Effect of Metal on Reduction Characteristics of Ceria for Ethanol Steam Reforming: in-situ XANES and Ambient-Pressure XPS study

Hyntae Sohn1, Ilgaz Soykal1, Franklin Tao2, Umit S. Ozkan1*
1The Ohio State University, Columbus, Ohio 43210 (United States)
2The University of Kansas, Lawrence, KS, 66045 (United States)
*ozkan.1@osu.edu

Introduction
Production of hydrogen from ethanol steam reforming (ESR) has attracted a lot of attention in the past decades, since it offers a potentially closed-loop carbon cycle if ethanol is derived from bio-sources. Noble metal based catalysts used in this process such as Pd, Pt, Ru and Rh show high catalytic activity [1]. However, the high cost of these metal catalysts is a limiting factor to make the process economically feasible. In our previous work, we have shown non-noble metal catalysts such as cobalt (Co) supported on ceria (CeO₂) to have high activity and stability for ESR. In recent studies, the support effects on the Co/CeO₂ catalyst performance have been investigated. It was found that different particle sizes and morphologies of ceria support affected the reduction state of cobalt, hence significantly altered the catalytic activity of Co/CeO₂ in ESR [2, 3]. The contribution of ceria support itself to the catalytic performance of Co/CeO₂ on ESR was also examined. Reduced state of ceria support (Ce⁴⁺) was active on ESR showing some extend of ethanol conversion and hydrogen yield [4]. In the present study, reduction characteristics of ceria were examined either with or without cobalt metal particles, using in-situ X-ray absorption spectroscopy (XAS) and ambient pressure X-ray photoelectron spectroscopy (XPS). Results indicate that the metal plays an important role in the reduction characteristics of Ce in ceria.

Materials and Methods
Two different particle sizes (3.5 nm-NP and 120 nm-MP) of the ceria support were prepared. Ceria nanopolyhedra (CeO₂-NP) were prepared via the solvothermal method and commercial ceria with a particle size in the 0.1 μm range (CeO₂-MP) was used for the larger size sample. After the support was prepared, cobalt was impregnated through incipient wetness impregnation method (IWI). The particles sizes of ceria was confirmed by transmission electron microscopy (TEM) images. Energy dispersive X-ray (EDX) spectroscopy was utilized to verify cobalt metal particles on the support in scanning transmission electron microscope (STEM) mode. Variation in the oxidation state of ceria under reaction conditions was quantified using in-situ x-ray absorption near edge structure spectroscopy (XANES) and ambient-pressure x-ray photoelectron spectroscopy (AP-XPS). The feed conditions for the in situ measurement were ethanol-to-water molar ratio of 1:10 in gas phase.

Results and Discussion

In-situ XANES and AP-XPS spectra were collected continuously during the first hour of ESR reaction over CeO₂-NP, MP and Co/CeO₂-NP, MP samples. Figure 1 shows a comparison of the oxidation states as a function of temperature for different ceria particle sizes with and without metal loading. The oxidation states are calculated using the XANES and AP-XPS spectra taken at the end of the first hour.

Figure 1. Comparison of extent of reduction in CeOx obtained from in-situ XANES and AP-XPS after 1 hour of ESR at 350, 400 and 450 °C

The extent of reduction is represented by the subscript x in CeOx. The reduction extent was increased (x decreased) as temperature was raised up to 450 °C in all samples. This observation was valid for both surface (AP-XPS) and bulk (XANES) measurements. This is attributed to the production of hydrogen during ethanol steam reforming which reduces the catalyst. From the XANES data, no bulk reduction for Co/CeO₂ and CeO₂-MP was observed. AP-XPS experiments, however, showed significant surface reduction for all samples. Similarly, extend of reduction measured by AP-XPS was higher than those measured by XANES in all samples, which indicates that surface is much more reduced than the bulk phase under ESR condition. Another interesting point is that in the presence of cobalt metal, the degree of reduction was lower compared to metal-free samples. This can be attributed to higher level of dissociation of water molecules in the presence of Co, and hence helping with the reoxidation step involved in ESR network.

Significance
This study examines the effect of metal on the reduction/reoxidation characteristics of ceria under steam reforming conditions using two in-situ techniques. Considering the wide use of ceria, these insights may help for other applications where ceria is used either as a support or as a catalyst.

References