Transient Studies
in Catalysis Science

Transient experiments

Transients **are introduced into a system by varying one or more state variables (p, T, flow)**

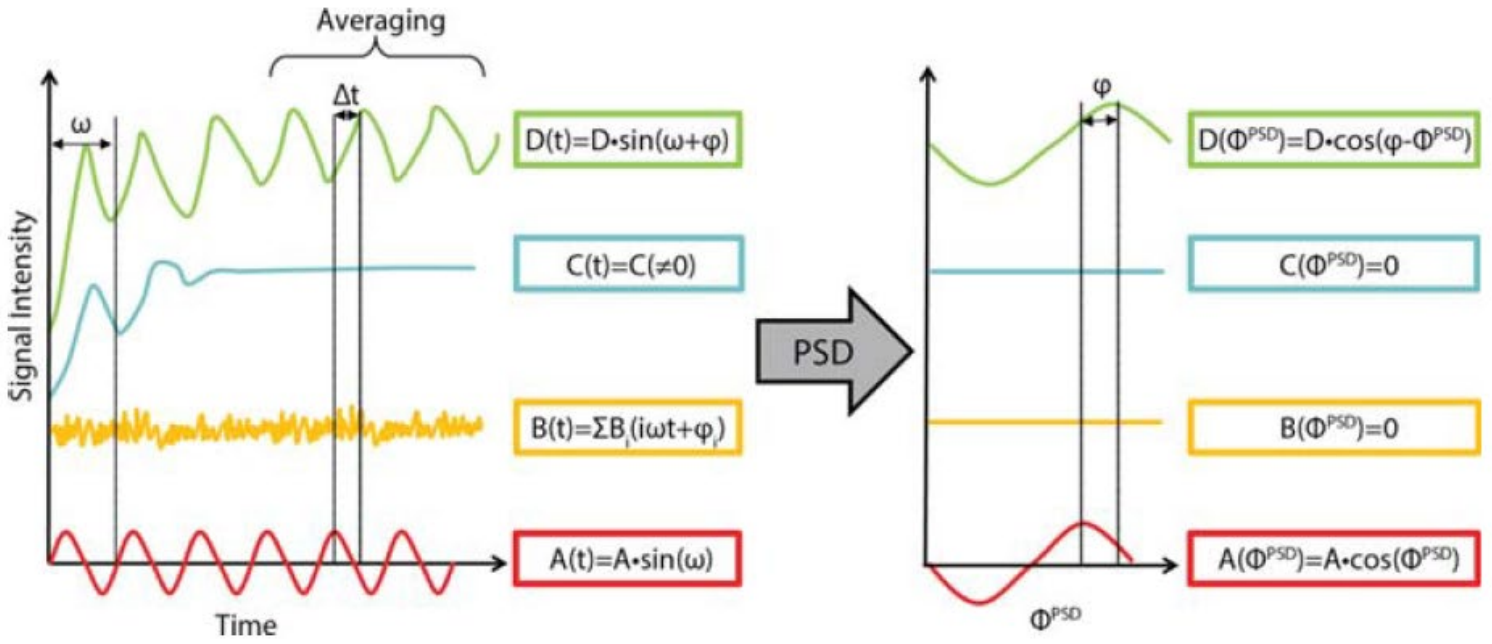


Transients produce changes in the chemical state of the catalyst and in the residence time of active spices



The response of the system tracks the periodicity of the transients

Urukawa et al, Chem Eng Science, 63 (2008) 4902



introduce a perturbation (p,T)

see response of the system:

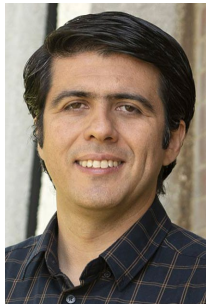
Variations in activity, catalyst structure and/or oxidation state

Key: High intensity of the beam in NSLS II allows to perform fast (10^{-3} –1 s) experiments with XRD, PDF and XAFS and match the response time of IR spectroscopy

Objective is to develop instrumentation for transient or pulse studies at beamlines of the NSLS II:

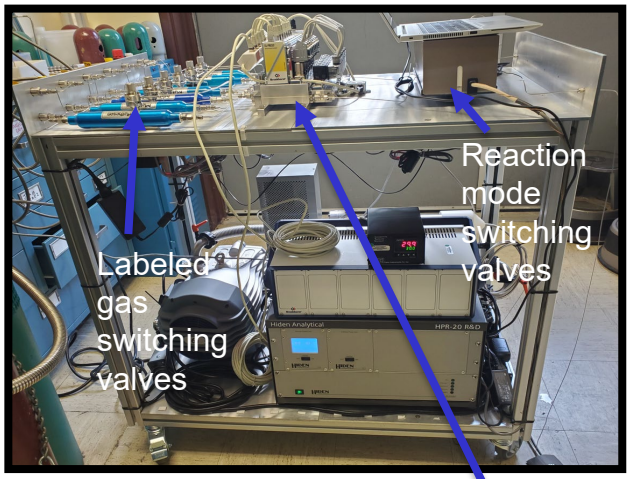
- ISS & QAS (technique: IR/XAFS)
- XPD2 (technique: IR/XRD & IR/PDF)
- IOS (technique: AP-XPS)

