

# Metal Ion Sites on Oxide Supports as Catalysts for the Water-Gas Shift and Methanol Steam Reforming Reactions

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## Objectives

The overall goal of this project is to elucidate the atomic-level interaction of Au, Cu, and Pt, with oxide supports, such as CeO<sub>2</sub>, ZrO<sub>2</sub>, ZnO, FeO<sub>x</sub>, and TiO<sub>2</sub> for reactions of interest in the production of hydrogen via the water-gas shift reaction and fuel processing reactions, especially methanol conversion reactions. One key objective is to understand the role of the support in these systems. Nanoshapes of the oxide supports are prepared to test structure sensitivity. Use of alkali promoters is investigated as a way to stabilize metal cations on any support, including earth-abundant oxides (silica,

alumina) and even carbon surfaces. Another major objective is the synthesis and detailed study of single atom alloys of PdCu, PtCu, PdAu, containing trace amounts of platinum or palladium, as new highly selective catalysts for reactions of methanol and other biomass-derived oxygenates.

## Abstract

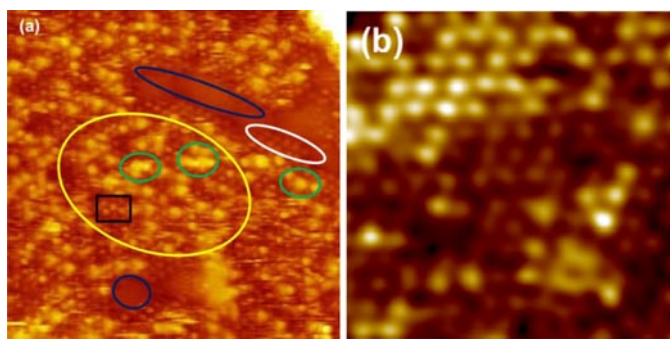
The work conducted this year was multi-pronged. For both the water-gas shift (WGS) and the methanol steam reforming (SRM) reactions, understanding the role of water on the surface is crucial. This was examined by STM and DFT studies of the Au/Fe<sub>3</sub>O<sub>4</sub>(111) model catalyst for the WGS reaction. Strongly bound OH species on the Fe<sup>III</sup> cations of the iron-terminated Fe<sub>3</sub>O<sub>4</sub>(111) surface do not allow CO adsorption. Only when Au adatoms are present (bound over the under-coordinated O atoms) on the iron oxide surface, is CO adsorption possible. This explains why the WGS reaction occurs at low temperatures on the Au/Fe<sub>3</sub>O<sub>4</sub> surfaces, but not on the gold-free iron oxide surfaces. Methanol activation is also studied over the same surfaces. In the case of methanol activation on copper catalysts, water was found to play an important catalytic role. Using high-resolution STM and temperature programmed reaction analysis, we found that six or more water molecules in the form of hydrogen bonded clusters act cooperatively to deprotonate each methanol molecule on an *oxygen-free* Cu(111) surface, stabilizing methoxy species on the copper step edges. The addition of isolated Pd atoms to the Cu(111) surface promotes this reaction, with methoxy dehydrogenating selectively to formaldehyde at higher temperatures. These results are fundamentally important when considering the mechanism involved in methanol reforming to products including CO, CO<sub>2</sub> and H<sub>2</sub>. In work with alkali promoted atomically dispersed Pt, we showed very high stability of core-shell Pt(Na)@SiO<sub>2</sub> materials under realistic WGS reaction conditions. More than half of the Pt existed as active Pt-O-(OH)-Na clusters in the silica shell and their activity was similar to that of Pt/CeO<sub>2</sub>. Na-promoted Pt on TiO<sub>2</sub> was prepared also last year and tested for formaldehyde oxidation at ambient conditions. This work was in collaboration with the Hong He group, of the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing. A new more efficient mechanistic pathway for the formaldehyde oxidation reaction was identified in that work. Alkali addition also effectively activates Pt on multi-wall carbon nanotubes, an otherwise inert material, to become an efficient catalyst for the WGS reaction at ~ 250-300 °C. Work on alkali promotion of gold catalysts continued this year with new experimental as well as computational findings supporting the model of a single metal center stabilized

by O and OH species supplied by the surrounding sodium atoms. Au-O- species on ceria were also found to catalyze the dehydrogenation of formic acid at close to ambient conditions. These findings are general and can be extended to other supports.

