Characterization of cobalt and cerium coordination environments for catalytic steam reforming of bio-derived liquids

DISSERTATION

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By

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Abstract

The demand for energy is projected to increase by 50% within the next 20 years. Currently 80% of the world’s energy is supplied by non-renewable fossil fuels. Due to the increasing effect of the greenhouse gases, carbon tax, which is a form of taxation levied on the fixed carbon content of the fuels is becoming a reality. These factors bring the need for renewable energy carriers with minimal carbon footprint. Hydrogen is a promising candidate for a viable and clean energy carrier with its high gravimetric energy density and as a potential for fuel cell applications. Fuel cells would increase energy efficiency by bypassing the thermodynamical constraints of the internal combustion engine. Moreover, refineries use considerable amounts of hydrogen for internal treatment which is supplied by steam methane reforming. Steam reforming of a bio-renewable source such as ethanol or acetaldehyde would allow for a closed carbon loop due to the sequestration of the carbon dioxide during plant growth via photosynthesis.

Traditional steam reforming catalysts are generally expensive due to their use of noble metals such as Rh. As opposed to the noble metals, cobalt is more economically feasible and ceria supported cobalt-based catalysts are promising candidates for steam reforming reactions. Previous work done in the Ozkan
research group with Co/CeO$_2$ catalysts has investigated effects such as surface-oxygen mobility, nature of the cobalt precursor and increasing the intimate contact between the support and the active metal. However, the nature of the active sites for the steam reforming reaction is still a topic of debate.

In this study the cobalt and ceria active sites were investigated under actual steam reforming conditions. These *in-situ* studies along with more conventional characterization methods enabled us to shed light into the active sites of the steam reforming reaction, namely Co$^{2+}$, Co$^0$, Ce$^{3+}$ and Ce$^{4+}$.

In the first chapter the background and literature survey on the subject is summarized followed by an overview of the reaction system. Chapter three focuses on comparing the effect of pretreatment of the catalysts and shows metallic Co sites to be more active. Moreover, Co sites were found to reduce under steam reforming conditions. After this milestone is established, chapter four delves into the effect of support morphologies and investigates the effect of different crystal planes on steam reforming which ultimately ties in with the reducibility of the cobalt species. Chapter five introduces the effect of particle size and shows how the surface chemistry is affected by synthesizing nano-scale particles.

According to the results acquired in this research, oxidized Co surfaces were found to catalyze ethanol dehydration reaction which produces acetaldehyde. An alternative pathway for acidic surfaces was found to produce ethylene via ethanol dehydration reaction, whereas, easily reducible surfaces
were found to be more active for hydrogen production. Tailoring the catalyst surface and controlling the extent of reduction were found to be essential in determining steam reforming activity.
Dedication

For Neslihan and all the other nut heads in my family who thought going to the other side of the world was probably a good idea. It was!
Acknowledgments

I am grateful to Prof. Umit S. Ozkan for her relentless pursuit in making my work and me better in every sense of the word. She was a much kinder Wolf Larsen (Jack London, Sea Wolf) to me who taught what it takes to stand on your own feet and follow your work through to the end. Be it a paper, a presentation or an experiment.

I appreciate Burcu Bayram for showing me the ropes and her great advice on literally any subject ranging from IR analysis to what kind butter you should buy on this continent. Dieter von Deak for smashing every stereotype about Americans within a week as well as being a great researcher and a great experimentalist. Hammers and wrenches made this work possible. Hyuntae Sohn for being everything a senior researcher can ask for and more. I would never allow anyone else to change my GC desktop colors to a disgusting red and yellow but this guy, he earned it. Deepika, Anshuman and Preshit for being such great people to work with and I gratefully acknowledge the rest of the HCRG as well.

Neslihan for putting up with ridiculous phrases like “I am going to US for five years” and “the ring has to be able to fit in a nitrile glove” as well as being the E=\hbar\nu of my life.
Vita

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**2006 – 2008**: Full scholarship for MS study awarded from The Scientific and Technological Research Council of Turkey
Publications


Fields of Study

Major Field: Chemical Engineering
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Chapter 1: Introduction

The developments in science and technology facilitate an ever increasing demand on the energy. Table 1 shows the energy consumption averages on the last two decades and despite the breakthroughs in renewable sources, fossil fuels are still used for more than 80% of the global consumption [1].

**Table 1.** Global energy consumption in 1000 TWh

<table>
<thead>
<tr>
<th>Year</th>
<th>Fossil</th>
<th>Nuclear</th>
<th>Renewable</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>83.37</td>
<td>6.1</td>
<td>13.1</td>
<td>102.6</td>
</tr>
<tr>
<td>2000</td>
<td>94.49</td>
<td>7.9</td>
<td>15.3</td>
<td>117.7</td>
</tr>
<tr>
<td>2008</td>
<td>117.8</td>
<td>8.3</td>
<td>18.5</td>
<td>144.6</td>
</tr>
<tr>
<td>Change in 2000-2008</td>
<td>22.6</td>
<td>0.4</td>
<td>3.2</td>
<td>26.2</td>
</tr>
<tr>
<td>% Growth in 2000-2008</td>
<td>23.9</td>
<td>5.1</td>
<td>20.9</td>
<td>22.3</td>
</tr>
</tbody>
</table>

Despite the 22% increase in total energy consumption, more than 1.3 billion of the world population does not have access to electricity. This indicates that energy consumption is very likely to increase with an increasing rate in the next few decades [2, 3]. Renewable sources have shown significant growth while still being behind fossil fuels. Nuclear power has not seen much growth. It should be noted that the incident in the Fukushima Daiichi nuclear power plant in 2011
may have an additional negative effect on the utilization of nuclear energy. Therefore it falls mostly on the renewable resources to supply the world’s energy due to the depletion of fossil sources. Moreover, fossil fuels tend to produce greenhouse gases in the form of CO\textsubscript{2}, CH\textsubscript{4} and NO\textsubscript{x} along with significant loss of efficiency with the internal combustion engine.

