Ethanol steam reforming over Co-based catalysts: Investigation of cobalt coordination environment under reaction conditions

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ARTICLE INFO

ABSTRACT

The transformations and the state of cobalt species during steam reforming of ethanol over Co/CeO_2 were investigated using in situ X-ray diffraction, controlled-atmosphere X-ray absorption fine structure, and X-ray photoelectron spectroscopy as well as steady state activity measurements. The catalyst was pretreated under an oxidizing or reducing atmosphere prior to characterization and activity testing to yield a Co_3O_4-rich or a Co^0-rich surface, respectively. While Co_3O_4 was found to be inactive for ethanol steam reforming, gradual activation of the oxidation-pretreated catalyst with temperature through reduction in Co_3O_4 took place under reaction conditions, and, over the activated catalyst, a mixture of both CoO and metallic Co were observed. Over the reduction-pretreated catalyst, metallic Co was partially oxidized to CoO during steam reforming of ethanol. The extent of cobalt reduction was observed to be independent of the initial state of the metal on the catalyst surface, and cobalt phase had the same composition under reaction above 450 °C.

1. Introduction

With the increasing demand on renewable energy technologies that leave minimal carbon footprint, research efforts on the production of hydrogen from renewable sources such as bio-derived oxygenates have been gaining momentum. In addition to having high gravimetric energy density and being a potential fuel for fuel cells, which allow more efficient energy conversion, when produced from bio-derived liquids, use of hydrogen as the energy carrier has minimal environmental impact due to the potential of recycling the CO_2 produced in the process via photosynthesis during plant growth [1]. The low sulfur content of the bio-derived liquids is another environmental advantage. Ethanol has emerged as a promising bio-derived liquid and received significant research attention because of its low toxicity and ease of handling, and the possibility of producing it from a variety of feedstocks that would not interfere with food or feed supply, such as lignocellulosic material.

Catalytic steam reforming is a cost-effective and efficient technology for hydrogen production from ethanol. A large number of catalytic systems have been reported to exhibit activity for the ethanol steam reforming (ESR) reaction, and these systems have been in a number of recent reviews [2–4]. Aupretre et al. [5] compared the catalytic activities of noble-metal-based (Rh, Pt) and non-noble-metal-based (Cu, Ni, Zn, and Fe) catalysts for ESR. These

authors reported Rh-based catalysts to possess superior catalytic activity in terms of both hydrogen yield and CO_2 selectivity. Similar studies in the literature have focused on noble-metal catalysts, such as Ru, Pd, Au, Re, Pt, Ir, and Rh [6–15] and reported high activities in a wide temperature and gas hourly space velocity range. Cobalt catalysts supported on a wide variety of metal oxide supports, such as zirconia, ceria, magnesia have shown promising ethanol steam reforming activities [16,17]; however, the nature of the cobalt active sites during the steam reforming reaction continues to be a topic of debate. Through ethanol, temperature-programmed desorption experiments carried out over a cobalt foil under ultra high vacuum conditions. Hyman and Vohs [18] showed that metallic cobalt sites were active in ethanol decarbonylation and Co^{2+} promoted dehydrogenation reactions to yield acetaldehyde species, while mostly complete oxidation products were observed over highly oxidized cobalt surfaces. The in situ magnetic characterization of cobalt during ethanol steam reforming over unsupported Co_3O_4 and metal oxide-supported cobalt catalysts was reported by Llorca et al. [19,20]. Over both types of catalysts, the authors observed the coexistence of an equilibrium state between reduced and oxidized phases of cobalt under reaction conditions. In a more recent study, Lin et al. [21] reported that the equilibrium state between CoO and Co^0 was governed by the feed stream composition as well as the catalyst pretreatment conditions. Similar results on the coexistence of Co^0 and CoO phases during ethanol steam reforming have been reported through in situ X-ray diffraction (XRD) studies on unsupported Co_3O_4 [22]. Batista

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et al. [23] reported that metallic cobalt sites constituted the active sites for ESR over cobalt-based catalysts. The metal–support interaction adds another level of complexity to the identification of active cobalt species for steam reforming of ethanol, and the nature of the ESR active sites remains as an important issue under debate.

Previously, through investigating the effect of a number different catalyst preparation methods and parameters, we have shown that strong metal–support interaction and high metal–support interface area were important factors that influence catalyst activity as well as stability [17,24–28]. The impregnation medium used for introducing the active metal onto the support [27] and the nature of cobalt precursor [24] was shown to play an important role in achieving high dispersion of cobalt species and thus, achieving high activity and stability over Co-based ethanol steam reforming catalysts. Novel catalyst synthesis techniques, namely solvothermal decomposition and reverse microemulsion, were also found to improve the catalyst activity by enhancing the intimate contact between the support and the active metal [28]. Furthermore, the nature of the support was found to play a key role in achieving high activity and stability by providing delivery of oxygen species to close proximity of ethoxy species and resulting in suppression of both sintering of cobalt and coke formation by enhancing oxidation of deposited carbon. In this context, ceria-based catalysts with significantly higher oxygen storage capacity and mobility were found to be highly active, selective, and stable for ethanol steam reforming [25]. Creation of oxygen vacancies through the introduction of a di-valent cation, such as Ca, resulted in further improvements in the hydrogen yields, turn-over frequencies, and lower liquid by-products [26]. In this paper, we present results of in situ and/or controlled-atmosphere investigation of the transformation and the state of cobalt species on a Co/CeO_2 catalyst during steam reforming of ethanol. The effect of two different pretreatment procedures, namely oxidizing and reducing pretreatment conditions, on the coordination environment of cobalt was studied using in situ X-ray diffraction, controlled-atmosphere X-ray absorption fine structure spectroscopy, and X-ray photoelectron spectroscopy in addition to steady state performance evaluations on oxidation- and reduction-pretreated catalysts. Evolution of species on the surfaces of oxidized and pre-reduced catalysts was also examined through in situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. It should be noted that there was no attempt to control the ratio of Co-to-CoO phases in the catalytic systems. Instead, the study focused on examining the evolution of the phases as the catalyst was exposed to the reaction medium for a certain length of time at each temperature.

