STRUCTURE AND ELECTRONIC PROPERTIES OF NI NANOPARTICLES DEPOSITED ON CERIA THIN FILMS

Ching-Rong "Ada" Chung

Mentor: Dr. Jing Zhou

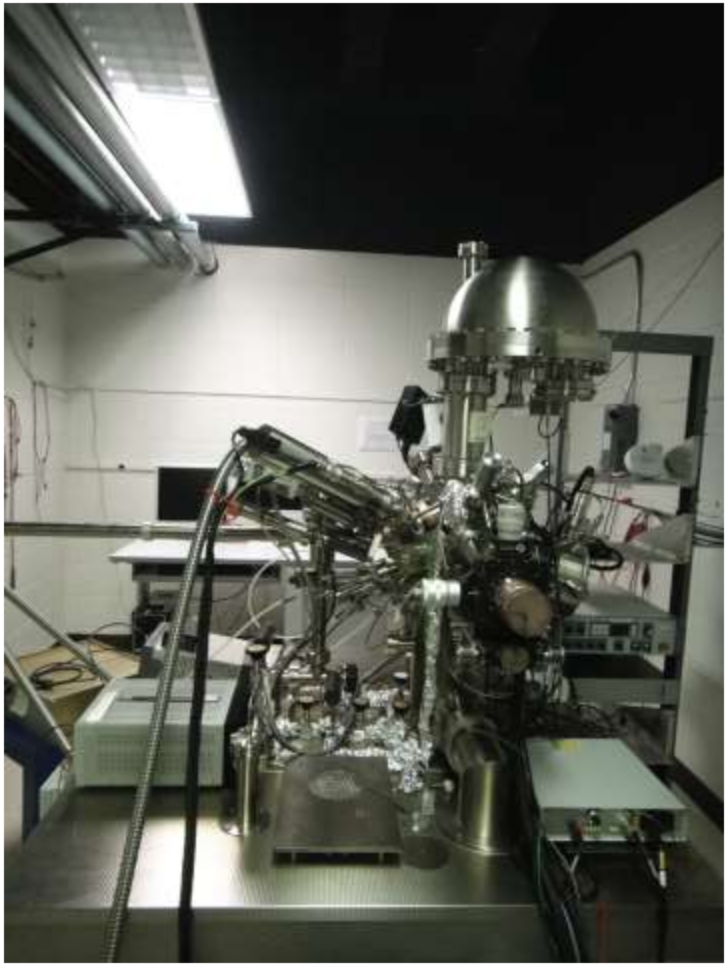
Department of Chemistry

University of Wyoming

Sponsored by EPSCoR Program

Overview

- Introduction
- Experimental Approach
- X-Ray Photoelectron Spectroscopy (XPS) Results
- Scanning Tunneling Microscopy (STM) Results



Ni with Ceria Support Creates Ecofriendly Energy Resources

Ethanol as fuels → + H_2O → **Ni/Ceria** Steam Reforming Unit → H_2, CO → Purifying Unit → H_2

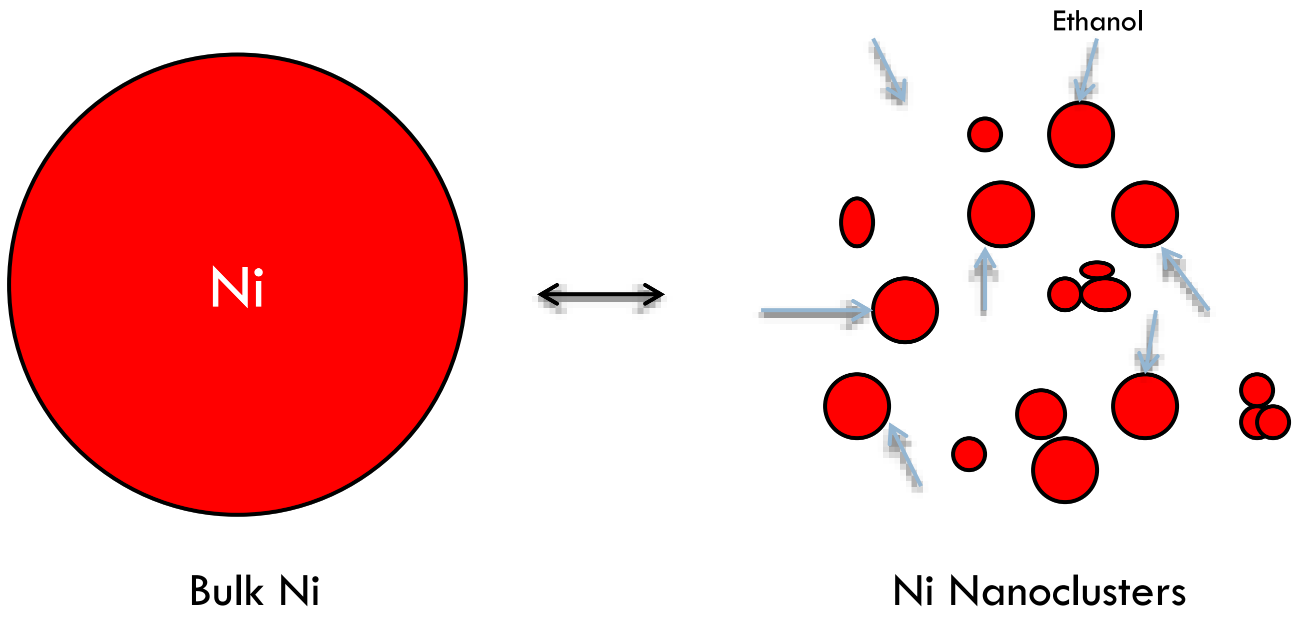
- Ni is a good catalyst
  - Inexpensive
  - Readily available
  - Highly Active
- But the system is not well understood

