The Effect of ZnO Addition on H₂O Activation over Co/ZrO₂ Catalysts

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Abstract

The effect of ZnO addition on the dissociation of H₂O and subsequent effects on cobalt oxidation state and ethanol reaction pathway were investigated over Co/ZrO₂ catalyst during ethanol steam reforming (ESR). Catalyst physical properties were characterized by BET, XRD, and TEM. To characterize the catalysts ability to dissociate H₂O, Raman spectroscopy, H₂O-TPO, and pulsed H₂O oxidation coupled with H₂-TPR were used. It was found that the addition of ZnO to cobalt supported on ZrO₂ decreased the activity for H₂O dissociation, leading to a lower degree of cobalt oxidation. The decreased H₂O dissociation was also found to affect the reaction pathway, evidenced by a shift in liquid product selectivity away from acetone and towards acetaldehyde.

1. Introduction

Steam reforming is a well-established industrial process for hydrogen production, currently ~49% of world hydrogen production is from steam reforming of methane [1]. Due to the increasingly stringent limitations on CO₂ emissions and increasing energy demands, steam reforming of renewable feed stocks such as methanol and ethanol has received extensive attention [2-5].

A wide range of catalysts have been investigated for ethanol steam reforming (ESR) [2, 4, 5].

Among those studied, supported cobalt catalysts have emerged as being particularly promising.

Noble metal catalysts have shown the highest activity for ethanol conversion, however, they also have shown a high selectivity to CH₄ at lower temperatures (e.g., below 500 °C) [6]. Ni and Co based catalysts have comparable activity for C-C cleavage, but Ni has demonstrated a higher selectivity to CH₄ than Co [4].

From studies of Co-based catalysts, it has been found that both cobalt oxidation state [7-14] and the reaction network [15-17] are significantly influenced by either the reaction conditions [7, 14, 18] or catalyst support [5, 8, 9, 11, 15-17, 19-21], which eventually led to different performances of the catalysts during ESR [5, 22]. Over model Co catalysts, it was found that while Co²⁺ is active for ethanol dehydrogenation reaction, Co⁰ is mainly responsible for C-C cleavage during ESR [12, 13]. These model studies have been further supported by recent work utilizing operando XAFS analysis to study the oxidation state of cobalt under realistic reaction conditions [7]. Our recent work also revealed that both the ratio of Co²⁺/Co⁰ [10, 11] and reaction network [23, 24] affected the selectivity to CH₄. For the former case, higher Co²⁺/Co⁰ ratio was found to favor CO methanation toward CH₄ [10]. For the latter case, acetone was found to be a key intermediate in ESR on Co/ZrO₂ [16] and acetone steam reforming resulted in the low CH₄

selectivity ($\leq 5\%$) [17, 25]. Over Co/CNF where acetaldehyde was identified as the only intermediate, a high CH_4 selectivity was observed ($\sim 10\%$) [17].

The general trends of catalyst support material are well known in regards to surface acidity and reducibility of the support [2, 15, 19]. Acidic supports tend to dehydrate ethanol to form ethylene while basic supports favor not only dehydrogenation of ethanol to acetaldehyde intermediate [2, 15, 26, 27], but also further condensation of acetaldehyde to acetone secondary intermediate [16, 22]. Reducible supports with high oxygen mobility (e.g., CeO_2) tend to give more stable performance in ESR, due to enhanced gasification of CH_x^* species, which limits both the quantity and stability of coke deposited [28-30]. More recently, it was found that the oxidation state of cobalt should be associated with the support chemistry [8, 9, 11]. Particularly, the addition of ZnO to the ZrO_2 was found to inhibit the metallic cobalt oxidation via water [11]. It is apparent that water must play a key role in oxidizing the active metal and carbon species as part of the redox cycle to minimize the deposition of coke on the catalyst. Unfortunately, there are relatively few studies correlating the dissociation of water with the catalytic performances in ESR. In this work, we investigated the impact that water dissociation has on both the cobalt oxidation state and the ESR reaction network, particularly the selectivity to acetaldehyde and acetone, and subsequent C_1 products.

