

II.B.2 Investigation of Reaction Networks and Active Sites in Bio-Ethanol Steam Reforming Over Co-Based Catalysts

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- 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 bio-ethanol steam reforming catalysts so that the work to develop precious metal free catalysts that can operate at lower temperatures with high yields and selectivities for hydrogen steam reforming from bio-ethanol can be guided by this knowledge. 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 Production section 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 2010 technical targets for hydrogen from bio-derived renewable liquids. Specific technical targets that would benefit from this study are the following:

- Production Energy Efficiency: 70%
- Contribution of Production to Capital Cost: 0.50 (\$/gge)

Accomplishments

- Understanding the reaction mechanism by exploring a complex network of reactions and reaction intermediates.
- Studying the deactivation mechanisms and developing strategies, based on catalyst formulation and modification, to improve stability while maintaining activity.
- Developing catalyst formulations that can achieve H₂ yields over 90% and no liquid by-products. No deactivation was observed in a 70-hour run.
- Developing novel catalyst synthesis techniques by changing the impregnation medium. Resulting catalyst much higher yields (83%) at much lower temperatures (350°C) compared to catalysts prepared in aqueous media.



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 solves issues 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 is structured into seven tasks occurring over the four-year project period. Each task is accompanied with milestones on a yearly basis. As a Go/No decision point at the end of Phase I (year two) technical progress must be shown in achieving the milestones set forth for the development of safety standards and catalyst preparation/initial characterization efforts. Additionally, catalyst performance with respect to temperature and gas hourly space velocity at the end of year two must warrant feasibility based on the initial economic analysis performed based on the DOE Distributed Hydrogen Production Technologies target goals. Scientific merit must be demonstrated by at least one peer reviewed publication to warrant the advanced studies in the following years.

Results

Based on the temperature-programmed desorption (TPD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) results illustrated in the quarterly reports of this year, a tentative reaction pathway for ethanol steam reforming over Co-based catalysts is proposed in Figure 1. In Scheme 1, the reactants (EtOH and water) molecules diffuse from gas phase to the surface of the catalyst. Then as demonstrated in Scheme 2, the ethanol molecules adsorb dissociatively on the Co sites, forming ethoxide species. Water, on the other hand, adsorbs on the