NASA uses hydrogen fuel to launch the space shuttles. Credit: NASA

+ **others**

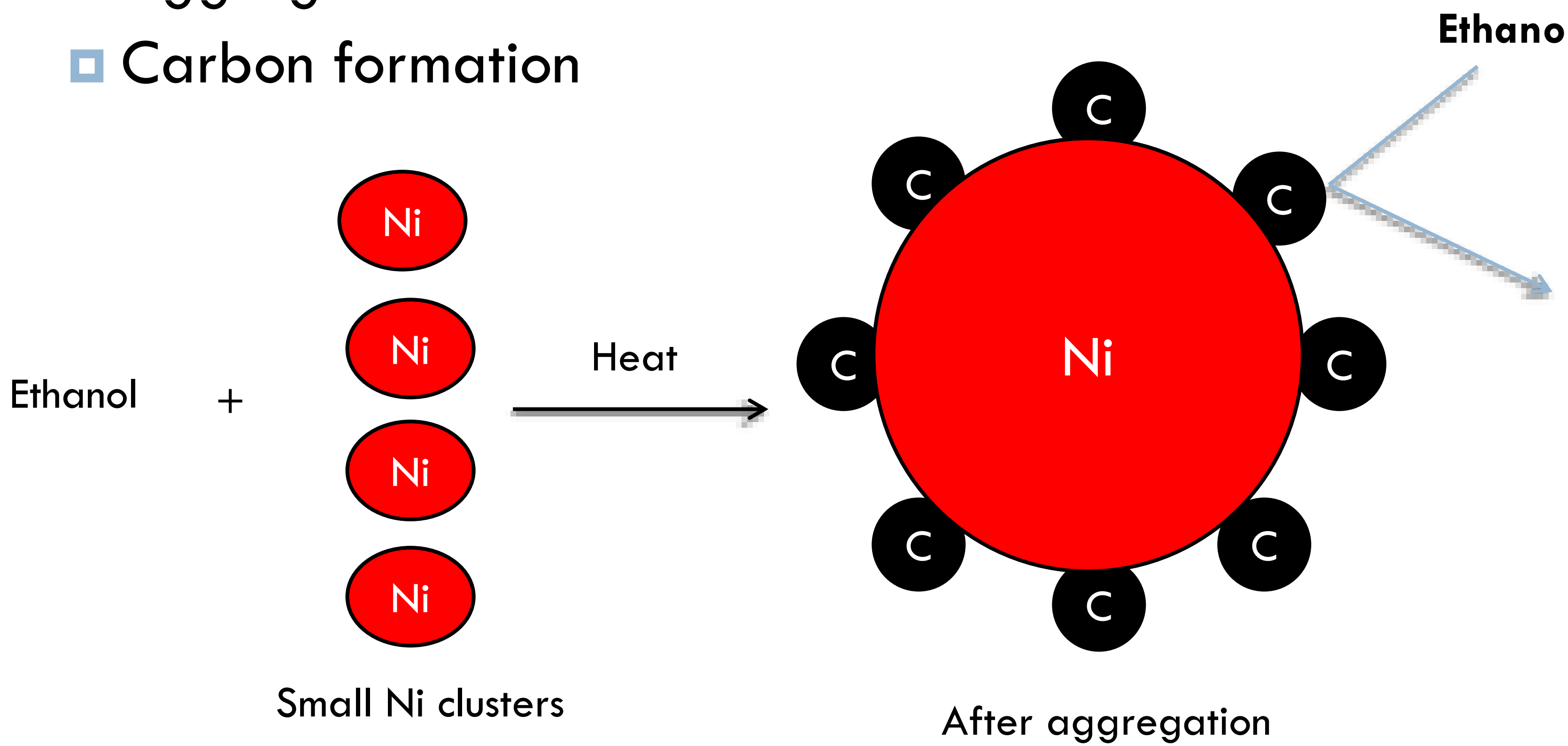
Size and Structure Do Matter

- Ni nanoparticle can increase the reactivity
  - Larger surface areas = Higher reactivity
- Structures of Ni can affect the reactivity



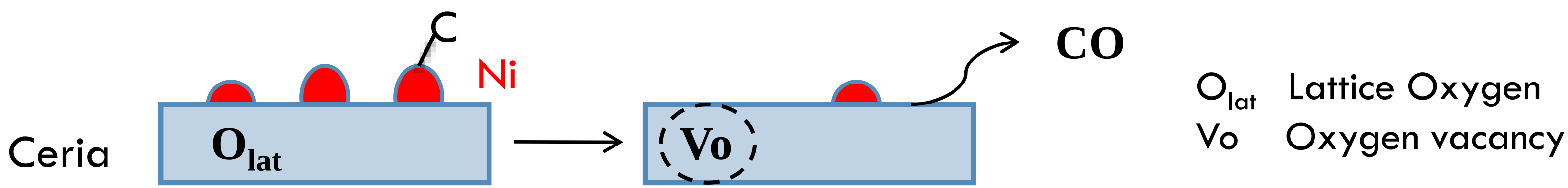
Problems of Using Pure Ni as the Catalyst

