Catalysis for Advanced Fuel Synthesis and Energy Conversion

Manipulation of C-H and C-O Bonds

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Internal contributors to the Chemistry Catalysis Program:

Principal investigators

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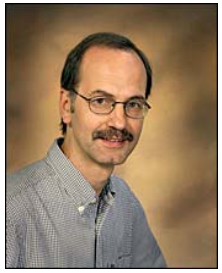

White

Postdocs

Palomino

Mahapatra

Liu

Grinter

Students

Luo

Vovchok

Zhang

Heterogeneous catalysis subtasks

Subtask 1

Activation and conversion of C-H bonds

- Development of in-situ techniques
- Methane conversion
- Steam reforming of alcohols

Subtask 2

Activation and conversion of C-O bonds

- CO_2 hydrogenation to alcohols
- Water-gas shift reaction

Nanostructure materials for catalysis

Subtask 3

- Well-defined mixed –metal oxide catalysts
- Inverse oxide/metal, carbide/metal and sulfide/metal catalysts

Subtasks 1 and 2 Focus: Manipulation of C-H and C-O bonds

Our objective is to obtain a fundamental understanding of catalytic processes associated with the manipulation of C-H and C-O bonds:

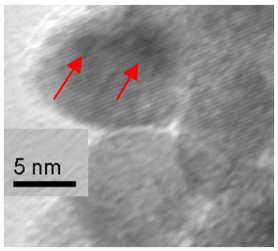
(i) Methane activation and conversion

(ii) The production of non-conventional fuels such as C1-C4 alcohols from CO_2/CO hydrogenation, and

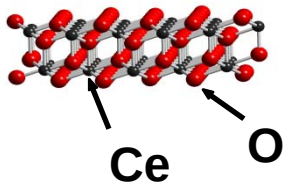
(iii) The production of hydrogen through ethanol steam reforming and the water-gas shift.

Manipulation of C-H and C-O bonds

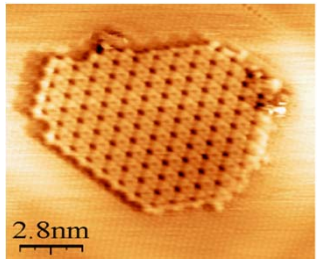
We work with powders and single crystals of metals and their compounds (oxides, carbides, sulfides and phosphides).



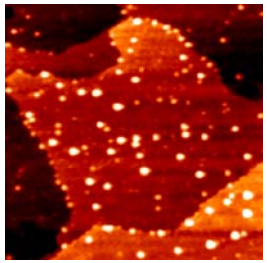
TEM: Au-CeO_2 powder



Slab model CeO_2(111)



STM: RuS_2 on Au(111)