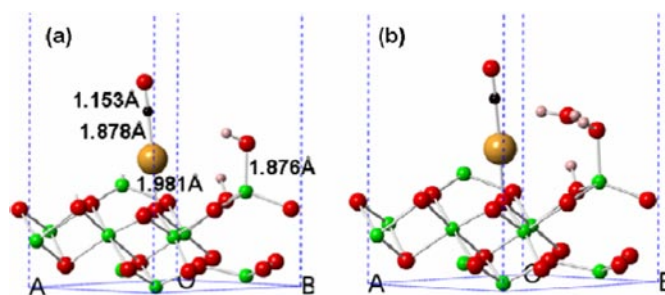
## Progress Report

### 1. Scanning Tunneling Microscopy and Theoretical Study of Water Adsorption on $\text{Fe}_3\text{O}_4$ and of the Water-Gas Shift Reaction on Au/ $\text{Fe}_3\text{O}_4$

The adsorption of water on iron oxide single crystal surfaces was investigated via Scanning Tunneling Microscopy (STM) and first-principle theoretical simulations<sup>1</sup>. Water species are observed only on the Fe-terminated  $\text{Fe}_3\text{O}_4(111)$  surface at temperatures up to 235 K, Fig. 1. Between 235 and 245 K we observed a change in the surface species from intact water molecules and hydroxyl groups bound to the surface to only hydroxyl groups atop the surface terminating  $\text{Fe}^{\text{III}}$  cations. DFT calculations confirm the identity of the surface species proposed from the STM images, finding that the most stable water species are the dissociated one (OH + H), with OH atop surface terminating  $\text{Fe}^{\text{III}}$  sites and H atop under-coordinated oxygen sites. Attempts to simulate the adsorption of CO on the hydroxylated surface fail because the only binding sites for CO are the surface  $\text{Fe}^{\text{III}}$  sites, which are blocked by the much more strongly bound OH. In order to promote this reaction, we simulated a surface decorated with gold atoms, Fig. 2. The Au ad-atoms cap the under-coordinated oxygen sites and dosed CO is found to bind to the Au ad-atom. This newly created binding site for CO not only allows for coexistence of CO and OH on the surface of  $\text{Fe}_3\text{O}_4$  but also provides collocation between the two species. These two factors explain



**FIGURE 1.** Topographic STM image of an iron oxide surface after dosing 0.15L of water at 235 K. (a) The image at 235K shows that the Fe-terminated  $\text{Fe}_3\text{O}_4(111)$  domain (yellow oval) has chemisorbed water species (marked by the black rectangle) and physisorbed water species (marked by green ovals) on it while the O-terminated  $\text{FeO}(111)$  (blue ovals) domains do not have any adsorbed water species; (b) The image at 245 K clearly shows only hydroxyl groups (bright features) on the Fe-terminated  $\text{Fe}_3\text{O}_4(111)$  surface.

