

## II.A.4 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.
  - Steam reforming.
- 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 interaction.
  - Sintering.

### Objectives

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

This is a university project, which is a systematic and detailed study aimed to provide fundamental answers to questions that are not readily solved in an industrial setting. The approach is an iterative one that combines catalyst synthesis, characterization and reaction engineering studies. 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
- Total hydrogen cost from bio-derived liquids: \$3.80/gge

### Accomplishments

- In an effort to increase the oxygen mobility of the catalysts, dopants with oxidation states lower than Ce (e.g., Ca) were used, leading to oxygen vacancies and changes in ceria lattice.
- Isotopic labeling studies provided insight for the overall reaction mechanism model, which was extended to take alternate reaction pathways into account.
- Novel synthesis techniques such as solvothermal, reverse microemulsion and colloidal crystal templating led to catalysts with much higher dispersion as well as superior catalytic performance (i.e., activity, selectivity, stability).
- Novel catalyst preparation methods utilizing reverse micro-emulsion techniques allowed for over 92% H<sub>2</sub> yield with high stability under more stringent conditions.
- Computational chemistry/molecular simulation studies on Co-CeO<sub>2</sub> systems were initiated as part of a collaborative effort.



### 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 lends itself very well to a distributed hydrogen production strategy and hence has the potential to offer solutions to problems associated with hydrogen storage and infrastructure. 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 examination of the cobalt-based catalyst system at every stage of its life history, from precursor stage to activation, deactivation and regeneration steps. The techniques used include catalyst synthesis studies, transient and steady-state reaction tests, and characterization using surface, bulk and molecular analysis techniques (both ex situ and in situ). 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. Understanding gained through molecular simulations is utilized in tailoring the catalyst surfaces for better performance.

### Results

Last year's effort had led to use of low-valence dopants such as Ca in ceria matrix to increase the oxygen mobility of the Co/CeO<sub>2</sub> catalysts. This was achieved by creating oxygen vacancies in the ceria lattice. Characterization results showed that Ca

doping also increased the CeO<sub>2</sub> unit cell size. X-ray diffraction studies were used to quantify the expansion. The diffraction patterns of CeO<sub>2</sub> and Ca<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.9</sub> are displayed in Figure 1. The peak broadening is a clear indication of smaller particle size. When the samples are compared, it is observed that the 28.56° peak for CeO<sub>2</sub> has shifted to 28.89° for Ca<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.9</sub>. Unit cell estimation based on the angles show an increase in the unit cell size from 5.4108 Å to 5.4151 Å. The increase is

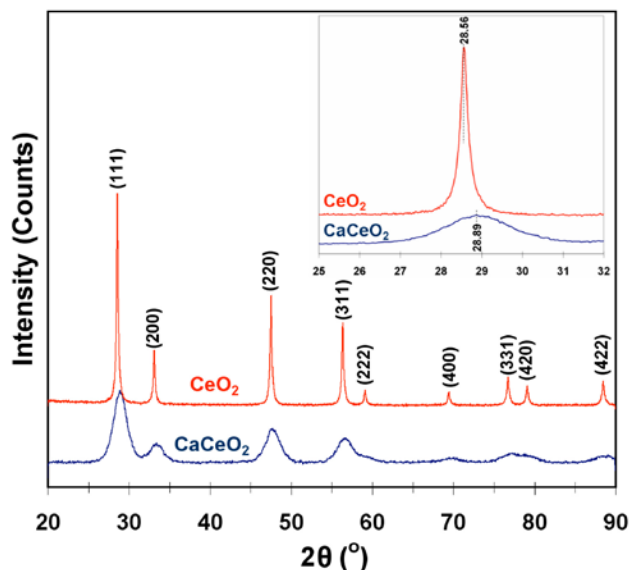


FIGURE 1. X-Ray Diffraction Patterns of CeO<sub>2</sub> and Ca<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.9</sub>

attributed to 10% calcium addition and it is in agreement with the literature [1-3].

