

## II.A.5 Investigation of Reaction Networks and Active Sites in Bio-Ethanol Steam Reforming over Co-Based Catalysts

Umit S. Ozkan (Primary Contact), Hua Song,  
Lingzhi Zhang

Department of Chemical & Biomolecular Engineering  
The Ohio State University (OSU)  
125 Koffolt Laboratories, 140 W. 19<sup>th</sup> Ave.  
Columbus, OH 43210  
Phone: (614) 292-6623; Fax: (614) 292-3769  
E-mail: ozkan.1@osu.edu

DOE Technology Development Manager:  
Sara Dillich

Phone: (202) 586-7925; Fax: (202) 586-2373  
E-mail: Sara.Dillich@ee.doe.gov

DOE Project Officer: Jill Sims

Phone: (303) 275-4961; Fax: (303) 275-4788  
E-mail: Jill.Sims@go.doe.gov

Contract Number: DE-FC36-05GO15033

Project Start Date: May 1, 2005  
Project End Date: April 30, 2010

- To study how the observed catalyst characteristics influence the reaction pathways for:
  - Oxygenate formation
  - Reverse water-gas-shift
  - Alkane and olefin formation
  - Coke deposition
- Determine how the chosen support material can influence metal dispersion and structure, and how it participates in:
  - Alcohol and water adsorption
  - Spillover of species
  - Intermediate and product formation
- Determine methods that can tailor the catalyst surface for optimum selectivity and activity by:
  - Site blocking
  - Chemical promotion
  - Active site density control
- Determine factors that degrade catalyst stability and optimize regeneration methods:
  - Pathways and active sites for coke formation
  - Loss of surface area under reaction
  - Metal-support compound formation
  - Sintering

### Objectives

Acquire a fundamental understanding of the reaction networks, active sites and deactivation mechanisms of potential bioethanol steam reforming catalysts to develop precious metal free catalysts that can operate at lower temperatures with high yields and selectivities for hydrogen steam reforming from bioethanol. More specifically:

- Determine the effect of catalyst synthesis methods on oxidation state, structure, metal dispersion, and particle size of cobalt-based bio-ethanol reforming catalysts using the following techniques:
  - Aqueous or organic impregnation
  - Co-precipitation
  - Sol-gel synthesis
  - Organometallic synthesis
  - Control of calcination and reduction conditions
- Determine oxidation states and chemical structures that are present in active catalysts that are exposed to:
  - Varying pre-treatment protocols
  - Differing levels of steam-to-carbon ratio during reaction
  - Oxidative and auto thermal operation
  - Different space velocities

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4.2.1) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Reformer Capital Costs
- (C) Operation and Maintenance (O&M)
- (D) Feedstock Issues

### Technical Targets

Bio-ethanol steam reforming over Co-based catalysts:

This project is a systematic and detailed study aimed to provide fundamental answers to questions that are not readily solved in an industrial setting. The results of this study will prevent interpreting erroneous information resulting from the screening of a large catalyst matrix by characterizing the parameters that lead to or inhibit the formation of active sites for reforming. The information obtained from the proposed study will address many

common problems associated with catalyst development, such as choice of materials, pre-treatment conditions, and factors controlling active site distribution, stability, and selectivity. Insights gained from these studies will be applied toward the design and synthesis of cost-effective and efficient reforming technologies that meet the DOE 2012 technical targets for hydrogen from bio-derived renewable liquids. Specific technical targets that would benefit from this study are the following:

- Production Energy Efficiency: 72.0%
- Contribution of Production to Capital Cost: 0.45 (\$/gge)

### Accomplishments

- Characterized the deactivation mechanism over Co-based catalysts.
- Modified catalyst formulation to achieve over 90% H<sub>2</sub> yields at temperatures below 500°C under neat conditions.
- Tested activity for steam reforming of various bio-derived liquids.
- Tested activity in the presence of impurities that are found in bioethanol.
- Used pre-reaction, post-reaction, and in situ characterization of catalysts and mechanistic studies to gain insight into the reaction networks, active sites and oxygen mobility and used these insights for tailoring catalyst surfaces for higher activity and stability.
- Initiated work on molecular simulation for rational design of the catalyst system (collaborative effort).
- Performed initial economic analysis using H2A model resulting in a production cost of \$3.46/kg. An independent analysis performed by Directed Technologies, Inc. using OSU data estimated the production cost as \$3.17/kg.
- Successfully completed the milestones for Phase One of the project and went through a go/no-go evaluation, which resulted in a “go” decision.



