

# V.N.12 Active Sites and Mechanism for the Water-Gas Shift Reaction on Metal and Metal/Oxide Catalysts (BNL FWP CO-027)

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and other applications. Our main objective is to obtain the knowledge necessary to predict the behavior, and ultimately design, improved cost-effective low temperature water-gas shift catalysts.

## Technical Barriers

*What is the active phase of WGS catalysts?* A central challenge is the difficulty of characterizing the active state of the catalyst at the elevated pressure and temperatures used for WGS operation. *In-situ* studies are needed to characterize the composition of metal-oxide catalysts and establish the general role of reduced metal nanoparticles vs. cationic metal centers.

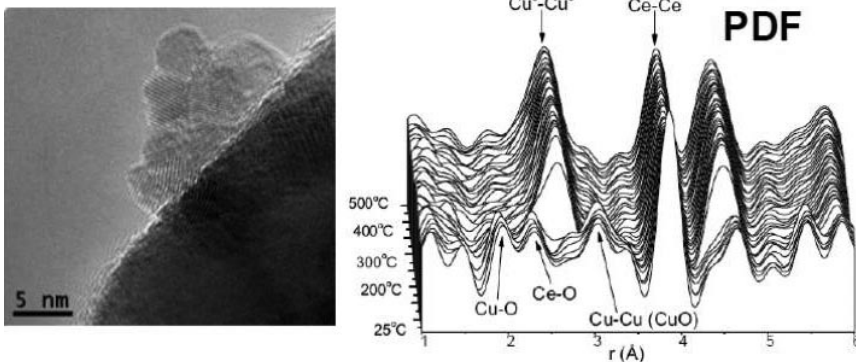
*What is the reaction mechanism?* A generally accepted mechanism for the WGS reaction does not yet exist. Alternatives include associative mechanisms (i.e. formation of HCOO, HOCO, CO<sub>3</sub> or HCO<sub>3</sub> intermediates) and the redox mechanism. Generally, the WGS involves the activation of water to release H<sub>2</sub> and the activation of CO to combine with the O left behind to release CO<sub>2</sub>. However, the problem is complex since metal nanoparticles and the oxide support can work in a cooperative way, facilitating different reaction steps.

## Abstract

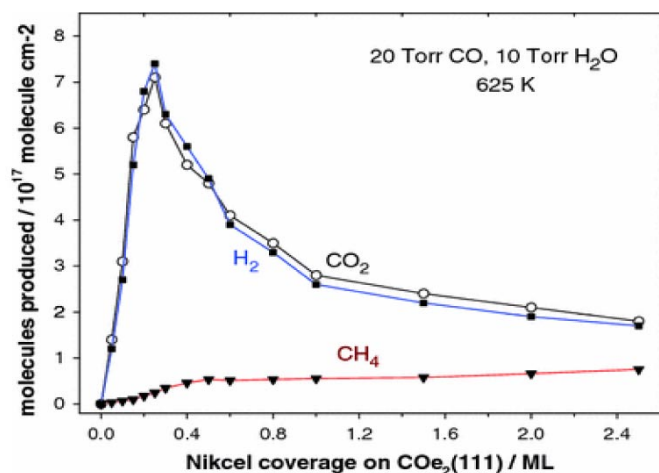
Current industrial catalysts for the water-gas shift reaction are commonly mixtures of Fe-Cr and Zn-Al-Cu oxides, used at temperatures between 350-500°C and 180-250°C, respectively. These oxide catalysts are pyrophoric and normally require lengthy and complex activation steps before usage. Improved catalysts are being sought, particularly for lower temperature (e.g., at T<150°C, equilibrium lowers the product CO concentration into ranges suitable for direct

## Objectives

Most hydrogen is currently derived from steam reforming of hydrocarbons (reacting steam with natural gas):  $C_nH_m + nH_2O \rightarrow nCO + (n-m/2)H_2$ . The reformed fuel contains substantial CO, which degrades the performance of the platinum catalysts used in polymer electrolyte membrane (PEM) fuel cell systems. The water-gas shift reaction (WGS:  $CO + H_2O \rightarrow H_2 + CO_2$ ) is a critical process in providing pure hydrogen for fuel cells



**FIGURE 1.** Left: TEM image of an inverse CeO<sub>2</sub>/CuO catalysts. Right: *In-situ* time-resolved PDF data for a CeO<sub>2</sub>/CuO catalyst during the WGS.