2. Experimental

2.1. Catalyst preparation

A Co/CeO_2 catalyst with 10 weight percentage nominal cobalt loading was prepared by a previously described incipient wetness impregnation route where commercial cerium (IV) oxide (Aldrich) is impregnated with an aqueous solution of cobalt (II) nitrate hexahydrate (Aldrich, 99.999%) [27]. Prior to impregnation, the ceria support was calcined at 550 °C for 3 h under air. Impregnation of cobalt on the support was carried out in five consecutive steps by drying the impregnated catalyst at 110 °C overnight in between impregnation steps to improve the homogeneity of the resulting catalyst. Following the final impregnation and drying step, the catalyst was calcined at 450 °C for 3 h under a flow of air.

2.2. Catalyst characterization

Surface area and pore volume measurements were obtained on a Micromeritics ASAP 2020 accelerated surface area and porosime-

try instrument, using krypton adsorption/desorption isotherms collected at liquid nitrogen temperature. The desorption branch of the isotherm was used to determine the BJH pore size distributions. Before measurement, the catalyst was degassed for 12 h at 130 °C under a vacuum better than 2 μm Hg. Prior to the surface area analysis of the reduced catalyst, a reduction step was performed in situ, using the same procedure outlined above. Krypton physisorption measurements showed BET surface areas of the CeO_2 support, oxidized Co/CeO_2 and reduced Co/CeO_2 catalysts to be 9 m^2/g, 7 m^2/g, and 10 m^2/g, respectively, while pore size distributions were consistent with a mesoporous material with pore size distributions centered at 17 nm.

The dispersion measurements were obtained using N_2O chemisorption technique outlined earlier by Jensen et al. [29]. For these measurements, 200 mg of the catalyst was packed in a ¼″ OD fixed bed quartz reactor with a quartz frit and placed inside a fast-response furnace (Carbolite, MTF 10/15/130). The sample was reduced in situ at 400 °C using 5% H_2 in He for 2 h. The reactor was then flushed with He at the same temperature and cooled under helium. N_2O chemisorption was performed by introducing a stream of 3%N_2O/He to the reactor at 40 °C. Species in the $m/z = 12$ to $m/z = 46$ range were monitored via an online mass spectrometer (MKS – Cirrus II). The mass spectrometer was calibrated for instrumental sensitivity factors and the contribution of $m/z = 28$ fragment of N_2O to the $m/z = 28$ trace. Throughout the experiment, N_2O and N_2 were the only species detected in the reactor effluent. For quantification of the N_2 formation, known volumes of N_2 were injected to the mass spectrometer under the same flow conditions with a 250 ml sample loop connected to an automated six-port valve. The number of O atoms consumed is calculated through N_2 evolution, and the number of surface Co sites is calculated after the Fickian diffusion correction, assuming 1:1 Co/O ratio. Due to the low surface area of the support, the dispersion of Co on the ceria surface was low ($\sim$1%).

The temperature-programmed reduction profiles (H_2-TPR) of Co/CeO_2 catalysts were collected on an online mass spectrometer (Cirrus II, MKS Instruments, 1–300 amu) operated in the selective ion-detection mode. Both $m/z = 2$ and $m/z = 18$ signals were monitored. 0.1 g of catalyst sample was packed inside a ¼″ OD quartz U-tube reactor made of quartz using quartz wool plugs. The catalyst was pretreated in He at 400 °C for 30 min followed by cooling to room temperature in He. Then, 5% H_2/He (30 cm^2/min) was introduced to the reactor at room temperature, and the mass signals were allowed to stabilize for at least 30 min before ramping the temperature at 10 °C/min to 650 °C.

The in situ XRD patterns during ethanol steam reforming over Co/CeO_2 were collected on a Bruker D8 Advance X-ray diffractometer with monochromatic Cu Kα radiation ($\lambda = 1.5418$ Å) through a tube operated at 40 kV and 50 mA and equipped with an Anton Paar HTK1200 controlled-atmosphere oven prior to the collection of in situ XRD patterns, and the catalyst samples were subjected to either an oxidation or a reduction pretreatment. The oxidation pretreatment involved heating the catalyst at 400 °C under air (30 ccm) for 30 min, and samples subjected to this pretreatment will be denoted as $Co/CeO_2(O)$. The pre-reduction step consisted of heating the catalyst to 400 °C under a flow of He (30 ccm) for 30 min followed by reduction for 2 h in 5% H_2/He (30 ccm) at the same temperature and purging with He (30 ccm) for 1 h at 450 °C. Samples subjected to this pretreatment will be denoted as $Co/CeO_2(R)$.

The ethanol steam reforming mixture contained ethanol and water at a molar ratio of 1-to-10 and an ethanol concentration of 0.3%. An O_2 trap was installed in the UHP helium line (VICI Valco Instruments, HP2 heated helium purifier) to remove any oxygen impurity that might be present in helium before it reaches the reactor. Throughout the XRD experiments, a linear heating rate of