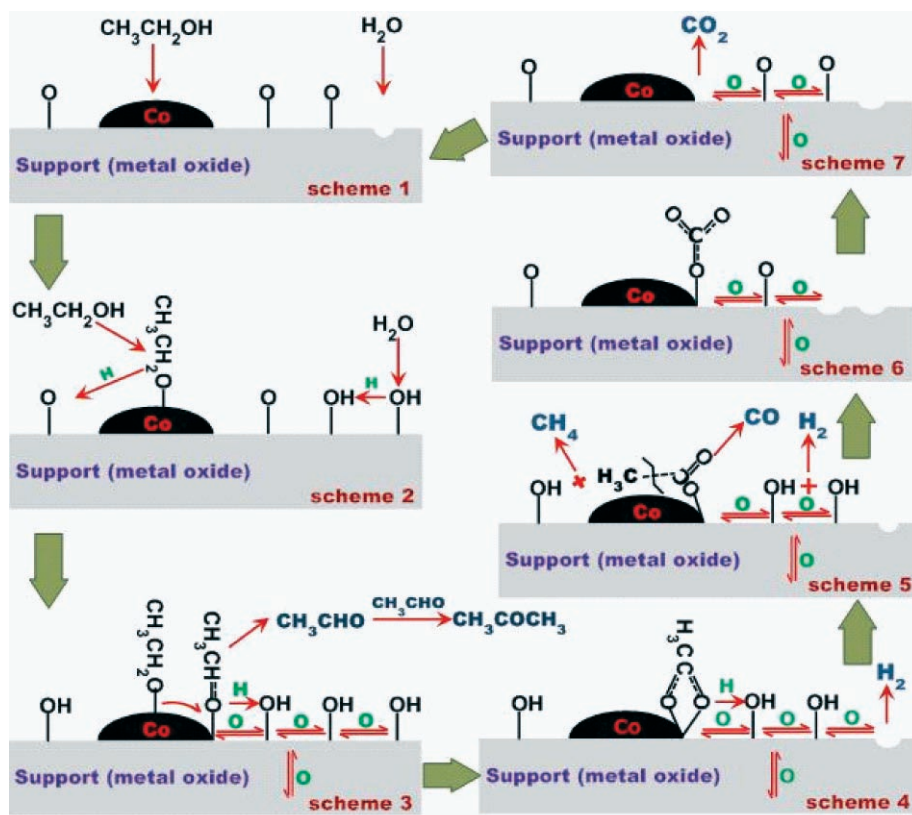


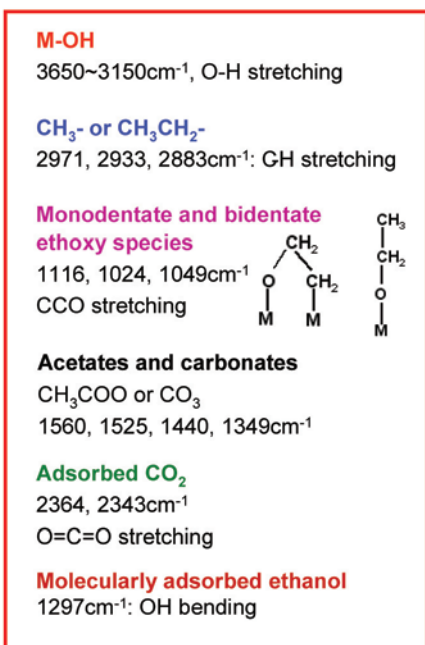
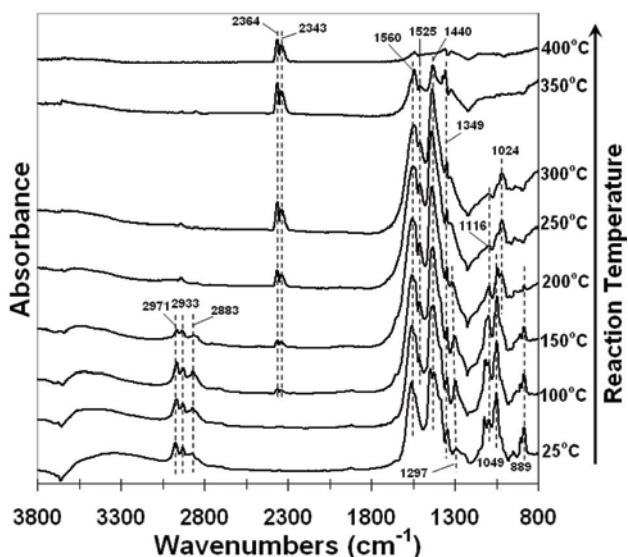
FIGURE 1. Proposed Reaction Mechanism for Ethanol Steam Reforming

support, forming hydroxyl groups. Subsequently, the ethoxide species will move to the interface of metal and oxide support and be oxidized by an additional hydrogen abstraction. Oxygen species from the surface are thought to be involved in forming acetaldehyde formation as shown in Scheme 3. Acetaldehyde molecules may lead to the formation of acetone through an aldol-condensation type reaction. Acetaldehyde species on the surface may further oxidize to acetate species, which can be facilitated by surface OH groups. The metal may be involved in C-C bond cleavage leading to the formation of single carbon species (Schemes 4-5). This step may account for the appearance of methane in the gas phase. The carbon-oxygen surface species may desorb or further oxidize to give carbonate species, especially on supports with high oxygen storage capacity (Scheme 6), which can desorb as CO_2 (Scheme 7).