- Ni becomes deactivated
  - Aggregation
  - Carbon formation

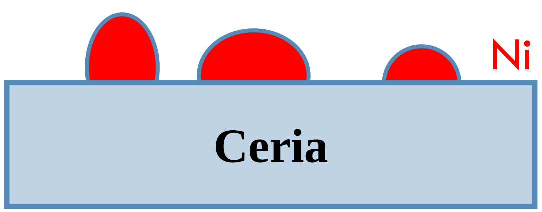


Ceria Support Provides a Potential Solution

- Ceria is reducible: $Ce^{4+} \longleftrightarrow Ce^{3+}$
- Ceria: CeO_2, Ce_2O_3, mixture of the two
- Oxidized Ceria: CeO_2
- Reduced Ceria: CeO_x (2<x<1.5)
- Ceria can eliminate carbon deposition on Ni



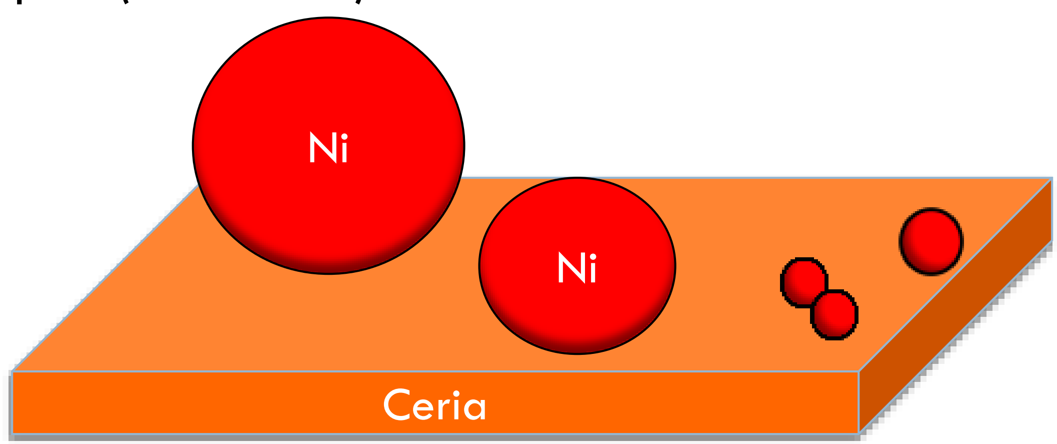
- Ceria can inhibit aggregation of Ni



Experimental Approach

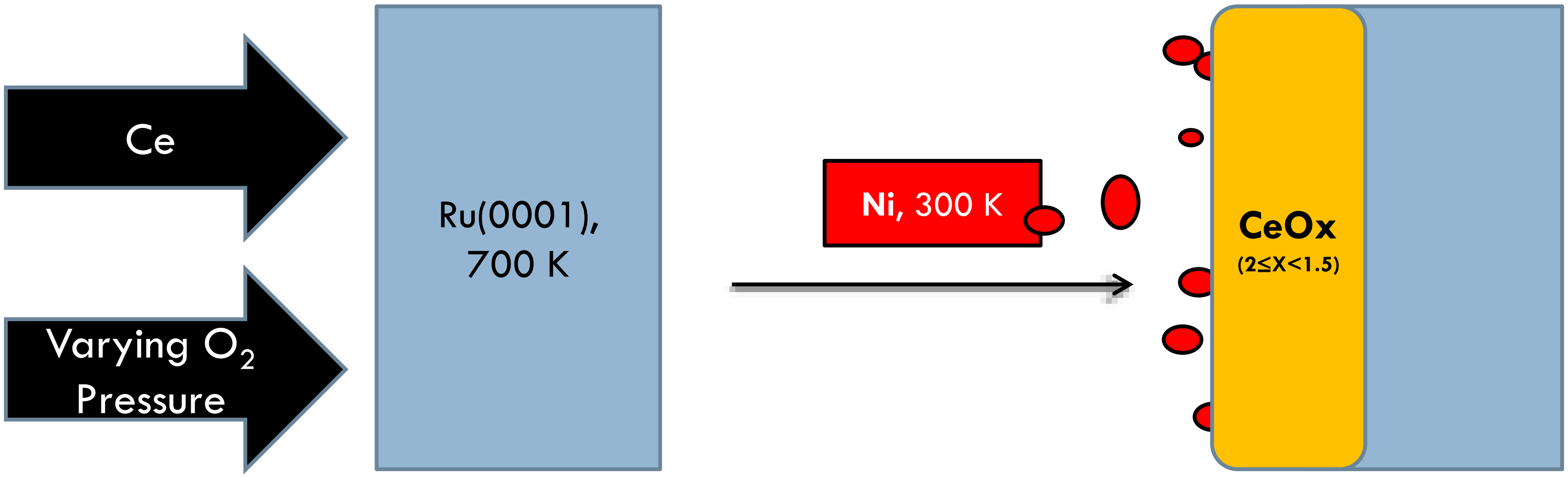
1. **Preparation of Ceria Supported of Ni**
2. **Structure and Electronic Characterization**
3. Ethanol Chemistry

- Ni catalytic reactivity can be affected by
  - Redox properties of ceria support (Ce^{4+}, Ce^{3+})
  - Ni and ceria interaction
  - Size
  - Structure

