Water-Gas Shift on Gold- and Copper-Oxide Catalysts: Active Sites and Reaction Mechanism

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Outline

• Motivation/objective

• Water-gas shift reaction on Au-CeO\textsubscript{2} powders

• Water-gas shift on Au/CeO\textsubscript{2}(110) surfaces

• Water-gas shift on CeO\textsubscript{x}/Au(111) surfaces
Motivation:

Most hydrogen is currently derived from the steam reforming of hydrocarbons:

\[ C_nH_m + nH_2O \rightarrow nCO + (n-m/2)H_2 \]

The reformed fuel contains 1-10% CO, which degrades the performance of the Pt electrode used in fuel cell systems.

The water-gas shift (CO + H_2O \rightarrow H_2 + CO_2) is used to remove the CO.
Recent studies indicate that ceria impregnated with gold nanoparticles is very active as a catalyst for the water-gas shift reaction being better than commercial Cu/ZnO catalysts.

- Fu et al, Science 301 (2003) 935

To improve the performance of the Au-ceria catalysts, we must:

- Identify what are the active phases. What active sites are making the catalysis?
- Determine the nature of the Au-CeO$_2$ interactions?
Our studies of XRD, photoemission and XANES/EXAFS show two types of nanoparticles in the gold-ceria catalysts:
- nanoparticles of metallic gold
- nanoparticles of gold oxide

What is the active phase of Au for the water-gas shift reaction?
- Stephanopoulus et al propose Au$^{+1}$ and Au$^{+3}$ as the active centers, Science 301 (2003) 935.
- In the early 1990s, Campbell, Norskov and coworkers found that Cu is the active phase in Cu/ZnO catalysts,
In-situ XRD and XAFS by Clausen et al corroborated this
To solve this controversy the water-gas shift was investigated over the following systems

- Water-gas shift reaction on Au-CeO$_2$ powders
- Water-gas shift on Au/CeO$_2$(110) surfaces
- Water-gas shift on CeO$_x$/Au(111) surfaces
Integral approach to catalysis:

Quantum-chemical modeling (DFT, MD, kinetic MC)

Chemistry associated with catalysis (surface science studies)

In-situ characterization of catalysts (xanes/exafs, tr-xrd)

Fundamental understanding of the behavior of active sites:
Rational design of better catalysts
National Synchrotron Light Source

Photoemission

XAFS

XRD
* Work with single crystals
  - Photoemission
  - X-ray absorption near-edge spectroscopy

* Work with high-surface area catalysts
  - *In-situ* Time-resolved x-ray diffraction
  - *In-situ* X-ray absorption near-edge spectroscopy
Water-gas shift reaction on:

• High surface area Au-CeO$_2$ and Cu-CeO$_2$ catalysts
Before reaction, as prepared:

The relative amount of $\text{AuO}_x$ increases when the total amount of gold decreases.

CeO$_2$ nanoparticles

powder Au/CeO$_2$ catalysts

Intensity / a.u.

Energy / eV

11900 11920 11940 11960 11980

0.0 0.2 0.4 0.6 0.8 1.0 1.2

0.5% Au 1.8% Au 2.4% Au 5.0% Au Au foil

Au L3 edge
In-situ measurements under atmospheric pressure for WGS reaction. The AuO_x becomes Au. The active phase consist of metal nanoparticles dispersed on CeO_{2-x}. 
In-situ XANES at Ce L₃-edge

Ceria is reduced under reaction conditions.
Water-gas shift reaction \((\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2)\) on CuO/CeO\(_2\)

**Figure 1.** TR-XRD patterns for 5\%CuO/CeO\(_2\) during the WGS reaction. (\(\lambda=0.921\text{Å}\))

Metallic Cu is the active phase

In agreement with the results of Campbell, Norskov, Clausen et al.
for Cu/ZnO:

**Figure 2.** Relative H\(_2\) concentrations in the products.
Summary

In-situ XANES and XRD studies show that the active phase of Au-CeO$_2$ and Cu-CeO$_2$ catalysts for the WGS reaction consist of metal nanoparticles dispersed on partially reduced CeO$_{2-x}$
Integral approach to catalysis:

Quantum-chemical modeling (DFT, MD, kinetic MC)

Chemistry associated with catalysis (surface science studies)

In-situ characterization of catalysts (xanes/exafs, tr-xrd)

Fundamental understanding of the behavior of active sites:
Rational design of better catalysts
Water-gas shift reaction on:

- Au and Cu nanoparticles supported on CeO$_2$(111), ZnO(0001) and TiO$_2$(110)
Model systems: Au and Cu on CeO$_2$(111)

For Au on CeO$_2$(111), the results of STM show 3D islands of Au with sizes of 2-4 nm (0.3-0.8 ML)
After exposing Au/CeO$_2$(111) surfaces to mixtures of \{CO + H$_2$O\} under WGS reaction conditions, post-reaction XPS characterization shows Au and partially reduced CeO$_{2-x}$(111)


Particle size matters: At the maximum activity metal particles with 2-4 nm in size.

**Question:** What is the role of the oxide?
Amounts of H$_2$ produced during the WGS reaction on 0.5 ML of gold or copper deposited on CeO$_2$(111) and ZnO(000$\bar{1}$).

* 20 Torr of CO and 10 Torr of H$_2$O at 625 K for 5 minutes in a batch reactor.
Oxide support matters.

**Question:** What is the role of the oxide?

What is the role of the oxide in the water-gas shift reaction?

Density functional calculations were performed to answer this question. Model catalysts:
- Cu(100) and Au(100) surfaces
- Free Cu and Au nanoparticles
- Cu/TiO$_{2-x}$(110) and Au/TiO$_{2-x}$(110) surfaces

Density functional calculations were performed with

-DMol³ code
-numerical basis set
-relativistic effective-core potentials
-PW91 functional
WGS on Cu(100) and on a Cu$_{29}$ nanoparticle

Cu surfaces and nanoparticle are able to catalyze the WGS reaction. In agreement with other works:

A $\text{Au}_{29}$ nanoparticle cannot catalyze the WGS reaction

Au systems exhibit a very low reactivity for the bonding or dissociation of $\text{H}_2\text{O}$
Au-TiO₂ surfaces exhibit high catalytic activity for the water-gas shift.

- For the Au-TiO₂ catalysts the oxide must play a very important role in the WGS process.
Model for Au/TiO$_{2-x}$(110)

We used this model to study the WGS reaction on Au/TiO$_{2-x}$(110).

Model used by Norskov et al. to study the oxidation of CO

The Au-TiO$_2$ interface helps in the dissociation of water and in the formation of a key HOCO intermediate.

Au(100) and Au(111) do not dissociate water well, but subsequent steps of the WGS are fine.

Performance of CeOx/Au(111) as a WGS catalyst?
Images of scanning tunneling microscopy for nanoparticles of CeO$_2$ dispersed on a Au(111) surface

Model catalyst for the water-gas shift
Production of hydrogen through the water-gas shift ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) on CeO$_2$/Au(111) catalysts

Photoemission indicates that there is a correlation between the concentration of O vacancies in the ceria nanoparticles and the catalytic activity.

Image of scanning tunneling microscopy for nanoparticle of CeO$_{2-x}$ dispersed on a Au(111) surface

CeO$_{2-x}$ with clusters of O vacancies. It dissociates water.
Proposed mechanism for the water-gas shift reaction

Water dissociates on O vacancies of the oxide, CO adsorbs on Au sites located nearby, and subsequent reaction takes place at the metal-oxide interface
Summary

*In-situ* XRD and XANES studies show that the active phase of Au-CeO$_2$ and Cu-CeO$_2$ catalysts for the WGS reaction consist of metal nanoparticles dispersed on partially reduced CeO$_{2-x}$

The catalytic activity of WGS catalysts containing Au or Cu supported on CeO$_2$(111) and TiO$_2$(110) depends strongly on the size of the metal nanoparticles.

Au nanoparticles alone are inactive for the water-gas shift because they cannot dissociate O-H bonds. The metal-TiO$_2$ and metal-CeO$_2$ interfaces play a direct role in the dissociation of water accelerating the WGS process.
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