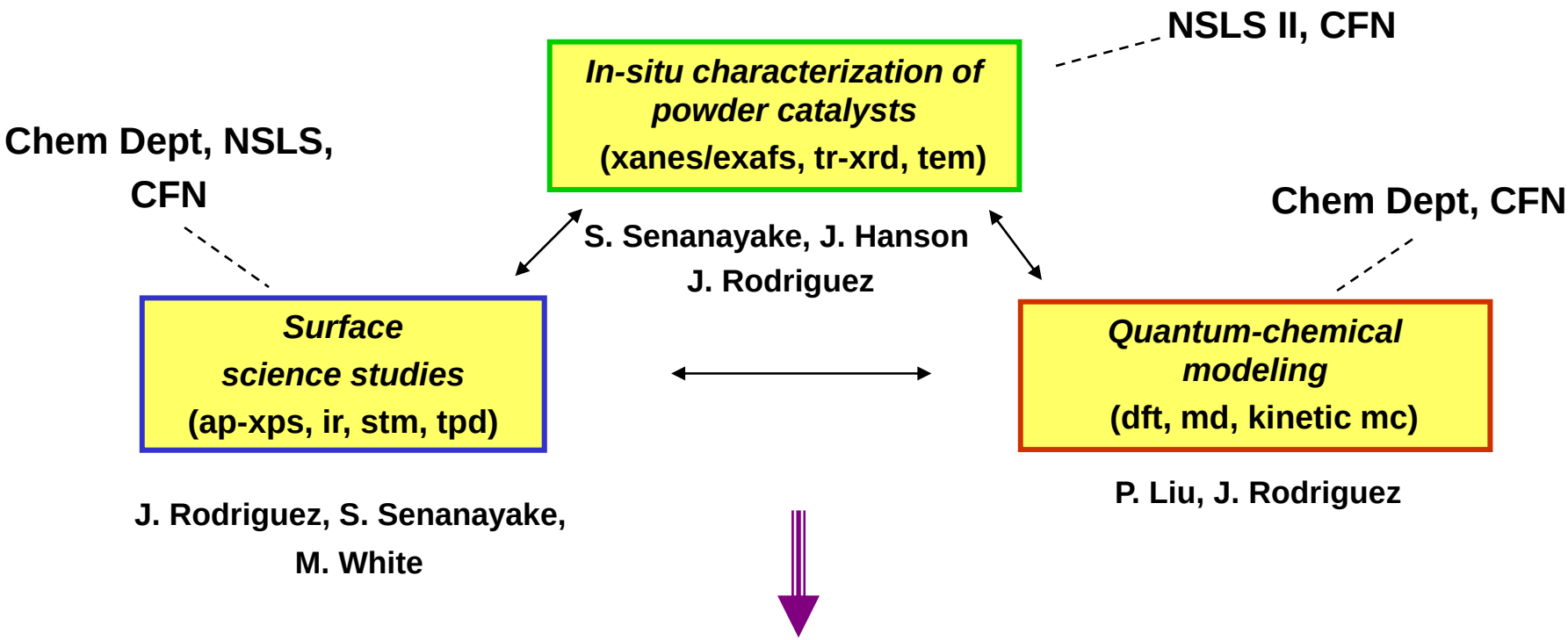


STM: Cu on TiO_2(110)

The phenomena responsible for the catalytic properties of these materials are not well understood:

- **active phase?**
- **role of ensemble and ligand effects?**
- **size effects?**
- **reaction mechanism?**

Integrated approach to catalysis:



Fundamental understanding of the behavior of active sites:

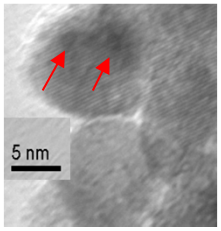
Rational design of better catalysts

NSLS I

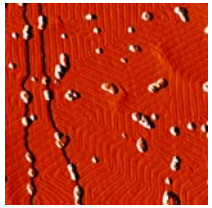
NSLS II

Challenge: **We need to characterize chemical transformations occurring in a wide range of materials and reaction times**

TEM image
Au/CeO_2



powder catalyst



STM image
for CeO_x/Au(111)

model single crystal

Multitechnique:

(XAFS, XRD, PDF, XFS/XRD, IR/XAFS)

Multitechnique:

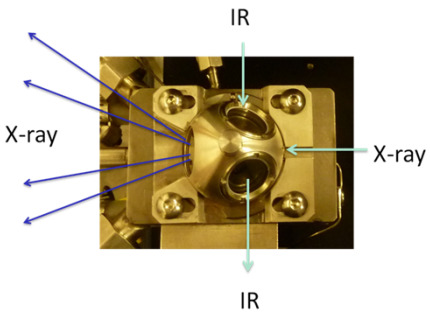
(PE, LEEM/PEEM, NEXAFS)

Strong interest in the development of techniques for *in-situ* characterization of structural, electronic and chemical properties

Partner Users in several beamlines, collaboration with Synchrotron Catalysis Consortium