**FIGURE 2.** Water-gas shift activity of Ni/CeO<sub>2</sub>(111) as a function of Ni coverage.

fuel cell use without further purification.). Ceria (Au, Cu or Pt on CeO<sub>2</sub>), titania (Au, Pd or Pt on TiO<sub>2</sub>) and molybdena (Ni, Cu and Au on MoO<sub>2</sub>) based nanostructured catalysts are very promising new candidates for high activity, lower temperature operation in WGS systems. However, the design and optimization of these and other metal/oxide WGS nanocatalysts are hindered by controversy about basic questions regarding the nature of the active sites and the reaction mechanism. Here, we follow a coordinated experimental and theoretical effort to better understand these promising metal/oxide catalysts, and to develop concepts for their improvement. The project combines research in three thrusts: (i) *in-situ* studies to determine catalyst structure, oxidation state and chemistry under reaction conditions; (ii) studies of relevant model systems, primarily based on nanoparticles supported on single crystal substrates; and (iii) computational modeling. By closely linking these three research thrusts, our goal is to provide strongly validated mechanistic and structural conclusions for the future design and optimization of nanostructured WGS catalysts.

## Progress Report

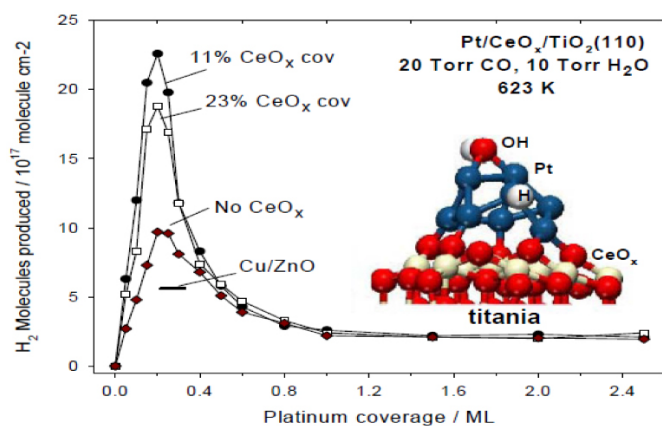
### In-situ studies of WGS catalysts with XRD, PDF, XAFS and TEM: Evolution of metal/oxide catalysts

The active phase of a series of metal/oxide powder catalysts (Pt/CeO<sub>2</sub>, Pt-Ru/CeO<sub>2</sub>, Pt/CeO<sub>x</sub>/TiO<sub>2</sub>, Au/CeO<sub>x</sub>/TiO<sub>2</sub>, Ce<sub>1-x</sub>Ni<sub>x</sub>O<sub>2-3y</sub>, CeO<sub>x</sub>/CuO) was investigated using a combination of *in-situ* time-resolved X-ray diffraction (XRD), Pair-distribution function (PDF) analysis, X-ray absorption fine structure (XAFS) and environmental TEM. Under reaction conditions most of these WGS catalysts underwent chemical transformations that drastically modified their composition with respect to that obtained during the synthesis process. The active phase of catalysts which combine Cu, Ni, Au or Pt with oxides such as CeO<sub>2</sub>,

