

Metallic Phases of Cobalt Based Catalysts in Ethanol Steam Reforming: The Effect of Cerium Oxide

Sean S.-Y. Lin¹, Do Heui Kim², and Su Y. Ha^{1*}

¹Department of Chemical Engineering, Washington State University, P.O. Box 642710, Pullman, WA 99164-2710 (USA)

²Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, PO Box 999, Richland, WA 99354 (USA)

*suha@wsu.edu

Introduction

The steam reforming of ethanol has been the focus of recent study as one of many promising technologies to supply portable hydrogen fuel. However, there is no commercial catalyst available to date to extract hydrogen from ethanol. Supported cobalt has been reported to possess noble-metal like activity for the C-C bond cleavage around 400°C to produce hydrogen from ethanol steam reforming. Metallic cobalt is believed to be the main active species in various supported cobalt catalysts [1]; but the enhancement of the catalytic activity due to the catalysts-support interactions is still elusive. In order to gain insight into cobalt-support interactions for designing a better supported catalyst system, questions regarding whether cobalt undergoes phase transformation during ethanol steam reforming and which phase is more active if phase transforms, need to be answered.

In this work, we have examined the phase transformation of cobalt and the corresponding catalytic activity in the steam reforming of ethanol. As evidenced through our *in situ* studies by XRD and DRIFTS, two metallic phases exist in cobalt under the reforming conditions and possess different activity for hydrogen production. The promoting effect of CeO₂ was found to hinder the phase transformation in hcp cobalt. More, the addition of CeO₂ to cobalt was shown to prevent the sintering of cobalt nanoparticles and increase hydrogen selectivity. This effect significantly increases the catalytic activity as compared with the unpromoted cobalt.

Materials and Methods

A nanocrystalline cobalt (II, III) oxide (Co₃O₄ <50 nm, Sigma-Aldrich) was used to study the phase transformation of cobalt and its corresponding catalytic activity through various hydrogen pre-reductions. For a comparative study, a cerium nitrate precursor, Ce(NO₃)₃·6H₂O (Alfa Aesar), was impregnated to Co₃O₄ followed by calcination in air at 500°C for 4 h to attain 10 wt% cerium promoted Co₃O₄, denoted as 10% Ce-Co₃O₄. The catalysts are characterized by BET, TPR, and TEM. A quartz packed-bed reactor coupled with GC was used for the catalyst testing. The *in situ* studies of the phase transformation and the surface chemistry on cobalt were carried out by XRD and DRIFTS, respectively.

Results and Discussion

The phase transformation of metallic cobalt from hexagonal to cubic phase in either hydrogen or reforming environments was confirmed by *in situ* XRD study (Figure 1). At reaction temperature of 350°C, hcp cobalt was stable and found to possess higher activity than fcc cobalt. This result was confirmed by the hydrogen production rate measured from reforming experiments, as well as by the surface chemistry from *in situ* DRIFTS study (Figure

2). To our best knowledge, it was discovered for the first time that the catalytic activity of cobalt toward hydrogen production from ethanol steam reforming is influenced by the crystalline structure. However, at typical reaction temperatures (400-500°C) of ethanol steam reforming, inexorable phase transformation of metallic cobalt from hcp to less active fcc phase will proceed as reforming temperature approaching to the onset temperature of its phase transformation at 420°C. We were able to stabilize the hcp cobalt phase at the reforming temperature up to 600°C by promoting cobalt catalysts with CeO₂. In addition to stabilizing the active cobalt phase at high reforming temperatures, CeO₂ prevents the sintering of cobalt nanoparticles in the pre-reduction process of Co₃O₄, as evidenced by their BET surface area (Table 1) and the TEM images. The cerium promoted cobalt catalyst also achieves a much lower CO selectivity and a higher H₂ yield as compared to that of the unpromoted hcp cobalt.

Table 1. Brunauer-Emmett-Teller surface area of Co₃O₄ and 10% Ce-Co₃O₄ catalysts pre-reduced at different temperatures under hydrogen

Catalyst	BET surface area (m ² /g)			
	Prior to reduction	350°C	450°C	600°C
Co ₃ O ₄	40.3	2.6	1.8	1.3
10% Ce-Co ₃ O ₄	28.2	26.7	23.2	15.2

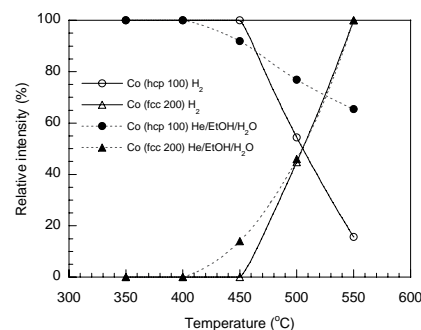


Figure 1. Peak evolutions of *in situ* XRD spectra corresponding to hcp Co and fcc Co under H₂ or ethanol/H₂O/He as a function of temperature.

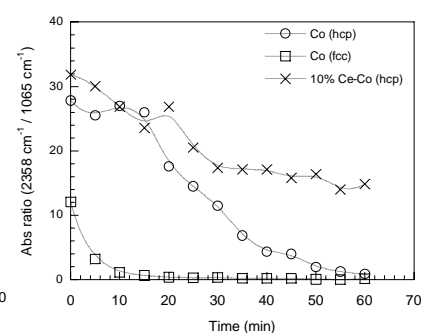


Figure 2. Ratio of IR absorbance (CO₂/EtOH; 2360/1065 cm⁻¹) as a function of time on Co catalysts under ethanol/H₂O/He at 350°C.

Significance

In this work the phase transformation in metallic cobalt during ethanol steam reforming was confirmed to influence the catalytic activity. A cerium promoted cobalt catalyst was found superior due to its ability to stabilize active crystalline phase and resist sintering.

Reference

1. Haryanto, A., Fernando, S., Murali, N., and Adhikari, S. *Energ Fuel* 19, 2098 (2005).