Instrumentation will be available for the BNL Catalysis Program and outside users

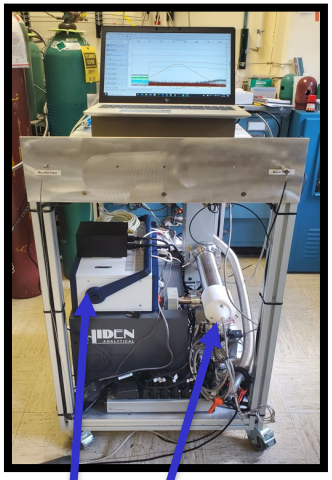


In the last year, Jorge Moncada (postdoc) has built an automatized transient /time resolved setup optimized for C1 Chemistry

Side view

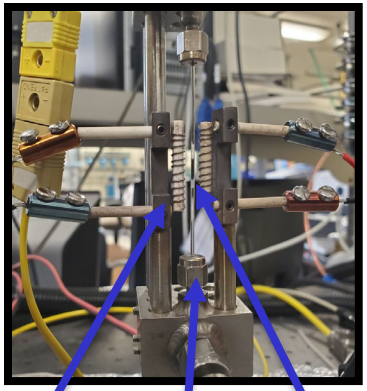


Front view



+

Reactor: Clausen Cell

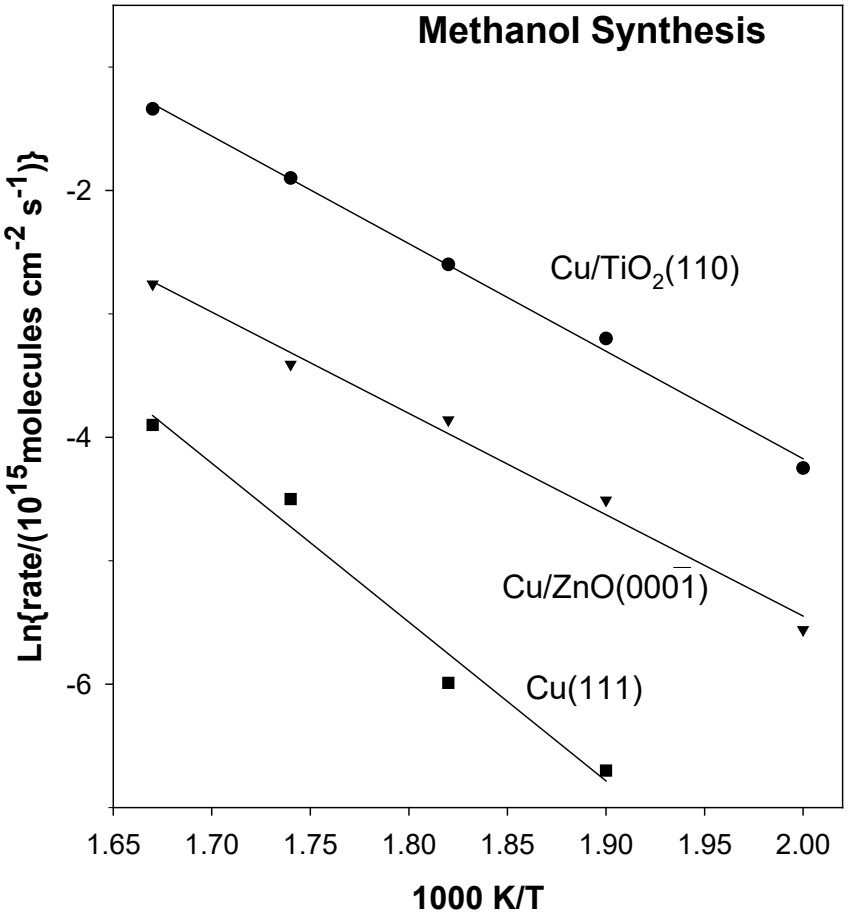


This portable unit will be taken to the NSLS II in 2022 to be used in operando studies with XRD, PDF and XAFS

Recent research on CO_2 hydrogenation:

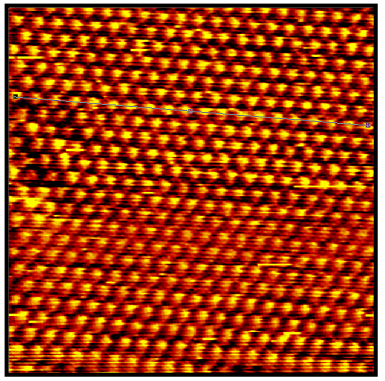
From model systems to powder catalysts
and transient studies

Metal- Oxide interfaces: CO_2 hydrogenation to methanol



$P(CO_2)$= 0.5 atm $P(H_2)$= 4.5 atm

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$



Cu(111)

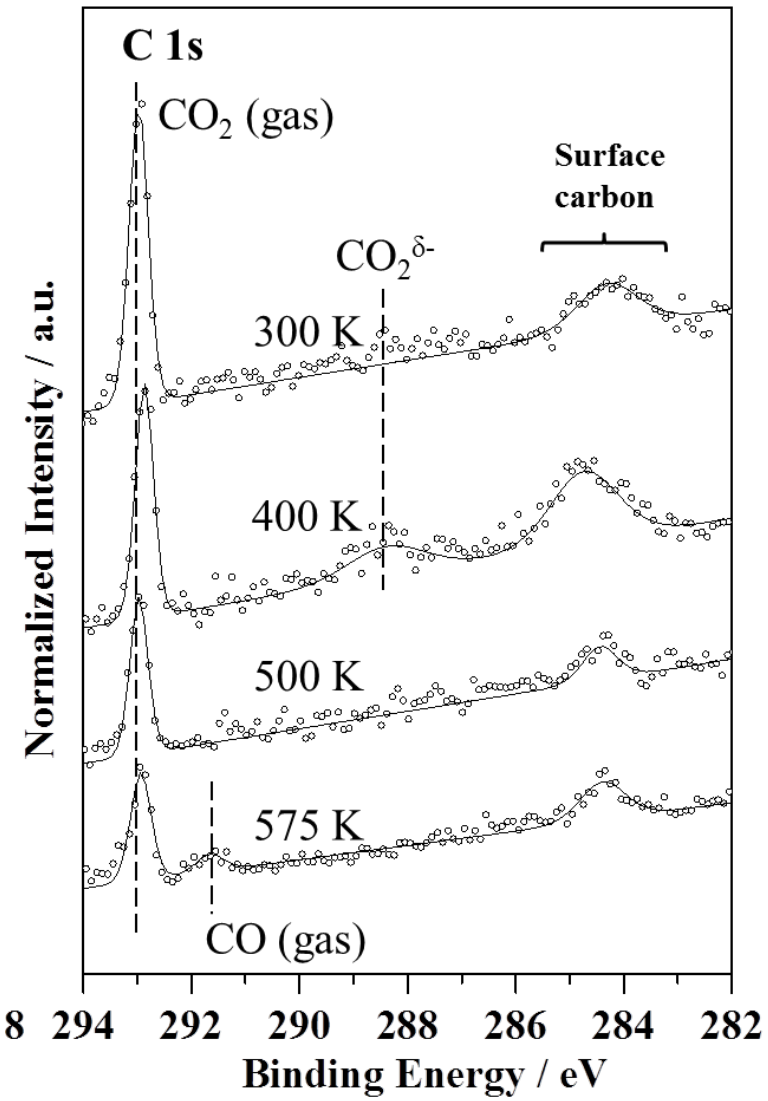
Pure Cu(111) is not a very good catalysts for CO_2 hydrogenation

Cu nanoparticles are more active than Cu(111) for the synthesis of methanol from CO_2 hydrogenation.

Kattel et al, Science 355 (2017) 1296

AP-XPS

On Cu(111)