Increasing impact of the greenhouse gases on the atmosphere bring the need for renewable energy carriers with minimal carbon footprint. Carbon tax, which is a form of taxation levied on the carbon content of the fuels was widely discussed for over two decades [4] and is becoming a reality with the recent implementation of new regulations adopted by the European airports [5]. Hydrogen is a promising candidate for a viable and clean energy carrier with its high gravimetric energy density and as a potential fuel for fuel cell applications, which may increase the fuel efficiency by bypassing the thermodynamical constraints of an internal combustion engine. However, the limitations of the current energy infrastructure require the need of an intermediate molecule which is more easily transportable. Transfer of liquids such as ethanol, butanol, acetaldehyde and dimethylether are economically feasible and on site or on board fuel reformers can supply hydrogen to the fuel cells where it can be converted to electricity and water. Provided that the feedstock for the bio-derivable liquids is cellulosic, the reforming step would operate with virtually no carbon footprint since the released CO\textsubscript{2} will be sequestered via photosynthesis.
during plant growth. Figure 1 shows the increase in ethanol production over the last decade.

![Figure 1: Production of ethanol in the world during the last decade, REN21, Renewables 2012 Global Status Report, 2012](image)

1.1 Steam Reforming Reaction

Steam reforming reaction, \[ C_nH_{2n+2}O + (2n-1) H_2O \rightarrow n CO_2 + (4n-1) H_2 \] is an endothermic reaction and plays a major role among catalytic hydrogen production strategies. 95% of the hydrogen is produced via steam reforming in United States [2]. Globally, over 50% of hydrogen production relies on natural gas reforming [6]. Bio-derived liquids are promising renewable alternatives for replacing natural gas and other fossil fuels. Traditional steam reforming catalysts are noble metal based. The work of Aupretre et al. [7] compares the catalytic
activities of Rh, Cu, Ni, Pt, Zn, Fe for steam reforming of ethanol and finds Rh-based catalysts superior in terms of hydrogen yield and CO\textsubscript{2} selectivity. Studies done over cobalt-based catalysts supported on calcium doped ceria lattices show promising ethanol conversions and hydrogen yields at temperatures as low as 400 °C [8]. The effect of support modification is of particular importance which shows that the surface species play a major role in steam reforming and under favorable surface conditions a non-noble metal based catalyst may become competitive. Therefore, it is necessary to investigate the evolution of surface species under steam reforming conditions to effectively tailor the sample to maximize the hydrogen yield and CO\textsubscript{2} selectivity. Recent years saw a rise in the number of publications on ethanol steam reforming with particular interest in noble metals like Rh, Ru, Re, Pd, Ir and Pt and more economical non-noble metals such as Ni, Cu and Co [7, 9-12]. Noble-metal catalysts have shown promising results in steam reforming activity with close to 90\% H\textsubscript{2} activities at the 500-600 °C under high gas-hourly space velocities (>10000 h\textsuperscript{-1}) [13-15]. However, the cost of these metals limits their use along with the availability and price fluctuations, which also affect their economical feasibility. For example, the prices of the rhodium metal bullion increased from $1000/ounce in 2003 to as much as $10000/ounce in 2008 just prior to the global recession after which it dropped by an order of magnitude due to the extensive use of Rh in automobile catalytic converters. However the prices are on the rise again in the recent years as can be seen in Figure 2. As an economically feasible alternative, cobalt
($2.5/ounce) catalysts supported on metal-oxide supports such as, zirconia, magnesia and ceria have been found to have high C-C bond cleavage activity and hydrogen yields for the steam reforming reaction in the temperature range of 300-500 °C [16, 17].

Figure 2 The price fluctuations of Rh metal bouillon between years 2000-2011, prices are based on London Stock Exchange

Previous research within the research group has focused on investigating the effect of a number different catalyst preparation methods and parameters. It was shown that strong metal-support interaction and high metal-support interface area were important factors that influence catalyst activity as well as stability [8, 17-21]. The impregnation medium used for introducing the active metal onto the support [20] and the nature of cobalt precursor [18] were 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 [21]. 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 [19], [17, 22]. Effect of oxygen mobility and OSC (Oxygen Storage Capacity) was investigated with other reactions such as CO oxidation, water gas shift and methane steam reforming in the literature [23-25]. In Song’s 2009 paper [19], which was a milestone for the project, it is explained how the labile oxygen of cerium oxide was able to provide the necessary oxygen to the surface carbon species oxidizing/gasifying carbon as soon as it forms on the surface, thereby preventing coking and enabling complete steam reforming even at higher space velocities. Also the ceria lattice was found to be stable in the 350-500 °C range which is the reaction temperature for ESR.
Creation of oxygen vacancies through the introduction of a di-valent cation, such as Ca, into the ceria matrix resulted in further improvements in the hydrogen yields, turnover frequencies and lower liquid byproducts [8].