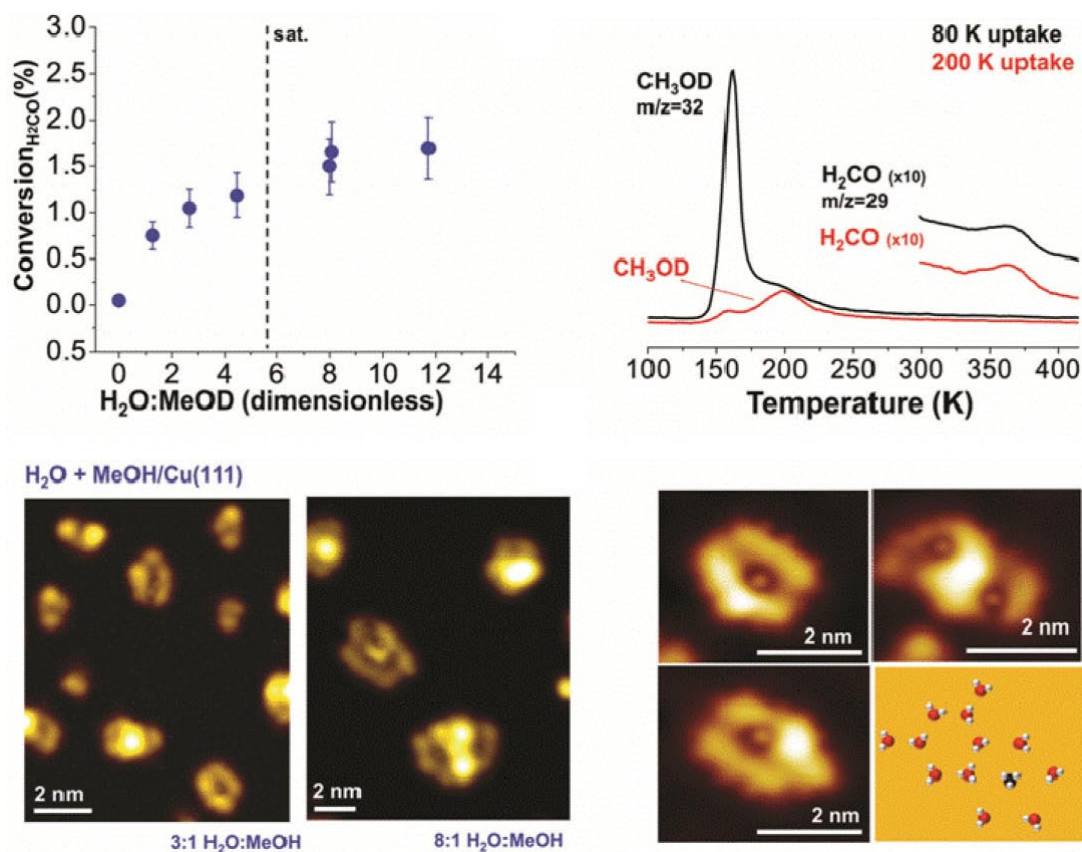


**FIGURE 2.** Optimized  $\text{H}_2\text{O}$  and CO adsorption on an Au-doped  $\text{Fe}_3\text{O}_4(111)$  surface (a) Dissociative water adsorption (b) Two  $\text{H}_2\text{O}$  molecule adsorption (Red: O atoms; Green: Fe atoms; Black: C atom; Orange: Au atom; Pink: H atoms).

the catalytic activity for the Water-Gas Shift Reaction on Au/ $\text{Fe}_3\text{O}_4(111)$  surfaces.

### 2. Water-Catalyzed Methanol Dehydrogenation to Formaldehyde

Copper catalysts have excellent activity and selectivity for methanol conversion to hydrogen and carbon dioxide by the SRM reaction. This product balance is dictated by the formation and weak binding of formaldehyde, the key reaction intermediate. It is widely accepted that oxygen adatoms or oxidized copper are required to activate methanol. By high-resolution STM and temperature programmed reaction testing, we found that six or more water molecules in the form of hydrogen bonded clusters act cooperatively to deprotonate each methanol molecule on an *oxygen-free* copper surface. Hydrogen-bonded networks of water comprise an active complex on which it is energetically favorable to bind a proton. On an atomically flat  $\text{Cu}(111)$  surface, where methoxy can only be formed as a transient species, the addition of hydrogen-bonded water complexes that stabilize H atoms drives O-H bond scission, leaving methoxy stabilized on Cu step edge atoms<sup>2</sup>. The addition of isolated Pd atoms to the  $\text{Cu}(111)$  surface promotes this reaction by allowing more methanol to remain on the surface at higher temperatures, where a greater degree of O-H bond activation can take place. Methoxy stabilized at Cu step edges and/or Pd atoms remains on the surface until it dehydrogenates selectively to formaldehyde at higher temperatures. The water-assisted dehydrogenation of methanol to formaldehyde comprises a new elementary step in the methanol steam reforming pathway. By studying well-defined surfaces, we have shown that both under-coordinated Cu step edge atoms and isolated Pd atoms at  $\text{Cu}(111)$  step edges can act as selective methanol dehydrogenation sites, as no decomposition of methanol to CO was observed<sup>2</sup>.



