

## V.P.13 *In-Situ* Studies of Active Sites and Mechanism for the Water-Gas Shift Reaction on Metal/Oxide Nanocatalysts

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### Objectives

The design and optimization of novel water-gas shift catalysts for the production of pure hydrogen depends on a better understanding of catalyst structure and function. We are carrying out a coordinated research program to understand the active sites and reaction mechanism for the water-gas shift on promising metal-oxide catalysts for industrial applications.

### Technical Barriers

Our goal is to develop the ability to predict, and ultimately design, improved cost-effective water-gas shift low temperature catalysts. These catalysts and the knowledge gained about their behavior will improve the performance and operation of industrial processes used for the production of pure hydrogen.

### Abstract

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 catalytic processes in the chemical industry and fuel cells. High purity hydrogen is needed in massive quantities for the synthesis of ammonia and nitrogen-based fertilizers and for essential hydrogenation processes within the food industry. Furthermore, improved air-tolerant, cost-effective WGS catalysts for lower temperature processing are needed to enable mobile fuel cell applications in a hydrogen fuel economy. The design and optimization of WGS catalysts depends on a better understanding of catalyst structure and function. We are carrying out a coordinated research program to understand the active sites and reaction mechanism for the WGS on promising metal-oxide catalysts. In the initial funding period, our studies with inverse oxide/

metal catalysts have shown the crucial role that an oxide can play in the WGS process. By combining nanoparticles of noble metals (Cu, Au and Pt) and ceria over a titania support, we have obtained extremely active WGS catalysts. Our work indicates that highly active WGS catalysts are bifunctional with the metal and oxide catalyzing different parts of the reaction. In the future, we will be working with three different types of catalyst configurations: metal/oxide, oxide/metal and mixed-metal oxide, with the aim of optimizing the performance of the metal and oxide phases. Our goal is to develop the ability to predict, and ultimately design, improved cost-effective WGS low temperature catalysts. Our approach exploits unique capabilities available for *in-situ* studies in the BNL catalysis programs, and at BNL facilities such as the National Synchrotron Light Source (NSLS) and the Center for Functional Nanomaterials (CFN).

### Progress Report

Since the start of this project 2.5 years ago, seventeen articles have been published by members of the research team examining different aspects of the WGS on metal/oxide catalysts (see separate list of publications). Work was done with high-surface area powders<sup>1-3</sup> and model catalysts,<sup>4,7</sup> combining sophisticated techniques for bulk and surface characterization<sup>1-6</sup> with state-of-the art theoretical calculations.<sup>5,7-11</sup> We have strategically directed part of our efforts to develop synchrotron-based techniques useful for *in-situ* characterization of catalysts and mechanistic studies: Quick XAFS, combined XRD/XAFS and combined XAFS/IR.

**A. In-situ XRD and XAFS studies of the WGS reaction on  $\text{CuFe}_2\text{O}_4$ ,  $\text{CuMoO}_4$  and  $\text{Ce}_{1-x}\text{Cu}_x\text{O}_2$ .** Cu-Fe oxides are used as WGS catalysts in several industrial processes.<sup>12-14</sup> The structure of  $\text{CuFe}_2\text{O}_4$  is known as an "inverse spinel" (Figure 1).<sup>2</sup> Copper ions sit predominantly on octahedral sites and iron atoms alternate between octahedral and tetrahedral sites. XRD data collected while performing the WGS on  $\text{CuFe}_2\text{O}_4$  showed that up to  $\sim 200^\circ\text{C}$ , there were no changes in the tetragonal structure of  $\text{CuFe}_2\text{O}_4$  and no WGS activity was detected.<sup>2</sup> From 200 to  $300^\circ\text{C}$ , CO attacks the oxide and partial reduction leads to the segregation of metallic Cu with the onset of WGS activity. At  $350^\circ\text{C}$ , one has an active WGS catalyst which contains a mixture of Cu,  $\text{CuFe}_5\text{O}_8$  and/or  $\text{Fe}_3\text{O}_4$ .<sup>2</sup> A Rietveld refinement gave a mole ratio of  $\sim 1$  for the diffraction lines of copper and the  $\text{CuFe}_5\text{O}_8/\text{Fe}_3\text{O}_4$  spinel.<sup>2</sup> *In-situ* experiments of x-ray absorption spectroscopy at the Cu