Formation of oxygen vacancies increases ESR activity, this has been observed experimentally [26-28]. Wang and Feng's proposed model [29] shows the surface density of atoms in ceria to be (111)>(100)>(110) and the energy of formation of oxygen vacancies also follow the same order. Thus, (110) surfaces have more oxygen vacancies. At first it may look like the (100) plane should have the higher density but this is not the case since for CeO$_2$, the (100) polar plane is composed of positively and negatively charged O layers. This structure is not stable at higher temperatures and relaxes into a low energy surface [30]. CeO$_2$ surfaces with higher (110) planes were expected to give higher hydrogen yields. There are two reasons for this behavior, the first one is explained above where the oxygen vacancies increase the oxygen mobility. The second one is a question of Co dispersion. Thereby, tailoring the planes and the support morphology is expected to have a significant effect on the catalyst performance.

Effect of different crystal morphologies on catalytic performance has been reported previously for bulk oxides [31-34] as well as for supports. Different morphologies of ceria were used for a variety of reactions, such as water-gas shift [35, 36], NO oxidation [37], methanol steam reforming [26, 28] and CO oxidation [38-40] as well as ethanol steam reforming with Rh as the active metal [41]. Godinho et al. [42] reported Ga doped ceria nanorods to be significantly
superior when compared to Ga doped on commercial ceria samples for ESR. There have also been several molecular simulation studies reporting on the varying catalytic characteristics of different crystal planes of ceria [43-47].

Work of Flytzani-Stephanopoulos and co-workers is of particular interest [26, 28, 36, 38, 48] where the crystal planes of ceria nano-rods, cubes and polyhedra were controlled and tailored for high gold dispersion and catalytic activity. It is reported that (110) and (100) ceria planes allow for higher Au dispersion due to the lower stability of these crystal planes, whereas the most stable (111) plane allows for minimal anion vacancies, thereby limiting oxygen mobility on the surface, which is line with the discussed model. These finds were in line with the theoretical work on the subject. Zhou et al., working on a similar problem, reported increasing oxygen vacancies in the ceria lattice with decreasing particle size [49] with two orders of magnitude difference between 4 nm and 60 nm particles.

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 Hymann and Vohs [50] 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$_3$O$_4$ and metal oxide-supported cobalt catalysts was reported by Llorca et al. [51, 52]. Over both types of catalysts, the authors observed the co-existence of an equilibrium state between reduced and oxidized phases of cobalt under reaction conditions. In a more recent study, Lin et al. [53] 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 co-existence of Co$^0$ and CoO phases during ethanol steam reforming have been reported through in situ X-ray diffraction (XRD) studies on unsupported Co$_3$O$_4$ [54]. Batista et al. [55] 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 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. Recent work of Hyman & Vohs [50] as well as Martono & Vohs [56] showed the activity of metallic cobalt foils for ethanol decarbonylation into CO, H$_2$, CH$_3$ whereas oxygenated Co species promoted dehydrogenation of ethoxides into acetaldehyde.

Hydrogen can be produced from ethanol through direct steam reforming reaction.

$$C_2H_5OH + 3 H_2O \rightarrow 6H_2 + 2 CO_2 \ (\Delta H_f = 348 \frac{kJ}{mol} \ at \ 25 ^\circ C)$$
The overall reaction is endothermic and would require energy input. The product distribution is governed by a very complex reaction network with many by-products. [17]. Some of the most common reactions are summarized below.

\[ C_2H_5OH \rightarrow CH_4 + H_2 + CO \text{ (decomposition of ethanol)} \]
\[ C_2H_5OH \rightarrow CH_3CHO + H_2 \text{ (dehydrogenation)} \]
\[ C_2H_5OH \rightarrow C_2H_4 + H_2O \text{ (dehydration)} \]
\[ C_2H_5OH + H_2O \rightarrow 2CO + 4H_2 \text{ (incomplete reforming)} \]
\[ 2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \text{ (dehydration synthesis/coupling)} \]
\[ CO + 3H_2 \rightarrow CH_4 + H_2O \text{ (methanation)} \]
\[ CH_4 + 2H_2O \rightarrow 4H_2 + CO_2 \text{ (methane steam reforming)} \]
\[ CO + 3H_2O \leftrightarrow H_2 + CO_2 \text{ (regular/reverse water-gas shift)} \]
\[ 2CO \rightarrow C + CO_2 \text{ (Boudouard reaction/coking)} \]

The reaction pathway starts with adsorption of water and ethanol. Figure 3 shows diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with a controlled environmental cell for 10% Co/CeO\(_2\) sample. Ceria particle size was 5 \(\mu\)meter, cobalt particles were around 60-100 nm. This sample is used mainly as a standard for comparison. The catalyst was pretreated under He at 400 °C for 30 minutes to clean out the catalyst surface followed by reduction by 5% H\(_2\)/He for 2 hours at the same temperature. Finally the temperature was raised to 450 °C and the surface was flushed with He again to remove water that may have
been formed during the reduction step. This is the typical reduction pretreatment method used throughout the work. 2.4cc water vapor was fed with 27.6cc He as carrier gas continuously to investigate adsorption of water vapor on the sample surface. Prior to spectra collection, IR backgrounds were collected and subtracted from the sample spectra.