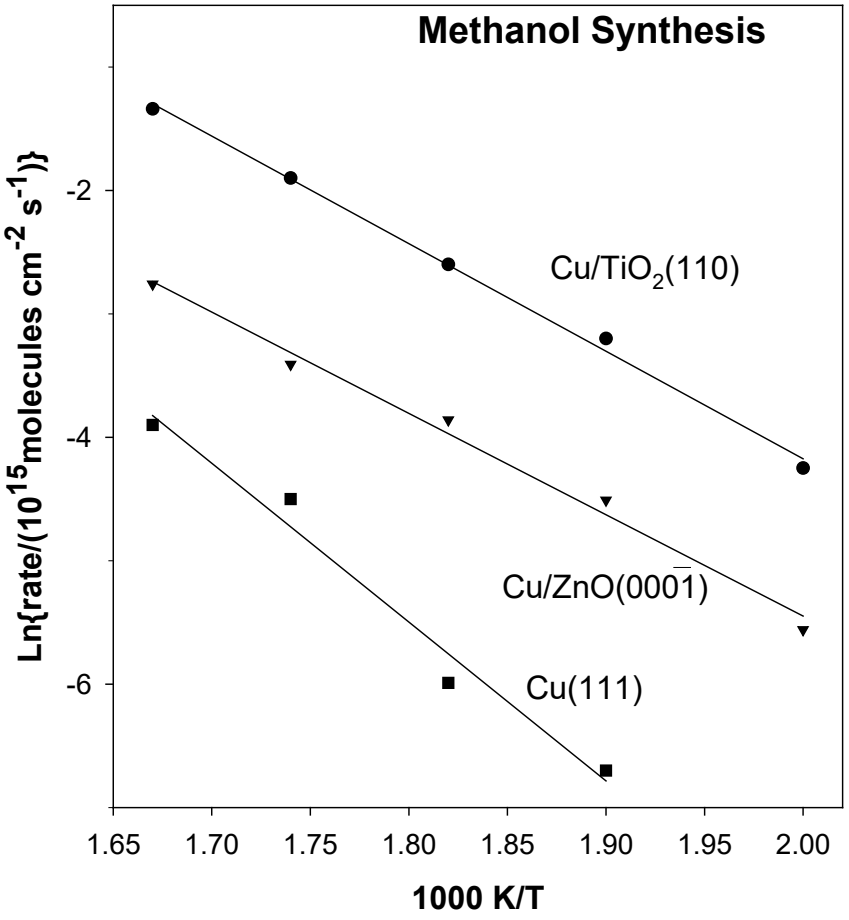


P= 50 mTorr CO_2, 200 mTorr H_2

Poor catalyst, only a small amount of adsorbed CO_2 on the surface.

Palomino et al, J Phys Chem B, 122 (2018) 794

Metal- Oxide interfaces: CO_2 hydrogenation to methanol



$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

Cu nanoparticles are more active than Cu(111) for the synthesis of methanol from CO_2 hydrogenation.

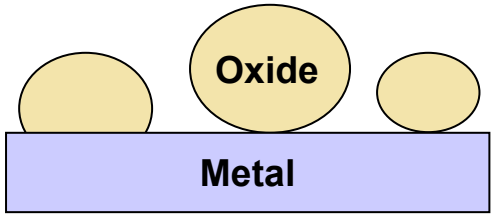
Background studies show that the oxide used as a support for Cu nanoparticles matters, with the catalytic activity increasing in the sequence:

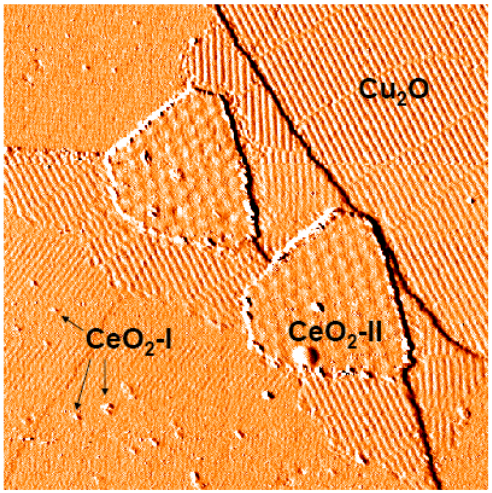
Cu < Cu/ZnO < Cu/TiO2

$P(CO_2)$= 0.5 atm $P(H_2)$= 4.5 atm

Yang, Liu, Rodriguez, White, Evans, PCCP, 12 (2010) 9909

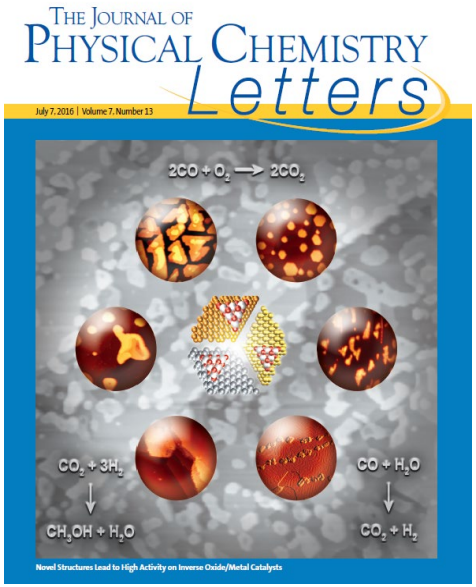
Nanocatalysis program at BNL: Preparation and characterization of highly active oxide/metal catalysts