2. Experimental Methods

2.1 Catalyst Synthesis

All catalysts were prepared via incipient wetness impregnation. The ZrO_2 support was synthesized by calcining $\text{Zr}(\text{OH})_4$ (MEL Cat XZO1247/01, 97+% purity) at $400\text{ }^\circ\text{C}$ ($3\text{ }^\circ\text{C}/\text{min}$) for 3 hours, then ramping to $500\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C}/\text{min}$ and holding for another 5 hours. ZnO support was made by decomposing $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Alfa Aesar 11559, 98+% purity) at $500\text{ }^\circ\text{C}$

(10 °C/min) for 3 hours; prior to the decomposition, the $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ precursor was dried at 125 °C (10 °C/min) for 2 hours. Metal precursors used were $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich 239267, 98+% purity) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich 228737, 98+% purity). Before impregnation, the ZrO_2 or ZnO was pre-dried at 80 °C for ~24 hours to remove the majority of adsorbed water. A calculated amount of metal precursor was dissolved in a given amount of deionized (DI) H_2O . The total volume of the metal precursor solution was set to reach the incipient wetness of the support surface. After the impregnation, the obtained wet powders were dried at ambient temperature for ~24 hours and then at 80 °C for 12 hours and then at 120 °C for 12 hours, after that the temperature was then ramped to 550 °C at 10 °C/min for 5 hours to complete the calcination. For ZnO doped catalysts cobalt and zinc precursors were dissolved into a single solution and the same process was followed.

Nomenclature used in this paper is as follows, 10 wt.% Co supported on ZrO_2 will be written as 10Co/ ZrO_2 , 10 wt.% Co with 1 wt%. Zn supported on ZrO_2 will be written as 10Co1Zn/ ZrO_2 , and 10 wt.% Co supported on ZnO will be written as 10Co/ ZnO .

2.2 Catalyst Characterization

Nitrogen physisorption experiments were performed on a Micromeritics 3020 TriStar II physisorption analyzer at -196 °C. The fresh catalysts were degassed under vacuum at 300 °C for 1 hour prior to measurement. Catalyst surface area was calculated using the Brunauer–Emmett–Teller (BET) model.

XRD patterns were collected using a Rigaku Mini-Flex X-ray powder diffractometer with a $\text{Cu-K}\alpha$ (incident wavelength = 0.15406 nm) radiation source at 40 kV and 15 mA. Diffraction patterns were collected from 20 to 80° (2 θ) using continuous accumulation with 0.01° step size at a rate of 1.5°2 θ /min. For reduced sample measurements diffraction patterns were collected from

40 to 55° (2 θ) using continuous accumulation with 0.01° step size at a rate of 0.25°2 θ /min.

Crystallite sizes were calculated from XRD patterns using the Scherrer equation. Preparation for the reduced samples consisted of reduction at 450 °C (5 °C/min) under 10% H₂/N₂ (50 SCCM) for 2 hours, followed by passivation at ambient temperature (25 °C) under 0.1% O₂/N₂ (50 SCCM) for 2 hours.

TEM images were collected on a Philips CM-200 equipped with a LaB₆ filament. An acceleration voltage of 200 kV was used during imaging. Catalysts were dispersed in ethanol using an ultra-sonic bath, the suspension was then loaded onto a copper grid coated with ultrathin lacy carbon for TEM imaging.

For particle size analysis, spherical particles were assumed and ImageJ software was used to calculate the diameter of the particles [31]. For statistical analysis over 100 particles were measured for each sample. From analysis using Origin software, the population distributions were determined to be log-normal, based on this mean and variance were calculated accordingly.

Pulsed water oxidation and water TPO (H₂O-TPO) experiments were performed on a Micromeritics AutoChem 2920. 50 mg of catalyst was loaded into a U-shaped quartz tube, sandwiched between two pieces of quartz wool. Outlet gases were monitored by both thermal-conductivity detector (TCD) and a Pfeiffer ThermoStar quadrupole mass-spectrometer (QMS).

For pulsed water oxidation, the catalyst was first reduced at 450 °C (5 °C/min ramp rate) for 2 hours under 10%H₂/Ar (50 SCCM), and then purged at 450 °C under He (50 SCCM) for 30 min. ~10%H₂O/He was generated by bubbling He (50 SCCM) through DI H₂O in a flask heated to 55 °C followed by a reflux at 45 °C. H₂O was then pulsed over the catalyst at 450 °C, and pulses were repeated until the catalyst surface was saturated monitored by TCD. QMS was used to monitor the effluent gases, particularly hydrogen. Following water pulses the catalyst was again

purged under He (50 SCCM) at 450 °C for 30 min, then cooled to 35 °C. To confirm degree of oxidation, H₂-TPR was run and H₂ uptake was quantified. Percentage oxidized by both H₂O pulses and H₂-TPR were calculated by taking the ratio of Co loaded and either H₂O taken up or H₂ consumed respectively. For H₂O-TPO, the catalyst was first reduced at 450 °C (5 °C/min ramp rate) for 2 hours under 10% H₂/Ar (50 SCCM). The catalyst was then cooled to 35 °C under He (50 SCCM). Next, the gas flow was switched to ~10% H₂O/He (50 SCCM) and the temperature was ramped to 500 °C at 10 °C/min.