**Figure 3.** In-situ water adsorption over 10% Co/CeO$_2$ sample

The broad band in the 3600-3200 cm$^{-1}$ region corresponds to OH groups and indicate dissociative desorption of water. The peak at 1687 cm$^{-1}$ is characteristic for molecularly adsorbed water [57]. The 2354 and 2323 cm$^{-1}$ are the CO$_2$ peaks and they evolve from surface carbonates which start
decomposing at higher temperatures. Carbonates persist on a sample even after the pretreatment. Figure 4 shows a complete steam reforming run for the same catalyst with water and ethanol in the feed stream [58]. The peak identification is as follows: $\nu_{as}(\text{CH}_3)$ at 2964 cm$^{-1}$, $\nu_s(\text{CH}_3)$ at 2931 cm$^{-1}$, $\nu$(CO) at 1049 cm$^{-1}$ and $\nu$(COO) at 844 cm$^{-1}$ modes of surface ethoxy species. Formation of ethoxy species is indicative of associative adsorption of ethanol onto the catalyst, yielding surface ethoxy and hydroxy species [24, 59-63]

**Figure 4.** In-situ DRIFTS spectra collected as a function of temperature during ethanol steam reforming over Co/CeO$_2$
Figure 5 shows an advanced reaction scheme which encompasses the reaction steps [64]. Water adsorbs dissociatively (scheme 1) and forming OH groups primarily on the ceria support. Molecularly adsorbed water is also observed, but desorbs readily at higher temperatures. Ethanol can adsorb on the Co species dissociatively (scheme 2) or molecularly (scheme 3), where adsorbed ethanol molecules can undergo decomposition into H₂, CO and CH₄ or they can also undergo dehydration and become ethylene (scheme 6). The ethoxide species coming from dissociated ethanol is the main reactionary pathway for ESR for our samples where the ethoxide species can get oxidized by the cobalt-support interface by losing another hydrogen atom into acetaldehyde. Acetaldehyde can desorb to the gas phase, decompose to CH₄ and CO or further oxidize to form acetic acid and surface acetate species. The formation of acetone might be derived from the aldol condensation of acetaldehyde, followed by a dehydrogenation and decarboxylation [64, 65]. The research group of Vohs reports acetaldehyde decarbonylation with oxidized surfaces and at low temperatures [50, 56]. The surface acetate species may follow multiple routes once they are formed. It is presumed that Cobalt plays a major role in the C-C bond cleavage and acetate species may break down to CH₄ and CO₂ which would desorb (scheme 7) or they may form formate and/or carbonate species. At this point it is worthwhile to note that both of the aforementioned groups are detected in the 1650-1400 cm⁻¹ region with the DRIFTS method and are difficult to differentiate. Formate species are assumed to break down to carbonates.
Figure 5. Possible steps for ethanol and reaction intermediates in ethanol steam reforming over supported catalysts. (This Figure is published in H. Song, X. Bao, C.M. Hadad, U.S. Ozkan, Catal. Lett. 141 (2011) 43-54, printed with the permission of the corresponding author)

which in turn becomes adsorbed CO₂ and desorbs from the surface. There are some points which are in question, e.g. acetate species may accumulate on the catalyst and lead to coking as seen in the work of Virginie et al. and de Lima et al.[66-68]. Moreover, certain ceria morphologies like the Co/CeO₂-nanorods where the cobalt dispersion is low but the surface area of the ceria is high would be highly resistant to coking but would not have enough Co active sites on the
sample to facilitate scheme 4 in Figure 5. Ethylene is encountered in the product stream on such samples and it does not necessarily lead to coking as depicted in Scheme 6. Nevertheless, Figure 5 summarizes the proposed reaction scheme.

Based on the results in the literature [69-71] and previous research within the group [72] a highly acidic surface such as Al₂O₃ and SiO₂ were found to promote ethanol dehydration which allows for high catalyst coking. Whereas a basic surface like CeO₂ would allow for ethanol dehydrogenation which would lead to acetaldehyde. Acetaldehyde is an important intermediate which paves the way for the final products CO₂ and H₂.
Chapter 2: Steam Reforming Reaction System

The steam reforming reaction system was a modified version of the system explained in [17]. It is used for ethanol, acetaldehyde, ethylene, ethane and dimethyl ether steam reforming at various stages of the project. Gases could be sent to the reactor at desired flow rates controlled by 8 Brooks Mass flow controllers. Liquid feeds were fed to the system via a Cole-Palmer pulse free syringe pump. Various syringes were used to prepare the reactant solutions. Syringes with 60 ml capacity were used for more concentrated reactant feeds and for longer experiments such as stability tests. Smaller syringes were used to have more precision in the reactant concentration but had a shorter lifetime. The liquid feed is fed into a 250 ml stainless steel evaporator kept at 230 °C s to evaporate all of the liquid mixture. The generated vapors are then carried with He and fed into the reactors. The gas lines were wrapped around with heating tape and insulation to keep the line temperature around 130 °C and prevent condensation of the liquids. The upstream region was labeled “A” and was controlled by a single Variac for heating purposes whereas the downstream sections were grouped under “B” and “C” regions with their own Variacs. This grouping enabled compartmentalization of the heating tapes and allowed for easier tracking when part of an electrical system failed due to constant heating.
during experiments. Thermocouples were distributed among the lines to ensure proper monitoring of temperature and were monitored via the Labview software. In order to monitor system temperature and pressure and automatic shutdown procedure, Labview software is installed and programmed for communication between the instruments and the computer terminals. NI SCC-TC02, SCC-SG24 and SCC-DO01 were boxes into the SC-2345 signal conditioning the connector block. These modules were chosen for monitoring pressure and pressure as well as controlling 8 solenoid valves which were installed right after the mass flow controllers to ascertain software control over the reaction feed. The NI PCI-6220 board was used for data transfer with a dedicated computer. It should be noted that the priority settings of the NI and SCC modules play a major role for the proper operation of the system. The solenoid valves are two-way automated valves which can stop the reactant flow depending on the pressure. Ethanol steam reforming reactions may lead to coking especially on acidic surfaces[69], which causes significant pressure drop. The pressure transducer located on the reactor upstream would alert the software and the program would stop the flow when the pressure reaches 10 psi in the lines. It should be noted that this feature has no control on the liquid feed and may result in flooding the lines with excess reactant. The evaporator may need to be emptied manually to remove excess liquid.