### Introduction

For hydrogen energy to fulfill its potential for protecting the environment, providing more efficient energy sources, and decreasing our nation's dependence on foreign oil, we need economical and efficient technologies for hydrogen production from renewable energy sources. Hydrogen production from ethanol through steam reforming offers solutions involved in hydrogen storage and infrastructure and lends itself

very well to a distributed hydrogen production strategy. The bio-ethanol produced by fermentation of biomass can yield an ethanol-water mixture already ideal for reforming without additional distillation steps. A review of the ethanol steam reforming literature shows that there is no consensus about an optimal catalyst, and a fundamental understanding of the relationships between catalytic properties and how these properties are affecting various reaction steps involved in this complex network is lacking.

The development of non-precious metal catalysts in this project will reduce the catalyst cost, while the lower operation temperatures will reduce the material cost for reactor systems and will also reduce the energy requirement for heating the feed mixture to high reaction temperatures. The catalyst will have high steam reforming activity, while being non-selective for various undesired side reactions, such as methanation, dehydration, dehydrogenation, coking, and reverse water-gas-shift reaction. The high yields to be achieved will help increase the production energy efficiency. The catalytic system will have high stability and well-understood regeneration mechanisms. High stability will reduce catalyst cost by prolonging the active life span of the catalyst. The regeneration mechanisms will be useful in reactivating the catalyst, rather than discarding the deactivated catalyst. The design of such catalysts will not be possible without a thorough understanding of the relationships between the catalyst preparation parameters, their structural and molecular characteristics and their reaction performance. The understanding acquired through this study will eliminate the need for costly trial-and-error efforts and will enable design of catalytic systems with the desired characteristics.

### Approach

The project encompasses a comprehensive study of precious-metal free catalyst systems (Co-based) for steam reforming of bio-ethanol and other bio-derived liquids for hydrogen production. The study includes examination of the catalyst at every stage of its life history, from precursor stage to activation, deactivation and regeneration steps, in an effort to understand the nature of active sites, the reaction networks and all underlying phenomena that determine the activity, selectivity and stability of these catalysts. The techniques used include catalyst synthesis studies, transient and steady-state reaction tests, and characterization studies using surface, bulk and molecular analysis techniques. The approach taken is not a consecutive execution of the tasks or steps in each task, but rather an iterative approach where the findings in one aspect of the study are utilized in a feed-back mechanism to plan, and modify the steps taken in another task.

**Results**

The impurity tolerance of the catalyst system is important for steam reforming crude ethanol directly without undergoing distillation and then re-mixing with water. Since the crude ethanol is much cheaper than pure ethanol, the development of the catalyst system with excellent impurity tolerance in the reactants will facilitate the further reduction of the hydrogen cost from ethanol steam reforming route. Based on the reported composition of the crude ethanol [1], a typical reactant liquid mixture is assumed to be composed of 1% glycerol, 1% lactic acid, 12% ethanol, and 86% water at volumetric percentage. The Co/CeO<sub>2</sub> catalyst displayed excellent reforming performance as shown in Figure 1. Ethanol is completely converted at temperatures as low as 350°C. Approximately 95% H<sub>2</sub> yield is achieved when the temperature is above 450°C. Acetaldehyde and acetone are main byproducts appearing at lower temperatures, but are not observed above 400°C. Methane steam reforming and reverse water-gas-shift in addition to bio-ethanol steam reforming (BESR) are the major reactions controlling the product distribution and H<sub>2</sub> yield at higher temperatures. More significantly, the high activity can be maintained up to 100 hrs without any sign of deactivation.

