

II.A.12 Investigation of Reaction Networks and Active Sites In Bio-Ethanol Steam Reforming Over Co-Based Catalysts

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Contract Number: DE-FC36-05GO15033

Start Date: May 1, 2005

Projected End Date: April 30, 2009

Objectives

Acquire a fundamental understanding of the reaction networks, active sites of 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 bioethanol 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:
 - 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 pretreatment protocols
 - Differing levels of steam-to-carbon ratio during reaction
 - Oxidative and auto thermal operation

- Different space velocities
- To study how the observed catalyst characteristics influence these reaction pathways:
 - Oxygenate formation
 - Reverse water-gas-shift (WGS)
 - Alkane and olefin formation
 - Coke deposition
- Determine how the chosen support material can influence metal dispersion and structure, and if it participates in the reaction by any of these means:
 - Alcohol and water adsorption
 - Spillover of species
 - Compound formation
- Determine methods that can tailor the catalyst surface for optimum selectivity and activity:
 - 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

Technical Barriers

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

- (A) Fuel Processor 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, pretreatment 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

- Successful launching of the project, building the experimental systems, and establishment of the experimental protocols
- Understanding the effect of synthesis parameters on the catalyst performance and establishing correlations
- Understanding the competing reaction networks
- Significant H₂ yields at high gas hourly space velocity (GHSV) and low temperatures in initial steady-state runs

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 WGS 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

This study will target development of a catalytic system that does not rely on precious metals and that can be active in a 350-550°C temperature range. The use of non-precious metals 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. Catalysts will have high steam reforming activity, while being non-selective for various undesired side reactions, such as methanation, dehydration, dehydrogenation, coking, and deactivation. This will help increase the hydrogen yield and prevent yield loss during reforming. It will also potentially eliminate costly separation processes. The ideal 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 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-go 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 GHSV 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

A reactor system (shown in Figure 1a) has been designed and constructed exclusively for this project, by which the catalytic performance for bio-ethanol steam reforming (BESR) and oxidative ethanol steam reforming (OESR) can be conveniently evaluated. The synthesized feed with designated molar ratio of water to ethanol or the crude ethanol solution obtained from the fermentation of biomass can be sent into the system

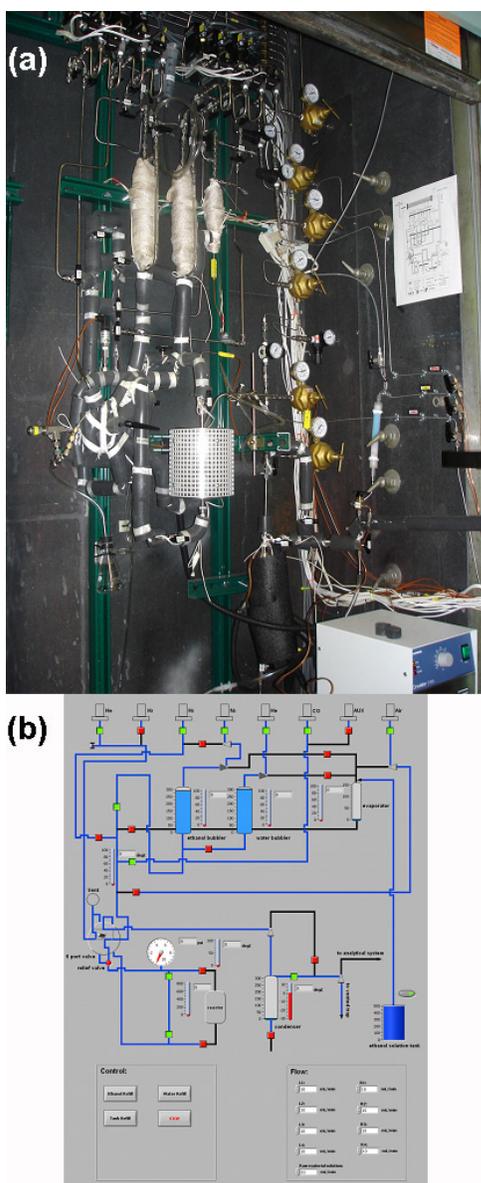


FIGURE 1. The Reactor System (a) and its User Interface (b)

either through bubblers or through the combination of a high performance liquid chromatograph (HPLC) pump and an evaporator. The sample pretreatment, reaction, and regeneration steps have been integrated into one system. The system has been automated through a LabView interface (shown in Figure 1b) and necessary safety features have been put in place. The reactant and product streams can be analyzed online by either being directly injected into a gas chromatograph (GC) or first passing through a condenser and then being sent into the GC separately. Analysis methods have been developed to identify and quantify the reaction products. An on-line mass spectrometer has also been installed for additional product analysis or for isotopic labeling studies. A detailed standard operating procedure (SOP) for this system has been established and personnel have been trained in operation and safety aspects of the system.