An online Shimadzu 2010 gas chromatograph carries out the analysis of the reaction products. Two different detectors are used with separate sample
injection valves and lines. The first line consists of heated lines, a 6-port valve with 250-microliter sample loop, a Q-bond column and a flame ionization detector (FID) for detection of hydrocarbon and liquid species. The reactant flow then enters a condenser and liquid species such as acetaldehyde, ethanol and water were removed from the product stream which is sent through a carboxen column to a pulsed discharge helium ionization detector (PDHID) to detect H₂, CO and CO₂ species. Figure 6 shows the flowchart of the reaction system and Figure 7 shows the Labview user interface.

The steam reforming system also has an ethanol and a water bubbler which enable an alternative method for feeding the reactants. Antoine vapor pressure calculations are used when calculating the flow rates of the carrier streams. The bubblers have some difficulties which limit their use significantly. It is assumed that the gas phase of the bubblers are always saturated which is an incorrect assumption, especially at high carrier flow rates the gas phases are far from equilibrium. This behavior increases the time the system takes to get into steady state. It is vitally important to work under steady feed conditions for correct calculation of the production and consumption rates, therefore evaporator, syringe pump assembly is the safer alternative. Keeping the evaporator at 230 °C which is far above the boiling points of water and ethanol enables the user to be on the safe side of the evaporation kinetics where all of the liquid feed is easily evaporated for flow rates up to 0.3 ml/hr.
The circulator chiller assembly from Techne® which cools down the condenser is also of particular importance for the system. The PDHID is very sensitive to water and it would show up as a major baseline shift around 10-15 minutes into the GC program depending on the temperature profile of the GC oven. This will damage the detector and affect CO₂ and ethylene responses. The condenser has to be kept around 0 °C at all times to prevent this from happening. This may be a challenge especially in the summer months when the room temperature is higher. Since ethylene glycol is a toxic substance, propylene glycol is preferred with the assembly. However, propylene glycol is viscous and between 50-70% dilution with distilled water was observed to give more cooling power. Care must be taken to make the circulator chiller assembly accessible in any configuration. If the chiller is set up upon a tray, this will also help significantly with the health and safety due to the coolant fluid which will inevitably spill during the maintenance cycle.
Figure 6 Steam reforming system flowchart
Figure 7 Steam reforming system user interface

The 6 port valves of the GC which control the shots are housed in a separate insulated oven which is controlled by one of the auxiliary heating ports built in the Shimadzu 2010. It is essential to keep the 6 port valves and their sample loops at the same temperature as the lines (130 °C) to prevent condensation in the loops themselves and also to regulate the amount of gas.
sent into the injector. The electronic board that is controlling these valves is called Aux4 on the GC and is not optimized for a high heating duty. Therefore, this port is prone to fail and needs to be replaced every 2-5 years. Sample calculations for the steady state activity calculations and feed flow rates were given in Appendix B.
Chapter 3: Effect of catalyst pretreatment

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3.1 Introduction

The transformations and the state of the cobalt species during ethanol steam reforming were investigated. The catalyst was pretreated under an oxidizing or reducing atmosphere prior to characterization and activity testing to yield a Co$_3$O$_4$-rich or Co$^0$ rich surface, respectively. While Co$_3$O$_4$ was found to be inactive for ethanol steam reforming, gradual activation of the oxidation-pretreated catalyst with temperature through reduction of Co$_3$O$_4$ 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.

3.2 Experimental

3.2.1 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%) [20]. Prior to impregnation, the ceria support was calcined at 550 °C for 3 hours 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 hours under a flow of air.

3.2.2 Catalyst characterization

Surface area and pore volume measurements were done on a Micromeritics ASAP 2020 accelerated surface area and porosimetry 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 hours 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 performed using N\textsubscript{2}O chemisorption technique outlined earlier by Jensen et al.[73]. For these measurements, 200mg the sample 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\textsubscript{2} in He for 2 hours. The reactor was then flushed with He at the same temperature and cooled under helium. N\textsubscript{2}O chemisorption was performed by introducing a stream of 3%N\textsubscript{2}O/He to the reactor at 40°C. Species in the m/z=12 to m/z=46 range were monitored via an on-line mass spectrometer (MKS – Cirrus II). The mass spectrometer was calibrated for instrumental sensitivity factors and the contribution of m/z=28 fragment of N\textsubscript{2}O to the m/z=28 trace. Throughout the experiment, N\textsubscript{2}O and N\textsubscript{2} were the only species detected in the reactor effluent. For quantification of the N\textsubscript{2} formation, known volumes of N\textsubscript{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\textsubscript{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 (~1%).

The temperature-programmed reduction profiles (H\textsubscript{2}-TPR) of Co/CeO\textsubscript{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 minutes followed by cooling to room temperature in He. Then 5% H₂/He (30 cm²/min) was introduced to the reactor at room temperature and the mass signals were allowed to stabilize for at least 30 minutes before ramping the temperature at 10°C/min to 650°C.