The reaction mechanism proposed in the last annual report is extended to take alternate pathways into account (Figure 2). The isotopic labeling techniques are coupled with surface analysis to shed light to the reaction pathways on the catalyst surface. The ethanol steam reactant mixture diffuse on the surface of the catalyst, where ethanol adsorbs dissociatively on cobalt sites, thereby forming ethoxide species on the metal. Simultaneously, water adsorbs on ceria and forms hydroxyl groups (Scheme 1). The single hydrogen atom from water can follow two pathways: 1) formation of OH groups with the surface oxygens, 2) reaction with an H atom from another molecule of adsorbed water to form H<sub>2</sub> which leaves the catalyst surface (Scheme 3). Ethoxide species stationed on the metal move to the metal-support interface and lose another hydrogen atom, thereby forming acetaldehydes (Scheme 4). The acetate species have two alternate pathways: they may form acetone through aldol-condensation reaction and desorb from surface. This is the cause of the acetone in the reactant stream. However, acetone is encountered at very low concentrations in temperatures above 350-400°C and the second pathway is more likely to be followed. The acetaldehyde species convert into acetate species through reaction with surface oxygen or hydroxyl groups (Scheme 5). The acetate species can follow different pathways. 1) Cobalt may cleave the C-C bond to form single carbon species (Scheme 7) and form CH<sub>4</sub>. The carbon-oxygen surface species