2.3 Catalyst Activity Evaluation

ESR activity tests were performed in a fixed-bed, single-pass quartz tube reactor (I.D., 6.5 mm). ESR reactions were carried out at 450 °C under atmospheric pressure. 50-100 mg of the catalyst (60-100 mesh) diluted 9x in SiC (70 mesh) was loaded and held in place using quartz wool. Prior to the reaction, the catalyst was reduced *in situ* at 450 °C (5 °C/min ramp rate) for 2 hours under 10% H₂/Ar (100 SCCM), followed by a N₂ purging (20 SCCM) for 60 min. An aqueous solution of H₂O and ethanol, 10:1 molar ratio, was fed to the evaporator (175 °C) using a Cole Parmer syringe pump. The vaporized H₂O/EtOH mixture was then carried to the reactor by flowing N₂. The ethanol partial pressure (P_{EtOH}) in the reactant gas was 7.4 kPa and WHSV was varied from 9.3 g_{EtOH}·g_{Catalyst}⁻¹·h⁻¹ to 18.5 g_{EtOH}·g_{Catalyst}⁻¹·h⁻¹ to control the ethanol conversion. A downstream cold trap (-5 °C) was used to capture the condensable components (e.g., unreacted H₂O/EtOH, acetaldehyde) in the effluent gas stream.

The dry gases (e.g., N₂, H₂, CO_x, CH₄) were analyzed with an on-line Agilent CP490 micro gas chromatograph equipped with 4 parallel columns (5Å molecular sieve, PPQ, Al₂O₃ and SiO₂) and thermal conductivity detectors (TCD) for quantifications. N₂ was used as an internal standard. Liquid products collected by the cold trap were analyzed by an Agilent 7890A gas

chromatograph with a 30 meter DB-FFAP column and flame ion detector (FID), acetonitrile was used as an internal standard. H₂-yield was calculated using equation 1.

$$\text{H}_2 \text{ yield} = (\text{H}_2 \text{ molar flow} / (6 \cdot \text{EtOH molar feed rate})) \cdot 100 \quad (1)$$

C₁ product yield was calculated using equation 2

$$\text{C}_1 \text{ yield} = ((\text{CO}_2 + \text{CO} + \text{CH}_4 \text{ molar flows}) / (2 \cdot \text{EtOH molar feed rate})) \cdot 100 \quad (2)$$

Ethanol conversion was calculated using equation 3

$$\text{EtOH conversion} = ((\text{EtOH in product liquid}) / (\text{EtOH in feed liquid})) \cdot 100 \quad (3)$$

Product selectivity was calculated using equation 4, integration is over the run time of the experiment to get total C of the product over the entire experiment.

$$\text{Selectivity} = (\int (\text{molar C flow of product}) / \sum (\text{all C in products over experiment})) \cdot 100 \quad (4)$$

2.4 *In situ* Raman characterization of cobalt oxidation by H₂O

In situ Raman spectra characterizing cobalt oxidation by H₂O were collected on a Horiba LabRAM HR Raman/FTIR microscope spectrometer, equipped with a 532 nm diode laser source (Ventus LP 532), a Synapse CCD (Charge Coupled Device), and an *in situ* cell (Linkam CCR1000). Samples were first reduced at 450 °C (5 °C/min ramp rate) for 2 hours under 10% H₂/He (50 SCCM) then cooled to ambient temperature. H₂O oxidation experiment was performed by bubbling He (10 SCCM) through H₂O at ambient temperature while the sample was heated to the target temperature and held for 30 min. Following the H₂O pretreatment, the sample was purged in flowing He (50 SCCM) for 30 min and then cooled down to ambient temperature where Raman spectra were collected.

3. Results and Discussion

3.1 Catalyst characterization

3.1.1 Effect of ZnO on physical properties

The results of physical properties are shown in Table 1. The ZrO_2 support was found to have a surface area of $50.6 \text{ m}^2/\text{g}$ and the ZnO support to have a surface area of $12.6 \text{ m}^2/\text{g}$. For both ZrO_2 and ZnO , the addition of 10wt% Co ($10\text{Co}/\text{ZrO}_2$ and $10\text{Co}/\text{ZnO}$) decreased the surface area to $41.0 \text{ m}^2/\text{g}$ and $8.9 \text{ m}^2/\text{g}$ respectively. $10\text{Co}1\text{Zn}/\text{ZrO}_2$ showed a further decrease of surface area to $35.0 \text{ m}^2/\text{g}$, possibly due to a strong interaction between the ZnO and the ZrO_2 .