The in-situ XRD patterns during ethanol steam reforming over Co/CeO₂ were collected on a Bruker D8 Advance X-ray diffractometer with monochromatic Cu Kα radiation (λ=1.5418 Å) through a tube operated at 40 kV and 50mA and equipped with an Anton Paar HTK1200 controlled atmosphere oven. Prior to the collection of in situ XRD patterns, 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 minutes and samples subjected to this pretreatment will be denoted as Co/CeO₂(O). The pre-reduction step consisted of heating the catalyst to 400 °C under a flow of He (30 ccm) for 30 minutes followed by reduction for 2 hours in 5% H₂/He (30 ccm) at the same temperature and purging with He (30 ccm) for 1 hour at 450°C. Samples subjected to this pretreatment will be denoted as Co/CeO₂(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 O₂ 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
12°C/min was used and the temperature was held constant at each temperature step for at least 30 minutes prior to the collection of the diffraction patterns. In order to investigate the progression of the reduction of cobalt oxide species, another experiment was conducted where, an oxidized catalyst was directly put under the abovementioned reaction stream at 500°C and in situ XRD patterns were collected as a function of time-on-stream. During these experiments the in situ XRD patterns were collected at 1 hour intervals for 12 hours. The identification of the crystalline phases through the collected diffraction patterns was done using the International Center for Diffraction Data (ICDD) database.

Controlled-atmosphere X-ray absorption fine structure (XAFS) data at the Co K-edge (7709 eV) were collected at the bending magnet beamline (5BM-D) of the Dow-Northwestern-DuPont Collaborative Access Team (DND-CAT) of the Advanced Photon Source, Argonne National Laboratories. The measurements were made in transmission mode with the Si(111) monochromator detuned by 30% to eliminate the higher order harmonics in the beam. The sample thickness was chosen to give an absorption edge jump of about 1.0 at the Co K-edge. The 10% Co/CeO₂ catalyst was mixed with SiO₂ at a ratio of 1:4 and finely ground (<150 mesh) to obtain a homogeneous mixture. Approximately 22 mg of the mixture was then pelletized in a 6 mm polished steel die and placed inside a 5 cm long quartz tube (6.5 mm ID) and supported with quartz wool plugs. The sample was then centered in a 45×2 cm controlled-atmosphere XAFS chamber that was fitted with Kapton® windows. The XAFS reactor set-up allowed
continuous flow of the reactants as well as the isolation of the catalyst sample. Although contact geometry of the catalyst with the gases in the XAS experiments does not simulate a true plug flow reactor (as described in a recent article[74]), this cell configuration has been used in many other studies reported in the literature [75, 76].

The catalyst in the controlled-atmosphere XAFS cell was pre-treated following either one of the pretreatment procedures outlined above. Ethanol steam reforming reaction mixture contained 0.3% of ethanol and 3% H₂O. The XAFS data on the pre-treated catalyst samples were collected following ethanol steam reforming at every 50°C in the 350-500°C region. At each temperature the catalyst was kept on-stream for 1 hour before flushing the cell with helium (100 ccm) for 15 minutes. The catalyst was cooled to room temperature under the helium atmosphere and sealed under the same atmosphere for data collection. The XAFS data were collected at room temperature under helium. Helium (UHP) was further purified by an O₂ trap (VICI Valco Instruments, HP2 heated helium purifier) installed upstream of the reaction chamber. Following data collection, the cell was heated to the next temperature under helium and the steam reforming feed was introduced. WinXAS data analysis software package was used for analysis of the collected XAFS data following standard procedures outlined in [77]. Phase shifts and backscattering amplitudes used for the analysis of the data were obtained from the experimental reference spectra collected on reference compounds; i.e. CoO and Co-foil. XANES reference spectra were obtained for
Co$_3$O$_4$, CoO and Co foil. The coordination parameters for Co-Co and Co-O-Co shells were obtained by isolation of the respective shells from the EXAFS spectrum using the difference method outlined earlier by Miller et al.[78]. The coordination numbers obtained through fitting the isolated shells are then divided by the fraction of that component obtained from XANES analysis for calculating the corrected coordination numbers. The large contribution from Co-Co shell did not allow isolation of the Co-O shell to obtain accurate coordination parameters.

Controlled-atmosphere X-ray photoelectron spectra of the Co/CeO$_2$ samples were collected in a Kratos AXIS Ultra X-ray photoelectron spectrometer, using monochromatized Al Kα (1486.7eV) X-ray source operated at 13kV and 10 mA. The surface chemical species of catalysts prepared as previously described were characterized before and after ethanol steam reforming reaction. The same reaction system as described in Section 2.3 for steady-state catalytic activity testing was used to treat the catalysts. After the reaction treatment had concluded, the system was flushed with ultra-pure helium for 15 min at rate of 30 ccm. The vertical plug flow reactor was sealed and removed from the reaction system. The catalyst sample was then cast into a pellet and transferred to the transfer arm of the spectrometer in a nitrogen atmosphere. The charge neutralizer was operated at a current of 2.0A and a filament bias of 1.3V. A complete survey spectrum, as well as spectra for the regions for O 1s, C 1s, Co 2p, and Ce 3d was collected for each catalyst sample. Collected data were corrected for charge shifting using standard C 1s binding energy of 284.5 eV.
XPS Peak 4.1 software package was used for curve fitting. Spectra baselines were determined using Shirley-type background fitting. Spectra were deconvoluted using Lorentzian-Gaussian combination peaks.

In-situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) experiments were performed using a Thermo NICOLET 6700 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a KBr beam splitter. The in situ cell consisted of a Smart Collector™ controlled-atmosphere chamber with ZnSe windows. Similar to the abovementioned XRD experiment, the catalyst was oxidized or reduced in situ following one the pretreatment procedures outlined above prior to introducing the steam reforming feed to the controlled-atmosphere chamber. Following the aforementioned treatment step, the temperature was raised to 500°C under helium flow and the background spectra were collected every 50°C, during cooling. At 25°C, another background spectrum was collected and the ethanol steam reforming feed with a water-to-ethanol molar ratio of 10:1 and 0.3% ethanol concentration was introduced to the DRIFTS chamber. The feed stream was obtained by flowing helium through two separate bubblers containing water and ethanol kept at room temperature. At each temperature, the reaction was allowed to progress for 30 minutes before collecting sample spectra while reactants are still flowing through the DRIFTS chamber. After the collection of the sample spectrum, the DRIFTS chamber was flushed with helium for 8 minutes and another sample spectrum was collected at the same temperature. Following the collection of this second
spectrum, the temperature was increased under the reaction feed and the procedure was repeated at 50°C intervals up to 500 °C. Any oxygen impurity in helium was removed by an O\textsubscript{2} trap (VICI VALCO Instruments, HP2 heated He purifier) prior to feeding the gas to the DRIFTS chamber.