150nm x 150nm

STM: $CeO_x/CuO_x/Cu(111)$



In an oxide/metal catalyst:

- **The oxide can have special structural and electronic properties**
- **One can use the oxide-metal interface in fundamental studies or technical applications**

Perspective article:
Rodriguez, Liu, Hrbek, Senanayake, Stacchiola, Graciani, Sanz, J. Phys. Chem. Lett. 2016, 7, 2627-2639

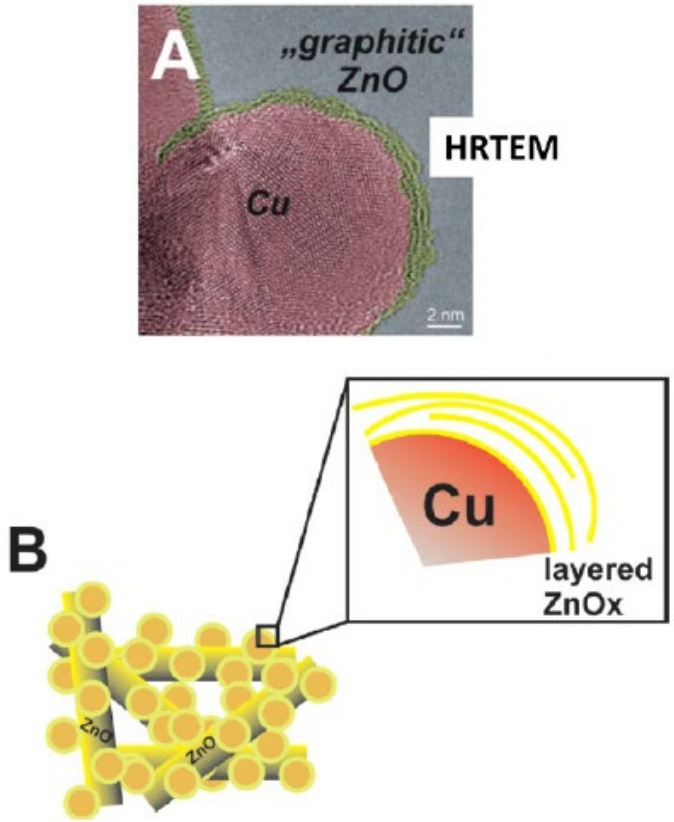


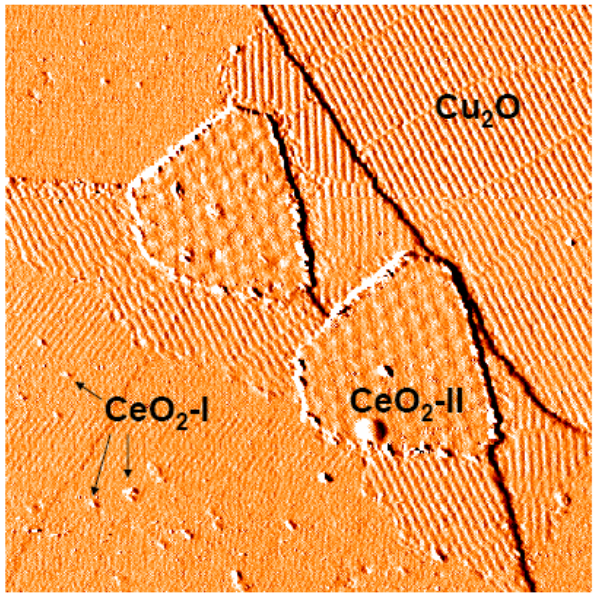
Figure 2. (A) HR-TEM image for a $Cu/ZnO/Al_2O_3$ catalyst after reduction in hydrogen. (B) Cartoon showing different components of a reduced $Cu/ZnO/Al_2O_3$ catalysts. Taken from ref 21. Copyright 2015 Wiley.

TEM studies for Cu/ZnO powder catalysts indicate that the active phase of the system consists of copper particles decorated with ZnO_x clusters

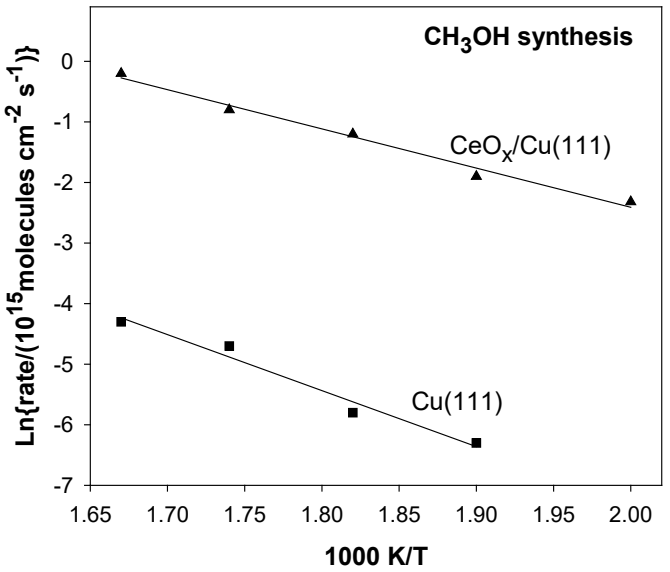
Active phase of the catalyst has an inverse oxide/metal configuration

