IV.A.15 Investigation of Reaction Networks and Active Sites in Bio-Ethanol Steam Reforming over Co-Based Catalysts

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Objectives

- Determine how the following catalyst synthesis methods affect oxidation state, structure, metal dispersion, and particle size of cobalt-based 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 under the following conditions:
  - Varying pre-treatment protocols
  - Differing levels of steam-to-carbon ratio during reaction
  - Oxidative and auto-thermal operation
  - Increased space velocities
- Study how the observed catalyst structures influence these reaction pathways:
  - 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 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 sites active 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 Hydrogen Production section 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
- E. Carbon Dioxide Emissions

Technical Targets

This project is a systematic and detailed study aimed to provide fundamental answers to questions that are not readily solved in an industrial setting due to lack of appropriate research facilities. The results of this study, which will focus on characterizing the parameters that lead to or inhibit the formation of active sites for reforming, will prevent interpreting erroneous information resulting from the screening of a large catalyst matrix. 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 production from bio-derived renewable liquids.

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 that have high steam reforming activity, while being non-selective for various undesired side reactions, such as methanation, dehydration, dehydrogenation, coking, and deactivation will be further developed. 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 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.

Accomplishments

- This is a new project; however, initial progress has been made.
- Items for building and installing the reactor system have been ordered.
- A safety review of the reactor design has been performed internally.
- Standard operating procedures for the reactor system have been developed.
- Analytical equipment to support the project has been identified and price quotations obtained.
- Personnel have been trained regarding reactor system construction and catalyst synthesis techniques.
- Review of the literature on ethanol steam reforming and related catalytic systems continues.
- Calcination and reduction temperature investigation on zirconia supported cobalt catalysts has begun.
- Hydrogen chemisorption analysis has been used for metal dispersion analysis of prepared catalysts for future correlation to catalytic activity.