3.2.3 Steady-state catalytic activity testing

The steady-state ethanol steam reforming activity data was collected in the 350-500°C range using a fixed bed flow reactor set-up using a 4mm ID quartz reactor with a quartz frit. For each run, a 100 mg batch of the Co/CeO\textsubscript{2} catalyst was packed inside the reactor. The reactor was placed inside a resistively-heated furnace (Carbolite, MTF 10/15/130) and the temperature was controlled by an Omega CSC232 PID temperature controller. Helium was used as the carrier gas and the reactants were introduced to the helium stream using a heated evaporator-syringe pump assembly. The reactants, water and ethanol, at a 10-to-1 molar ratio, were fed to an evaporator maintained at 230°C, using pulse-free syringe pumps (Cole-Parmer). The gas lines in contact with the reactant gas stream were heated to 130°C to prevent condensation. For the reaction experiments, the feed stream to the reactor constituted of 0.8% ethanol and 8% water in helium at a WHSV of 2.7 g EtOH (g cat)\textsuperscript{-1} hr\textsuperscript{-1}. The steady-state reaction experiments were run in the kinetically controlled regime by maintaining the reaction conditions away from equilibrium at all temperatures during the activity testing experiments. By using the Weisz-Prater criterion for internal diffusion
effects and Mear’s Criterion for external diffusion effects, it was verified that there were no transport limitations in the system. The reported reactant conversion and product yield values are representative of the catalytic activity after steady state was reached at each temperature. Prior to the catalytic activity tests the catalyst samples were subjected to either an oxidation or a reduction pretreatment as outlined in Section 3.2.2.

The quantitative analysis of the reactor effluents was carried out by on-line gas chromatography (Shimadzu Scientific 2010) equipped with a Carboxen® column coupled with a pulsed discharge helium ionization detector (PDHID) which was used to separate and detect H₂, CO and CO₂ and a Q-Bond column with a flame ionization detector (FID) to separate and detect the hydrocarbon species. The carbon balances were always better than 95%.

Average turn-over frequency (TOF) for H₂ formation was defined as

\[ \text{TOF} = \frac{\text{mole of } H_2 \text{ produced/sec}}{\text{mole of Co on the surface}} \]

TOFs were also calculated for the Co⁰ and Co⁺² sites individually. In these calculations, it was assumed that, at a given temperature, a Co⁰ site had the same TOF whether it was in a pre-reduced catalyst matrix or not. The same assumption was used for the Co⁺² sites. At each temperature, TOFs for the two sites (TOF_{Co⁰} and TOF_{Co⁺²}) were calculated using the following two equations:

\[
\begin{align*}
(n_{Co⁰})_O x(\text{TOF}_{Co⁰}) + (n_{Co⁺²})_O x(\text{TOF}_{Co⁺²}) &= (\text{molecules of } H_2 \text{ produced/sec})_O \\
(n_{Co⁰})_R x(\text{TOF}_{Co⁰}) + (n_{Co⁺²})_R x(\text{TOF}_{Co⁺²}) &= (\text{molecules of } H_2 \text{ produced/sec})_R
\end{align*}
\]
where subscripts “O” and “R” refer to the catalysts that went through oxidation and reduction pretreatments, respectively. The terms $n_{\text{Co}^0}$ and $n_{\text{Co}^{+2}}$ represent the number of Co$^0$ and Co$^{+2}$ sites, respectively, calculated from XANES data for each catalyst at each temperature.

3.3 Results and Discussion

3.3.1 Temperature-programmed Reduction

The reduction characteristics of the Co/CeO$_2$ catalyst was investigated by temperature programmed reduction technique in the 50-650°C range. The H$_2$ consumption profile as a function of temperature is presented in Figure 8 together with deconvolution of the H$_2$ uptake profile for quantitative analysis. During the TPR experiment, H$_2$ uptake was observed as a well-resolved doublet in the 250-500°C region and the doublet was curve-fitted with two symmetric peaks with maxima corresponding to 330°C and 400°C. Such a two-component reduction profile for reduction of Co/CeO$_2$ has been previously reported [22] and is consistent with a stepwise reduction scheme, where the first consumption feature is associated with reduction of Co$_3$O$_4$ to CoO while the second one arises from reduction of CoO to metallic Co. There were no H$_2$ consumption features that could be associated with the onset of the reduction of the ceria support in the temperature range the TPR experiment was carried out. The assignment of the H$_2$ consumption maxima was further verified by calculating the area under each fitted component. The area ratio of the second fitted component to the fist fitted component was calculated to be 3 which is in agreement with the stoichiometry
of stepwise Co$_3$O$_4$ to CoO to Co$^0$ reduction and further verifies the peak assignments.