Fig. 1 shows the XRD of the supported cobalt catalysts. Over $10\text{Co}/\text{ZrO}_2$ (Fig. 1a), and $10\text{Co}1\text{Zn}/\text{ZrO}_2$ (Fig. 1b), strong peaks at 24.3, 28.3, 31.6, 34.4, 35.4, 41.0, 49.3, and 50.3, with minor peaks at 38.7, 45.0, 45.4, 54.2, 55.6, 57.4, 58.0, 60.2, 61.8, 62.9, 65.7, 71.3, and 75.3 corresponding to typical peaks of the tetragonal phase of ZrO_2 (JCDPDS PDF card 00-036-0420). In addition, one strong Co_3O_4 peak at 36.9 can be clearly resolved. Both $10\text{Co}/\text{ZrO}_2$ and $10\text{Co}1\text{Zn}/\text{ZrO}_2$ showed shifts in the 45.4 and 60.2 peaks, most likely due to overlap with the Co_3O_4 peaks at 44.8 and 59.2 respectively. These observation suggest the formation of Co_3O_4 species. Over Co/ZnO , the strong peaks at 31.8, 34.5, 36.3, 47.6, 56.6, 62.9, and 68.0, as well as minor peaks at 66.4, 69.1, 72.6, and 77.0, suggest the Wurtzite structure of the ZnO support (JCPDS PDF card 00-036-1451). Additional peaks at 31.2, 38.4, 44.8, 55.6, 59.2, and 65.2, along with the formation of a shoulder at 36.6 reveal the formation of Co_3O_4 species (JCPDS PDF card 00-042-1467). Co_3O_4 peak at 36.3 was used for $10\text{Co}/\text{ZrO}_2$ and $10\text{Co}1\text{Zn}/\text{ZrO}_2$ crystallite calculations, while Co_3O_4 peak at 44.8 was used for $10\text{Co}/\text{ZnO}$ to accommodate for peak overlaps. For the reduced samples (supporting information Fig. S1) the metallic cobalt peak at 44.2 was used to estimate the crystallite size of the cobalt particles. Peak deconvolution software was used to estimate the cobalt peak area due to the strong overlap with ZrO_2 .

TEM data, shown in Fig. 2, indicated that the particle size distribution for all catalysts was log-normal, also summarized in Table 1. Over $10\text{Co}/\text{ZrO}_2$, the average Co_3O_4 particle size was found

to be 18.2 nm. The addition of Zn (10Co1Zn/ZrO₂) did not significantly change the average particle size, 17.2 nm. It was observed that the addition of Zn did help to minimize the frequency of occurrence of larger particles (Fig. 2B). Over 10Co/ZnO, the average Co₃O₄ particle size was found to be 26.1 nm. While it is not typical to identify the average particle size as being larger with TEM than with XRD, there are two interpretations for the observation in this work. 1), the contrast between the Co₃O₄ and both ZrO₂ and ZnO is not very well pronounced, as they have similar diffraction patterns and atomic densities. Only the large particles are differentiated from the support material by TEM. 2), XRD provides information about the crystallite size, not directly the particle itself; the big particles observed by TEM could be secondary particle of aggregated smaller Co₃O₄ crystallites.

3.1.2 Effect of ZnO on H₂O Dissociation

To study the ability of the catalyst to dissociate H₂O, Raman spectroscopy of H₂O oxidation of Co⁰, pulsed H₂O oxidation with TPR, and H₂O-TPO were used. A summary of the results is shown in Table 2.

Operando Raman study of cobalt oxidation by H₂O

Raman spectra for the oxidation of Co over 10Co/ZrO₂ and 10Co1Zn/ZrO₂ are shown in Fig. 3 - A and -B. Fresh catalysts for both 10Co/ZrO₂ and 10Co1Zn/ZrO₂ showed features assigned to ZrO₂ support at 175/184, 325, 366, 468, 515, and 612 cm⁻¹ and cobalt oxide species at 485 and 674 cm⁻¹ [32, 33]. The strong ZrO₂ doublet at 184 and 175 cm⁻¹ is most likely masking the 195 cm⁻¹ peak of cobalt oxides. The ZrO₂ support, 10Co/ZrO₂, and 10Co1Zn/ZrO₂ all displayed Raman bands typical of monoclinic ZrO₂ in the fresh catalyst evidenced by the typical peaks at 175/184 cm⁻¹ and peaks at 325, 366, 468, 515, and 612 cm⁻¹ [23, 34]. This is contrast to the XRD pattern shown in Fig. 1, where the tetragonal ZrO₂ was observed. B-K Kim et al. found that

