Activity and Stability of Ceria Supported Bimetallic Ni-Au in the Reforming of Ethanol

By Sakun Duwal

Outline

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→Experimental

→Results

→Conclusions

Introduction

$CH_3CH_2OH + H_2O \xrightarrow{Ni\text{-}Au/CeO_2} 2CO + 4H_2$ Steam Reforming of Ethanol $\Delta H_R = +260$ kJ/mol

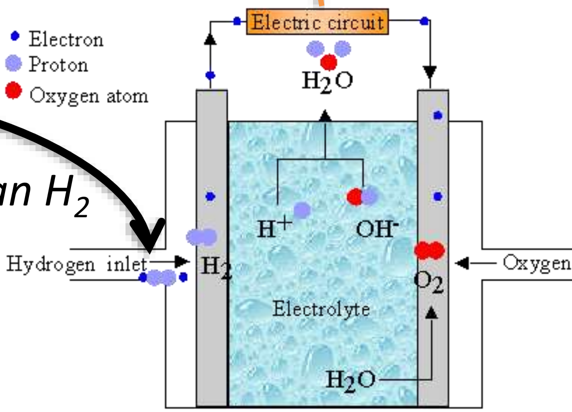
Water Gas Shift (WGS) reaction

$CO + H_2O \xrightarrow{Au/CeO_2} CO_2 + H_2$

$CO + 1/2O_2 \rightarrow CO_2$

CO oxidation

Pure Clean H_2



G.A Deluga, et al. Science 303, 993, (2004)
http://www.ceb.cam.ac.uk/pages/fuel-cells.html

Why Nickel and Gold?

Nickel (Ni)

- **Advantage**
  - Highly active in producing H_2
  - Cheap
  - Abundant
- **Disadvantage**: Can rapidly deactivate owing to coke formation and sintering during the reforming process

Gold (Au)

- High catalytic activity
- Retards coke formation

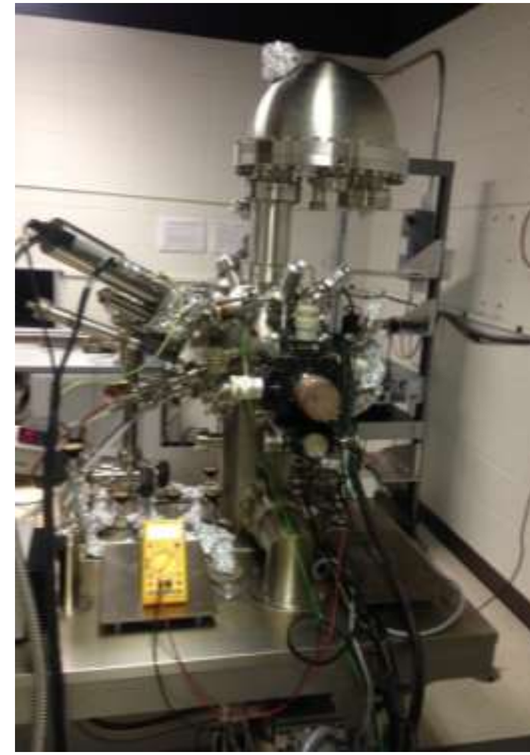
Y. Zhou and J. Zhou, J. Phys. Chem. C, 2012, 116 (17), 9544-9549.