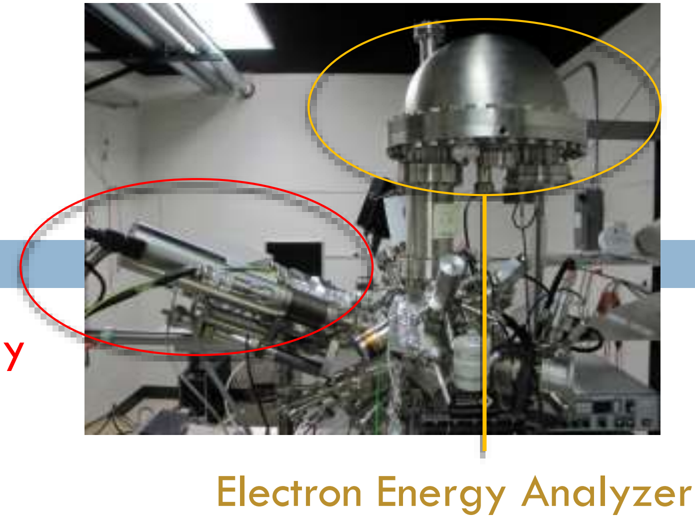


Preparation of Ceria and Deposition of Ni particles

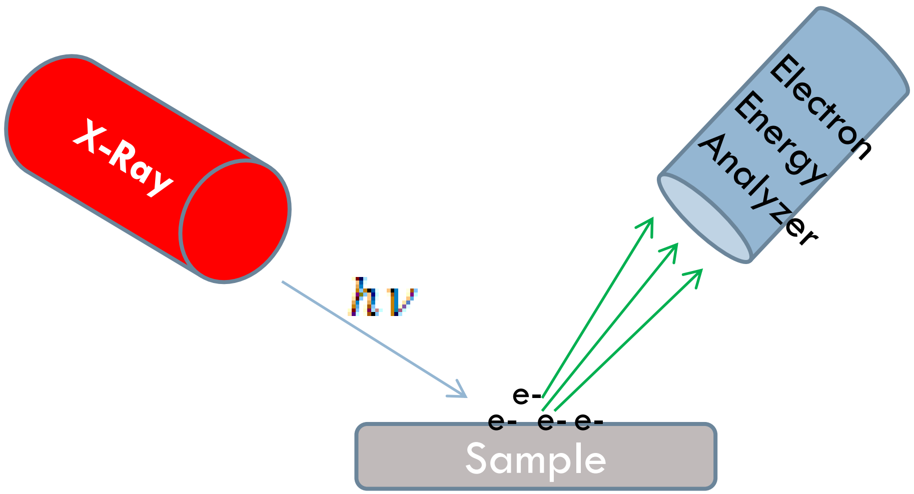
- Two types of ceria:
  - Oxidized ceria, CeO_2
  - Reduced ceria, CeO_x
- Ultra high Vacuum Condition: pressure: 10^{-11} Torr