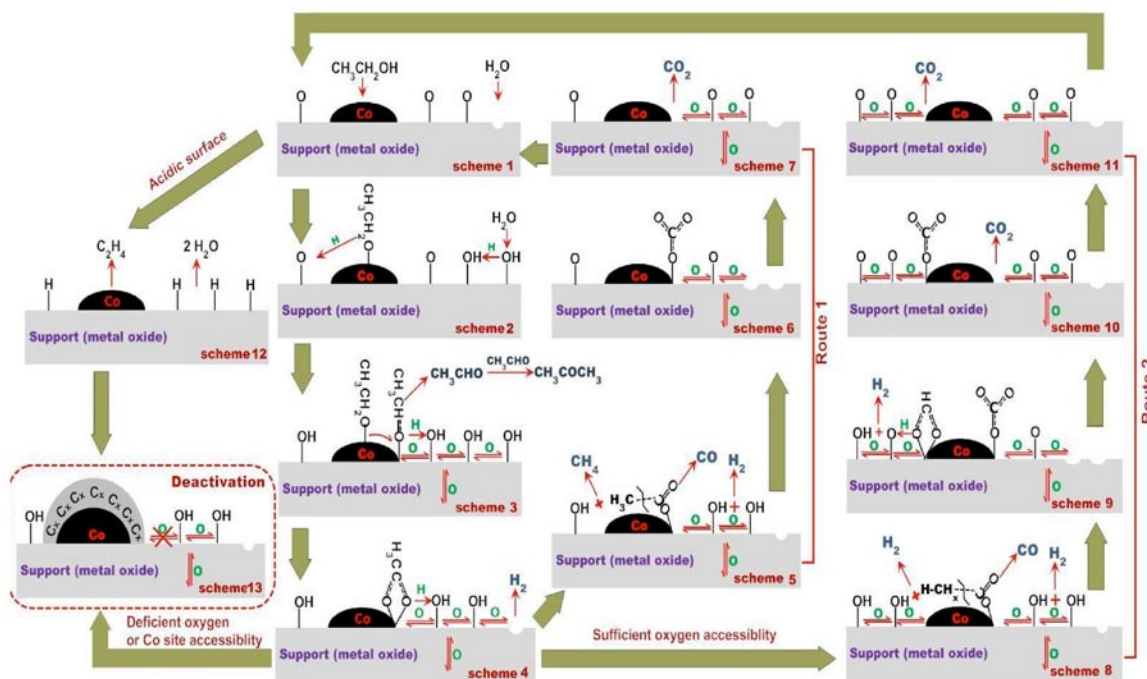


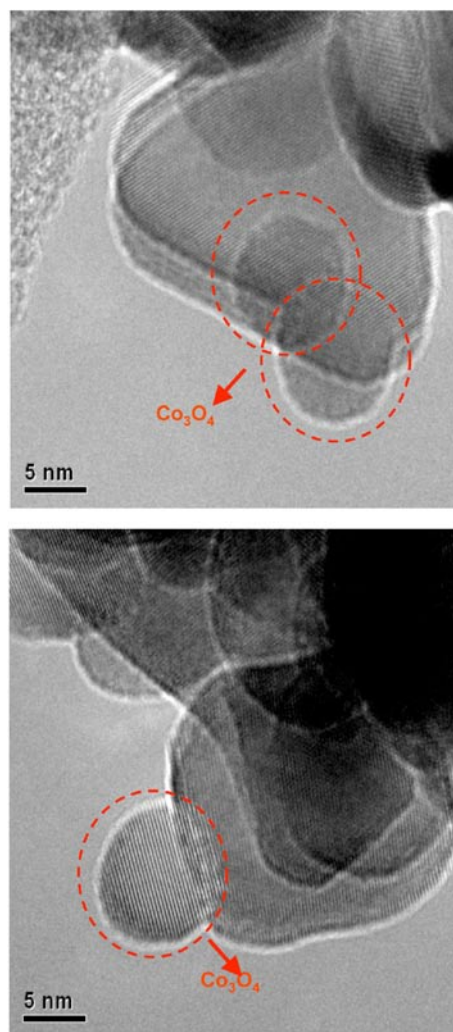
FIGURE 2. Proposed Reaction Mechanism for Ethanol Steam Reforming over Supported Co Catalysts

desorb or get further oxidized to form carbonate species. Supports with high oxygen capacity and mobility allow  $\text{CO}_2$  to desorb from the surface (Schemes 8 and 9, First Route). 2) In the second route, if the oxygen is easily accessible to the  $\text{CH}_3$  species, further oxidation will take place (Scheme 10) via both hydrogen subtraction and oxygen addition and formates will form on the surface through formaldehyde intermediates (Scheme 11). The catalyst surface gets regenerated through  $\text{CO}_2$  desorption (Scheme 13) and the catalyst becomes ready for another cycle, independent of the reaction pathway taken. If the surface is highly acidic, ethanol dehydration may dominate the reaction pathway and result in the formation of  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_4$  which are the major precursors to coke due to polymerization, as described in Scheme 2 and 6. If the oxygen mobility in the catalyst is not high enough, the acetate species may remain on the surface and lead to coke formation, as reported earlier by Lima and Erdohelyi [4,5].

The cobalt particle size is controlled more effectively via reverse micro-emulsion technique. Surfactants are added to encapsulate the cobalt particles in a limited hydrophilic environment to increase cobalt dispersion and prevent reagglomeration at high temperatures. Tetrahydrofuran addition prevents the support from embedding the metal completely and silylation of the metal oxide support is achieved by adding hexamethyldisilazane to improve the chemical compatibility between the support surface and the organometallic micelle, to further increase the metallic dispersion. The exact technique can be found in the work of Martinez et al. [6,7]. Figure 3 shows two transmission electron microscopy images of  $\text{Co}/\text{CeO}_2$  catalysts prepared by the reverse microemulsion method.  $\text{Co}_3\text{O}_4$  particles are highlighted with the red circles. Around 90% of the oxides are found to have particle sizes between 6 and 7 nm. Furthermore the cobalt particles are noticeably embedded onto the surface of the ceria support, which leads to enhanced dispersion of the metal. This is due to the silylation of the metal oxide. Figure 4 shows the catalytic activity results of the  $\text{Co}/\text{CeO}_2$  catalyst prepared by the microemulsion technique. The catalyst has over 90%  $\text{H}_2$  yield at 350°C and above at weight hourly space velocities twice as high as those used for other catalysts. Catalysts that are kept on line over 120 hours at 400°C show no sign of deactivation. The novel synthesis technique gave much better results than the incipient wetness impregnation method.