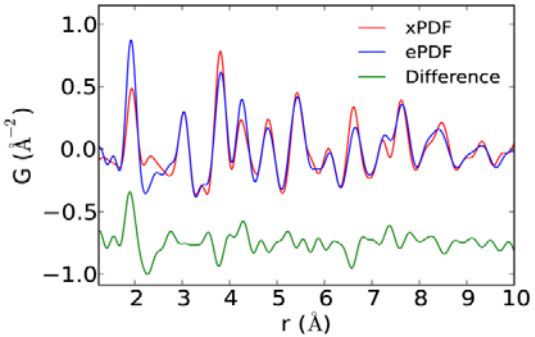
Catalysis at the NSLS-II: Unique tools for studying relationships between structure and reactivity

Combined XRD or XAFS with IR



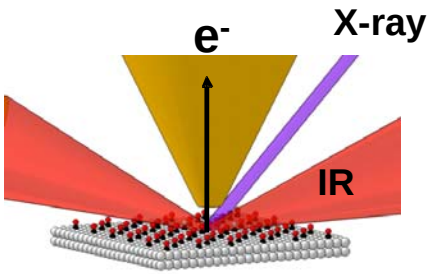
XPD, QAS, ISS beamlines

In-situ X-ray and electron PDF



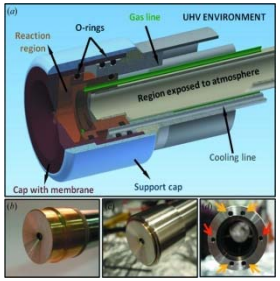
XPD-2 beamline and ETEM at CFN

AP-XPS + IR



CSX-2 beamline

Soft X-ray absorption

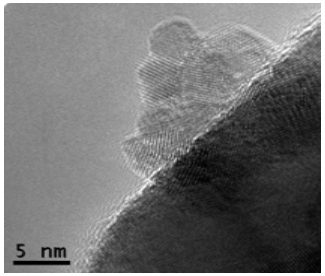


CSX-2 beamline

Studies with *In-situ* XRD, PDF and XAFS indicate that catalysts are dynamic entities that evolve under WGS reaction conditions

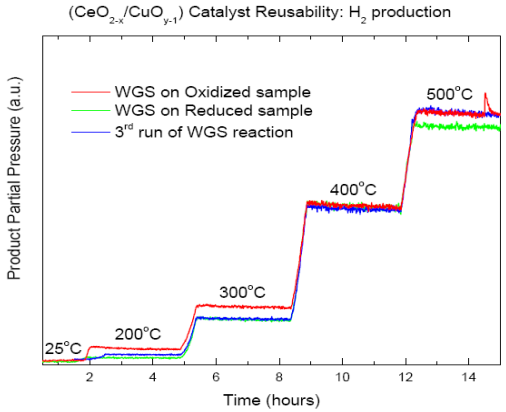
Water-gas shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$) on CeO_X/CuO

TEM

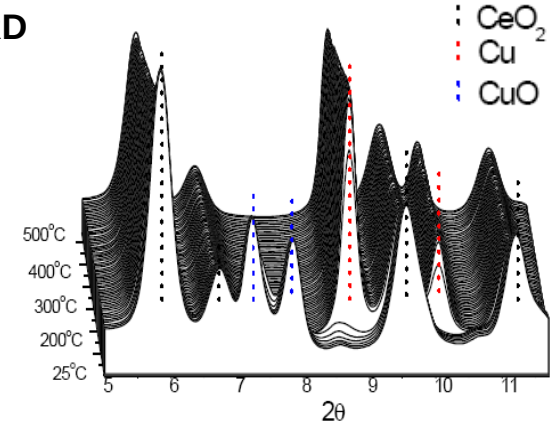


room temperature

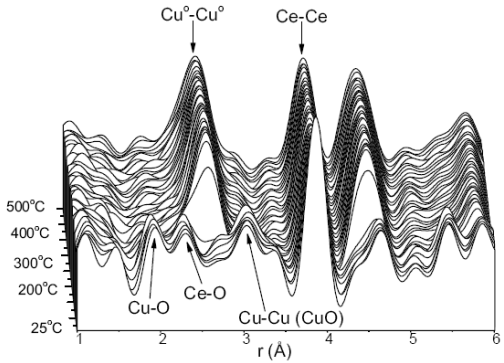
Activity



XRD



PDF



$CeO_2/CuO \rightarrow CeO_x/Cu$

Catalyst is a dynamic entity that changes under reaction

- Rodriguez, Hanson, Senanayake, Stacchiola, Phys. Chem. Chem. Phys. 15 (2013) 12004
- Rodriguez, Hanson et al, J. Phys. Chem. C, 114 (2010) 3580