**Figure 3.** Upper left panel shows conversion of methanol to formaldehyde (370 K) as a function of water coverage adsorbed with 0.15 ML of partially deuterated methanol (CH<sub>3</sub>OD) on Cu(111). The vertical line indicates saturation of the monolayer. The upper right panel shows TPR profiles of methanol adsorbed at 85 K and 200 K on Cu(111); in each case, water was co-adsorbed on the surface at 85 K. The lower STM panels show co-adsorption of methanol and water at 5 K after annealing to 60 K leads to the formation of new structures. High resolution STM images reveal a new structure consisting of a ring of hydrogen-bonded water molecules surrounding a deprotonated methanol molecule. In this configuration, the water molecules act in concert to deprotonate the methanol molecule to methoxy, which appears as a localized protrusion in the cluster<sup>2</sup>.

### 3. Silica-encapsulated platinum catalysts for the low-temperature water-gas shift reaction

Encapsulated platinum in core-shell Pt@SiO<sub>2</sub> materials was prepared by a reverse microemulsion method. With alkali ion addition, the Pt-Na@SiO<sub>2</sub> or Na(IMP)-Pt@SiO<sub>2</sub> materials show very good activity for the low-temperature WGS reaction, Fig. 4. Promotion by Na is independent of the point of addition<sup>3</sup>.

The active Pt-O<sub>x</sub>(OH)-Na species in the silica shell stabilize both the Pt and Na ions, dissociate water, and regenerate surface hydroxyl groups. The apparent activation energy for the WGS reaction over Pt-based catalysts is independent of the support structure and type.

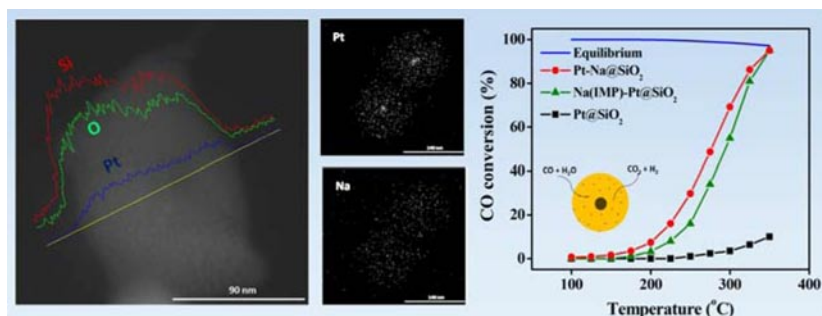
### 4. Alkali-promoted Pt/TiO<sub>2</sub> opens a new pathway to formaldehyde oxidation at ambient temperatures

In work carried out with alkali-promoted Pt/TiO<sub>2</sub> catalysts, we found that the key steps for HCHO oxidation