Lunkenbein, Behrens, Schlogl et al. Angew Chem. Int. Ed. 54 (2015) 4544-4548

Methanol synthesis on CeOx/Cu(111)



150nm x 150nm



under reaction

Cu^{1+} → Cu^0

Ce^{4+} → Ce^{3+}

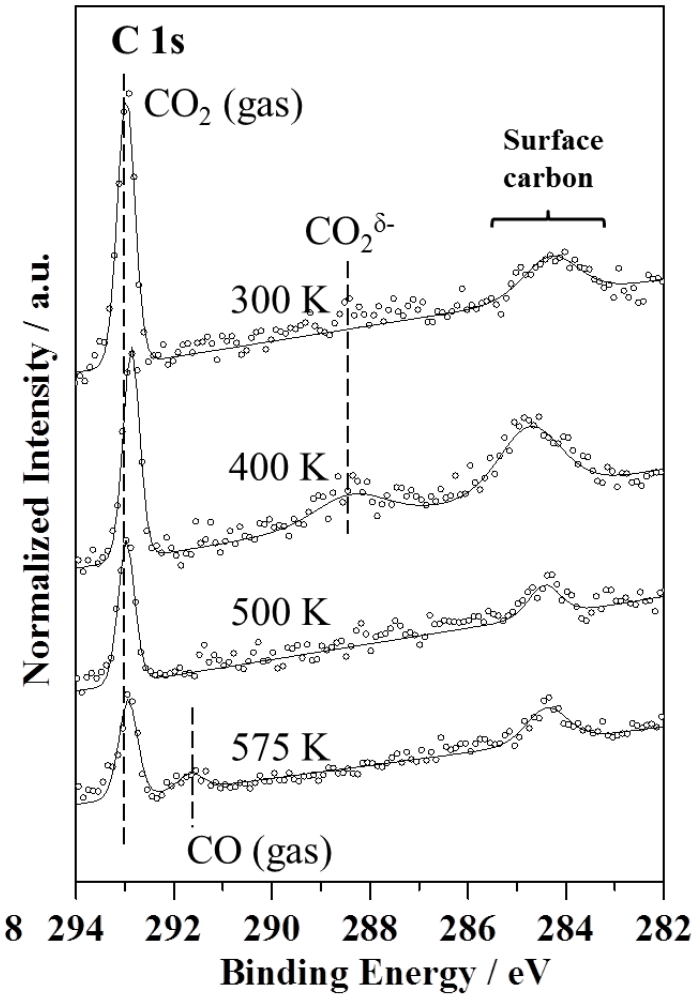
P(CO2)= 0.5 atm P(H2)= 4.5 atm
Top trace : 20% of Cu covered by ceria

The ceria nanoparticles enhance the reactivity of the copper surface, oxide plays active role