TiO<sub>2</sub> and CeO<sub>x</sub>/TiO<sub>2</sub> essentially involved nanoparticles of the reduced metals. The oxide support underwent partial reduction and was not a simple spectator, facilitating the dissociation of water and in some cases modifying the chemical properties of the supported metal. Therefore, to optimize the performance of these catalysts one must take into consideration the properties of the metal and oxide phases. Figure 1 shows a TEM image and PDF data for an inverse CeO<sub>x</sub>/CuO powder catalysts. In the TEM image, taken for the as-prepared catalysts, one can see crystallites that in many cases exhibit a (111) surface termination. The PDF results for water-gas shift reaction conditions show a simultaneous disappearance of the Cu-O vector of CuO with the appearance of a Cu-Cu vector for metallic copper. These data, and *in-situ* results obtained for other catalysts in our group, indicate that a WGS metal/oxide catalyst is a dynamic entity that changes with reaction conditions.

### Metal-oxide interactions and the activity of water-gas shift catalysts

A series of model catalysts {CeO<sub>x</sub>/Cu(111), CeO<sub>x</sub>/Au(111), Pt/CeO<sub>2</sub>(111), Ni/CeO<sub>2</sub>(111), Pt/TiO<sub>2</sub>(110), Pt/CeO<sub>x</sub>/TiO<sub>2</sub>(110)} was used to study fundamental aspects of the water-gas shift reaction. These studies revealed that the oxide component of the catalyst can affect the reaction process in two different ways. First, the presence of O vacancies in the oxide greatly facilitates the dissociation of water. Second, the electronic properties of the metal can be affected by interactions with the oxide producing special chemical properties. This is the case in the Ni/CeO<sub>2</sub>(111), Pt/CeO<sub>2</sub>(111) and Pt/CeO<sub>x</sub>/TiO<sub>2</sub>(110) systems. In Figure 2, small coverages of Ni on CeO<sub>2</sub>(111) are highly active for the water-gas shift reaction and do not produce methane, although bulk Ni is a very good catalyst for the methanation of CO. The electronic properties of Ni and Pt nanoparticles deposited on CeO<sub>2</sub>(111) and CeO<sub>x</sub>/TiO<sub>2</sub>(110) have been examined using core and valence photoemission. The results of valence photoemission point to a new type of metal-support interaction which produces large electronic perturbations for small Ni and Pt particles in contact with ceria. The Ni/CeO<sub>2</sub>(111), Pt/CeO<sub>2</sub>(111) and Pt/CeO<sub>x</sub>/TiO<sub>2</sub>(110) systems exhibited a density of metal d states near the Fermi level that was much smaller than that expected for bulk metallic Ni or Pt. The electronic perturbations induced by ceria on Ni made this metal a very poor catalyst for CO methanation, but transformed Ni into an excellent catalyst for the production of hydrogen through the water-gas shift reaction (Figure 2) and the steam reforming of ethanol. Furthermore, the large electronic perturbations seen for small Pt particles in contact with ceria significantly enhanced the ability of the admetal to adsorb and dissociate water made it a highly active catalyst for the water-gas shift reaction (Figure 3). The behaviour seen for Ni/CeO<sub>2</sub>(111), Pt/CeO<sub>2</sub>(111) and Pt/CeO<sub>x</sub>/TiO<sub>2</sub>(110) systems illustrates the positive effects derived from electronic metal-support interactions and points to a promising approach for



**FIGURE 3.** Water-gas shift activity of Pt/TiO<sub>2</sub>(110) and Pt/CeO<sub>x</sub>/TiO<sub>2</sub>(111) as a function of Pt coverage.

improving or optimizing the performance of metal/oxide catalysts.