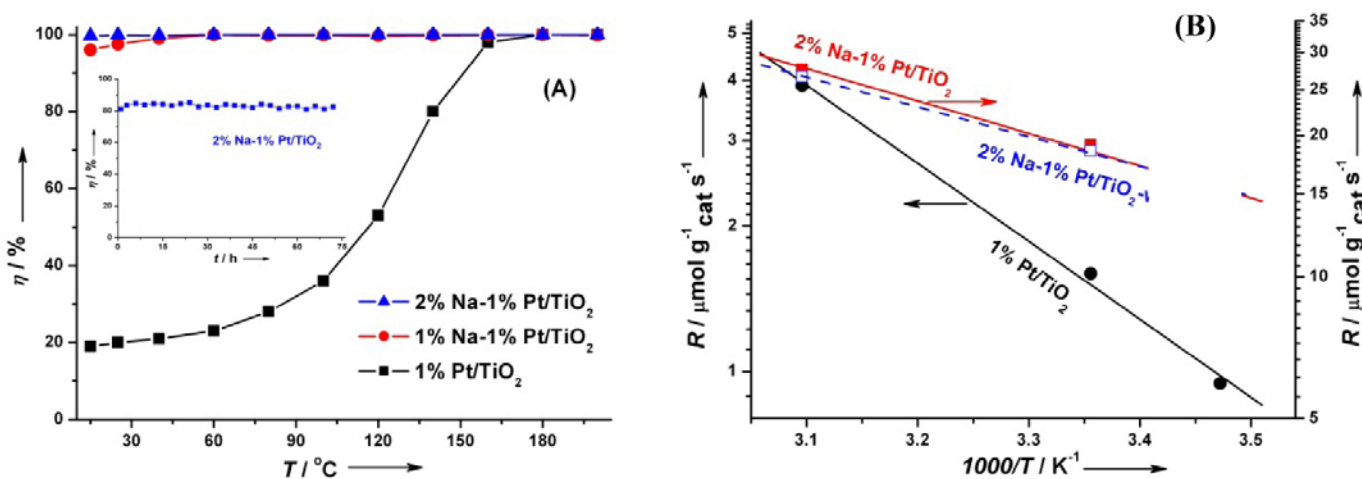
(including O<sub>2</sub>, HCHO and H<sub>2</sub>O activation) take place on the atomically dispersed Pt-O(OH)<sub>x</sub>-alkali species, which alters the ambient-temperature HCHO oxidation pathway by promoting the reaction between surface OH and formate species at room temperature, and thus greatly enhancing the HCHO oxidation activity<sup>4</sup>. Such OH activation by alkali ion addition may apply to other volatile organic compound oxidation reactions and to other metals.

### 5. Dehydrogenation of formic acid on atomically dispersed gold on ceria

In new work with supported gold on ceria, we have found that atomically dispersed gold species catalyze the decomposition of formic acid through the dehydrogenation pathway at near-ambient temperatures. Au-O-Ce sites on the {110} surfaces of ceria nanorods prepared by hydrothermal methods have high activity and excellent stability for formic acid dehydrogenation<sup>5</sup>. Mechanistic insights from this study



**FIGURE 4.** (left panel) Elemental linescans of as prepared Pt@SiO<sub>2</sub> after air calcination at 400 °C; and STEM/EDS of Pt, Na in the same. (right panel) CO conversion profiles in steady-state tests of WGS reaction over Pt@SiO<sub>2</sub>, Pt-Na@SiO<sub>2</sub> and Na(IMP)-Pt@SiO<sub>2</sub> catalysts (2%CO–10%H<sub>2</sub>O–He, 70 mL/min, contact time = 0.09 g s/mL).

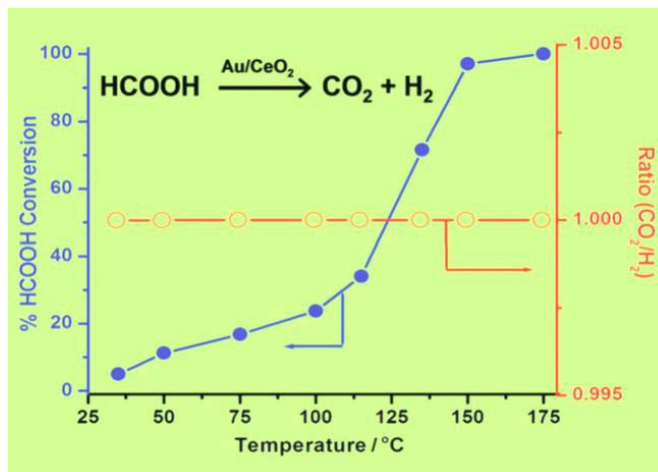


**FIGURE 5.** (A) HCHO conversion ( $\eta$ ) over x wt.% Na-1 wt.% Pt/TiO<sub>2</sub> (x = 0, 1 and 2) catalysts as a function of temperature. HCHO 600 ppm, O<sub>2</sub> 20 vol.%, RH: ~50%, He bal.; total flow rate: 50 cm<sup>3</sup> min<sup>-1</sup>, and GHSV 120,000 h<sup>-1</sup> (inset: stability test of 2% Na-1% Pt/TiO<sub>2</sub> at 25 °C, GHSV = 300,000 h<sup>-1</sup> with same other reaction conditions); (B) HCHO oxidation rate (R) over 1% Pt/TiO<sub>2</sub>, 2% Na-1% Pt/TiO<sub>2</sub> and 2% Na-1% Pt/TiO<sub>2</sub>-washed catalysts.