Although the catalyst systems developed so far are exclusively designed for ethanol steam reforming, their applicability for reforming other bio-liquids can be an important advantage if acceptable activity as well as stability can be acquired, since a variety of organic compounds will be produced after fermentation of biomass. Table 1 summarizes the H<sub>2</sub> yields achieved for various commonly used bio-derived liquids at temperatures 450°C and above over a 10%Co/CeO<sub>2</sub>

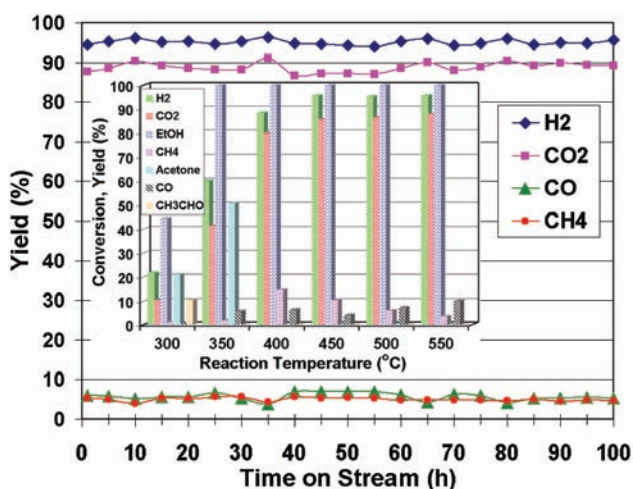
catalyst prepared through incipient wetness impregnation (IWI) using ethanol as the solvent for the Co precursor. Generally, a minimum of 80% hydrogen yield is achieved for all bio-derived liquids tested.

**TABLE 1.** The Hydrogen Yields for Various Bio-Derived Liquids over 10%Co/CeO<sub>2</sub>

Bio-derived liquids	% H <sub>2</sub> Yield
Methanol	> 95% at 450°C
1-propanol	> 90% at 500°C
2-propanol	> 80% at 550°C
Butanol	> 85% at 550°C
Dimethyl ether	> 80% at 550°C

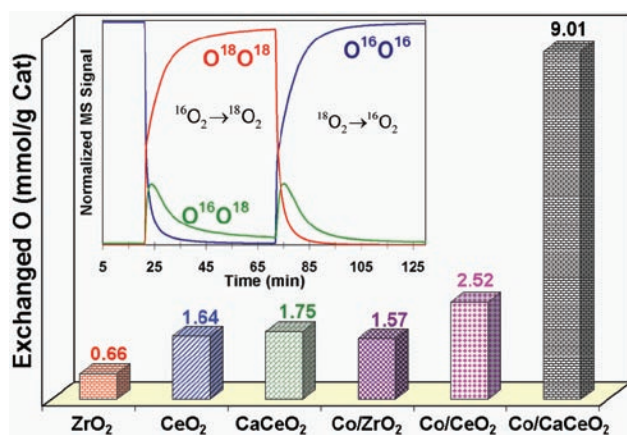
The post-reaction characterization studies were performed over spent catalysts. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) characterization showed that in addition to amorphous carbon, carbon nanofibers were also formed over 10%Co/ZrO<sub>2</sub> with varying diameters. The cobalt particles appeared to be encased at the tip of the fibers. The carbon fibers are seen to vary in diameter substantially, depending on the size of the Co particle that catalyses its growth. While most of the fibers are shorter with diameters around 20 nm, there are some fibers with much larger diameters (~150 nm). Compared to the average size of the Co particles of freshly reduced samples, some of the Co particles encased in carbon fibers appear to be much larger, suggesting that there may have been sintering of Co particles during reaction, resulting in larger particle sizes. The catalysts which contained ceria (10%Co/10%CeO<sub>2</sub>-ZrO<sub>2</sub>) showed no fiber formation even after 110 hrs time-on-stream experiment. TEM analysis at high resolutions suggested that the CeO<sub>2</sub>-added catalyst followed an “extrusion” mechanism in coke deposition, where carbon is not allowed to dissolve and diffuse into the metal particle, inhibiting fiber formation. Over the Co-ZrO<sub>2</sub> catalysts, the Co particles seem to be lifted off the surface by the fiber growth mechanism, over the ceria-modified catalysts, the Co particles remain anchored on the surface.