because the monoclinic ZrO_2 has much stronger Raman activity that Raman spectroscopy can provide a better metric for measuring the ratio of monoclinic/tetragonal ZrO_2 when the monoclinic fraction is small [34]. Additionally, from C. Li and M. Li's study of the phase transformations of ZrO_2 it appears that monoclinic ZrO_2 will form on the surface first, while the bulk of ZrO_2 remains in the tetragonal phase [23]. Based on this literature, Raman spectroscopy identifying monoclinic ZrO_2 on the surface and XRD identifying tetragonal ZrO_2 in the bulk is not surprising. Following reduction, the cobalt oxide features at 485 and 674 cm^{-1} were greatly diminished, however, they were not completely removed. This suggested that even following 2 h at 450 °C, some surface Co remained in the oxidation state, possibly due to strong interaction with the ZrO_2 support, consistent with our previous studies [16]. In addition, features ascribed to tetragonal ZrO_2 appeared, evidenced by the peaks at 147 and 249 cm^{-1} , the leading edge of the 325 cm^{-1} peak, and the shift up of the 612 cm^{-1} peak to 622 cm^{-1} [23, 34]. It has been observed that under reducing conditions the tetragonal phase of ZrO_2 can be stabilized despite the monoclinic phase typically being more stable [35]. Following water exposure at 30 °C, the cobalt oxide features at 485 and 674 cm^{-1} were observed to increase again, suggesting that oxidation is occurring. Looking closely at the cobalt oxide peak intensity at 674 cm^{-1} and the adjacent ZrO_2 peak intensity at 612 cm^{-1} , it was found that 10Co/ ZrO_2 had a ratio of 1.22 and 10Co1Zn/ ZrO_2 had a ratio of 1.02. This suggests that more oxidation occurred over 10Co/ ZrO_2 than over 10Co1Zn/ ZrO_2 . In addition, following H_2O exposure the features for tetragonal ZrO_2 again begin to diminish. The decrease of tetragonal ZrO_2 is most likely due to the reforming of monoclinic ZrO_2 , which has been observed to be enhanced in the presence of water [24, 36]. As temperature increases (Supporting Fig. S3 -A and -B), the cobalt oxide features continued to grow,

suggesting continued oxidation. Similarly, the features ascribed to tetragonal ZrO_2 continued to decrease while those features associated with monoclinic ZrO_2 increased.

Over $10\text{Co}/\text{ZnO}$, the features of cobalt oxide were observed on the fresh sample (Fig. 3-C). In addition to the peaks at 482 and 674 cm^{-1} , the peak at 190 cm^{-1} was also visible. It is of note that the cobalt oxide peaks were not as well defined over $10\text{Co}/\text{ZnO}$ as they were for either $10\text{Co}/\text{ZrO}_2$ or $10\text{Co}1\text{Zn}/\text{ZrO}_2$. This may be due to the strong interaction between ZnO and CoO and the possibility of a solid oxide solution of ZnO and CoO forming. Peaks assigned to ZnO were also observed at 95 , 316 , 430 , 519 , and a very broad peak at 1090 cm^{-1} [37, 38]. Following reduction, the cobalt oxide features were again diminished but not completely removed. Low temperature H_2O exposure at $50\text{ }^\circ\text{C}$ showed no change in the cobalt oxide features, suggesting that no additional oxidation occurred. With H_2O exposure at $150\text{ }^\circ\text{C}$ growth was observed in the cobalt oxide features, suggesting that oxidation had begun.

To summarize the data from Raman spectroscopy, all catalysts showed strong Raman peaks for cobalt oxide over the fresh sample. Following reduction, the intensity of the cobalt oxide peaks was greatly diminished but not eliminated. Following H_2O exposure at $30\text{ }^\circ\text{C}$, only $10\text{Co}/\text{ZrO}_2$ and $10\text{Co}1\text{Zn}/\text{ZrO}_2$ showed growth of the cobalt oxide features. Following H_2O exposure above $50\text{ }^\circ\text{C}$ $10\text{Co}/\text{ZnO}$ showed growth of the cobalt oxide features as well. Of the catalysts investigated, $10\text{Co}/\text{ZnO}$ appeared to have the lowest activity for H_2O dissociation leading to cobalt oxidation, again matching well with literature [39, 40]. The comparison of $10\text{Co}/\text{ZrO}_2$ and $10\text{Co}1\text{Zn}/\text{ZrO}_2$ was more challenging as both showed oxidation at the lowest temperature H_2O exposure investigated. Examining the ratio of the cobalt oxide peak intensity at 674 cm^{-1} and the adjacent ZrO_2 peak intensity at 612 cm^{-1} , it was found that $10\text{Co}/\text{ZrO}_2$ had a ratio of 1.22 and $10\text{Co}1\text{Zn}/\text{ZrO}_2$ had a ratio of 1.02 , suggesting that more oxidation occurred over $10\text{Co}/\text{ZrO}_2$.