## Future Directions

We will be using a combination of experiment and theory to continue our studies on the behavior of WGS nanocatalysts that contain three different types of oxides: Ceria- (Cu/CeO<sub>2</sub>, Au/CeO<sub>2</sub>, Pd/CeO<sub>2</sub>, Pt/CeO<sub>2</sub>), titania- (Au/TiO<sub>2</sub>, Pd/TiO<sub>2</sub>, Pt/TiO<sub>2</sub>) and molybdena-based (Au/MoO<sub>2</sub>, Cu/MoO<sub>2</sub>, Ni/MoO<sub>2</sub>) systems. The future research can be divided into three major thrusts:

*i) In-situ Characterization of High-Surface Area Powder Catalysts.* In the next years we will perform systematic experiments that will focus on examining the chemical state and structural/morphological properties of metal/oxide WGS catalysts using a unique suite of techniques (XAFS, XRD, TEM) for *in-situ* characterization. A new capability for environmental transmission electron microscopy (ETEM) is being established at the Center for Functional Nanomaterials (CFN) in BNL. The new ETEM is a custom-designed instrument for advanced *in-situ* electron microscopy, including experiments for chemical reaction and crystal growth in various gas environments. It is the first of its kind and will be applied for three dimensional (3D) tomography and near-edge x-ray absorption spectroscopy with powder catalysts. After the structural and morphological characterization of the catalysts, experiments that use IR spectroscopy to probe the WGS reaction mechanism will be carried out. We will be able to validate or discard controversial claims. The combination of *in-situ* XANES, XRD, TEM and IR spectroscopy will allow us to establish meaningful correlations between structure and reactivity that can be directly used to improve the performance of WGS industrial catalysts. The studies described in this part of the proposal will give basic information that will be used in the other two parts of the project for modeling the catalytic process at an atomic level and for testing fundamental concepts.

*ii) Experimental Studies with Model Well-defined Catalysts.* The powder nanocatalysts under study in the previous part are complex by nature. Investigators have a limited control over the structural and electronic properties that can affect the chemical reactivity of the system. This makes it difficult to study basic phenomena associated with the water-gas shift reaction: How does the reaction change with particle size, what is the nature of the electronic interaction between the admetal and oxide support, are electronic effects more important than structural or ensemble effects, is the oxide a simple spectator, how does the reaction rate depend on the oxide surface structure?

In this part of the project, we plan to do WGS studies on several well-defined model catalysts. These model systems will be used to examine fundamental issues that have been raised from *in-situ* studies of high-surface area powder catalysts and will provide results that are essential for the theoretical work described in the next section. Metal nanoparticles will be deposited by physical vapor deposition on single crystal oxide surfaces. Another type of model will involve “inverse” catalysts consisting of oxide nanoparticles supported on Au(111), Cu(111) and Pt(111) single crystals. We have been successful preparing nano-arrays of MoO<sub>x</sub>, TiO<sub>x</sub> and CeO<sub>x</sub> on Au(111). We also know how to prepare CeO<sub>x</sub>/Cu(111) “inverse” model catalysts. The model systems are flexible and can be modified to test new concepts or hypothesis that will come from the future theoretical studies. Since we will be dealing with new materials or catalyst configurations, these studies also can give novel ideas on what should be considered when designing new industrial catalysts.

*In-situ* data collected with IR spectroscopy and moderate-pressure XPS on the well-defined metal/oxide and oxide/metal systems will point to key intermediates in the WGS reaction mechanism and will be extremely useful as a check-point in the theoretical studies described in the next section.

*(iii) Theoretical Studies of WGS Reaction Mechanism and the Behavior of Active Sites.* Despite extensive efforts, there are some issues involved in the WGS reaction that cannot be addressed directly by experiment. What is the detailed reaction pathway including the geometries and energetics of reactants, possible intermediates and transition states? On which sites does the reaction take place? How are the WGS activities of metal and metal oxide nanoparticles affected by differences in their electronic structure and geometry associated with particle size and shape, the metal oxidation state, the support, and particle↔support interactions?