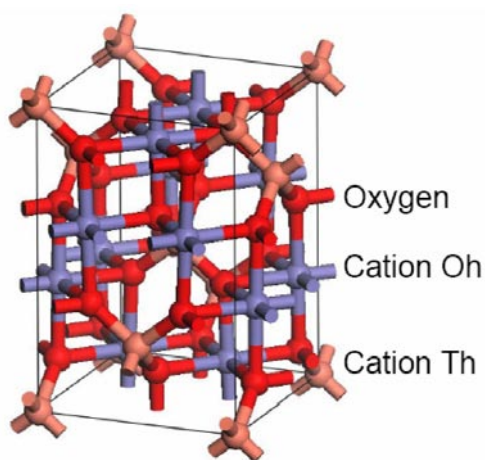


FIGURE 1. Structure of  $\text{CuFe}_2\text{O}_4$

K-edge indicated that essentially all the  $\text{Cu}^{2+}$  initially present in  $\text{CuFe}_2\text{O}_4$  was reduced to metallic  $\text{Cu}^0$ .<sup>2</sup> Our XRD and XAFS results point to metallic copper as an active species for the WGS.<sup>2</sup> This is consistent with studies performed in our group for the water-gas shift on  $\text{CuMoO}_4$ ,  $\text{Ce}_{1-x}\text{Cu}_x\text{O}_{2-x}$ , and  $\text{CuO-ZnO}$  powder catalysts.<sup>1,3</sup> In all of these systems, catalytic activity was seen only after a  $\text{Cu}^{2+} \rightarrow \text{Cu}^0$  transformation. A highly active phase consists of metallic Cu dispersed on a partially reduced oxide support ( $\text{MoO}_2$ ,  $\text{CeO}_{2-x}$ ,  $\text{Fe}_3\text{O}_{4-x}$ ).<sup>1-3</sup> These studies help to solve a long debate about the oxidation state of Cu in oxide-based WGS catalysts.<sup>3,15</sup>

**B. WGS activity of Cu nanoparticles supported on well-defined oxide surfaces.** Since  $\text{CuFe}_2\text{O}_4$ ,  $\text{Ce}_{1-x}\text{Cu}_x\text{O}_2$ ,  $\text{CuO-ZnO}$ , or  $\text{CuMoO}_4$  show significant water-gas shift activity only when the Cu cations in the mixed-metal oxide are reduced to metallic copper, Cu nanoparticles were deposited on a series of well-defined oxide surfaces and their WGS activity was measured in a batch reactor.<sup>6,9</sup> The WGS activity of the Cu nanoparticles supported on  $\text{MgO}(100)$  was 2-3 times larger than that of  $\text{Cu}(100)$ .<sup>6</sup> Even better WGS catalysts were obtained when Cu was deposited on  $\text{CeO}_2(111)$  or  $\text{TiO}_2(110)$ .<sup>6,9</sup> An apparent activation energy of 13.8 kcal/mol was found for the WGS on  $\text{Cu/MgO}(100)$ .<sup>6</sup> This is smaller than the value of 15.2 kcal/mol observed on  $\text{Cu}(100)$ , and substantially larger than the values of 7-9 kcal/mol seen for the apparent activation energies of the  $\text{Cu/CeO}_2(111)$  and  $\text{Cu/TiO}_2(110)$  catalysts.<sup>6,9</sup> Post-reaction surface characterization pointed to the lack of O vacancies in the  $\text{Cu/MgO}(100)$  catalysts.<sup>6</sup> This is in contrast to results found for  $\text{Cu/CeO}_2(111)$  and  $\text{Cu/TiO}_2(110)$ , where the oxide support exhibits a significant concentration of O vacancies as a consequence of the WGS reaction.<sup>6,9</sup> The oxygen vacancies present in  $\text{Cu/CeO}_2(111)$  and  $\text{Cu/TiO}_2(110)$  could help in the

dissociation of the water molecule and reduce the apparent activation energy for the WGS process.<sup>9</sup>

**C. WGS reaction on inverse  $\text{CeO}_x/\text{Cu}(111)$  and  $\text{CeO}_x/\text{Au}(111)$  catalysts: Active role of the oxide.**