Properties of Ceria

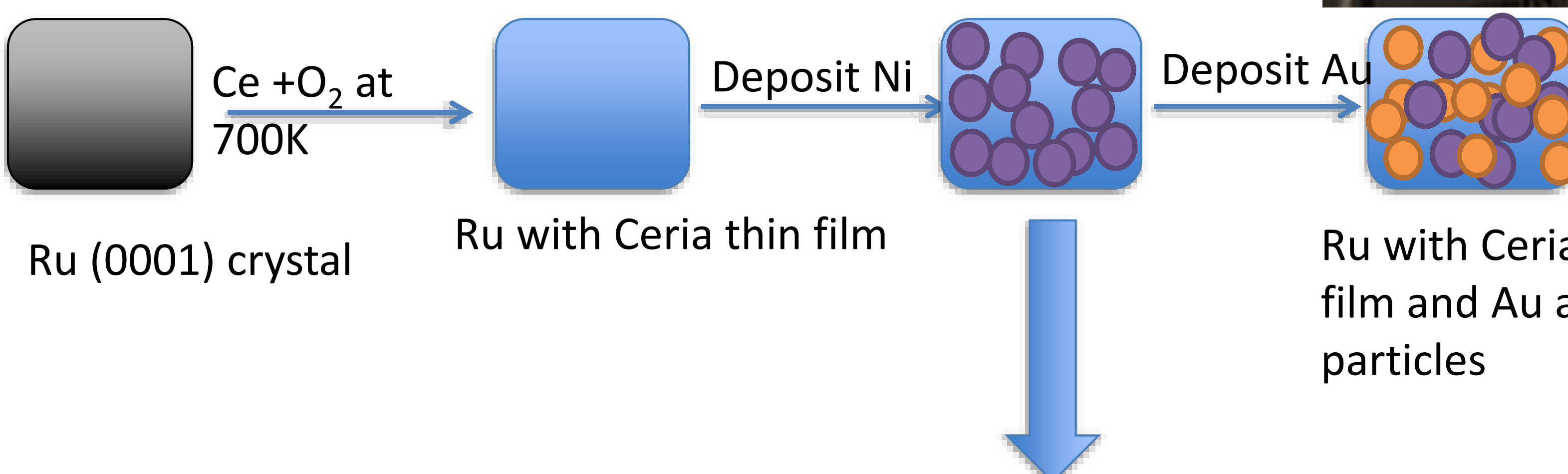
- Good oxygen storage capacity
- Redox properties
- Improves the stability and catalytic performance of Ni catalysts
- Dispersion of Ni particles on ceria diminishes the coke formation

Zhou et al. J.Phys.Chem.lett.2010,1, 609-615

Experimental

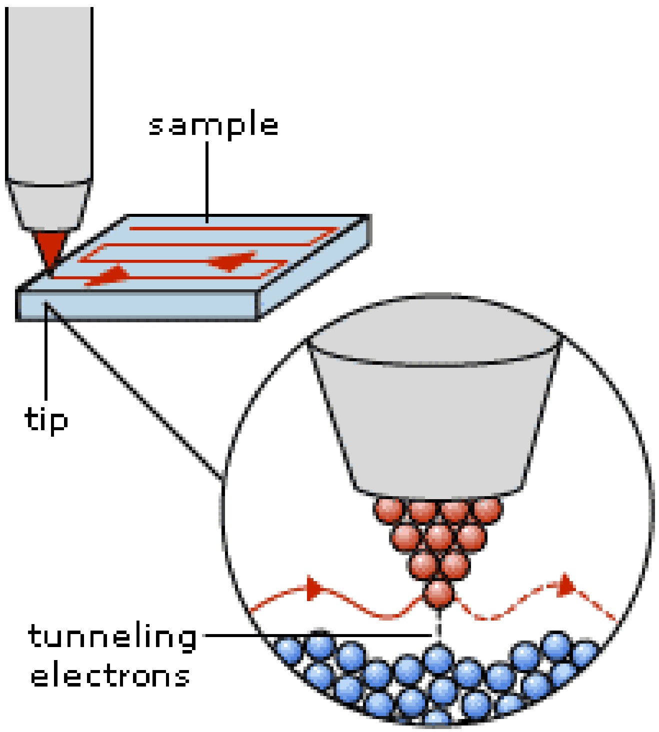


❖Growth process



- ❖ Characterization using Scanning Tunneling Microscopy (STM)
- ❖ Activity Study using Temperature Programmed Desorption (TPD)