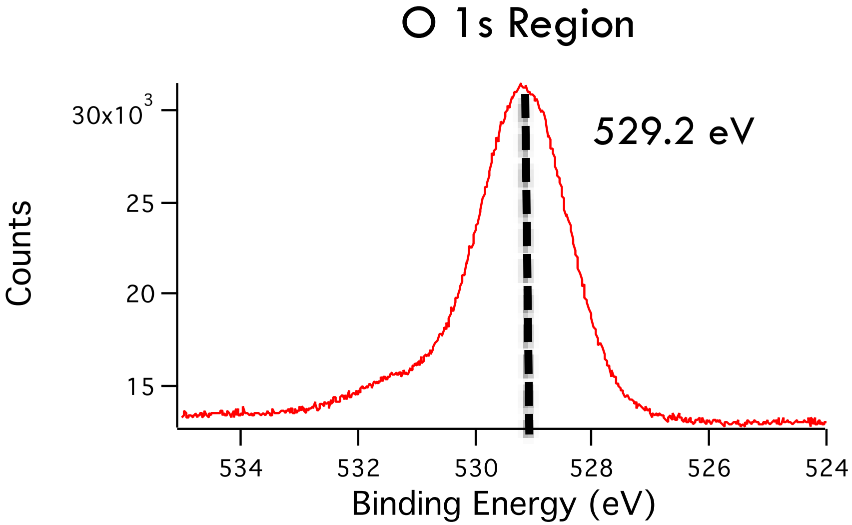


Basic Principle of XPS

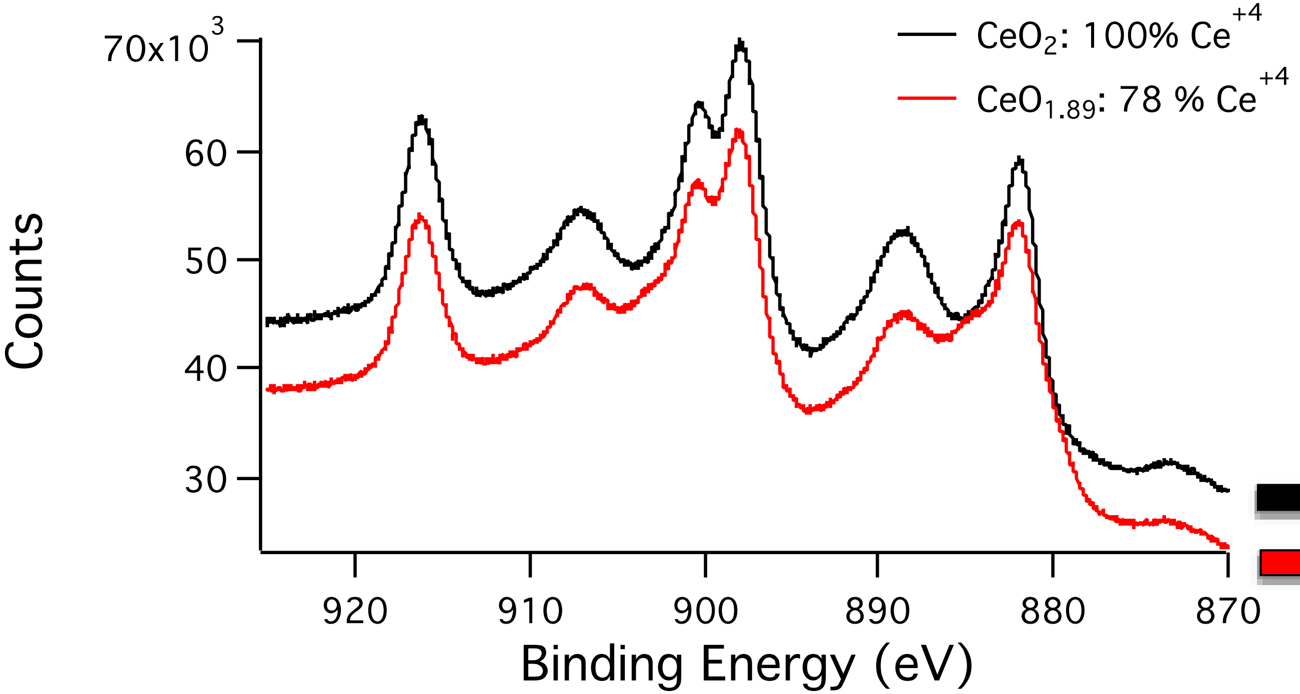


- Utilizes photoelectric effect
- Binding Energy = Energy of X-Ray (hv) – Kinetic Energy (KE)
- Provides "finger print " identity and the oxidation state of a sample





X-Ray Photoelectron Spectroscopy of Ce 3d

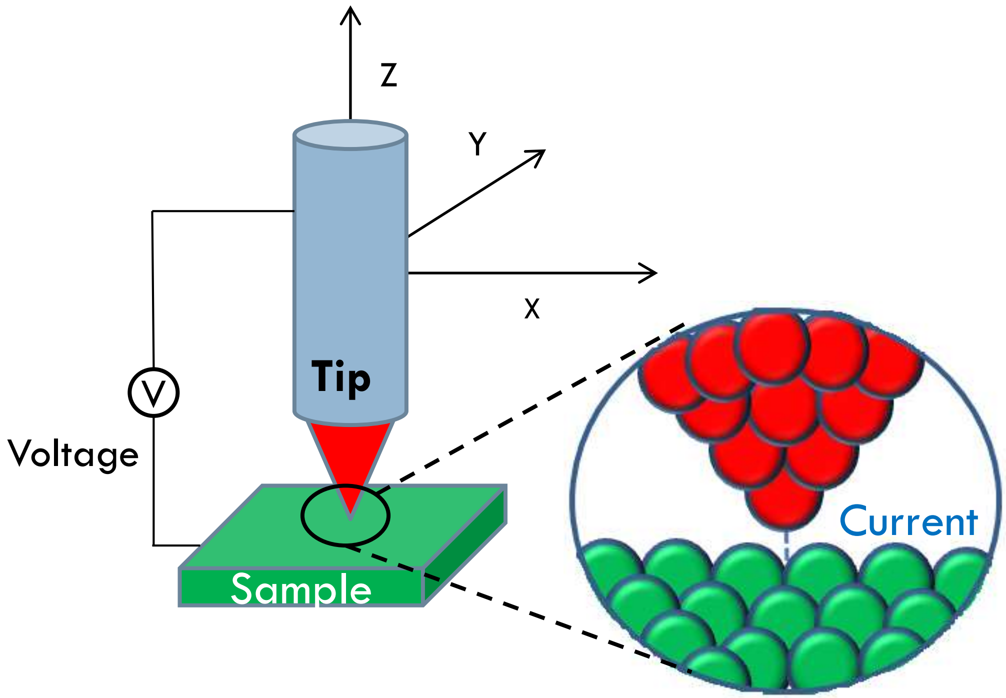


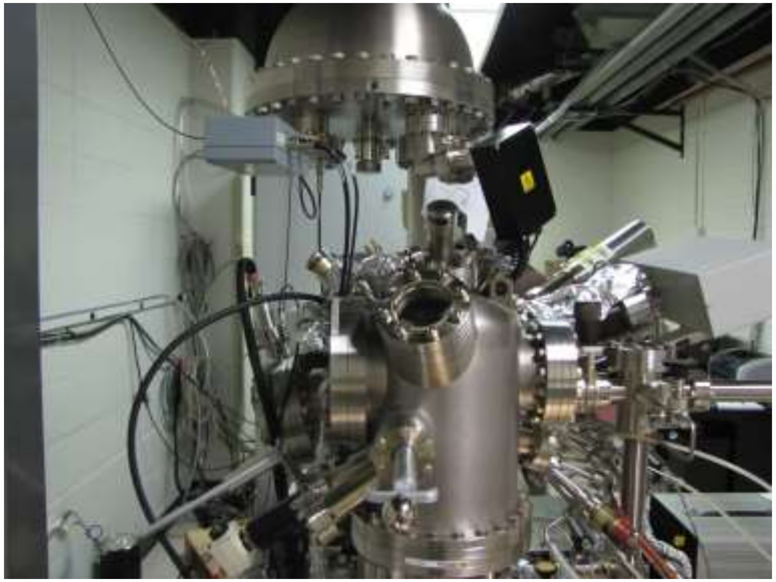
Oxygen Pressure:
2 x 10^{-7} Torr

Oxygen Pressure:
8 x 10^{-8} Torr

Basic Principle of Scanning Tunneling Microscopy

- Requires a sharp metal probe, a conductive sample, voltage supply, and a constant feedback loop
- Generate atomic resolution images of the surface