Several studies dealing with metal/oxide powder catalysts and the WGS indicate that the oxide plays a direct role in the reaction,<sup>13,16</sup> but due to the complex nature of these systems there is no agreement on what exactly this role is. To address this issue, we performed experiments on inverse  $\text{CeO}_x/\text{Au}(111)$  and  $\text{CeO}_x/\text{Cu}(111)$  catalysts.<sup>5,7</sup> After depositing Ce atoms on  $\text{Cu}(111)$  under an atmosphere of  $\text{O}_2$ , one obtains  $\text{CeO}_x/\text{Cu}_2\text{O}/\text{Cu}(111)$  systems.<sup>5</sup> Upon reaction with CO, the  $\text{Cu}_2\text{O}$  is easily reduced and one obtains  $\text{CeO}_x/\text{Cu}(111)$  inverse catalysts.<sup>5</sup> The oxidation state of Ce in these systems is a mixture of  $\text{Ce}^{3+}/\text{Ce}^{4+}$ . The deposition of ceria nanoparticles on top of  $\text{Cu}(111)$  produces a phenomenal increase in the WGS activity.<sup>5</sup> A comparison of the WGS activities of  $\text{CeO}_x/\text{Cu}(111)$  and  $\text{Cu/CeO}_2(111)$  shows that an optimization of the physical and chemical properties of the oxide component is as important as the optimization of the properties of the metal component.<sup>5</sup>

**D. Controlling the nature of mixed-metal oxide catalysts at the nanometer level: High WGS activity of  $\text{M/CeO}_x/\text{TiO}_2(110)$  surfaces ( $\text{M} = \text{Au}, \text{Cu}, \text{Pt}$ ).**

Recently, there has been a strong interest in understanding phenomena associated with the deposition of oxide nanoparticles on the surface of a second (host) oxide.<sup>17</sup> At BNL, STM, photoemission, and density-functional calculations were used to study the behavior of ceria nanoparticles deposited on a  $\text{TiO}_2(110)$  surface.<sup>4</sup> The titania substrate imposed non-typical coordination modes on the ceria nanoparticles. In the  $\text{CeO}_x/\text{TiO}_2(110)$  system, the Ce cations adopt a geometry and an oxidation state (+3) which are quite different from those seen in bulk ceria or for ceria nanoparticles on metal substrates.<sup>4,10</sup> The results of STM show the formation of  $\text{Ce}_2\text{O}_3$  dimers which form small linear arrays on top of the  $\text{TiO}_2(110)$  substrate (see Figure 2). An increase in the stability of the  $\text{Ce}^{3+}$  oxidation state leads to an enhancement in the chemical and catalytic activity of the ceria nanoparticles.<sup>4,10,11</sup> The co-deposition of ceria and gold nanoparticles on a  $\text{TiO}_2(110)$  substrate generates catalysts with an extremely high activity for the production of hydrogen through the water-gas shift reaction (see Figure 3).  $\text{Au/CeO}_x/\text{TiO}_2(110)$  was found to be much more active than  $\text{Au/TiO}_2(110)$  or even  $\text{Au/CeO}_2(111)$ .<sup>4</sup> On the  $\text{TiO}_2(110)$  surface, the ceria nanoparticles help to disperse the Au atoms and to dissociate the water molecule.<sup>4,10,11</sup> While Au surfaces and nanoparticles interact poorly with water,<sup>8</sup> density-functional calculations predict an exothermic process for the dissociation of water on  $\text{CeO}_x/\text{TiO}_2(110)$  with almost no activation barrier.<sup>10,11</sup> The enhanced stability of the  $\text{Ce}^{3+}$  state in  $\text{CeO}_x/\text{TiO}_2(110)$  is an example of structural

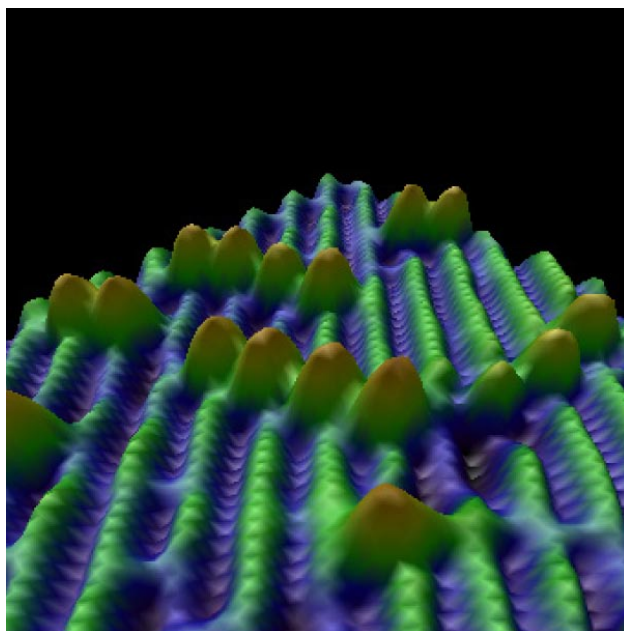


FIGURE 2. STM image for the deposition of  $\text{CeO}_x$  on  $\text{TiO}_2(110)$ <sup>6</sup>