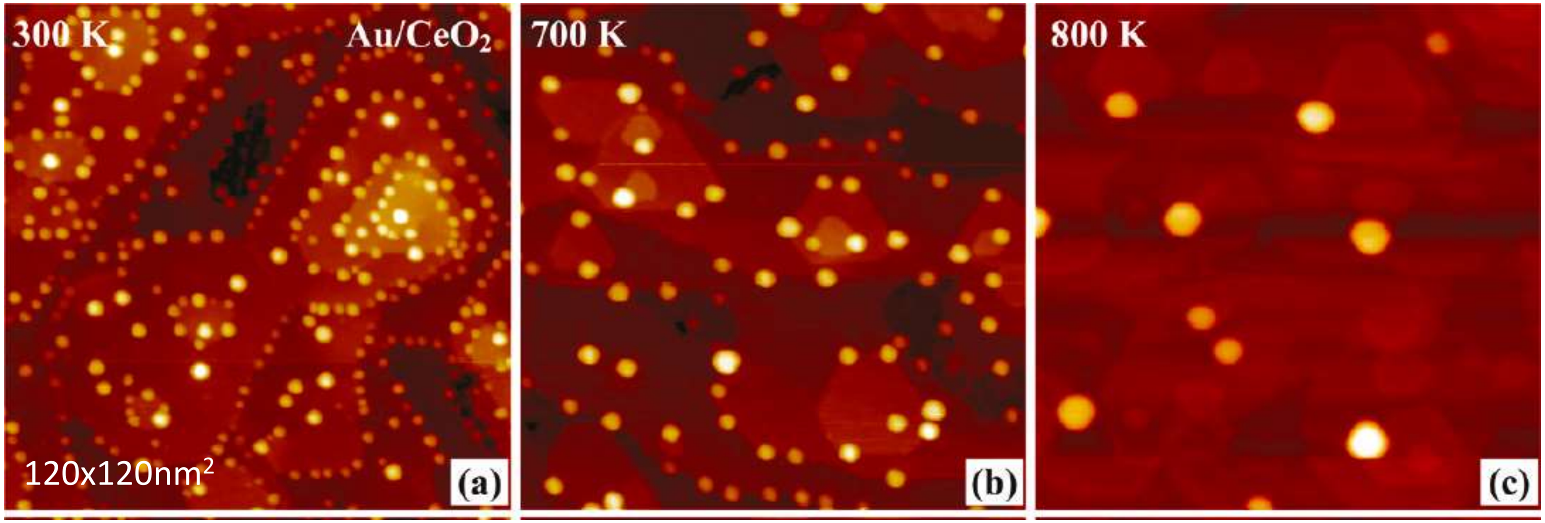
Scanning Tunneling Microscopy (STM)



- ❖ A sharp probe approaches the surface
- ❖ Current starts to tunnel
- ❖ Tip scans across the surface
- ❖ Enables to take an image of sample to study morphology