A preliminary flow chart of an industrially realistic ethanol steam reforming process has been drawn by Aspen® for economic analysis. In this process, the feed streams are ethanol produced from the fermentation of biomass and water. Air is also included for oxidative steam reforming. Two reformers are included in the flow chart in order to make the process continuous when one reactor is taken off-line. When the catalyst within one reformer is deactivated, another reformer with fresh or regenerated catalyst can be switched online. Downstream high-temperature WGS and low-temperature WGS are employed to minimize CO concentration in the stream. Finally, a pressure swing adsorption (PSA) unit is used to concentrate the hydrogen to designated purification for distribution. The energy and power integration has been incorporated into the process to save the energy consumption and reduce the cost.

A series of cobalt-based catalysts with different supports and addition of various promoters have been prepared by incipient wetness impregnation and sol-gel methods. The initial effort has been focused on the 10%Co/ZrO₂ calcined at different temperatures from 250°C to 550°C.

The metal dispersion of the synthesized catalysts has been measured using a H₂ chemisorption technique. Metal dispersion has been found to correlate closely with the catalytic activity. The effect of calcination temperature, reduction temperature, and reduction time on metal dispersion has been evaluated. The optimized parameters (those that give the highest metallic surface) area are found to be 400°C, 350°C, and 2 h, respectively.

The calcination process has been studied for 10%Co/ZrO₂ with thermo-gravimetric analysis mass spectrometry (TGA/MS) equipment. H₂O, CO₂, and NO_x have been observed to elute from the sample sequentially during the decomposition of the cobalt precursor Co(NO₃)₂•6H₂O.

After the calcination, the cobalt precursor is decomposed to Co_3O_4 , which is identified from the x-ray photoelectron spectroscopy (XPS), Raman, and x-ray diffraction (XRD) data. Raman data have shown complete coverage of the surface.

The reducibility of 10%Co/ZrO₂ after calcination has been examined through the combination of temperature-programmed reduction (TPR) and TGA experiments. Figure 2 shows the TPR profiles for the samples calcined at different temperatures. The first small peak comes from residual nitrate from the catalyst preparation, which has been confirmed by the simultaneous MS signal. At calcination temperatures below 400°C, the precursor is not decomposed completely. The first reduction peak is due to $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ transformation and the second reduction peak represents further reduction to metallic Co ($\text{Co}^{2+} \rightarrow \text{Co}$), which has been verified by measuring hydrogen consumption. The calcination temperature that leads to the greatest reducibility (i.e., lowest reduction temperature) is also found to give the maximum metallic surface area, showing the existence of a correlation between calcination temperature and these two parameters.

The reduction step has also been optimized using the cobalt dispersion criterion. Following reduction at 350°C for 2 h, the catalyst is found to be a mixture of Co^{2+} and Co^0 oxidation states, as seen through XPS and TPR analyses. In addition, transmission electron microscopy (TEM) images show that the size of cobalt particle is reduced significantly after reduction.

The adsorption uptake of ethanol, one of the reactants of BESR, has been tested through ethanol

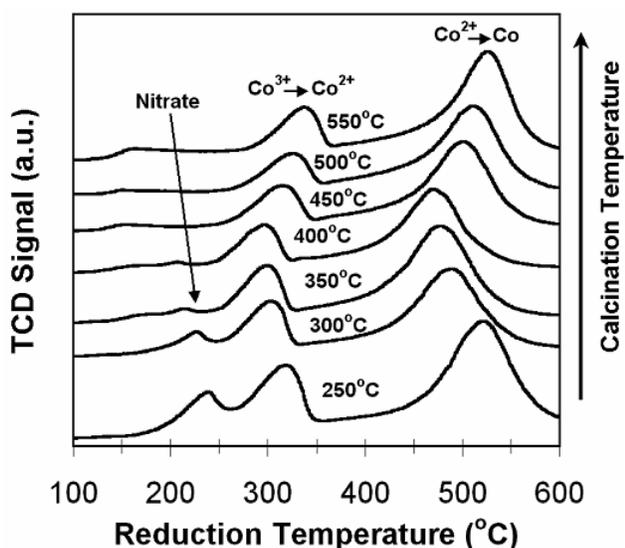


FIGURE 2. TPR profiles of the Samples Calcined at Different Temperatures

pulse chemisorption experiment (Figure 3a). As shown in Figure 3b, the maximum ethanol uptake was observed at the sample reduced at 350°C for 2 h. When compared with the results from the hydrogen chemisorption described above, the maximum ethanol uptake is seen to coincide with the maximum metallic surface area, which supports our assertion that metallic cobalt species constitute the active sites for ethanol adsorption during BESR.