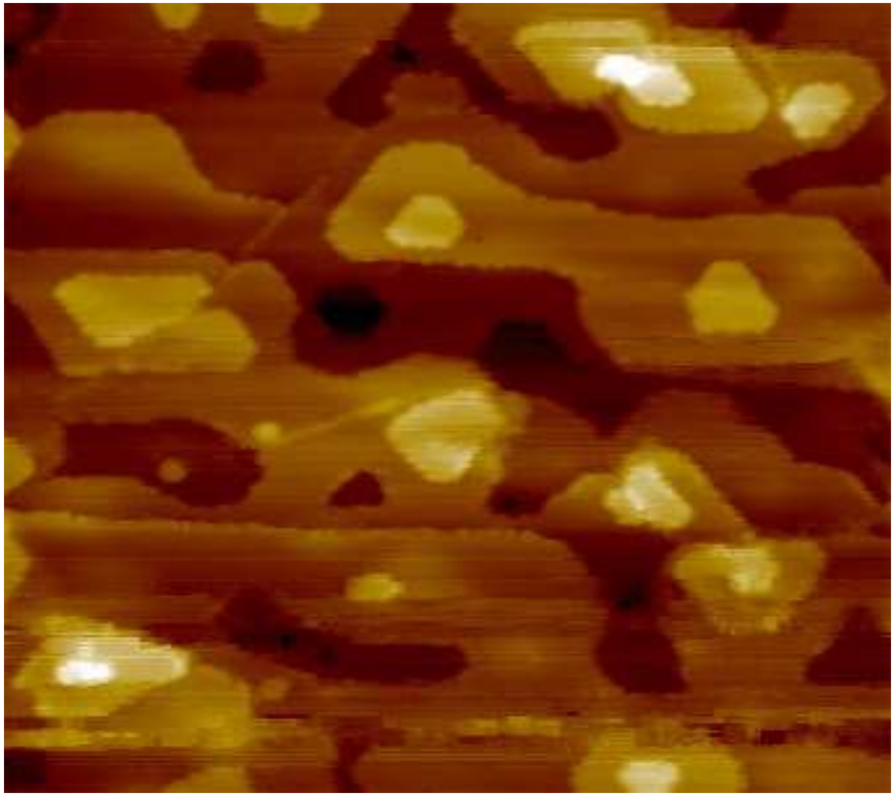




STM Results

- Characteristic of Ceria:
  - Flat terraces
  - Layers

CeO_2 at 300 K



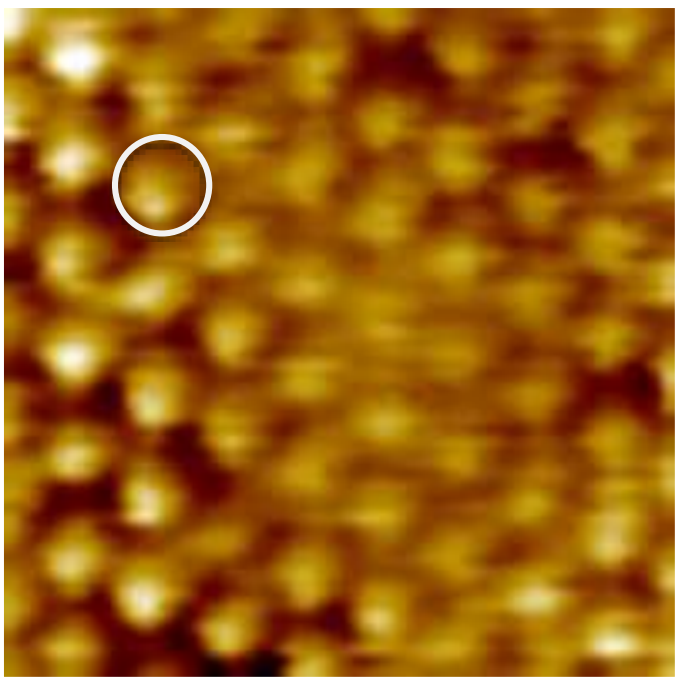
100 x 100 nm^2

Ceria at the Atomic Scale

- Ce atoms are observed
- More oxygen vacancies on $CeO_{1.88}$

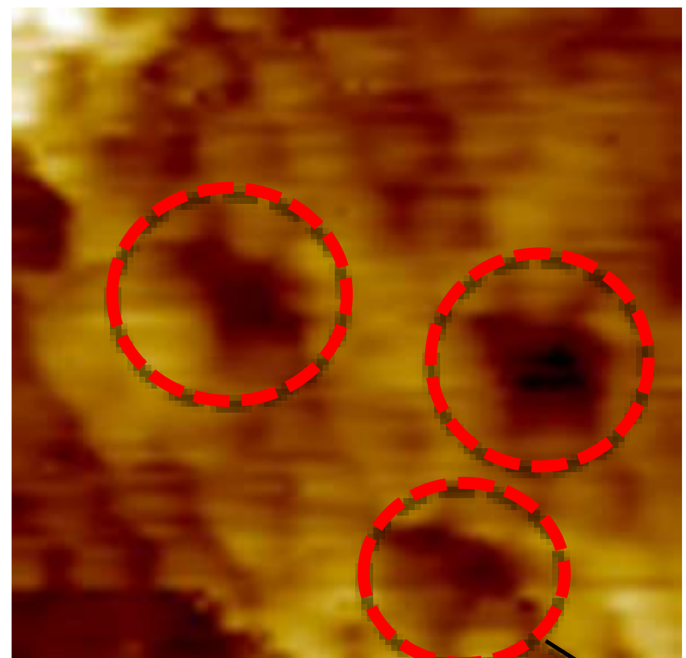
Oxidized Ceria (CeO_2)

Individual Ce atom



3 nm x 3 nm

Reduced Ceria ($CeO_{1.88}$)