Although Co/ZrO_2 had promising activity, time-on-stream experiments showed coke formation at high temperatures (500°C and above). The deactivation mechanism was examined by incorporating X-ray diffraction (XRD), laser raman spectroscopy (LRS), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis-differential scanning calorimetry/mass spectrometry (TGA-DSC/MS) techniques. From the results of LRS, two broad peaks centered at 1340

and 1590 cm^{-1} are observed over $10\%\text{Co}/\text{ZrO}_2$ sample after time-on-stream experiment. These bands are characteristic of disordered carbonaceous deposits [1]. The band located around $1,340\text{ cm}^{-1}$ is known as the D line and the band at $1,590\text{ cm}^{-1}$ is recognized as the G line, which is very sensitive to the extent of two-dimensional graphitic ordering. With the insight gained through the deactivation studies, new catalyst formulations were developed incorporating ceria and other lanthanide elements. These new formulations provided much higher activity at lower temperatures, with no coking on the surface. *In situ* DRIFTS experiments provided an explanation for the enhanced activity at low temperatures. A comparison of DRIFT spectra taken during ethanol TPD or ethanol+water TPD experiments showed that over the ceria-containing samples, the appearance and disappearance of surface species took place at much lower temperatures. This can be explained by the high oxygen storage capacity of ceria. DRIFT spectra taken during ethanol TPD over Co/CeO_2 catalyst is presented in Figure 2 as an example. Time-on-stream experiments over these catalysts showed no sign of coking on the surface, even after 110 hours on stream.

A strong promotion effect has been observed after making modifications to the $10\%\text{Co}/\text{ZrO}_2$ catalyst



High oxygen storage capability of ceria facilitates the appearance and disappearance of the reaction intermediates at much lower temperatures

FIGURE 2. *In situ* DRIFTS during Ethanol TPD over Co/CeO₂ Catalyst

system. Figure 3 shows the product distribution and time-on-stream performance of 10%Co/20%La₂O₃-CeO₂ catalyst at 450°C. Over this catalyst, a hydrogen yield over 90% was maintained for over 70 hours. At this temperature and using the same feed conditions, the hydrogen yield that would be obtained at equilibrium is only 71%, showing that we are clearly in the kinetically controlled regime. The only other products formed besides H₂ and CO₂ are CH₄ (less than 5%) and CO (less than 8%). It appears that this catalyst is very promising both for activity and stability performance it has

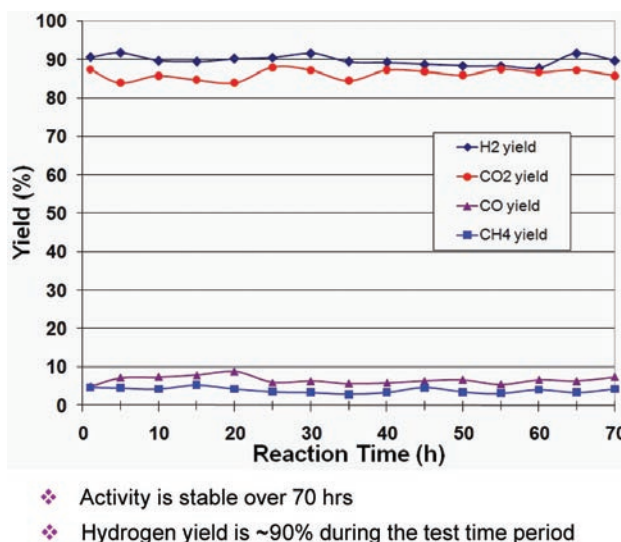


FIGURE 3. Best Performing Catalysts: Product Distribution and Time-On-Stream Performance on 10%Co/20%La₂O₃-CeO₂

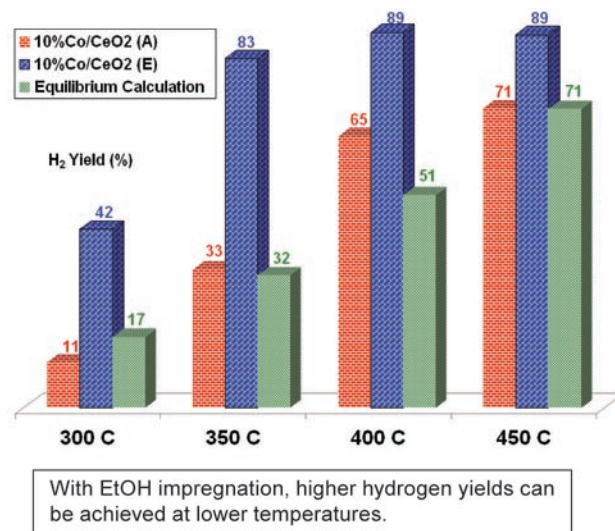


FIGURE 4. Effect of the Impregnation Medium on Activity (Aqueous vs. Ethanol) H₂O:EtOH=10:1 (Molar Ratio) WHSV=0.48 gEtOH/gCat/h, GHSV=~20,000h⁻¹ C_{EtOH}=2%

exhibited and will be further investigated in the coming year.