### Conclusions and Future Directions

- Oxygen mobility is enhanced with Ca doping.
- Isotopic labeling and in situ characterization provide new insights into the reaction mechanism.
- Novel synthesis techniques such as solvothermal, reverse microemulsion and colloidal crystal



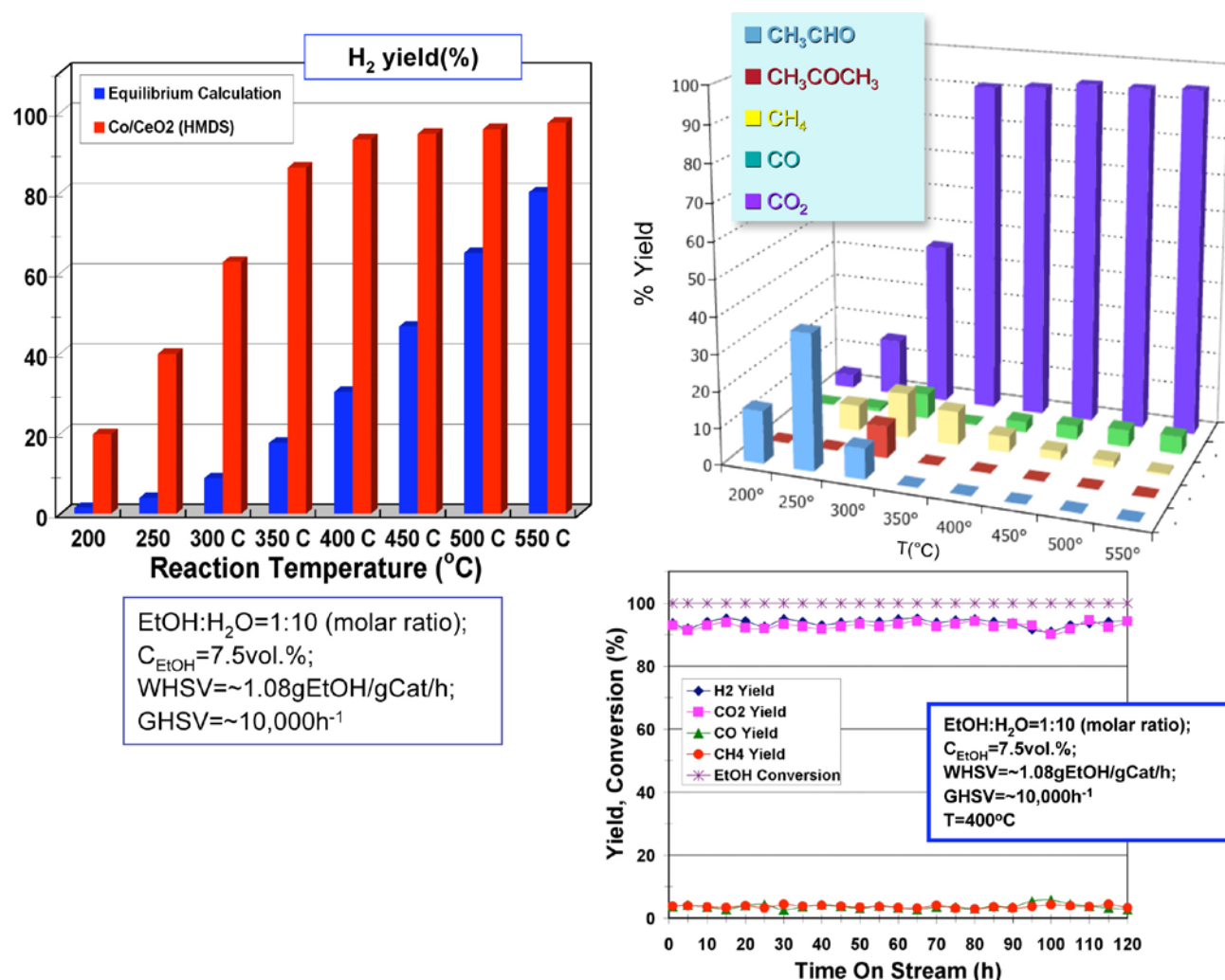
**FIGURE 3.** High Resolution Transmission Electron Microscopy Images of  $\text{Co}/\text{CeO}_2$  Catalyst Prepared by a Reverse Microemulsion Technique

templating led to catalysts with much higher dispersion as well as superior catalytic performance (i.e., activity, selectivity, stability).