http://www.nobelprize.org/educational/physics/microscopes/scanning/index.html

Monometallic Au/CeO_2 STM images

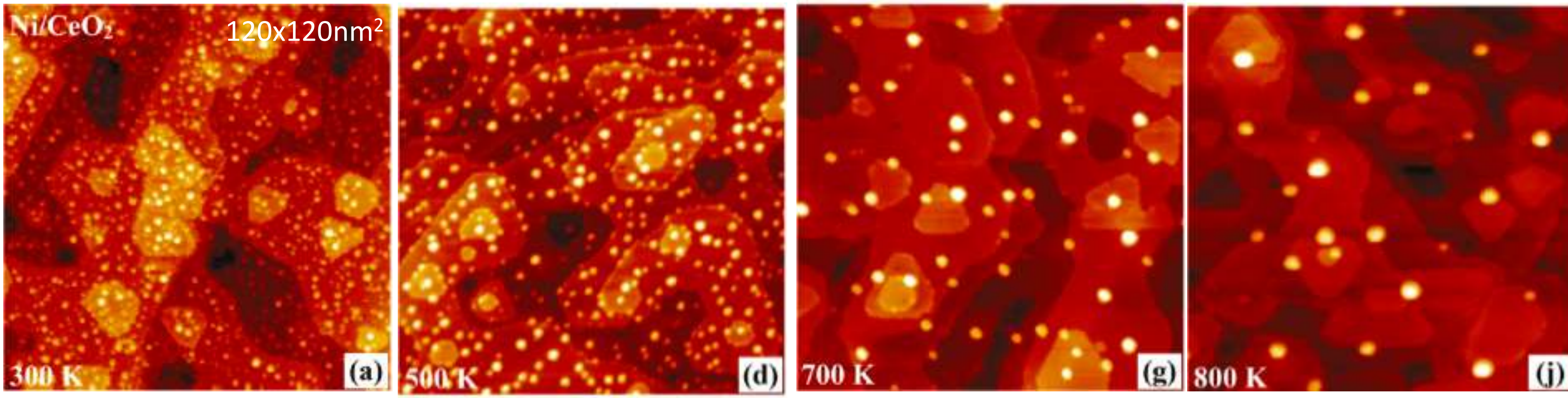


Width: 2.5 nm	Width: 3.8 nm	Width: 5.2 nm
Height: 0.7 nm	Height: 1.0 nm	Height: 2.0 nm
Density: $4.1 \times 10^{12}/cm^2$	Density: $0.9 \times 10^{12}/cm^2$	Density: $0.1 \times 10^{12}/cm^2$

- Flat, bright and hexagonal shaped gold nanoparticles
- STM line profile to measure height and diameter
- At 800k, the particles aggregate to form big particles

Zhou et al. J.Phys.Chem.Lett.2010,1, 1447-1453
Zhou et al. J.Phys.Chem.lett.2010,1, 609-615

Monometallic Ni/CeO_2



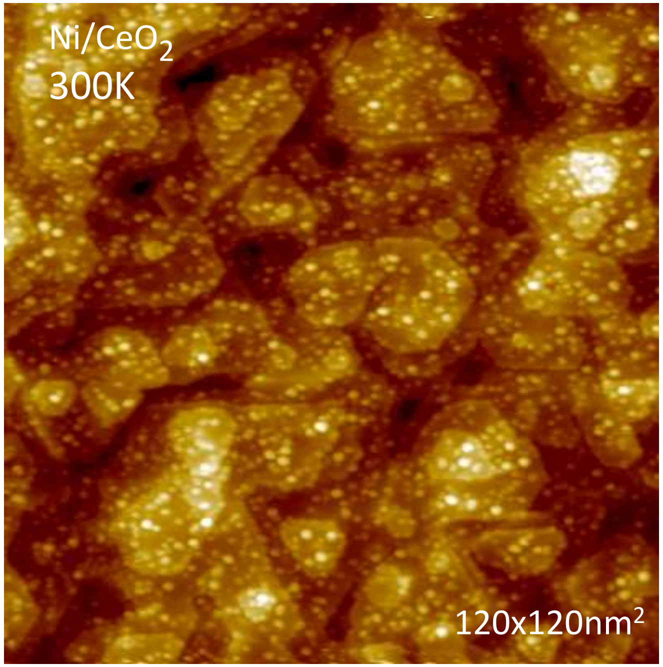
Width: 1.6 nm
Height: 0.4 nm
Density: $8.2x10^{12}/cm^2$