point to the use of trace amounts of gold to achieve robust and cost-effective catalysts.

### 6. Other Work with atomically dispersed supported gold and platinum

Alkali addition was effective in activating Pt on any support, including platinum on multi-wall carbon nanotubes, an otherwise inert material. Pt-O-(OH)-Na clusters on the carbon nanotube walls catalyze the WGS reaction at ~ 250-300 °C<sup>6</sup>. Work on alkali promotion of gold catalysts continued this year with new experimental as well as computational findings supporting the model of a single gold atom stabilized by O and OH species supplied by the surrounding sodium atoms. Results from this work will be included in the annual report.



**FIGURE 6.** Decomposition of formic acid with dispersed gold on ceria

## Future Directions

A comprehensive and complementary approach is followed to elucidate the metal-oxide interaction at the atomic scale. Since last year, we have also added an important new dimension to the project on the atomic metal-to-metal interaction with the preparation of single atom alloys. Work with methanol reactions on PdCu and PtCu SAAs will continue both with model catalysts and their nanoparticle analogs. In other STM work, methanol on the Au/Fe<sub>3</sub>O<sub>4</sub>(111) model catalyst is currently under investigation. This work will be concluded in the first part of the next reporting period; and the results will be transferred to nanoshapes for further study under ambient pressure. The synthesis, characterization and evaluation of Au and Cu and their surface alloys on nanoshapes of ZnO, TiO<sub>2</sub> and (Zn) ZrO<sub>2</sub> for WGS, SRM, and ethanol reactions will continue. The desired outcome is a good mechanistic understanding of the chemistries under investigation and the reaction-induced evolution of the key catalyst structures in order to propose general catalyst design guidelines for the reactions of interest to this project.

## Publication list acknowledging the DOE grant DE-FG02-05ER15730— this reporting period

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3. Wang, Y, Zhai Y, Pierre, D, Flytzani-Stephanopoulos, M., “Silica-encapsulated Platinum Catalysts for the low-temperature Water-gas Shift Reaction”, *Appl. Cat. B* **2012**, 127, 342- 350.
4. Zhang, C, et al., “Alkali-Metal-Promoted Pt/TiO<sub>2</sub> Opens a More Efficient Pathway to Formaldehyde Oxidation at Ambient Temperatures”, *Angewandte Chemie International Edition*, **2012**, 51, 9628-9632.
5. Yi, N, Saltsburg, H., Flytzani-Stephanopoulos, M, “Efficient and Stable Hydrogen Production through Dehydrogenation of Formic Acid on Atomically Dispersed Gold on Ceria”, *ChemSusChem*, **2013**, DOI: 10.1002/cssc.201200957.
6. Zugic, B, Bell, DC, Flytzani-Stephanopoulos, M, Activation of Platinum Supported on Carbon for the Low-Temperature Water-Gas Shift Reaction, **2013**, submitted.
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9. Lawton, TJ, Kyriakou, G, Baber, AE, Sykes, ECH, “An Atomic Scale View of Methanol Reactivity at the Cu(111)/CuO<sub>x</sub> Interface” *ChemCatChem*, Accepted, **2013** DOI: 10.1002/cctc.201200810
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11. Yang, M, Allard, LF, Flytzani-Stephanopoulos, M. “Atomically Dispersed Au-(OH)<sub>x</sub> Species Bound on Titania Catalyze the Low-temperature Water-Gas Shift Reaction”, *J. Am. Chem. Soc.*, **2013**, DOI: 10.1021/ja312646d.