The TPRxn experiments for the 10%Co/ZrO₂ calcined at 400°C and reduced at different temperatures have been performed using on-line mass spectrometry and the results of which are shown in Figure 4. Ethanol conversion takes off between 200 and 250°C, which is accompanied by H₂ formation. The very low temperature for the onset of the H₂ production is very encouraging. Small quantities of acetone, methane and diethyl ether are seen in a narrow temperature window between 300 and 400°C. CO formation becomes more significant at higher temperatures, possibly due to steam reforming of the cracking products or reverse-water gas shift reaction.

The maximum amount of hydrogen for the catalyst reduced at different temperatures has also been plotted

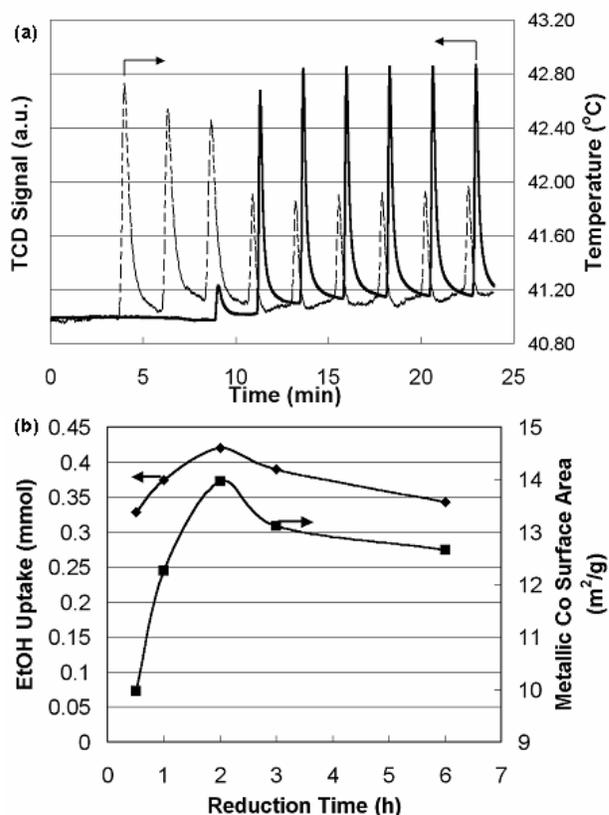


FIGURE 3. Ethanol Pulse Chemisorption over 10%Co/ZrO₂ (a) Ethanol Signal and Temperature Variation in each Pulse (B) Variation of Ethanol Uptake and Metallic Surface Area with Reduction Time

as a function of reduction temperature in order to compare with the chemisorption results. As can be seen from Figure 5, the TPRxn results agree closely with the chemisorption results. The reduction temperature which leads to the maximum H₂ formation is also the reduction temperature which gives the highest metallic surface area. The correlation between the cobalt dispersion and the catalytic performance on BESR seen here further supports our assertion that the higher the cobalt dispersion is, the higher the hydrogen yield will be.

Some initial steady-state reaction experiments have also been performed by using the reactor system described above. In Figure 6, the data are presented in the form of ethanol conversion and product yield. Yield for H₂ is defined as:

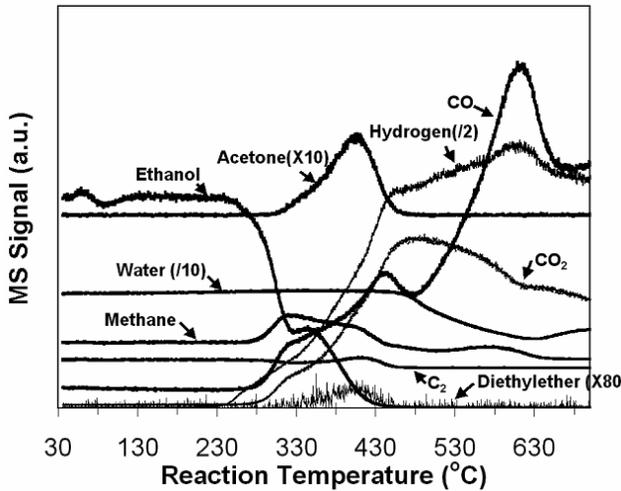


FIGURE 4. Concentration Profiles of Different Products during TPRxn over 10%Co/ZrO₂