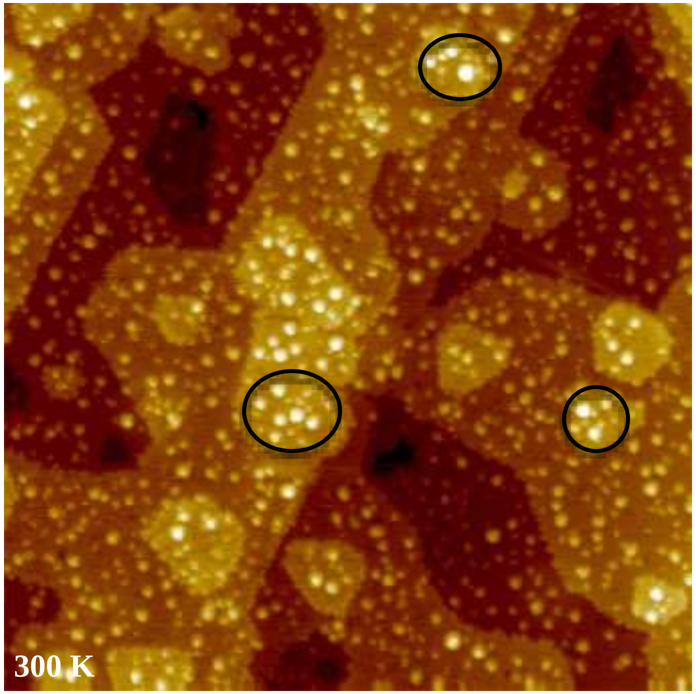
3 nm x 3 nm

Oxygen vacancies

Ni Deposited on Ce

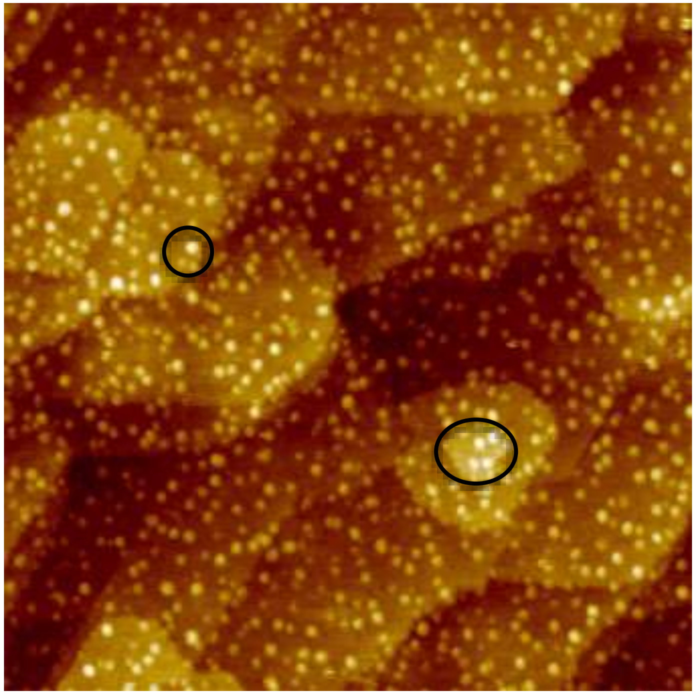
- Ni nanoparticles can form
- Ni can form nanoclusters