Width: 2.0 nm
Height: 0.7 nm
Density: $4.6\ x10^{12}/cm^2$

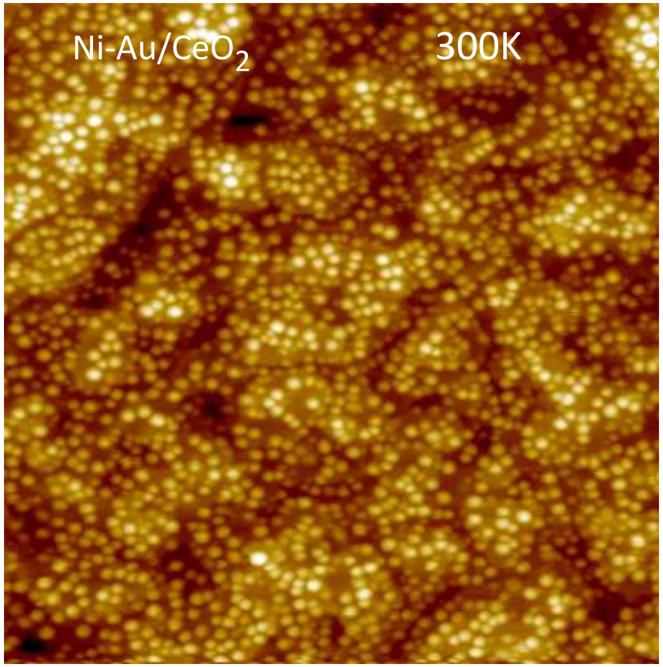
Width: 3.4 nm
Height: 1.0 nm
Density: $0.7\ x10^{12}/cm^2$