In situ and post-reaction characterization of catalysts showed oxygen mobility to play a significant role in improving catalytic performance, including activity and stability by facilitating complete ethanol oxidation to CO<sub>2</sub>. Isotopic oxygen exchange technique has been widely accepted as a useful tool for investigating oxygen mobility in oxides [2-4]. The inset of Figure 2 shows the typical profiles collected during <sup>16</sup>O<sub>2</sub>-to-<sup>18</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub>-to-<sup>16</sup>O<sub>2</sub> switches. All the signals are normalized by the total counts. During the first switch, <sup>16</sup>O<sup>16</sup>O signal (m/z=32) decreases, accompanied by a rise of <sup>18</sup>O<sup>18</sup>O signal (m/z=36). The <sup>16</sup>O<sup>18</sup>O signal (m/z=34) is shown to go through a maximum. The



**FIGURE 1.** Ethanol conversion and product distribution over 10%Co/CeO<sub>2</sub> (EtOH IWI) during crude ethanol steam reforming at different temperatures. (Reaction parameters: H<sub>2</sub>O:EtOH=23.5:1 (molar ratio), GHSV ~15,000 h<sup>-1</sup>, WHSV=0.2g EtOH/gCat/h, and C<sub>EtOH</sub> ~1%) and the corresponding time-on-stream data at 450°C.

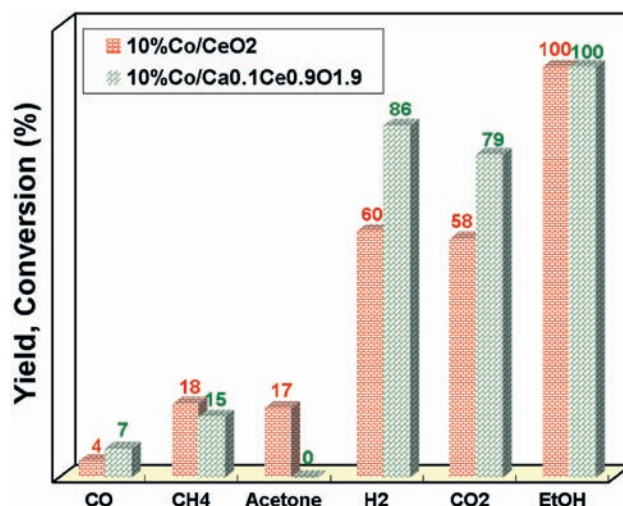




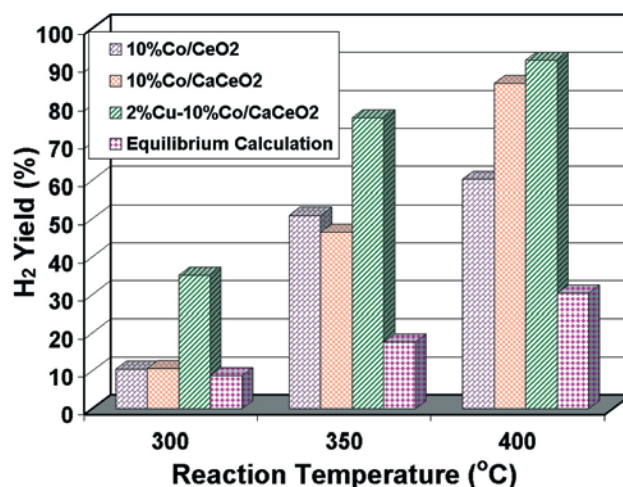
**FIGURE 2.** Oxygen mobility over  $ZrO_2$ ,  $CeO_2$ ,  $Ca_{0.1}Ce_{0.9}O_{1.9}$ ,  $10\%Co/ZrO_2$ ,  $10\%Co/CeO_2$ ,  $10\%Co/Ca_{0.1}Ce_{0.9}O_{1.9}$  measured using  $^{16}O_2/^{18}O_2$  switch.

