Hydrogen Production from Steam Reforming of Bio-Ethanol over Non-Precious Metal Catalysts

Hua Song, and Umit S. Ozkan*
Department of Chemical and Biomolecular Engineering
The Ohio State University, Columbus, OH 43210, USA
*E-mail: ozkan.1@osu.edu

Introduction

Bio-Ethanol Steam Reforming (BESR) offers an environmentally friendly route to produce hydrogen. The development of non-precious metal catalyst systems with high activity, selectivity, and stability makes the technique economically competitive and promising for the future.

In this study, the significances of active metal particle size and inherent oxygen mobility over cobalt-based catalyst during BESR have been evaluated through steady state reaction and catalyst characterization studies. The relationship between catalyst properties and activity has been established and a tentative BESR reaction mechanism, which can guide rational design of catalyst systems, has been proposed with the support of experimental results. H_2 yields around 90% have been achieved at temperatures below 450°C. In addition, the deactivation mechanism has been explored and catalysts with modified formulations have been developed to achieve long term stability while maintaining high activity.

Materials and Methods

Catalysts Preparation. Versatile synthesis methods including impregnation, precipitation, hydrothermal, solvothermal, colloidal crystal templating, and nanocasting techniques have been used to achieve desired catalysts with specific morphology and particle size.

Catalytic Tests. The catalytic performance measurement and analysis methods used were reported elsewhere [1, 2].

Catalysts Characterization. Catalysts were characterized using N_2 physisorption, chemisorption, isotopic labeling, XRD, XPS, TPR, TPD, TGA, DSC, LRS, DRIFTS, TEM, SEM, and EPR techniques. Detailed experimental procedures can be found in [1-3].

Results and Discussion

Through studies performed over ZrO_2- and CeO_2-supported cobalt catalysts, the high oxygen mobility of the catalyst was found not only to suppress the carbon deposition and help maintain the active surface area, but also allow delivery of oxygen to close proximity of ethoxy species, promoting complete oxidation of carbon to CO_2, and resulting in higher hydrogen yields [3]. Overall, oxygen accessibility of the catalyst plays a significant role on catalytic performance during BESR. After further modification by incorporating Ca into the support CeO_2 lattice, catalytic performance was further improved. Table 1 shows the catalytic activity comparison between the samples with and without Ca doping at relatively lower temperatures (i.e., 400°C).

Table 1. Conversion (%) and product distributions (Yield %) over 10%Co/CeO_2 and 10%Co/$Ca_{0.1}Ce_{0.9}O_{1.9}$ at 400°C (Reaction parameters: H_2O:EtOH=10:1 (molar ratio), GHSV=~5,000h^{-1}, WHSV=0.54gEtOH/gCat/h, and C_{EtOH}=~7.5%.)

Catalyst	H_2	CH_4	CO	CO_2	Acetone	EtOH
10%Co/CeO_2	60	18	3.9	58	17	100
10%Co/ $Ca_{0.1}Ce_{0.9}O_{1.9}$	85.6	14.7	6.8	78.6	0	100

The promotion effect of Ca addition is seen in product distribution as well. The improvement of H_2 yield under neat reaction condition can be mainly ascribed to the disappearance of liquid byproduct (i.e., acetone). The only gas byproducts under these conditions when the support is doped with Ca are CH_4 and CO. Through characterization techniques such as isotopic labeling, TPR, pulse chemi-sorption, CO-O_2 switch, and ESR, the improvement of the catalytic performance with Ca doping of the Co-CeO_2 catalyst system could be attributed to the creation of oxygen vacancies, resulting in much higher oxygen mobility, as shown in Fig.1.

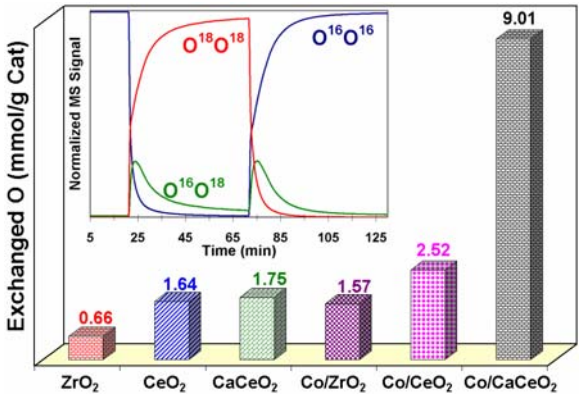

Figure 1. Oxygen mobility over ZrO_2, CeO_2, $Ca_{0.1}Ce_{0.9}O_{1.9}$, 10%Co/ZrO_2, 10%Co/CeO_2, 10%Co/$Ca_{0.1}Ce_{0.9}O_{1.9}$ measured using $^{16}O_2/^{18}O_2$ switch.

Significance

The knowledge acquired through this study will bring us closer to designing catalytic systems that can be utilized for distributed hydrogen production strategies from renewable sources.

References

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2. Song, H., Zhang, L.Z, and Ozkan, U.S. *Green Chem.* 9, 686 (2007).
3. Song, H, and Ozkan, U.S. *J. Catal.* (*In Press*, DOI: 10.1016/j.jcat.2008.11.006)