Figure 4 shows the results from a recent set of experiments where the catalysts synthesis was modified by changing the impregnation medium. Two Co/CeO₂ catalysts prepared in aqueous versus ethanol solutions were compared for activity. The most exciting aspect of this set of results is the very high activity (83% H₂ yield) at temperatures as low as 350°C obtained over the catalyst prepared in an ethanol solution. At this

temperature, the catalyst which was prepared in an aqueous medium gives only 33% hydrogen yield.

Conclusions and Future Directions

- CeO₂ supported cobalt catalyst is shown to be a promising candidate for bio-ethanol steam reforming with excellent activity and stability.
- A catalyst system with high cobalt dispersion and oxygen mobility is crucial for achieving high activity and stability.
- Primary mode of deactivation over Co-based catalyst is coking on the surface.
- Ceria has high oxygen storage capacity and oxygen mobility which can prevent carbon deposition resulting in higher stability.
- Re can favor the C-C bond breakage which can facilitate formation of single-carbon products.
- The proposed reaction mechanism will be further investigated and supported by additional characterization techniques.
- The economic analysis will be completed and updated with the modified catalyst formulations and a better understanding of the kinetic and mechanistic behavior of the corresponding catalyst system.
- A more robust catalyst system will be developed to afford more stringent reaction conditions.

FY 2007 Publications

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*, *in press*.
2. Song, H., Zhang, L., Ozkan, U.S., "Effect of Synthesis Parameters on the Catalytic Activity of Co/ZrO₂ for Bio-ethanol Steam Reforming", *Green Chemistry*, 9(2007) 686-694.
3. Song, H., Zhang, L., Ozkan, U.S., "Promotional Effects on Co-Based Catalysts in Bio-ethanol Steam Reforming", submitted to *International Journal of Hydrogen Energy*.

Presentations

1. Song, H. and Ozkan, U.S., "Fuel Cell Grade Hydrogen Production from the Bio-Ethanol Steam Reforming over Co-based Catalysts: An Investigation of Reaction Networks and Active Sites" *Ohio Fuel Cell Symposium*, Canton, Ohio, May 2006. (Poster Presentation)
2. Song, H., Zhang, L., Ozkan, U.S., "Investigation of bio-ethanol system reforming over cobalt-based catalysts", 232nd *ACS National meeting & exposition*, San Francisco, CA, September 2006. (Keynote Lecture)
3. 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*, Baltimore, MD, October 2006.
4. Song, H., Zhang, L., and Ozkan, U.S., "Catalytic Hydrogen Production from Renewable Sources" *OSU-Honda Research Forum*, Columbus, Ohio, February 2007. (Poster Presentation)
5. Song, H., Zhang, L., Ozkan, U.S., "Investigation of Reaction Networks and Active Sites in Steam Reforming of Bio-ethanol over Cobalt based Catalysts" 233rd *ACS National Meeting*, Chicago, IL, March 2007.
6. Song, H., Zhang, L., Ozkan, U.S., "Hydrogen Production from Renewable Sources over Cobalt-based Nanocatalyst", *Ohio Nanosummit 2007*, April 2007, Akron, OH. (Poster Presentation)
7. Song, H., Zhang, L. and Ozkan, U.S., "Hydrogen Production from Bio-ethanol Steam Reforming over Cobalt-based Catalysts" 20th *North American Meeting of North American Catalysis Society*, Houston, TX, June 2007.

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2. Llorca, J., Homs, N., Sales, J., Piscina, P.R. *J. Catal.* 209(2002) 306.