$^{16}O^{18}O$  formation is derived from the dissociative adsorption of  $^{18}O_2$  and subsequent recombination of the  $^{18}O$  atom created and  $^{16}O$  atom originally attached to the sample. This mechanism has been referred to going through a “three-atom complex” by Winter [5]. The doubly labeled oxygen results from a “four-atom” complex on the surface. Following the  $^{18}O_2$ -to- $^{16}O_2$  switch, relaxation and rise curves are essentially identical as well as the signal for the cross-labeled oxygen. After integrating the peak areas of corresponding oxygen species, the amount of exchanged oxygen atoms was calculated using a technique described previously in the literature [6] for the two bare supports and ceria- and zirconia-supported catalysts. As seen in Figure 2, not only the  $CeO_2$  support, but also the  $CeO_2$  supported Co sample presents notably higher oxygen mobility than their zirconia counterparts. Moreover, when Ca is introduced into the  $CeO_2$  support lattice, a great enhancement of oxygen mobility is observed resulting from the creation of oxygen vacancies due to the lower valence state of Ca compared with Ce. The improved activity is demonstrated in Figure 3. The product distributions at  $400^\circ C$  indicate that higher hydrogen yield (86%) is acquired without the formation of any liquid byproducts (e.g., acetone) over Ca incorporated catalyst under neat conditions.

Through further modifications, more promising catalyst formulations are achieved, giving 90%  $H_2$  yields under neat reaction conditions. As can be seen in Figure 4, the addition of a second non-precious metal (i.e., Cu in this study) improves the catalytic activity especially at lower temperatures, compared with the Co-only samples, indicating that there exists a synergistic interaction between these impregnated active metals. This observation shows potential in industrial applications, because it will facilitate the cost reduction while achieving competitive catalytic performance compared to its precious metal counterparts.



**FIGURE 3.** Conversion and Product Distributions over  $10\%Co/CeO_2$  and  $10\%Co/Ca_{0.1}Ce_{0.9}O_{1.9}$  at  $400^\circ C$  (Reaction parameters:  $H_2O:EtOH=10:1$  (molar ratio),  $GHSV \sim 5,000 h^{-1}$ ,  $WHSV=0.54g EtOH/gCat/h$ , and  $C_{EtOH} \sim 7.5\%$ )



**FIGURE 4.** The effect of Non-Precious Metal Promoter on the Catalytic Activity of  $10\%Co/CeO_2$  during BESR (Reaction parameters:  $H_2O:EtOH=10:1$  (molar ratio),  $GHSV \sim 5,000 h^{-1}$ , and  $C_{EtOH} \sim 7.5\%$ )

## Conclusions and Future Directions

- The catalyst system formulated has strong tolerance to the reactant impurities and high flexibility to other bio-derived liquids.
- Deactivation mechanism has been examined and catalyst formulations have been modified to achieve higher stability.
- Oxygen mobility has been shown to play a significant role on improving catalytic performance.
- Excellent catalytic performance was achieved under neat reaction conditions through catalyst

formulation modifications and control of catalyst particle growth.

- Kinetic and mechanistic studies will be coupled with catalyst characterization under reaction conditions to obtain kinetic parameters.
- Long term time-on-stream experiments will be performed (e.g., >100 hrs under neat reaction conditions).
- Accelerated deactivation and regeneration studies (e.g., higher carbon to steam ratio and gas hourly space velocity, GHSV) will be performed.
- Economic analysis will be tuned based on updated catalyst system knowledge database and the new H2A model.
- Collaborative molecular simulation work using density functional theory calculations will be performed and used to guide rational catalyst design.

### Special Recognitions & Awards/Patents Issued

1. A poster named “Hydrogen Production from Biorenewable Resources over Non-Noble Metal Catalysts for Fuel Cell Applications” has received the second place in the 2008 Ohio Fuel Cell Symposium Poster Competition.

