

V.G.2 Catalysis and Electrocatalysis for Fuel Synthesis: Hydrogen Production and the Water-Gas Shift

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Program Scope

The water-gas shift reaction (WGS: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) is a critical process in providing pure hydrogen for fuel cells and other applications. Improved air-tolerant, cost-effective WGS catalysts for lower temperature processing are needed. Ceria-, titania- and molybdena-based catalysts are expected to be the next generation of WGS catalysts for industrial applications. The design and optimization of these WGS catalysts depends on a better understanding of their structures and functions. This project involves a coordinated research program to understand the active sites and reaction mechanism for the WGS on these promising metal/oxide catalysts. Our goal is to develop the ability to predict, and ultimately design, improved cost-effective WGS low temperature catalysts. Our approach exploits a uniquely powerful combination of synthetic and characterization methods for both model systems and industrially relevant powder catalysts. It utilizes unique capabilities for in situ studies using time-resolved X-ray diffraction (XRD), X-ray absorption spectroscopy, photoemission, infrared spectroscopy, and transmission electron microscopy (TEM). Most experiments are closely coupled to theoretical studies on the chemisorption of the reactants, the stability of possible intermediates, and activation barriers for elementary reaction steps, providing critical guidance in developing a complete picture of the links between catalyst structure and reaction mechanism in this important process for the production of pure hydrogen.

FY 2016 Highlights

(1) A new type of metal-support interaction that can be quite useful for the rational design of highly active water-gas shift catalysts was discovered and is under study.

- (2) Studies carried out using inverse oxide/metal catalysts showed the important role played by the oxide phase in the WGS reaction. This led to a shift of paradigm for the design of WGS catalysts. The optimization of the properties of the oxide phase is as important as the optimization of the metal phase.
- (3) Highly active powder catalysts that combine Au or Pt and CeO_2 nanoparticles on a titania substrate were prepared and fully characterized.
- (4) New tools were developed for the in situ characterization of WGS catalysts. A new instrument will combine X-ray absorption fine structure (XAFS) with infrared or Raman spectroscopy. This new instrumentation will allow us to perform unique mechanistic studies.

A series of model catalysts [$\text{CeO}_x/\text{Cu}(111)$, $\text{CeO}_x/\text{Au}(111)$, $\text{Pt}/\text{CeO}_2(111)$, $\text{Ni}/\text{CeO}_2(111)$, $\text{Pt}/\text{TiO}_2(110)$, $\text{Pt}/\text{CeO}_x/\text{TiO}_2(110)$] 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 $\text{Ni}/\text{CeO}_2(111)$, $\text{Pt}/\text{CeO}_2(111)$ and $\text{Pt}/\text{CeO}_x/\text{TiO}_2(110)$ systems. In Figure 1, small coverages of Ni on $\text{CeO}_2(111)$ are highly active for the WGS reaction and do not produce

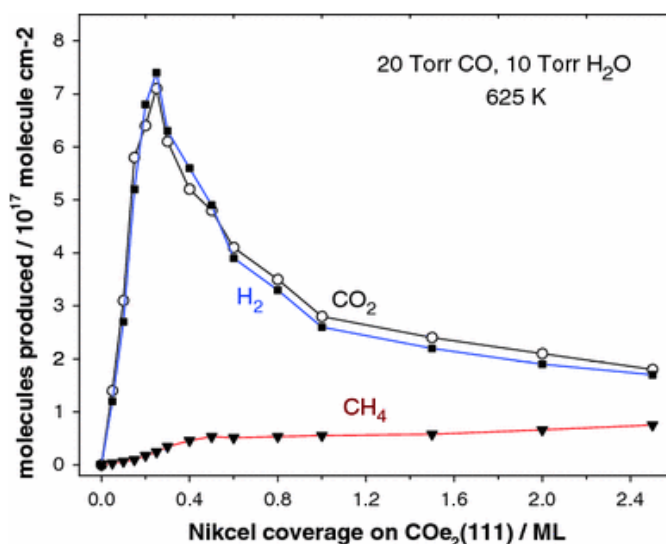


FIGURE 1. Water-gas shift activity of $\text{Ni}/\text{CeO}_2(111)$ as a function of Ni coverage.