Scientific strategy: **Use oxide and carbide supports to modify the reactivity of metals**

- **Metal-oxide interfaces**
  - **Ethanol steam reforming (ST1)**
  - **Methane conversion (ST1)**
  - **Water-gas shift reaction (ST2)**
  - **CO_2 hydrogenation to methanol (ST2)**

- **Metal-carbide interfaces**
  - **Water-gas shift reaction (ST2)**
  - **CO_2 hydrogenation to methanol (ST2)**

ST1: C-H bond conversion

ST2: C-O bond conversion

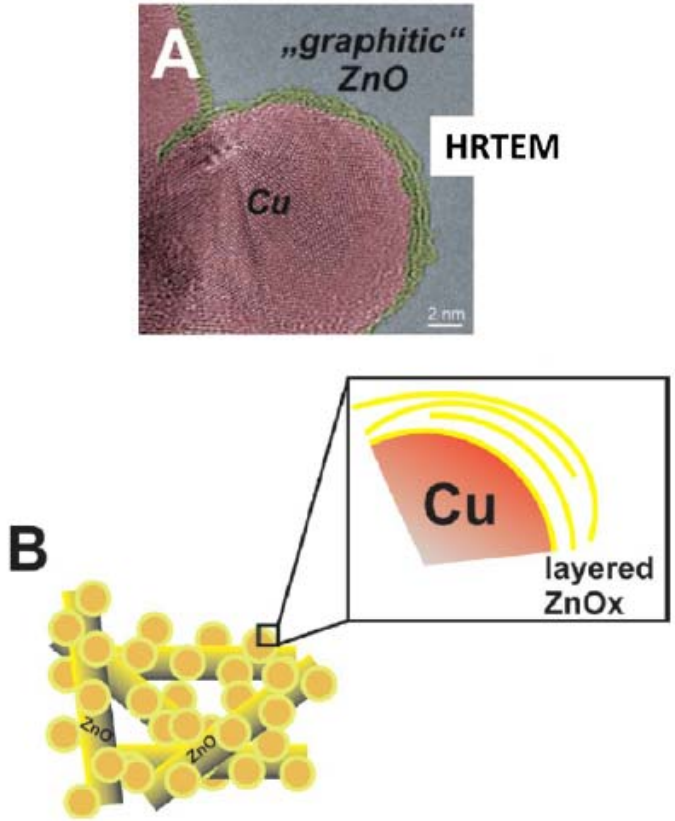
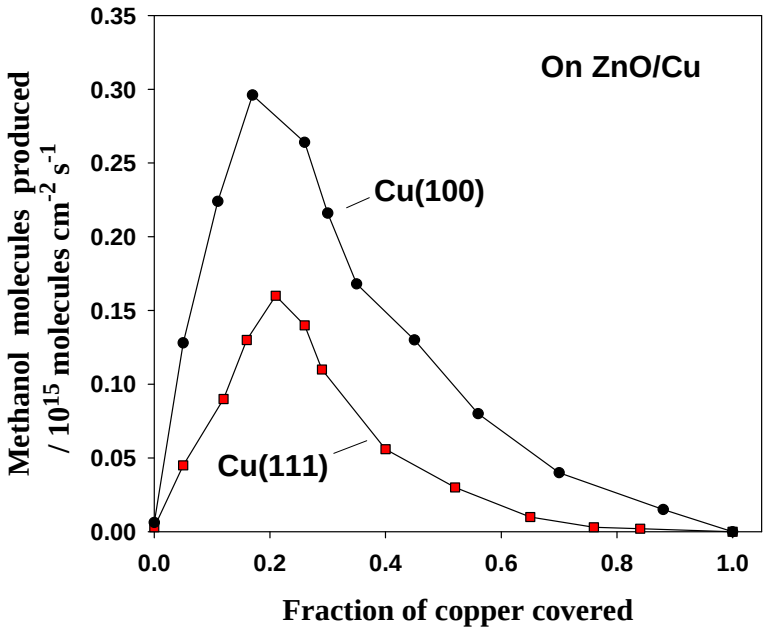