### FY 2008 Publications/Presentations

1. Song, H., Zhang, L., Watson, R.B., Braden, D., Ozkan, U.S., “Investigation of Bio-ethanol Steam Reforming over Cobalt-based Catalysts” *Catalysis Today*, 129, 346-354 (2007).
2. Song, H., Zhang, L., Ozkan, U.S., “Promotional Effects on Co-Based Catalysts in Bio-ethanol Steam Reforming”, *Proceedings of the 2<sup>nd</sup> International Hydrogen Energy Congress*, July 2007.
3. Song, H., Zhang, L., Ozkan, U.S., “Catalytic Hydrogen Production from Bio-Ethanol Steam Reforming”, *Tri-State Catalysis Society Symposium*, Lexington, KY, November 2007.
4. Song, H., Zhang, L., Ozkan, U.S., “Investigation of Bio-Ethanol Steam Reforming over Cobalt based Catalysts”, *U.S. Department of Energy Bio-derived Liquids to Hydrogen Distributed Reforming Working Group Kick-Off Meeting*, Laurel, MD, November 2007.
5. Song, H., Zhang, L. and Ozkan, U.S., “Catalytic Hydrogen Production from Bio-ethanol on Co-based Catalysts,” *2nd International Hydrogen Energy Congress*, Istanbul, Turkey, July 2007.
6. Ozkan, U.S., “Catalytic Hydrogen Production” *Turkish Catalysis Society Workshop*, Keynote Lecture, Istanbul, Turkey, July 2007. (Invited lecture)

7. Song, H., Zhang, L., Ozkan, U.S., “Hydrogen Production from Bio-ethanol Steam Reforming over Cobalt-based Catalysts” *20<sup>th</sup> North American Meeting of North American Catalysis Society*, Houston, TX., June 2007.

8. Ozkan, U.S., “Catalytic Hydrogen Production through Steam Reforming, Water Gas Shift, and PROX Reactions”, Technical University of Eindhoven, Eindhoven, The Netherlands, October 2007. (Invited lecture)

9. Ozkan, U.S., “Catalytic Hydrogen Production,” *Universite Claude Bernard, Lyon, France*, October 2007. (Invited lecture)

10. Song, H., Zhang, L., Ozkan, U.S., “Hydrogen Production from Bio-derived Liquids over Cobalt-Based Catalysts” *Prepr. Am. Chem. Soc. Div. Fuel Chem.*, 53(1) (2008).

11. Song, H., Ozkan, U.S., “Hydrogen Production from Biorenewable Resources over Non-Noble Metal Catalysts for Fuel Cell Applications”, *2008 Ohio Fuel Cell Symposium*, May 2008.

12. Song H., Zhang, L., Ozkan, U.S., “Hydrogen Production from Bio-derived Liquids over Cobalt-Based Catalysts”, *235<sup>th</sup> ACS National meeting & exposition*, New Orleans, LA, April 2008.

13. Song, H., Zhang, L., Ozkan, U.S., “Catalytic Hydrogen Production from Bio-Derived Liquids over Non-Noble Metal Catalysts” *OAI Poster Session*, Columbus, OH, February 2008.

14. 2008 DOE hydrogen Program Review, Washington, D.C., June 2008. Presentation PD-5.

15. Song, H., Zhang, L., Ozkan, U.S., “Hydrogen Production from Bio-derived Liquids over Cobalt-Based Catalysts” *14<sup>th</sup> International Congress on Catalysis*, Seoul, Korea, July 2008 (accepted).

16. Song, H., Ozkan, U.S., “Ethanol Steam Reforming over Co-based catalysts: Role of oxygen mobility”, Submitted to *Journal of Catalysis*.

### References

1. Akande, A.J., Idem, R.O., Dalai, A.K., *Appl. Catal. A: Gen.* 287 (2005) 159.
2. Driscoll, S.A., Ozkan, U.S., *J. Catal.* 97 (1993), 11524.
3. Ozkan, U.S., Cai, Y., *J. Catal.* 149 (1994) 375.
4. Ozkan, U.S., Cai, Y., Kumthekar, M.W., *J. Catal.* 149 (1994) 390.
5. Winter, E.R.S., *J. Chem. Soc. A*, 2889 (1968).
6. Hargreaves, J.S.J., Jackson, S.D., Webb, G., Imperial College Press (2006) 115.