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Water-induced formation of cobalt oxides over supported cobalt/ceria–zirconia catalysts under ethanol-steam conditions

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ABSTRACT

The water-induced formation of cobalt oxides by the re-oxidation of metallic cobalt in pre-reduced 10% Co/CeO_2–ZrO_2 catalyst was verified by in situ temperature-programmed reduction (TPR) and in situ X-ray Photoelectron Spectroscopy (XPS) studies under various ethanol-steam conditions at 450 °C. The formation and transformation of water-induced cobalt oxide species during the reaction were influenced by the pre-reduction conditions as well as the feed stream composition. Our results suggest that the surface composition of the cobalt species (e.g. Co, CoO, and CoO_x) in the 10% Co/CeO_2–ZrO_2 catalyst, initially determined by the catalyst pre-treatment conditions, changed toward an equilibrium state governed by the feed stream composition as the reaction proceeded. In addition, the reducibility of the ceria sites may play a significant role in the formation of such water-induced cobalt oxide species, as the redox process involves both cobalt and ceria sites in the ethanol-steam environment. Finally, the effect of the water-induced cobalt oxides in the 10% Co/CeO_2–ZrO_2 catalyst was investigated under ethanol and ethanol-steam conditions, particularly for the carbon–carbon (C–C) bond cleavage of ethanol. The water-induced formation of cobalt oxides in the catalyst was not observed to affect the cleavage, in either ethanol-rich (e.g. ethanol decomposition) or steam-rich (e.g. ethanol steam reforming) conditions. This result could be explained by our in situ studies, which revealed the redox exchange between reduced cobalt and oxidized cobalt in a feed stream with a changing water-to-ethanol ratio.

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1. Introduction

Catalysts for hydrogen production through ethanol steam reforming (ESR) have been carefully studied and summarized in the recent literature [1–4]. Precious metals such as Rh, Pt, and Pd have been found to be effective catalysts. Rh, in particular, is the most active because the formation of five-member ring oxametallacycles over Rh surfaces during the dehydrogenation of ethanol facilitates the C–C bond cleavage of the adsorbed ethoxide species, when compared with the acetaldehyde formed over Pd surfaces, which can lead to acetone formation [5,6]. However, larger-scale applications of ESR would be impractical using expensive Rh-based catalysts.

As an inexpensive alternative for ethanol reforming applications, Co-based catalysts have attracted much attention recently; their activity for efficient C–C bond cleavage around 400 °C has been reported to be similar to that of precious metal catalysts [7,8]. The similarity in terms of activity for the C–C bond cleavage is not surprising, as revealed by density function theory (DFT) calculations that the oxametallacycic intermediate is more stable over Rh and Co surfaces than over other transition metals [6].

In addition, the catalytic properties of Co-based catalysts that determine the reaction turnovers and the product selectivity in a kinetic-controlled regime during ESR are found to be strongly influenced by the supporting materials, such as Al_2O_3, MgO, ZnO, SiO_2, and ZrO_2 [7–11]. The Co-support interactions and their influence on catalytic performance over supported Co catalysts have been a research focus in the steam reforming of ethanol. Based on what has been found in supported metal catalysts [12] and our previous findings [13,14], it is generally believed that C–C bond cleavage takes place on metallic Co surfaces, while the support plays a dual role, physically stabilizing Co nanocrystallites and chemically facilitating the oxidation process by activating water molecules or releasing lattice oxygen.

Although metallic Co was shown to be responsible for the activity in several ethanol reforming studies using bulk and supported Co catalysts [14–18], owing to the difficulty of characterizing Co species over support surfaces in *operando* conditions, the true identity of its active centers in ESR is still elusive. Furthermore, the

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coexistence of metallic Co and Co oxides (CoO_x) was observed and seems unavoidable in a steam-rich environment given by a high steam-to-carbon feed condition; it is a challenging task to differentiate cobalt species with different oxidation states and correlate the composition of the bulk cobalt to catalytic properties, especially when they are coupled with Co-support interactions.

The presence of CoO_x, or more precisely, the re-oxidation of metallic Co to CoO_x, is also an interesting topic in supported Co-based Fischer–Tropsch catalysts. The negative effect of water on catalyst activity in Fischer–Tropsch synthesis could be linked to the formation of inactive cobalt oxides; however, the issue remains controversial [19–23]. In the case of ESR, however, very few papers address the effect of water on the oxidation of cobalt, and the discussion is mostly limited to the bulk cobalt catalysts [16,17]. The assumption that the metallic cobalt is stable and acts as the active center is generally made in studies of supported cobalt catalysts for ESR, in which the activity and stability are measured, and the cobalt-support interactions are discussed for the pre-reduced metallic cobalt only. Therefore, in steam reforming conditions or reactions involving steam, the redox exchange between the reduced and oxidized cobalt species and their interactions with support surfaces as well as adsorbed molecules should not be overlooked, as the nature of the active sites is still under investigation.

This work examines the formation of CoO_x species over supported $Co/CeO_2–ZrO_2$ catalysts in different ethanol-steam conditions including ethanol steam reforming, water-assisted ethanol decomposition, and ethanol decomposition reactions. Supported $Co/CeO_2–ZrO_2$ was chosen as a model catalyst system because its high activity toward hydrogen production via ethanol steam reforming has been shown to be closely related to the reducibility of cobalt and the cobalt-support interactions [13,24].