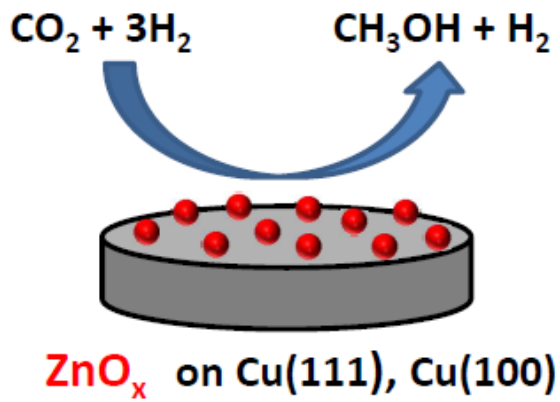
Figure 2. (A) HR-TEM image for a $Cu/ZnO/Al_2O_3$ catalyst after reduction in hydrogen. (B) Cartoon showing different components of a reduced $Cu/ZnO/Al_2O_3$ catalysts. Taken from ref 21. Copyright 2015 Wiley.

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



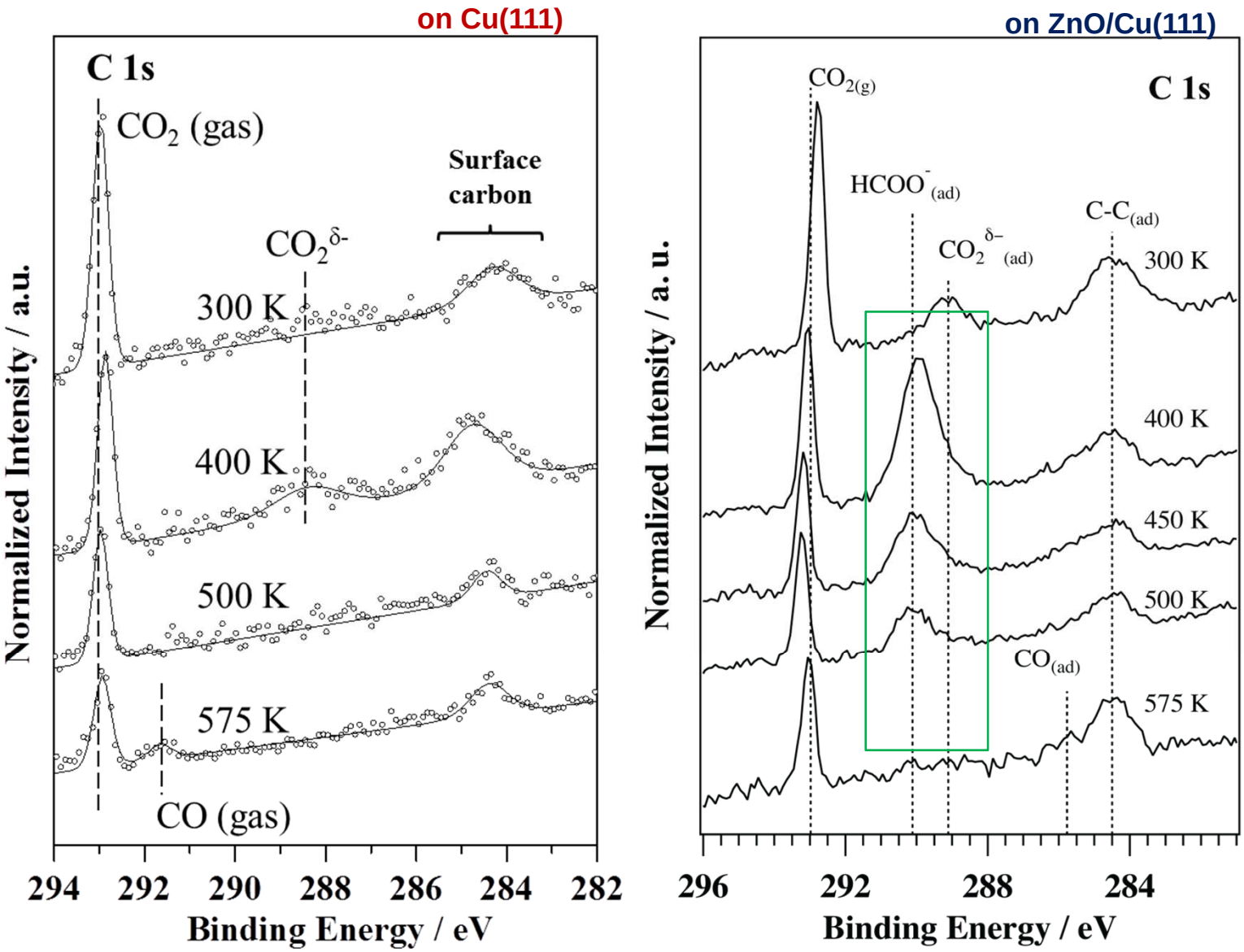


The creation of a metal-oxide interface enhances the rate for CO_2 hydrogenation to methanol

The nanoparticles of ZnO have specific electronic properties not seen for bulk ZnO (synchrotron data and DFT calculations)

Rodriguez et al, Science, 355, 1296-1299 (2017).

CSX-2: AP-XPS, 100 mTorr of CO_2 and 500 mTorr of H_2



New intermediate appears at the ZnO-copper interface

Major achievements of Subtask-2 in the last three-years

Catalytic Manipulation of C-O bonds

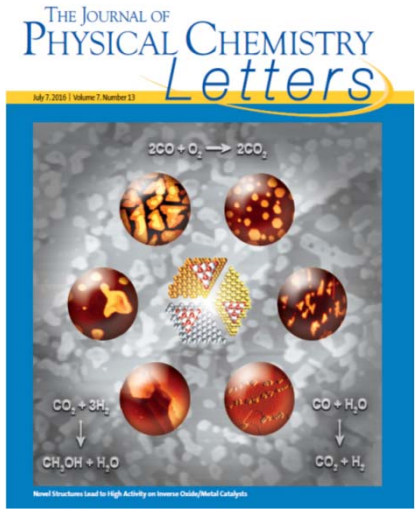