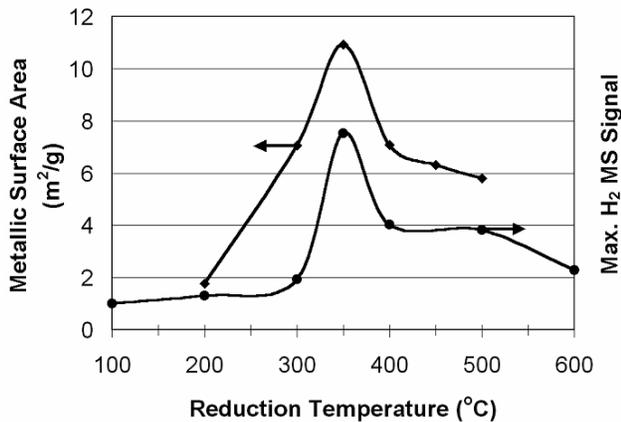


FIGURE 5. The Correlation between Cobalt Dispersion and Catalytic Performance

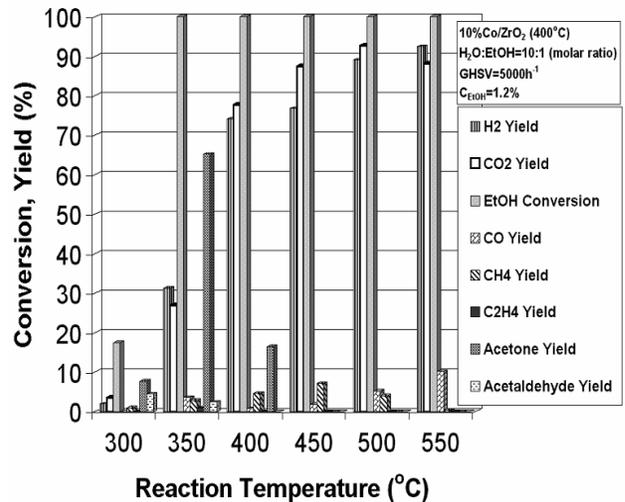


FIGURE 6. The Steady-State Reaction Data for 10%Co/ZrO₂ Calcined at 400°C

$$H_2 \text{ Yield} = 100 \times (\text{Moles of } H_2 \text{ produced}) / \{6 \times (\text{moles of ethanol fed})\}$$

Yield for carbon-containing products is defined as:

$$\text{Yield of product A} = 100 \times (\text{moles of A produced}) \times (\# \text{ of C in A}) / \{2 \times (\text{moles of ethanol fed})\}$$

The most striking result is the very high H₂ yield that is achieved at 550°C. The H₂ yield at this temperature is 92% at 550°C, which is equivalent to 5.5 mols of H₂ produced per mol of ethanol fed. What is also worth noting is that the only H-containing product observed at this temperature besides H₂ and CO₂ is CO. At lower temperatures, in addition to the main products which are expected to be formed during BESR reaction, (i.e., H₂ and CO₂), small quantities of acetone, CO, CH₄, C₂H₄, and acetaldehyde were also observed at different levels. As seen in the figure, above 350°C, the ethanol conversion is complete, hence the yield of H₂ is determined by the competing reactions, including ethanol decomposition, dehydration, dehydrogenation, methanation and WGS reaction. Although these are very preliminary data taken without any optimization, the results are very promising.

Conclusions and Future Directions

- ZrO₂ supported cobalt catalyst is shown to be a promising candidate for BESR.
- The metal dispersion and reducibility have been shown to be important parameters in determining catalytic activity.
- Initial steady-state experiments show the potential for getting very high H₂ yield. They also point out to the importance of understanding the reaction

networks since H₂ yield is determined by the competing reactions.

- Kinetic and mechanistic investigations will be initialized coupled with in-situ characterization.
- Energy and mass balances and economic analysis will be performed by using Aspen[®].
- Catalyst system optimization will be continued.
- Catalyst deactivation and regeneration characteristics will be investigated.
- Reproducibility experiments will be performed.

FY 2006 Publications/Presentations

1. Watson, R.B., Ozkan, U.S., Matter, P.H., Braden, D., Song, H., "Alcohol Steam Reforming for Hydrogen Production" presented at the Annual Meeting of the American Institute of Chemical Engineers, Cincinnati, OH, November 2005.
2. Ozkan, U.S., Song, H., Watson, R.B., Zhang, L., "Investigation of Bio-ethanol Steam Reforming over Co-based Catalysts" presented at the ACS National Meeting, Atlanta, GA, March 2006.
3. Ozkan, U.S., Song, H., Watson, R.B., Zhang, L., "Investigation of Bio-ethanol Steam Reforming over Co-based Catalysts" *Prepr. Am.Chem.Soc. Div.Petr.Chem.*, 2006, 51(1)24.
4. Ozkan, U.S., Song, H., Zhang, L., "Investigation of Bio-ethanol Steam Reforming over Co-based Catalysts" presented at the DOE Annual Merit Review Meeting, Arlington, VA, May 2006.