Ethanol steam reforming over Co-based catalysts: Role of oxygen mobility

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ABSTRACT

The effect of oxygen mobility on the bio-ethanol steam reforming of ZrO_2- and CeO_2-supported cobalt catalysts was investigated. The supported catalysts were prepared by incipient wetness impregnation (IWI) and characterized through N_2 physisorption, X-ray photoelectron spectroscopy, temperature programmed oxidation, laser Raman spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy, O_2 pulse chemisorption, isotopic labeling, and transmission electron microscopy techniques at various life stages of the catalyst. The results indicated that the catalyst deactivation was due mostly to deposition of various types of carbon on the surface although cobalt sintering could also be contributing to the deactivation. The addition of ceria was found to improve the catalytic stability as well as activity, primarily due to the higher oxygen mobility of ceria.

1. Introduction

As the wide-spread application of fuel cells becomes closer to reality, increased attention has been focused on hydrogen production technologies. Bio-ethanol steam reforming (BESR) offers an environmentally friendly route for hydrogen production from renewable sources, with potentially little contribution to green house effect, since CO_2 can be recycled through photosynthesis during the plant growth. Bio-ethanol can be obtained from fermentation of biomass (e.g. sugar cane, cellulose, corn). Because of its low toxicity and ease of deliverability, ethanol steam reforming lends itself very well to a distributed-production strategy. Development of a non-precious catalytic system with high activity and stability will be an important step in making this technique economically competitive.

With increased interest in hydrogen as an energy carrier for fuel cells, studies in the literature on ethanol steam reforming catalysts have also increased significantly in recent years. Catalysts utilized are mainly Ni, Cu, Co and supported noble metals, such as Rh, Ru, Re, Pd, Ir and Pt [1–4], which have been reviewed by Haryanto et al. [5] and Vaidya et al. [6]. Although supported noble metal catalysts have been shown to have significant activity in 500–600 °C range and at high space velocities [7–9], high cost of these metals limits their application. As a less expensive alternative, cobalt-based catalysts have been reported to have superior ethanol steam reforming performance due to their high activity for C–C bond cleavage at temperatures as low as 350–400 °C [10–12]. At these temperatures, researchers have reported good selectivity to CO_2 and H_2 with CH_4 being the only by-product.

Catalyst deactivation during BESR has been reported over various catalyst systems [13–16], especially over supported Ni catalysts [17–24]. Furthermore, in most of these studies, the metal sintering and the deposition of carbonaceous species such as amorphous carbon, carbon filament, and carbonate species have been recognized as the main causes of catalyst deactivation. The number of studies examining the activity of supported cobalt catalysts is fewer [25–27], most detailed studies being reported by Llorca and co-workers [11,12,28–32] and the most commonly used support being ZnO.

In recent years, increased attention has been given to the role of oxygen mobility in improving the catalytic stability during BESR through preventing metal particles from sintering [33,34] and suppressing the formation of carbonaceous species by gasification. While most of these studies are focused on the utilization of CeO_2 or ZrO_2–CeO_2 mixed oxide supported noble-metal catalysts [35–37], the importance of a similar phenomenon for non-precious metal catalysts such Co has received much less attention.

In our earlier publications [38,39], we have reported on the catalytic activity of Co/ZrO_2 catalysts in ethanol steam reforming and the effect of synthesis parameters on catalytic performance. In this study, we focus on the deactivation behavior of these Co-based catalysts and the effect of the oxygen mobility of the support on catalytic activity and stability. Ceria, which is known for its high oxygen storage capacity, has been reported to enhance the catalytic activity and stability in several reactions

such as CO oxidation, water–gas shift, and steam reforming of methane [40–42]. In this paper, the role of CeO_2 addition in improving the stability of Co-based catalysts, as examined through characterization studies that included N_2 physisorption, X-ray photoelectron spectroscopy (XPS), temperature-programmed oxidation (TPO), laser Raman spectroscopy (LRS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), O_2 pulse chemisorption, $^{16}O_2/^{18}O_2$ exchange, and transmission electron microscopy (TEM) techniques, is reported.

2. Experimental

2.1. Catalysts preparation

Supported cobalt catalysts with 10 wt% metal loading were prepared in air by incipient wetness impregnation from cobalt(II) nitrate hexahydrate (Aldrich 99.999%) aqueous solutions. The pure supports used were ZrO_2 (Saint Gobain, surface area: 55 m^2/g, pore volume: 0.21 cm^3/g) and CeO_2 (powder <5 μm, 99.9% Aldrich, surface area: 71 m^2/g, pore volume: 0.34 cm^3/g). The 10 wt%CeO_2–ZrO_2 support was prepared by impregnating the ZrO_2 support using an aqueous solution of cerium(III) nitrate (Aldrich 99.999%). All the supports were calcined for 3 h in air at 500 °C prior to metal impregnation. After repeating the impregnation of cobalt precursor and drying steps (at 95 °C) as many times as determined by the pore volume of the corresponding supports, the resulting samples were calcined at 400 °C for 3 h in the air and stored for use. The term "fresh sample" is used to represent the sample after calcination; the "reduced sample" denotes the sample reduced at 400 °C for 2 h; and the "spent sample" refers to the sample after reduction treatment and exposure to reaction atmosphere for various time periods.