Pulsed H₂O oxidation/H₂-TPR

In order to further confirm the results from Raman spectroscopy, pulsed H₂O oxidation was also used to quantify the activity of the catalysts for H₂O dissociation and oxidation. By pulsing H₂O over reduced catalysts at reaction temperature (450 °C) the uptake of H₂O and the production of H₂ can be tracked. Fig. 4-A shows the peak areas for H₂ ($m/z = 2$) produced during H₂O pulsing. 10Co/ZrO₂ and 10Co1Zn/ZrO₂ show very similar profiles with a lower initial peak followed by an increase to the highest peak area for the second pulse and peak areas gradually decreasing with subsequent pulses. 10Co/ZnO showed a slightly different profile with a high initial peak followed by rapid decrease of H₂ produced. From H₂O uptake, 12.2% of the Co⁰ on 10Co/ZrO₂ was oxidized and 11.9% of the Co⁰ on 10Co1Zn/ZrO₂ was oxidized, for 10Co/ZnO only 6.6% of the Co⁰ was calculated to be oxidized. Saturation, defined as peak areas being less than 10% different from the average final peak area, occurred after 11 pulses for 10Co/ZrO₂, 10 pulses for 10Co1Zn/ZrO₂, and only 4 pulses for 10Co/ZnO. To help confirm the extent of oxidation via pulsed H₂O oxidation, H₂-TPR was run following pulsed H₂O oxidation and a purge to remove excess H₂O (Fig. 4-B). TPR for 10Co/ZrO₂ showed two primary reduction peaks centered at 288 and 402 °C. 10Co/ZrO₂ also showed the highest fraction of high temperature reduction species. 10Co1Zn/ZrO₂ also showed 2 primary reduction peaks centered at 268 and 400 °C. 10Co/ZnO showed multiple reduction peaks over a wide temperature range. 10Co/ZnO also showed the highest fraction of low temperature reduction species. From these profiles it was calculated 16.7%, 9.4%, and 9.2% of the Co⁰ had been oxidized in 10Co/ZrO₂, 10Co1Zn/ZrO₂, and 10Co/ZnO respectively. It further confirms that 10Co/ZrO₂ was the most active catalyst for H₂O dissociation and oxidation, followed by 10Co1Zn/ZrO₂, and 10Co/ZnO had the lowest activity for H₂O dissociation and oxidation.

H₂O-TPO

Additionally, H₂O-TPO was also used to investigate the activity of the catalysts to dissociate H₂O and oxidize Co⁰. H₂O-TPO profiles of the H₂ (m/z = 2) signal from on line QMS are shown in Fig. 5. Both 10Co/ZrO₂ and 10Co1Zn/ZrO₂ show an initial oxidation peak at 47 °C. In addition, however, a broad shoulder extending up to 100 °C was observed on 10Co/ZrO₂, suggesting more oxidation at low temperatures. Although 10Co1Zn/ZrO₂ also showed a broad shoulder from 50-100 °C, the intensity is significantly smaller than that of Co/ZrO₂. Over 10Co/ZnO the initial oxidation peak temperature was at 51 °C. There was no shoulder on the initial oxidation peak. The onset of oxidation observed here matched well with those observed during Raman spectroscopy.

In summary, 10Co/ZrO₂ showed the highest extent and activity for oxidation of Co⁰ in the presence of H₂O while 10Co/ZnO showed the lowest. 10Co1Zn/ZrO₂ displayed an intermediate degree of H₂O dissociation and oxidation, as would be expected from coating some of the more active ZrO₂ surface with less active ZnO. These results also matched well with the following ESR selectivity to acetaldehyde and acetone, as dissociation of H₂O is critical to the conversion of acetaldehyde to acetone.

3.2 Effect of ZnO on Ethanol Steam Reforming

The ESR activity of the catalysts are shown in Fig. 6. The 10Co/ZrO₂ catalyst showed a 12.2% C₁ product yield and 13.5% H₂ yield at a total ethanol conversion of 41.6%. The gas products were predominantly C₁ products with CO₂ being the most abundant at 19.3% selectivity, followed by CO and CH₄ at 5.3% and 1.5% selectivity respectively. A small amount of ethylene was observed with selectivity of 2.7%, ethane was also detected, however, the selectivity was <0.5% and was not considered significant. The majority of products produced were collected in

the liquid phase. Acetaldehyde showed a selectivity of 27.4% while acetone had a selectivity of 39.4%. Ethyl acetate and acetic acid were also observed in the liquid products with 0.9% and 3.3% selectivity respectively. Acetone, acetaldehyde, ethyl acetate, and acetic acid have all been reported previously intermediates of the ESR reaction pathway [17, 26, 41, 42]. Additionally, the requirement of water for conversion of ethanol to acetone via acetaldehyde has also been reported [43-45]. The high selectivity of acetone, especially being higher than the selectivity to acetaldehyde suggests that the conversion of acetaldehyde to acetone is very facile over the $10\text{Co}/\text{ZrO}_2$.