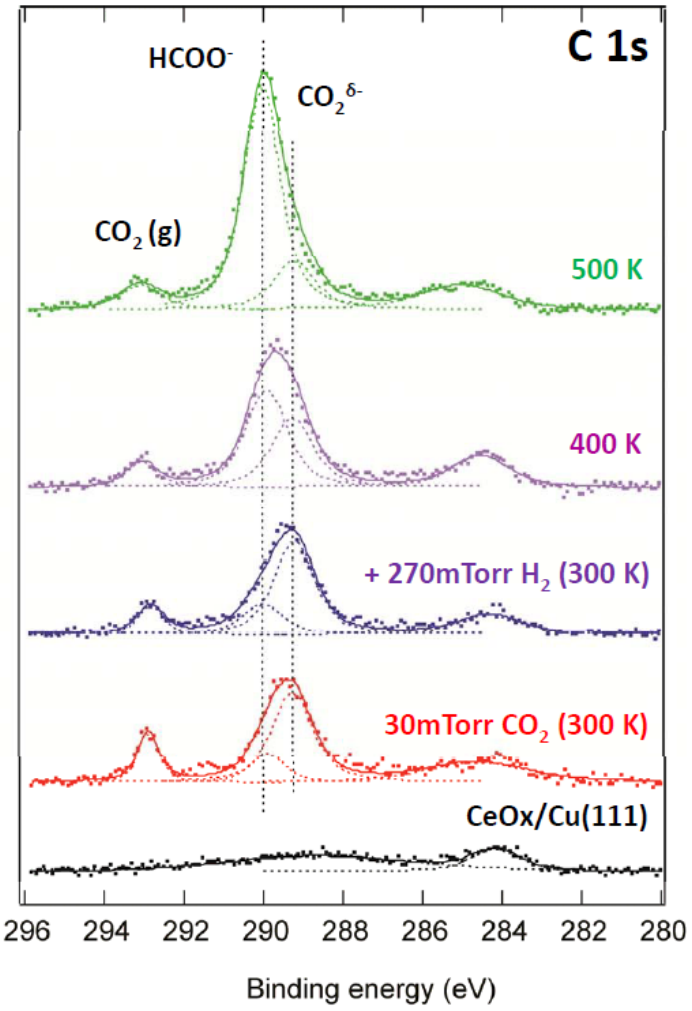
Graciani et al, Science 345 (2014) 546

AP-XPS: 30 mTorr CO_2 and 270 mTorr H_2

On Cu(111)



On CeO_x/Cu(111)

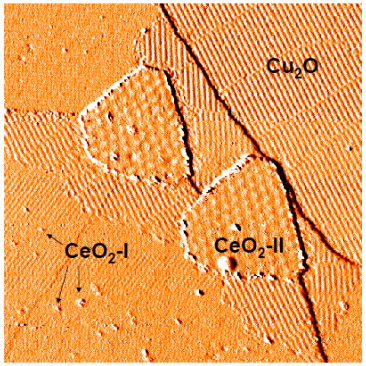


Senanayake et al, J Phys Chem C 120 (2016) 1778

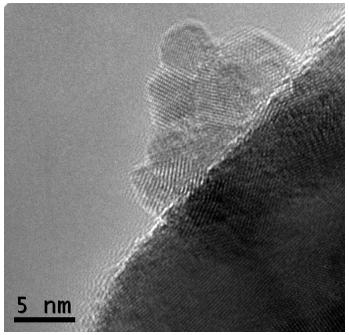
CO_2 hydrogenation catalyst engineered from model systems:

Model catalyst → Technical catalyst

$CeO_2/CuO_x/Cu(111)$ → CeO_2/CuO powder

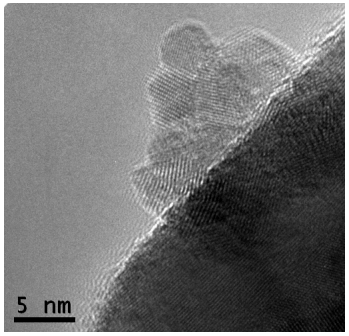


150nm x 150nm



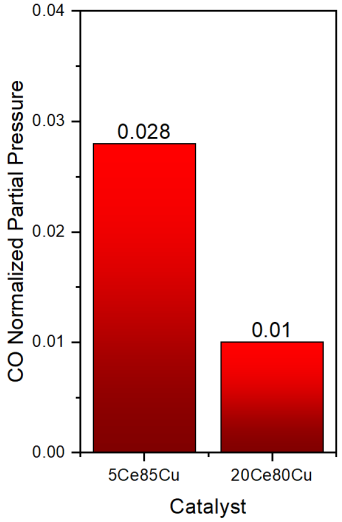
Rodriguez et al, J. Phys. Chem. Lett. 7 (2016) 2627