2.2. Catalysts characterization and reaction performance measurement

The surface areas of the fresh and spent catalysts were measured using nitrogen adsorption at 77 K (Micromeritics ASAP 2010). Before each measurement, the sample was degassed under 130 °C overnight to remove any impurities adsorbed from the atmosphere during storage.

XPS analysis was performed using an AXIS His, 165 Spectrometer manufactured by Kratos Analytical with a monochromatized Al$K\alpha$ X-ray source. 2.3 V voltage was chosen to make the charge balance. A stainless steel sample holder was used. Survey scans were performed to identify all the elements within the sample, followed by more detailed regional scans for Co 2p, C 1s, O 1s, Zr 3d orbitals in order to achieve the high resolution for these elements of interest. A controlled-atmosphere transfer chamber was used for transferring the sample to the XPS instrument without exposure to atmosphere.

Temperature-programmed oxidation (TPO) experiments were performed using Autochem-2920 (Micromeritics) with an online mass spectrometer (MS) (MKS Instruments, 1–300 amu). The samples were first pretreated at 300 °C with He for 30 min in order to remove adsorbed contaminants during storage. After cooling down to room temperature under helium, 10%O_2/He (30 ml/min) was introduced into the reactor and TPO experiments were subsequently performed with a heating rate of 10 °C/min after the MS signal was stable.

Raman spectra were taken with a LabRAM HR-800 spectrometer equipped with an OLYMPUS BX41 microscope (50× magnification) and a CCD detector. An argon ion green laser (514.5 nm, operated at 3 mW) was used as the excitation source during spectra collection.

O_2 pulse chemisorption experiments were conducted using AutoChem II 2920 (Micrometrics) connected with a Cirrus Mass Spectrometer (MKS Instruments, 1–300 amu). Catalysts of ∼200 mg

were sandwiched between two layers of quartz wool and subjected to an oxidative cleaning step in air for 30 min, at the calcination temperature of the sample, followed by a reduction step at 400 °C for 2 h. After the system was flushed with He to remove any moisture, the O_2 pulses were introduced at 300 °C. The $m/z = 32$ signal was continuously detected by the MS until there was no variation between two consecutive peaks.

$^{16}O_2/^{18}O_2$ exchange experiments were performed using a Thermo Finnegan Trace Ultra DQC GC/MS. ∼50 mg samples were placed in a U-tube quartz reactor. Following a cleaning step under He at 400 °C for 30 min to remove impurities adsorbed during storage, the reactor was cooled down to 300 °C, at which temperature the $^{16}O_2/^{18}O_2$ exchange took place. The $m/z = 32$, 34, and 36 (mass-to-charge ratio) signals were monitored by the mass spectrometer during the exchange process. 10% Ar was included in the 2% $^{16}O_2$/He stream to account for the gas-phase hold-up time, as described previously [43–45]. In addition, blank experiments were also performed and showed no exchange in the gas phase when no catalyst was present.

The TEM experiments were performed by using Philips Tecnai TF-20 TEM instrument operated at 200 kV. An X-ray analyzer for EDS is incorporated into the instrument for elemental analysis under STEM mode for improving image contrast between C and Co phases. The sample was first dispersed in ethanol and supported on Lacey-formvar carbon on a 200 mesh Cu grid before the TEM images were recorded.

DRIFTS was performed with a Thermo NICOLET 6700 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a KBr beam splitter. The in situ experiments were performed using a Smart collector DRIFT environmental chamber with ZnSe windows. Following the pretreatment under He at 400 °C for 30 min and reduction under 5%H_2/He at 400 °C for 2 h, the environmental chamber was heated to 450 °C for 1 h under He for removing moisture generated from the reduction step. The reactant vapors generated from a two-bubbler system were then flowed over the sample for 1 h at room temperature using He as a carrier gas. The sample was then flushed with He for 10 min. Spectra were taken at pre-set intervals while the sample temperature was ramped from 25 to 500 °C.

The catalytic performance measurement and analysis methods used were reported elsewhere [38]. Briefly, all catalysts were first pretreated at 400 °C for 30 min. under He and then reduced in situ at 400 °C for 2 h under 5%H_2/He. The reactant liquid consisting of ethanol and water at 1:10 molar ratio was delivered into an evaporator. The generated reactant vapor was carried by He and introduced into the reactor. The dilution ratio varied between 40 and 75 (inert-to-ethanol molar ratio). For neat experiments, gas phase reactants were directly fed to the reactor without dilution with an inert gas. Subsequently the catalytic performances were tested in the temperature range of 300 to 550, in 50 °C increments. The catalyst was held at each temperature for at least 2 h. At the end of the catalytic test, the flow of EtOH + H_2O was stopped and the catalyst was cooled under He stream. The hydrogen yield is defined as H_2 yield % $= \frac{\text{moles of } H_2 \text{ produced}}{6 \times (\text{moles of ethanol fed})} \times 100$. The time-on-stream (TOS) tests were performed at 450 °C for different time periods depending on the deactivation rate of various samples. The spent samples after TOS experiments were cooled down to room temperature under helium before characterization.

The turnover frequency (TOF) reported in the paper is calculated based on the ethanol conversion rate divided by the total available metallic cobalt active sites contained over the samples charged in the reactor. The cobalt dispersion is estimated using a H_2 chemisorption technique, which is described in detail previously [38].