Several in situ techniques including diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS), temperature-programmed reduction (TPR), and X-ray Photoelectron Spectroscopy (XPS) were used to characterize the formation of water-induced CoO_x over supported $Co/CeO_2–ZrO_2$ in various ethanol-steam mixtures. The re-oxidation of metallic Co and a transient exchange between metallic Co and CoO_x were found to be associated with water-to-ethanol ratios in the feed stream. Furthermore, the Co–Ce interaction in the catalyst was demonstrated, as the extent of reduction for the Ce species in the $CeO_2–ZrO_2$ support was found to play a key role in the re-oxidation/re-reduction of the supported cobalt species in ethanol-steam conditions.

2. Experimental

2.1. Catalyst preparation and activity evaluation

Incipient wetness impregnation was used for the synthesis of supported $Co_3O_4/CeO_2–ZrO_2$. Commercial nanocrystalline $CeO_2–ZrO_2$ (Ce/Zr atomic ratio close to 3, Sigma-Aldrich) was impregnated with cobalt nitrate, $Co(NO_3)_2·6H_2O$ (Alfa Aesar), followed by calcination at 500 °C in air for 4 h to form supported cobalt oxides on $CeO_2–ZrO_2$ (10 wt.% cobalt). This sample is denoted as 10% Co–CZ. A detailed characterization of the physical properties of this catalyst, such as crystalline structure, surface area, pore volume, and morphology, has been carried out in our previous study [24].

The catalytic activity of 10% Co–CZ was evaluated in a series of catalyst testing experiments. Approximately 100 mg catalyst was charged into an 8-mm-ID quartz packed-bed reactor inside a Watlow temperature-controlled furnace at atmospheric pressure. Gas flows were controlled with Brooks Mass Flow Controllers (Model 5850E). The catalyst was pre-reduced under 20 sccm hydrogen flow at 450 °C for 2 h before the activity evaluation. After the pre-reduction, degassed ethanol or a degassed ethanol–water mixture was injected into the reactor with a syringe pump and vaporized in a pre-heater containing an SiC bed with a 10-sccm helium carrier gas. Ethanol was fed at a constant weight hourly space velocity (WHSV) of 1.58 h^{-1} in all the streams. The product stream was passed through a two-stage condenser to remove water, unconverted ethanol, and any other possible liquid by-products before the gas analysis. The effluent composition was analyzed using an SRI gas chromatograph equipped with a thermal conductivity detector (TCD), molecular sieve 13X, and Hayesep D columns, capable of separating and measuring H_2, CH_4, CO, CO_2, C_2H_6, and C_2H_4. The catalyst performance was analyzed in terms of the carbon–carbon (C–C) cleavage conversion of ethanol and the formation rate of gaseous products. This rate was calculated on the basis of the catalyst mass. The C–C cleavage conversion of ethanol was defined using a carbon basis molar ratio, the ratio of gaseous C1 compounds (CH_4, CO, and CO_2) in the product stream to the ethanol in the feed stream:

$$\text{C—C cleavage conversion}(\%) = \left(\frac{CH_4 + CO + CO_2}{C_2H_5OH \times 2}\right) \times 100$$

2.2. In situ TPR

Temperature-programmed reduction (TPR) experiments were performed using a Micromeritics ChemiSorb 2720 equipped with a thermal conductivity detector (TCD). In a typical in situ TPR experiment, approximately 40 mg of sample was held by quartz wool and placed in a U-shaped quartz tube, where a syringe pump delivered an ethanol–water mixture through a customized stainless tube (0.042″ OD and 0.027″ ID) positioned above the sample . Thermocouples were directly in contact with the quartz tube of the sample section. The H_2-TPR profiles were recorded at a ramping rate of 10 °C/min from 25 °C to 850 °C and a 40-sccm flow rate of 10% H_2–Ar mixture. Depending on the measurement type, different thermal pre-treatments were used before the H_2-TPR profile was recorded. The sample was pre-oxidized for all the measurements to eliminate possible surface contamination before the pre-reduction and titration procedures. The sample was pre-oxidized at a 40-sccm flow rate of 5% O_2-helium at 500 °C for 30 min. Pre-reduction of the sample was performed at a 40-sccm flow rate of the 10% H_2–Ar mixture at a desired temperature for 1 h. The water titration or ethanol–water titration was performed at a 40-sccm flow rate of Ar at 450 °C with a liquid volume of 0.025 ml at a feed rate of 0.5 ml/h. The liquid (water or ethanol–water) for the titration was degassed to remove any dissolved O_2. The blank H_2-TPR profile was obtained by carrying out the same procedure (pre-oxidation, pre-reduction, water titration) over a sample tube filled only with quartz wool to ensure there was no interference in the TCD signal.

2.3. In situ DRIFTS

CO chemisorption was carried out by diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Perkin-Elmer System 2000 FTIR spectrometer with a liquid-nitrogen-cooled MCT detector. A Harrick Scientific HVC-DR2 reaction chamber mounted inside the spectrometer provided temperature-controlled flow-through atmospheres for catalyst pre-treatments for CO chemisorption. The path of the infrared beam inside the sample compartment was purged with nitrogen to eliminate water and CO_2 noise during the measurements.

Three different pre-treatments were used for the sample powders (~140 mg) before CO chemisorption. A hydrogen or helium flow of 30 sccm was introduced into the reactor chamber at