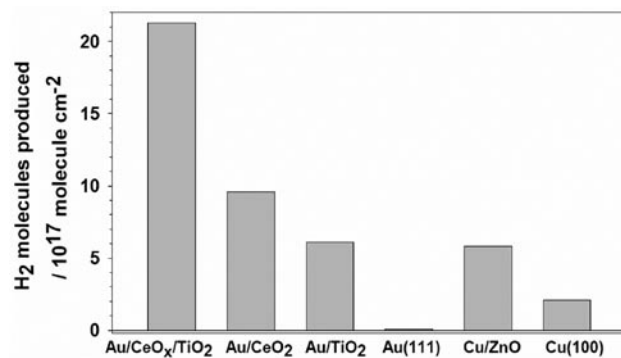
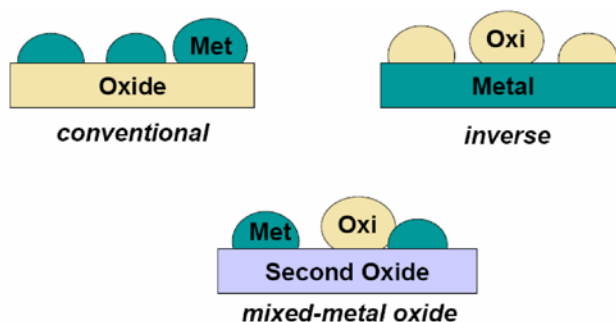


FIGURE 3. WGS activity of  $\text{Au/CeO}_x/\text{TiO}_2(110)$ ,  $\text{Au/CeO}_2(111)$ ,  $\text{Au/TiO}_2(110)$  and  $\text{Cu/ZnO}(000\bar{1})$ .<sup>6</sup> The reported values for the production of  $\text{H}_2$  were obtained after exposing the catalysts to 20 Torr of CO and 10 Torr of  $\text{H}_2\text{O}$  at 352°C for 5 minutes.<sup>6</sup>

promotion in catalysis documented for the first time on the atomic level.<sup>4</sup> Thus, the exploration of mixed-metal oxides at the nanometer level may open new avenues for optimizing catalysts through stabilization of non-conventional surface structures with special chemical activity.<sup>4,10,17,18</sup> The  $\text{Cu/CeO}_x/\text{TiO}_2(110)$  and  $\text{Pt/CeO}_x/\text{TiO}_2(110)$  systems are also excellent WGS catalysts.<sup>10</sup> In the future, we plan to extend this type of studies to high-surface area powders. A first set of studies for a  $\text{Pt/CeO}_x/\text{TiO}_2$  powder shows a very good WGS catalyst.<sup>18</sup>



## Future Directions

The studies described above indicate that highly active water-gas shift catalysts are bifunctional with the metal and oxide catalyzing different parts of the reaction. To optimize these complex systems one must understand the nature of the active sites in each component of the catalyst and determine how they interact with the reactants ( $\text{CO}$ ,  $\text{H}_2\text{O}$ ) and possible intermediates ( $\text{OH}$ ,  $\text{HOCO}$ ,  $\text{HCOO}$ ,  $\text{CO}_3$  and  $\text{HCO}_3$ ) of the WGS.<sup>19</sup> In the future, we plan to work with catalysts in which the oxide phase contains or combines ceria, titania and molybdena. Cu, Au, Pd or Pt will constitute the metal phase. This selection of oxides and metals is based in our previous studies. The high WGS activity of ceria- and titania-based catalysts is well documented in the literature.<sup>15,16,20</sup> They are expected to be the next generation of WGS catalysts for industrial applications. We will identify methodologies for developing highly efficient WGS catalysts optimizing the performance of the metal and oxide phases. The scheme at the left shows the three different configurations in which a metal and an oxide will be combined in our catalysts. The most complex and promising is the mixed-metal oxide configuration in which nanoparticles of a metal and an oxide can interact with the reactants.<sup>4,10,18</sup> Our experience indicates that a coordinated approach is necessary to address fundamental issues for the WGS on metal/oxide catalysts. Thus, we propose three research thrusts: (i) *in-situ* studies; (ii) model system studies; and (iii) theoretical calculations. The overarching questions of catalyst state, reaction mechanism, and nanoparticle size and morphology interconnect these thrusts. As in the past, we will be taking advantage of a unique set of techniques available at BNL for *in-situ* studies (XRD, XAFS, TEM, IR, XPS). The experiments will 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 structure and mechanism in this important process.

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