methane, although bulk Ni is a very good catalyst for the methanation of CO. The electronic properties of Ni and Pt nanoparticles deposited on $\text{CeO}_2(111)$ and $\text{CeO}_x/\text{TiO}_2(110)$ 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/ $\text{CeO}_2(111)$ Pt/ $\text{CeO}_2(111)$ and Pt/ $\text{CeO}_x/\text{TiO}_2(110)$ 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 (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 WGS (Figure 2). The behavior seen for Ni/ $\text{CeO}_2(111)$, Pt/ $\text{CeO}_2(111)$ and Pt/ $\text{CeO}_x/\text{TiO}_2(110)$ systems illustrates the positive effects derived from electronic metal-support interactions and points to a promising approach for improving or optimizing the performance of metal/oxide catalysts.

The active phase of a series of metal/oxide powder catalysts (Pt/ CeO_2 , Pt-Ru/ CeO_2 , Pt/ $\text{CeO}_x/\text{TiO}_2$, Au/ $\text{CeO}_x/\text{TiO}_2$, $\text{Ce}_{1-x}\text{Ni}_x\text{O}_{2-3}$, CeO_x/CuO) was investigated using a combination of in situ time-resolved XRD, Pair-distribution function (PDF) analysis, 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_2 , TiO_2 and $\text{CeO}_x/\text{TiO}_2$ 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. Figures 3 shows a TEM image and PDF data for an inverse CeO_x/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 to water-gas shift reaction conditions and 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.

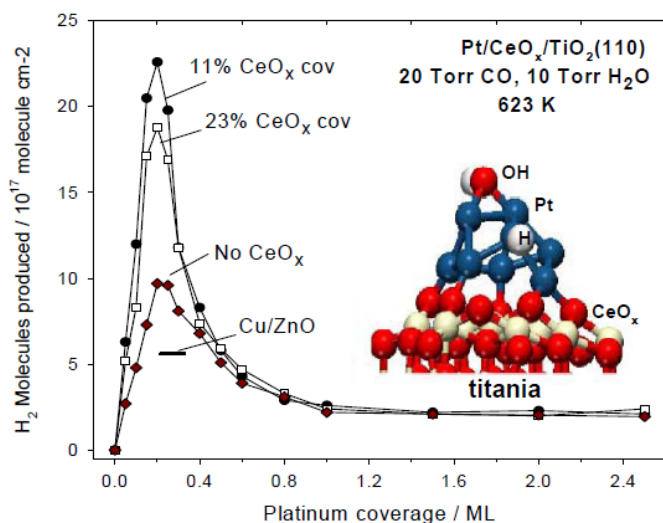


FIGURE 2. Water-gas shift activity of Pt/ $\text{TiO}_2(110)$ and Pt/ $\text{CeO}_x/\text{TiO}_2(111)$ as a function of Pt coverage.

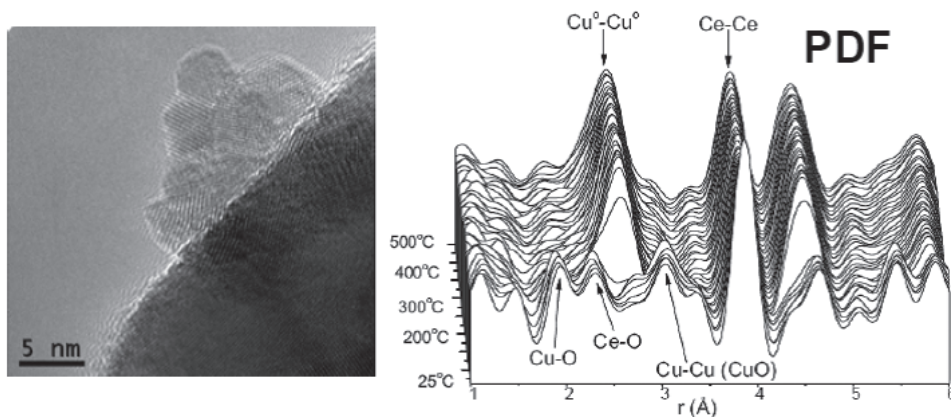


FIGURE 3. Left: TEM image of an inverse CeO_x/CuO catalyst. Right: in situ time-resolved PDF data for a CeO_2/CuO catalyst during the WGS.