The addition of a small amount of ZnO, $10\text{Co}1\text{Zn}/\text{ZrO}_2$, increased the C_1 product yield to 12.7%, H_2 yield to 15.3%, and overall ethanol conversion to 51.1%. The selectivity to gas products, however, decreased. CO_2 , CO, and CH_4 selectivity all decreased to 17.5%, 3.9%, and 1.2% respectively. Ethylene selectivity also decreased to 1.4%, ethane selectivity remained $<0.5\%$. While the gas product distributions remained relatively similar, the liquid product selectivity changed significantly. The selectivity to acetaldehyde increased to 36.9% while the selectivity to acetone decreased to 33.2%, ethyl acetate selectivity remained at 0.9% and acetic acid selectivity increased slightly to 4.5%. The large shift in acetaldehyde selectivity can be attributed to a combination of effects. First is that the dehydrogenation reaction converting ethanol to acetaldehyde is more active over basic catalysts than over acidic catalysts, ZnO has higher basicity than ZrO_2 [46]. Second, that the conversion of acetaldehyde to acetone requires H_2O dissociation [17, 44], which is suppressed by the addition ZnO on the ZrO_2 support as evidenced by the afore mentioned Raman, H_2O uptake, and H_2O -TPO data. A decrease in H_2O dissociation is further supported by the increase in CO selectivity. The water-gas shift (WGS) reaction is cited as operating in parallel with, or as part of, the ESR reaction mechanism, the WGS reaction

is also cited as being more dependent on H_2O and H_2O dissociation than it is on CO adsorption [15, 26, 39, 40, 47].

Over $10\text{Co}/\text{ZnO}$ the residence time was doubled to keep conversion similar to $10\text{Co}/\text{ZrO}_2$ and $10\text{Co}1\text{Zn}/\text{ZrO}_2$, the C_1 product yield was found to be 12.9% with a H_2 yield of 15.5% and an overall ethanol conversion of 52.0%. The CO_2 selectivity was close to that over $10\text{Co}1\text{Zn}/\text{ZrO}_2$ at 17.7%, while the CO and CH_4 selectivity increased to 6.8% and 2.1% respectively. Ethylene selectivity was 2.3% and ethane selectivity remained $<0.5\%$. The selectivity to acetaldehyde continued to increase to 54.7% and acetone selectivity dropped to only 5.1%, ethyl acetate selectivity increased slightly to 1.2% and acetic acid selectivity increased significantly to 10.0%. The low activity on Co/ZnO can be, in part, explained by the difference in surface area shown in section 3.1. Notably, the further shift in acetaldehyde and particularly acetone selectivity indicate the importance of H_2O dissociation. $10\text{Co}/\text{ZnO}$ has more than sufficient basic sites for conversion of ethanol to acetaldehyde, however, it is not able to convert the acetaldehyde to acetone effectively. This is also evidenced by the CO selectivity being the highest among the catalysts.

From the ESR activity testing, it does appear that the ability of the catalyst to dissociate and activate H_2O could be ranked as $10\text{Co}/\text{ZrO}_2 > 10\text{Co}1\text{Zn}/\text{ZrO}_2 > 10\text{Co}/\text{ZnO}$ as evidenced by both the CO_2/CO ratio and the acetone/acetaldehyde ratios. H_2O dissociation and Co oxidation in presence of H_2O were more directly tested to confirm this hypothesis and are outlined in Section 3.1.2.

4. Conclusion

The effects of ZnO and thus H₂O dissociation were investigated on 10Co/ZrO₂ for the steam reforming of ethanol. The data suggests that ZnO decreased the ability of 10Co/ZrO₂ to dissociate water. This was directly reflected in Raman spectroscopy of catalysts during H₂O exposure, pulsed H₂O oxidation coupled with H₂-TPR, and H₂O-TPO where cobalt oxidation was consistently more facile over 10Co/ZrO₂ than over 10Co1Zn/ZrO₂. This also matched well when comparing to 10Co/ZnO, which showed the least facile and lowest degree of oxidation. The dissociation of H₂O was also reflected in ESR product distribution, shifting the most favored product from acetone over 10Co/ZrO₂ to acetaldehyde over 10Co/ZnO. Based on this and prior work it appears that the dissociation of H₂O on the catalyst surface can be tuned by adding a promoting material, in this case ZnO, to adjust the product distribution and the oxidation stability of cobalt. With a higher degree of H₂O dissociation, the catalyst will favor acetone formation from acetaldehyde, which can lead to more complete steam reforming; however, the oxidation of cobalt is also more facile, leading to a decrease in the C-C cleavage. With lower degree of H₂O dissociation, the catalyst will favor acetaldehyde formation and acetaldehyde steam reforming, which can limit the extent of steam reforming; the oxidation of cobalt is also less facile, helping to increase C-C cleavage.