Ni/CeO_2



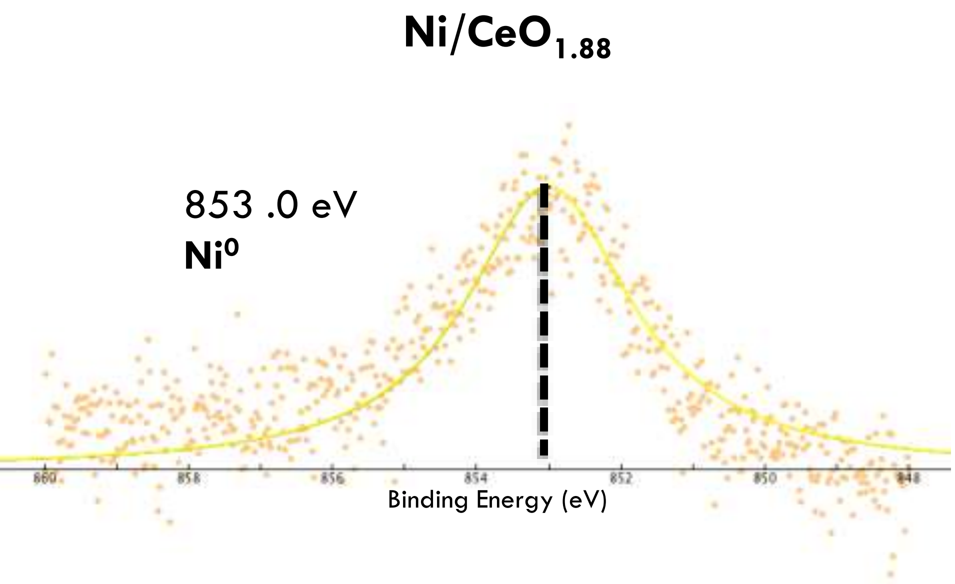
100 x 100 nm^2

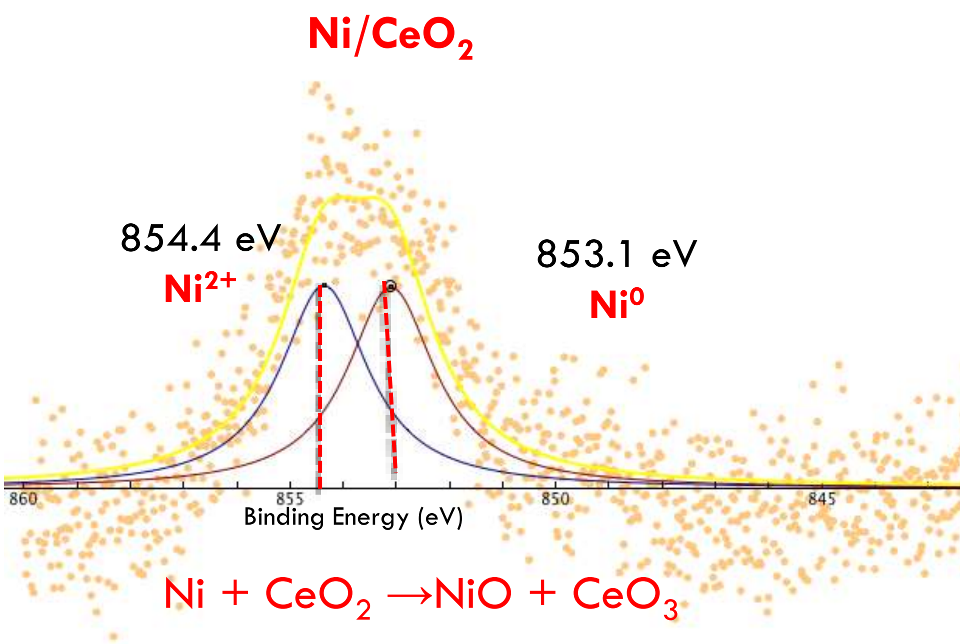
Ni/$CeO_{1.88}$



100 x 100 nm^2

Ni 2p XPS Spectra

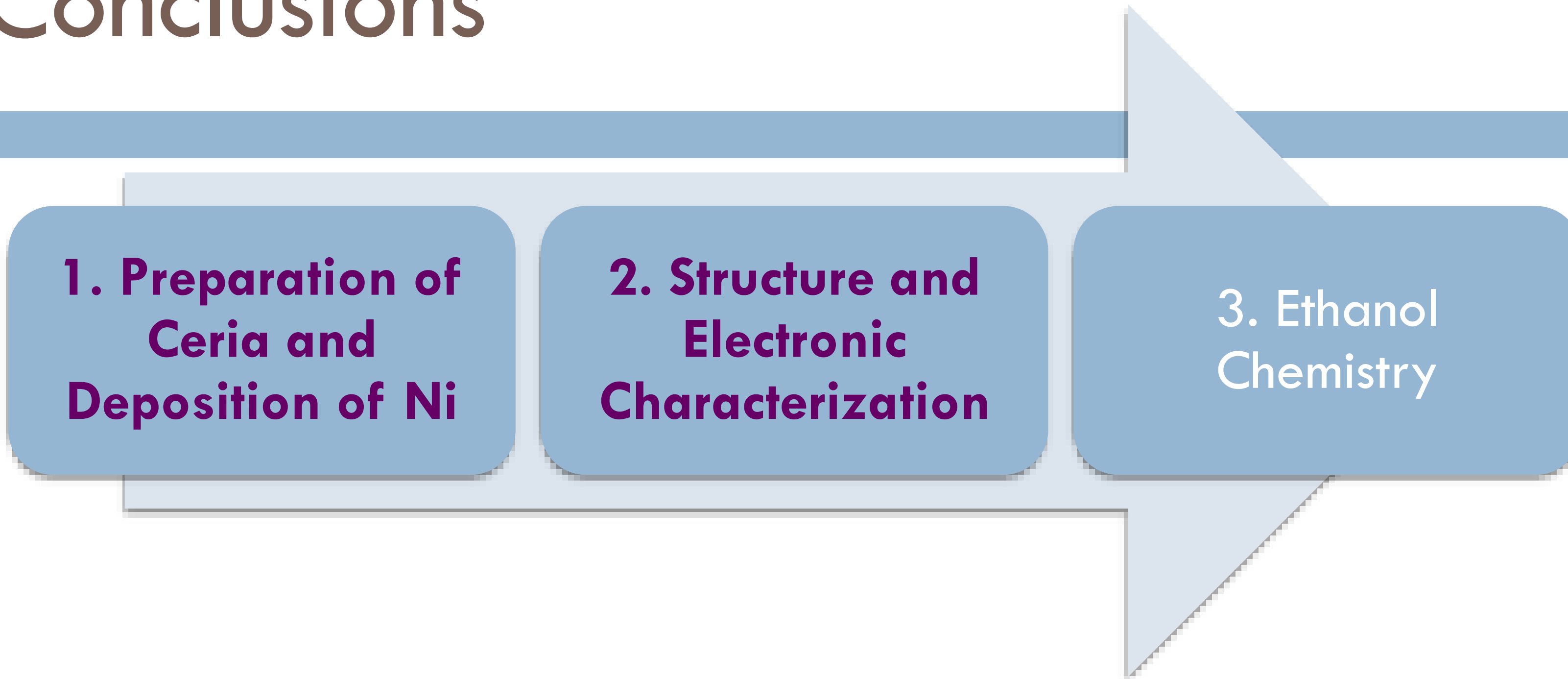




- Metallic Ni can form on the reduced ceria
- NiO and metallic Ni can form on the oxidized ceria

Tao et al *Surface Science* **2008**, 602, 2769-2773

Conclusions



- Different Ce thin films can be prepared
- Ni nanoclusters can form
- Reduced ceria have more oxygen vacancies
- Ni remains metallic state on the reduced ceria
- NiO can form on the oxidized ceria.

Acknowledgements

- Dr. Jing Zhou
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