- Discovery of the important role played by metal-support interactions in active catalysts for the water-gas shift and CO_2 hydrogenation.

- Design of metal-oxide, metal-carbide, and metal-sulfide interfaces active as catalysts for the water-gas shift and CO_2 hydrogenation.

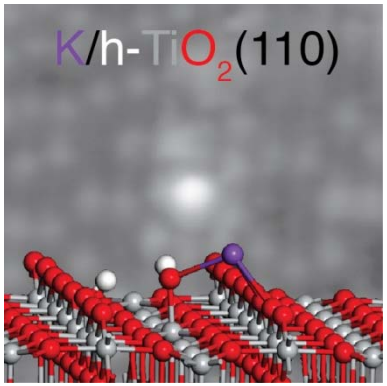
- Identification of HOCO as a key intermediate for the water-gas shift.

- *Operando* studies showed the dynamic nature of metal/oxide and metal/carbide catalysts during the water-gas shift and C-O conversion

- Discovery of the high surface mobility of K as a promoter of the activity of catalysts used for the water-gas shift and CO_2 hydrogenation.



C-O conversion on Inverse catalysts



Subtask 2 was the intellectual leader for 31 publications. 2 in *Science*, 3 in *Angew Chem*, 2 in *JACS*, 3 in *ACS Catal*., 3 in *J. Phys. Chem. C, 2* in *Accounts of Chem. Res.* 1 in *J. Catal*., and 3 in *Phys. Chem. Chem. Phys*. Four invited review articles and book chapters.