Width: 4.5 nm
Height: 1.1 nm
Density: $0.3\ x10^{12}/cm^2$

Bimetallic Ni-Au/CeO_2 at Room Temperature

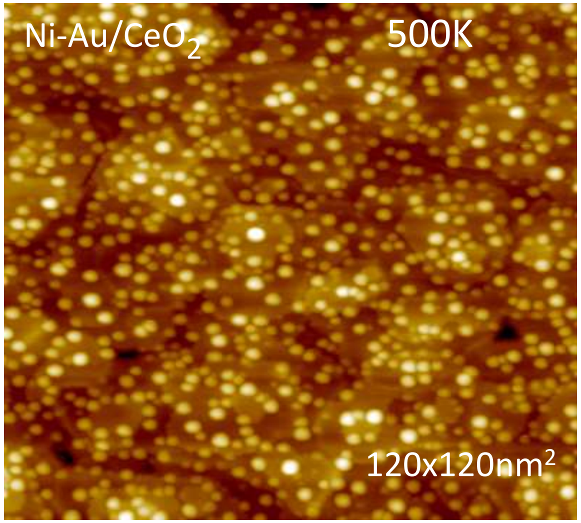


Width: 2.3 nm
Height: 0.3 nm
Density: $6.8 \times 10^{12}/cm^2$

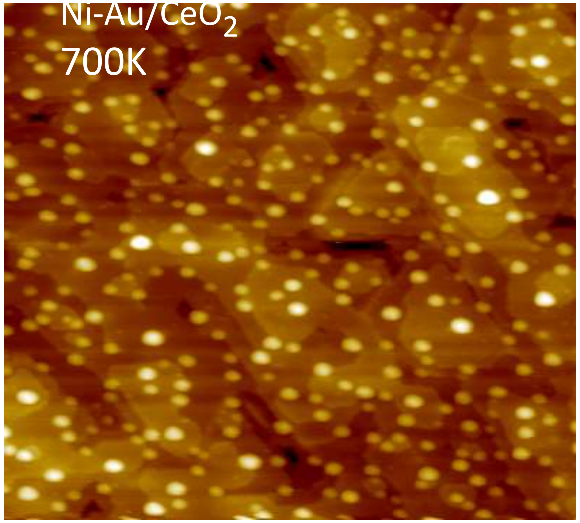


Width: 2.5 nm
Height: 0.4 nm
Density: $9.6 \times 10^{12}/cm^2$

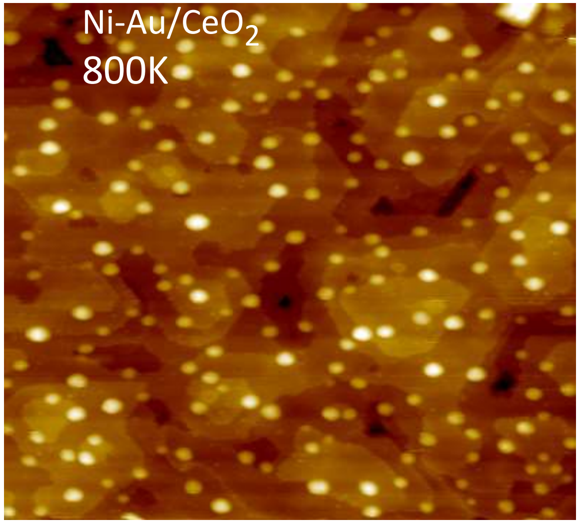
Temperature Dependent Study of Bimetallic Ni-Au/CeO_2



Width: 3.3 nm
Height: 0.7 nm
Density: $5.5 \times 10^{12}/cm^2$



Width: 3.4 nm
Height: 1.1 nm
Density: $2.4 \times 10^{12}/cm^2$

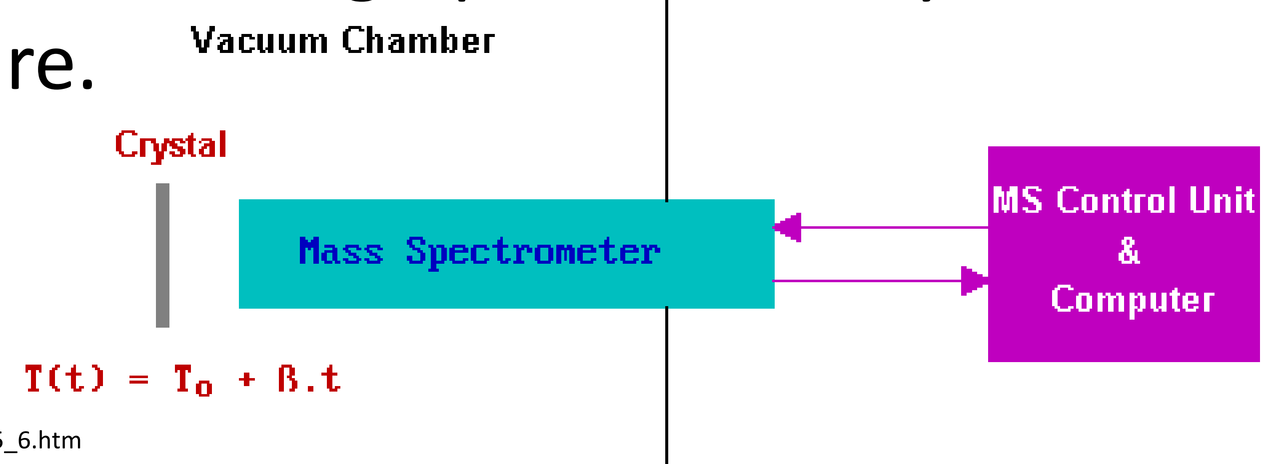


Width: 3.9 nm
Height: 1.3 nm
Density: $1.4 \times 10^{12}/cm^2$

- Increase in Diameter for Bimetallic Ni-Au : 31%
- Increase in Diameter for Monometallic Au: 51%
- Increase in Diameter for Monometallic Ni:64%