- The effect of oxygen in the feed stream on product distribution as well as catalyst deactivation will be examined.
- Other bio-derived liquids will be used as feed.
- 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. Ozkan, U.S., Song, H., “Hydrogen Production from Steam Reforming of Ethanol over Calcium Modified  $\text{Co}/\text{CeO}_2$  Catalyst”, (*In Process*).



**FIGURE 4.** Hydrogen Yield, C-Containing Product Distribution and Time-On-Stream Performance over a Co/CeO<sub>2</sub> Catalyst Prepared by a Reverse Microemulsion Technique

## FY 2009 Publications/Presentations

### Books

1. *New Catalyst Synthesis Techniques*, special issue of Topics in Catalysis, Guest editor, U.S. Ozkan, Springer Publisher, Volume: 49, 2008.
2. *Design of Heterogeneous Catalysts: New Approaches based on Synthesis, Characterization and Modeling*, Ed. U.S. Ozkan, Wiley-VCH, 2009.

### Journal Articles

1. Song, H., Ozkan, U.S., "Ethanol Steam Reforming over Co-based Catalysts: Role of Oxygen Mobility" *Journal of Catalysis*, **261** 70-78(2009).
2. Song, H. and Ozkan, U.S., "The Role of Impregnation Medium on the Activity of Ceria-supported Co Catalysts for Ethanol Steam Reforming," *J. Molecular Catalysis*, submitted.

3. Song, H. Ozkan, U.S., "Changing the Oxygen Mobility in Co/Ceria Catalysts by Ca Incorporation: Implications for Ethanol Steam Reforming" *Journal of Physical Chemistry*. Invited paper. Submitted.
4. Song, H. and Ozkan, U.S., "Effect of Cobalt Precursor on the Performance of Ceria-Supported Cobalt Catalysts for Ethanol Steam Reforming," submitted to *Applied Catalysis A*.
5. Song, H., Tan, B., Ozkan, U.S., "Novel Synthesis Techniques for Preparation of Co/CeO<sub>2</sub> as Ethanol Steam Reforming Catalysts," submitted to *Catalysis Letters*.

### Conference Presentations

1. 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.
2. 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.

3. 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.
4. Song, H. Zhang, L., Ozkan, U.S., "Hydrogen Production from Bio-ethanol over Co-based Catalysts," presented at the 2008 American Chemical Society Fall Meeting, Philadelphia, PA, 2008.
5. Song, H., Zhang, L., Ozkan, U.S., "Catalytic Hydrogen Production from Bio-renewable Resources" 2<sup>nd</sup> International Symposium on Bioenergy and Bioprocess Technology, Qingdao, China, October 2008.
6. Song, H., Zhang, L., Blohm, K., Ozkan, U.S., "Hydrogen Production from Bio-Ethanol Steam Reforming over Co-Based Catalysts", 2008 AIChE Annual National Meeting, Philadelphia, PA, November, 2008.
7. Song, H., Ozkan, U.S., "Hydrogen Production from Steam Reforming of Bio-Ethanol over Non-Precious Metal Catalysts," 21<sup>st</sup> Meeting of the North American Catalysis Society, San Francisco, CA, June 2009.

#### Invited Lectures

1. "Steam reforming of ethanol over Co-based catalysts: Active sites and reaction networks," University of Berkeley, Lawrence Berkeley National Laboratory, Berkeley, CA, March 2009.
2. "Catalytic Hydrogen Production from Bio-ethanol through Steam Reforming". USDOE Hydrogen Program Review Meeting, Washington, D.C., May 2009.

#### References

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2. V. Thangadurai, P. Kopp, J. Power Sources 168 (2007) 178-183.
3. W. Huang, P. Shuk, M. Greenblatt, Solid State Ionics 100 (1997) 23-27.
4. Erdöhelyi, J. Raskó, T. Kecskés, M. Tóth, M. Dömök, K. Baán, Catal. Today 116 (2006) 367-376.
5. S.M. Lima, A.M. Silva, U.M. Graham, G. Jacobs, B.H. Davis, L.V. Mattos, F.B. Noronha, Appl. Catal. A: Gen. 352 (2009) 95-113.
6. Martínez, G. Prieto, Catal. Comm. 8 (2007) 1479-1486.
7. Martínez, G. Prieto, J. Catal. 245 (2007) 470-476.