We will be performing calculations on systems similar to those under study in the previous sections (i) and (ii). When going from extended surfaces to isolated nanoparticles and oxide supported nanoparticles, the effects of size, shape, and metal↔oxide interactions on the catalysis will

be determined. Our calculations on these materials will be coordinated with extensive experiments, especially for the model catalysts discussed in section (ii), so that meaningful comparisons can be made. Our DFT study of a system will start with the calculation of the reaction pathway, where the computationally identified possible intermediates can be compared with the results from our experimental *in-situ* studies. With the calculated information on the energetics of intermediates and transition states, a micro-kinetic model will be developed to estimate the catalytic activity. In addition, features of the reaction pathway obtained from static DFT studies will be explored by molecular dynamics (MD) simulations. With this close interaction between theory and experiment, we should be able to provide definitive information about the behavior of WGS catalysts. The DFT calculations will be carried out using the DMol<sup>3</sup>, CASTEP and VASP codes. For a few of these systems, we will perform MD simulations using the algorithms available in CASTEP, VASP or CPMD. We will also augment the micro-kinetic model calculations with kinetic Monte Carlo (KMC) simulations.

### Publication list: 20 papers published or in press

1. Gonzalez, Ines et al, A Comparative Study of the Water Gas Shift Reaction over Platinum Catalysts Supported on CeO<sub>2</sub>, TiO<sub>2</sub> and Ce-modified TiO<sub>2</sub>. *Catal. Today* **2010**, *149*, 372-379.
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5. Barrio, Laura et al, Unusual Physical and Chemical Properties of Ni in Ce<sub>1-x</sub>Ni<sub>x</sub>O<sub>2-y</sub> Oxides: Structural Characterization and Catalytic Activity for the Water Gas Shift Reaction. *J. Phys. Chem. C*, **2010**, *114*, 12689-12697.
6. Barrio, Laura et al, Unraveling the Active Site in Copper-Ceria Systems for the Water-Gas Shift Reaction: *In Situ* Characterization of an Inverse Powder CeO<sub>2-x</sub>/CuO-Cu Catalyst. *J. Phys. Chem. C*, **2010**, *114*, 3580-3587.
7. Senanayake, Sanjaya et al, Water-Gas Shift and CO Methanation Reactions over Ni-CeO<sub>2</sub>(111) Catalysts. *Topics in Catal.* **2011**, *54*, 34 - 41.
8. Barrio, Laura et al, *In situ* characterization of Pt catalysts supported on ceria modified TiO<sub>2</sub> for the WGS reaction: influence of ceria loading on catalytic behavior. *Phys. Chem. Chem. Phys.*, **2012**, *14*, 2192-2202.
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11. Rodriguez, Jose, Supported Gold in CO Oxidation, the Water-gas Shift, and DeSOx Reactions, book chapter for *Supported Metals in Catalysis*, 2<sup>nd</sup> Edition (Editors: James Anderson and Marcos Fernandez-Garcia), Imperial College Press, London, 2012 (invited book chapter).
12. Senanayake, Sanjaya et al, Nanopatterning in CeO<sub>x</sub>/Cu(111): A New Mechanism for Surface Reconstruction and Enhancement of Catalytic Activity. *J. Phys. Chem. Letters*, **2012**, *3*, 839-843.
13. Bruix, Albert et al., A New Type of Strong Metal-Support Interaction and the Production of H<sub>2</sub> through the Transformation of Water on Pt/CeO<sub>2</sub>(111) and Pt/CeO<sub>x</sub>/TiO<sub>2</sub>(110) Catalysts. *J. Am. Chem. Soc.* **2012**, *134*, 8968-8974.
14. Xu, Weiqian et al. *In situ* Studies of CeO<sub>2</sub>-supported Pt, Ru, and Pt-Ru Alloy Catalysts for the Water-gas Shift Reaction: Active Phases and Reaction Intermediates. *J. Catal.* **2012**, *291*, 117-126.
15. Kubacka, Anna et al, Tungsten as an Interface Agent Leading to Highly Active and Stable Copper-Ceria Water Gas Shift Catalyst. *Applied Catal. B : Environmental*, **2012**, *132/133*, 423-432.
16. Ramirez-Reina, Tomas et al, *Operando* Characterization of Iron-promoted Ceria-Alumina Gold Catalysts during the Water-gas Shift Reaction. *Catal. Today*, **2013**, *205*, 41-48.
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