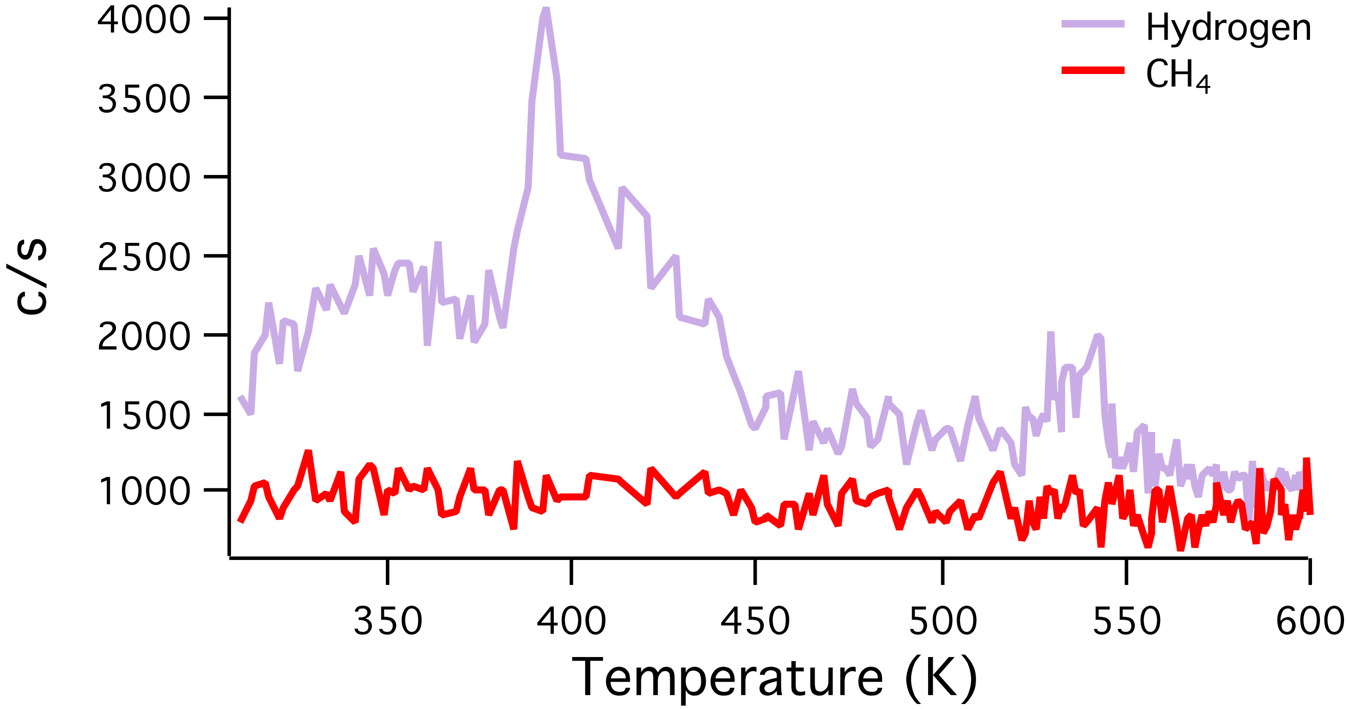
Temperature Programmed Desorption (TPD)

- Involves adsorption of ethanol onto the surface of catalyst
- Heat crystal with catalyst by linearly increasing temperature
- The detector, mass spectrometer helps to obtain the data as a graph of intensity versus temperature.



http://www.chem.qmul.ac.uk/surfaces/scc/scat5_6.htm

Ethanol Reaction on Ni/CeO_2



❖ **Active for Hydrogen production**

❖ **Ceria plays a key role to reduce methane formation**

Conclusions

- Bimetallic Ni-Au/Ceria retards the sintering process

- H_2 production was observed for Ni/CeO_2

Future Work

❖ Study the activity of bimetallic Ni-Au/CeO_2

Acknowledgements

- Dr. Jing Zhou
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- UW School of Energy Resources

Thank you!

Adsorption and Decomposition of Ethanol on Ni

same signal versus temperature behavior as the (less intense) signal from the ethanol parent molecular ion, and this behavior was the same for all isotopic ethanol molecules. Also shown in table 1 are the mass species derived from the observed products of ethanol decomposition on Ni(111).

The ethanol flux *at the crystal surface* per unit pressure behind a calibrated 2 μm conductance was estimated using a measurement of this quantity for CO.

Gates et al *Surface Science* **1986**, 171, 111 – 134.