Start of transient studies for CeO_2/CuO powder

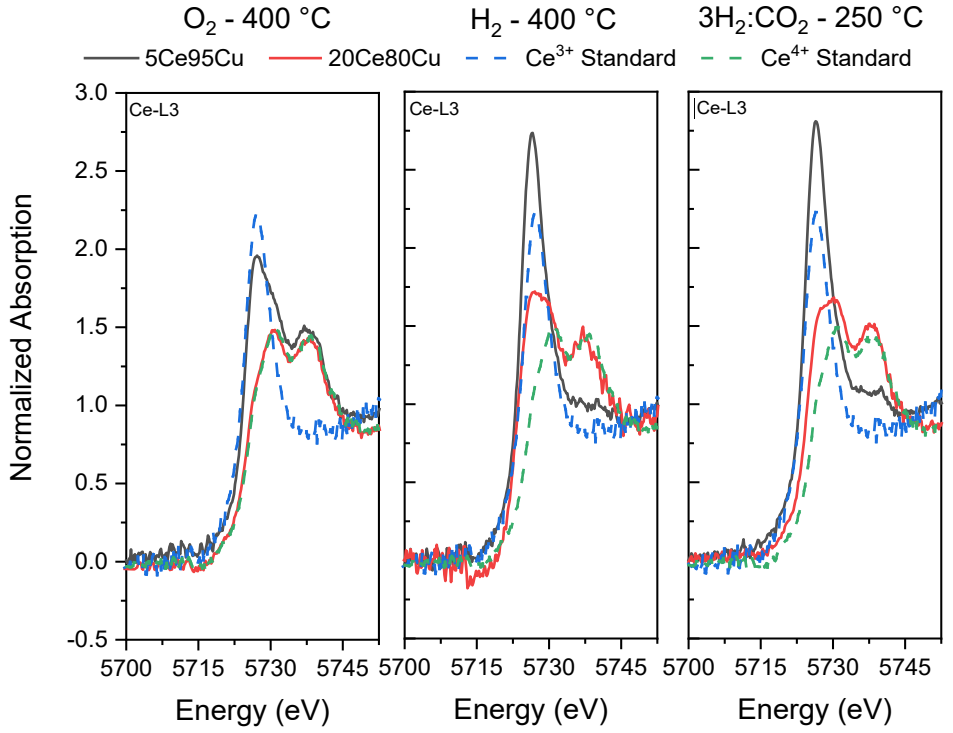


TEM: CeO_2/CuO

$CO_2 + H_2 \rightarrow CO + H_2O$



In-situ XANES: Ce L_{III} edge



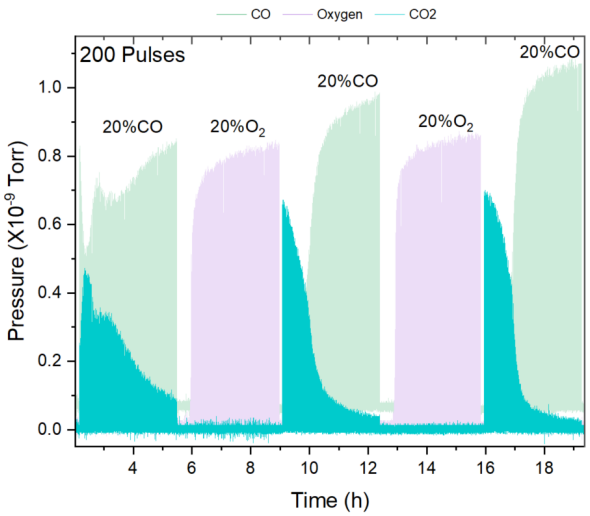
- Ce^{4+} transforms into Ce^{3+} in the presence of H_2 or CO_2/H_2

- The amount of Ce^{3+} correlates with catalytic activity

Results – redox studies in progress

Cycles for reduction and oxidation of CeO_2/CuO: CO + $0.5O_2$ → CO_2

Mass spectrometer (new instrument)



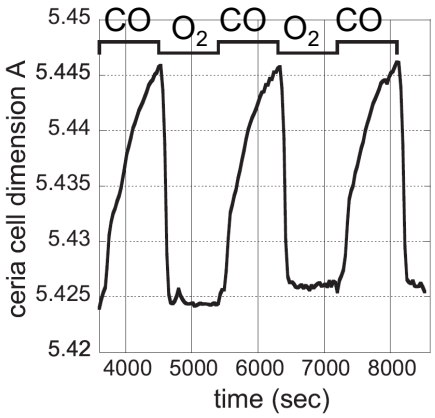
CO pulses:

- **CO(gas) + O-oxide → CO_2(gas) + Vacancies-oxide**

O_2 pulses:

- **O_2(gas) + 2Vacancies-oxide → O-oxide**

separate in-situ XRD studies



CO pulses:

- **Reduce CuO and CeO_2, creation of O vacancies and Ce^{3+} expanding the lattice in the oxide**

O_2 pulses:

- **Remove O vacancies and reduces oxide lattice**

Future work

- Develop instrumentation for transient or pulse studies at beamlines of the NSLS II:
  - ISS & QAS (technique: IR/XAFS)
  - XPD2 (technique: IR/XRD & IR/PDF)
  - IOS (technique: AP-XPS)

- Systematic transient studies exploring the behavior of CeO_2/CuO powders. Identify
  - active sites
  - reaction mechanism

  to optimize catalytic performance.

- **Collaborators:**

Transient studies: J Moncada, J Hanson

Development of in-situ techniques: J Hanson, J Hrbek, S Senanayake

CO2 Hydrogenation:

BNL: J Hrbek , S Senanayake, D Stacchiola, P Liu, J Hanson, M White, R Palomino, S Kattel, S Ma, X Wang, F Yang, D Grinter, M Mahapatra

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