

Hydrogen Production from Bio-Ethanol Steam Reforming over Co-based Catalysts

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Introduction

Bio-ethanol Steam Reforming (BESR) offers an attractive route for H₂ production from renewable sources. It is environmentally friendly, has the potential of being carbon neutral and is amenable to a distributed energy generation strategy. Because of the advantages it offers, there have been many studies focusing on BESR over different catalytic system.

In this study, cobalt based catalysts were prepared by either an impregnation or a sol gel technique. Effect of synthesis parameters on the catalytic activity and stability was investigated [1]. Subsequent modifications were made to the initial catalyst system by incorporating a second oxide in the support or a second active metal in order to improve stability while maintaining activity. The corresponding catalytic activities were evaluated and the effect of Gas Hourly Space Velocity (GHSV) was examined. The reaction network and reaction intermediates were also investigated using *in-situ* spectroscopy techniques.

Materials and Methods

Catalysts Preparation. Supported cobalt catalysts with 10wt% metal loading were prepared in air by incipient wetness impregnation from cobalt (II) nitrate hexahydrate aqueous solutions. Calculated amount of cerium (III) nitrate hexahydrate and rhenium (III) chloride were added into the aqueous solutions to produce the modified catalysts. The support used was ZrO₂ (Saint Gobain) with a surface area and pore volume of 31m²/g, 0.21cm³/g, respectively. After repeating the impregnation and drying steps (at 95°C) as many times as determined by the pore volume of the ZrO₂ support, the resulting samples were calcined at 400°C for 3h in the air. Sol gel catalysts were prepared using Zr propoxide. For abbreviation, the synthesized 10%Co/ZrO₂, 1%Re-10%Co/10%CeO₂-ZrO₂, and 10%Co/10%CeO₂-ZrO₂ were denoted as 10Co/Zr, 1Re-10Co/10Ce-Zr, and 10Co/10Ce-Zr respectively.

Catalytic Tests. Catalytic tests were performed using a tubular reactor. The feed was diluted in a carrier gas and the reactants were fed using separate bubblers. Detailed descriptions of the reactor system, operating procedure and the analysis methods can be found in [1].

Catalysts Characterization. Catalysts were characterized using BET, XRD, XPS, TPD, TGA, DSC, LRS and DRIFTS techniques.

Results and Discussion

The effect of synthesis conditions, such as calcination and reduction temperature and the sol gel parameters was examined and the catalytic performance was found to be a strong function of these parameters. As determined by the H₂ chemisorption studies, ethanol

conversion is found to correlate closely with metal dispersion and hence, the metallic Co sites. The product distribution, on the other hand, is determined by a complex network of competing reactions, including BESR, methanation, WGS, dehydration, and dehydrogenation. The effect of gas space velocity was evaluated from 5,000~94,000h⁻¹. Product distribution was found to change significantly with GHSV. At 500°C, the formulation that consisted of 10%Co/ZrO₂ was found to achieve 92% H₂ yield, which is equivalent to 5.5 mols of H₂ produced per mol of ethanol fed. In addition, ethanol can be fully converted at temperatures as low as 350°C. What is also worth noting is that at temperatures above 475°C, the only other product besides hydrogen and CO₂ is CO, making H₂ the only H-containing product. When this formulation was modified by incorporation of CeO₂ and Re, the low temperature activity of the catalyst increased significantly, giving over 70% H₂ yield at temperatures as low as 350°C.

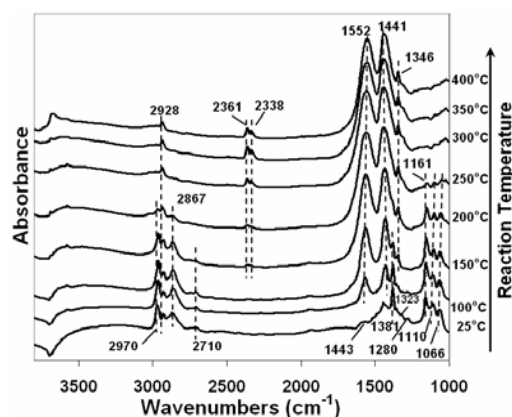


Fig. 1 DRIFT spectra taken over Co/ZrO₂ during ethanol TPD

Fig.1 shows DRIFT spectra taken during TPD following adsorption of ethanol at room temperature. At room temperature, the primary species are molecularly adsorbed ethanol and bidentate and monodentate ethoxy species as seen through the vibration bands located at 1323 ($\delta(\text{CH}_3)$) and 1280cm⁻¹ ($\delta(\text{OH})$), the C-H stretching (2970, 2928, 2867, 2710 cm⁻¹), CH₃ bending (1443, 1381 cm⁻¹), and CCO stretching (1161, 1110, 1066 cm⁻¹) bands. With increasing temperature, ethoxy species are replaced by acetate and formate species (1552, 1441, 1346 cm⁻¹). Starting around 150°C, adsorbed CO₂ begins to appear (2361, 2338 cm⁻¹). Similarity between the species formed following ethanol and

acetaldehyde adsorption suggests common paths between the reforming of these two species.

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. Laosiripojana, N., Assabumrungrat, S. *Appl. Catal. B: Env.* 29, 66 (2006).