Acknowledgements

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The Effect of ZnO Addition on H₂O Activation over Co/ZrO₂ Catalysts

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Table 2 Comparison of H₂O dissociation over different supports

Table 1: Physical properties of catalyst

Sample	BET Surface Area [m ² /g]	Oxide Crystallite Size ^a [nm]	Oxide Particle Size ^b [nm]	Metal Crystallite Size ^a [nm]
ZrO ₂	51	-	-	
ZnO	13	-	-	
10Co/ZrO ₂	41	18	18	8
10Co1Zn/ZrO ₂	35	14	18	8
10Co/ZnO	9	19	26	15

^a Calculated from XRD using Scherrer equation^b Estimated from TEM using log-normal distribution

Table 2 Comparison of H₂O dissociation over different supports

Sample	Raman Spectra	H ₂ O Pulse Oxidation		H ₂ O-TPO
	Ox. Onset [°C]	H ₂ O-Pulse ^a [% Ox.]	H ₂ -TPR ^b [% Ox.]	Ox. Peak [°C]
10Co/ZrO ₂	30	12.8	16.7	49
10Co1Zn/ZrO ₂	30	12.1	9.4	49
10Co/ZnO	50	6.4	9.2	51

^a Calculated from H₂O uptake from m/z = 18

^b Calculated from calibrated TCD signal

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Fig. 1. XRD patterns for (a) 10Co/ZrO₂; (b) 10Co1Zn/ZrO₂; (c) 10Co/ZnO. Peak icons: α = Co₃O₄; γ = ZrO₂; ζ = ZnO.

Fig. 2 TEM images and particle size distributions from TEM images for A) 10Co/ZrO₂; B) 10Co1Zn/ZrO₂; C) 10Co/ZnO. For each analysis, at least 100 particles were measured. Yellow circles were added to help identify Co particles.

Fig. 3 Plot A – 10Co/ZrO₂; Plot B – 10Co1Zn/ZrO₂; Plot C – 10Co/ZnO. Raman spectra for: α – fresh catalyst; β – reduced catalyst; χ – H₂O exposure at 30 °C; δ – H₂O exposure at 50 °C; ϵ – H₂O exposure at 150 °C; ϕ – H₂O exposure at 250 °C; κ – H₂O exposure at 350 °C. Cobalt oxide peaks highlighted by dashed line.

Fig. 4. Plot A – H₂ (m/z = 2) peak areas during H₂O pulsed oxidation; Plot B – TPR profiles following H₂O pulsed oxidation. α – 10Co/ZrO₂, reduction peaks marked by dash line; β – 10Co1ZnO/ZrO₂, reduction peaks marked by dash-dot line; χ – 10Co/ZnO, reduction peaks marked by dot line.

Fig. 5 QMS $m/z = 2$ signal for H₂O-TPO A – 10Co/ZrO₂; B – 10Co1Zn/ZrO₂; C – 10Co/ZnO

Fig. 6. ESR at 450 °C, H₂O:EtOH = 10:1 molar, $P_{\text{EtOH}} = 7.4$ kPa, WHSV was varied from 9.3 $\text{g}_{\text{EtOH}} \cdot \text{g}_{\text{Catalyst}}^{-1} \cdot \text{h}^{-1}$ to 18.5 $\text{g}_{\text{EtOH}} \cdot \text{g}_{\text{Catalyst}}^{-1} \cdot \text{h}^{-1}$ to control the total ethanol between 40%-50%. Other products is the cumulative selectivity of ethylene, ethane, ethyl acetate, and acetic acid.

Figure 1

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Figure 2-A

Figure 2-B

Figure 2-C

Fig. 2 TEM images and particle size distributions from TEM images for A) 10Co/ZrO₂; B) 10Co1Zn/ZrO₂; C) 10Co/ZnO. For each analysis, at least 100 particles were measured. Yellow circles were added to help identify Co particles.

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Figure 3-B

Figure 3-C

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Figure 4-A

Figure 4-B

Fig. 4. Plot A – H_2 ($m/z = 2$) peak areas during H_2O pulsed oxidation; Plot B – TPR profiles following H_2O pulsed oxidation. α – $10\text{Co}/\text{ZrO}_2$, reduction peaks marked by dash line; β – $10\text{Co}1\text{ZnO}/\text{ZrO}_2$, reduction peaks marked by dash-dot line; χ – $10\text{Co}/\text{ZnO}$, reduction peaks marked by dot line.

Figure 5

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Figure 6

Fig. 6. ESR at 450 °C, H₂O:EtOH = 10:1 molar, P_{EtOH} = 7.4 kPa, WHSV was varied from 9.3 g_{EtOH}·g_{Catalyst}⁻¹·h⁻¹ to 18.5 g_{EtOH}·g_{Catalyst}⁻¹·h⁻¹ to control the total ethanol between 40%-50%. Other products is the cumulative selectivity of ethylene, ethane, ethyl acetate, and acetic acid.

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Graphical Abstract