3.3.2 In-situ X-ray Diffraction

The transformation of Co-phases during steam reforming of ethanol at different temperatures over Co/CeO$_2$(O) and Co/CeO$_2$(R) catalysts was investigated using in situ XRD technique. Figure 8 shows the in-situ XRD patterns collected during ethanol steam reforming over Co/CeO$_2$(R). XRD patterns for the pristine and reduced catalysts are provided for comparison. The XRD pattern for the pristine catalyst was obtained at room temperature before the catalyst treatment. Three diffraction peaks at 2Θ values of 31°, 33° and 37° were resolved over the pristine catalyst. The well-resolved peak at 33° corresponds to diffraction by (200) plane of CeO$_2$ in face-centered cubic cerianite structure (ICDD #34-394). The cerianite phase persists throughout the pretreatment and ESR stages, regardless of the conditions under which the catalyst was pretreated. Crystallite size calculations using Scherrer’s method over the (200) plane of CeO$_2$ yielded an average ceria crystallite size of approximately 60 nm and did not show any changes in the crystallite size of this phase during ethanol steam reforming over this catalyst, regardless of the pretreatment conditions.
The remaining 31° and 37° peaks were associated with the (220) and (311) planes of Co$_3$O$_4$ (ICDD #42-1467). The XRD pattern for the catalyst after reduction pretreatment was obtained at room temperature under an inert flow. Following reduction treatment, the peaks associated with Co$_3$O$_4$ disappeared and the formation of a new diffraction peak at 44° together with two weakly resolved peaks at 36.5° and 42.4° was observed. The well-resolved peak located at 44° corresponds to the (111) plane of metallic cobalt (ICDD #15-806), while the 36.5° and 42.4° peaks were associated with the (111) and (200) planes of CoO (ICDD #5-0562). The peaks at 31° and 37° are attributed to the (220) and (311) planes of Co$_3$O$_4$.
With the introduction of the reaction feed over Co/CeO$_2$(R) at 300°C, a decrease in the intensity of the peak associated with metallic cobalt phase (44°) and a concomitant increase in the intensities of CoO peaks (36.5° and 42.4°) were observed. This observation suggests a partial re-oxidation of metallic cobalt species to CoO. The CoO phase persisted under reaction conditions at 350°C, but further increase in the reaction temperature resulted in the reduction of CoO to form metallic cobalt species, as suggested by a decrease in the intensity of CoO diffraction peaks and increase of the 44° peak, which was associated with metallic cobalt. The in-situ XRD pattern collected after 30 minutes on stream of ethanol steam reforming at 500°C suggest that metallic Co is the major cobalt phase observed to exist together with the cerianite phase of CeO$_2$. Although very weak, the diffraction line that corresponds to the CoO phase still exists following reaction at 500°C, as seen in Figure 9.

As discussed above, re-oxidation of metallic cobalt on the pre-reduced catalyst was observed during ethanol steam reforming at 300°C. One plausible explanation for this re-oxidation phenomenon is oxygen migration from the support to metallic cobalt moieties to result in cobalt oxide species. Labile oxygen species of the CeO$_2$ support play an important role in improving the activity and stability of Co-based steam reforming catalysts not only by suppressing coke formation, but also by promoting oxygen delivery to close proximity of ethoxy species to enable higher hydrogen yields [19].
Another plausible explanation is the re-oxidation of metallic cobalt moieties with oxygen from dissociative adsorption of water from the reaction mixture. Similar observations on the conversion of metallic Co to CoO under the reaction conditions have been previously reported [53, 79] and the extent of the re-oxidation was found to be influenced by the ethanol-to-water ratio over a 10% Co/CeO$_2$-ZrO$_2$ catalyst [53].

With the aim of providing further insight to this phenomenon, a Co/CeO$_2$ catalyst was reduced under 5%H$_2$/He at 450°C for 2 hours and then, kept in helium atmosphere at the same temperature while XRD patterns were collected at one hour intervals after switching to the inert atmosphere. The reduction temperature used for this experiment was higher than the temperature used in pre-reduction procedure prior to reaction experiments. In agreement with the results discussed above, the XRD pattern collected immediately after switching to the inert atmosphere shows the presence of metallic Co phase (44°) together with the cerianite phase (33°) (Figure 10).
Figure 9 In situ XRD patterns collected as a function of temperature during ethanol steam reforming over Co/CeO$_2$(R).
Figure 10 In-situ XRD patterns collected as function of time-on-stream during inert treatment of Co/CeO$_2$(R) at 400°C.

No change in the X-ray diffraction patterns was observed over a period of 10 hours of inert treatment of the reduced Co/CeO$_2$ catalyst at 450°C. It should be noted that the temperature chosen for inert treatment of the catalyst (450°C) was higher than the temperature where re-oxidation of cobalt was observed under reaction conditions (300°C) to promote re-oxidation phenomenon arising from the mobility of oxygen species. Although partial re-oxidation of cobalt
species was observed within one hour of the introduction of ESR feed to the reaction chamber, the experiment the inert treatment of a pre-reduced Co/CeO$_2$ catalyst did not show formation of oxidized cobalt species over a period of 10 hours. These results suggest that, during reaction at 300°C, the re-oxidation of metallic cobalt was caused primarily by dissociative adsorption of water from the gas phase. It should be noted that this result does not rule out the possibility of oxygen diffusion from the support. In fact, our previous work has shown oxygen from ceria to be readily accessible [8]. It is possible that there may have been some oxygen replenishment from the ceria support, but the extent of reoxidation may have been insufficient to provide any long-range order for an oxide phase to be detected by the XRD technique.

The progression of the reduction of cobalt species from Co$_3$O$_4$ to metallic cobalt during ethanol steam reforming was further investigated by keeping the catalyst under ethanol steam reforming feed stream at 500°C while monitoring the transformation of cobalt phases by in situ XRD. Figure 12 shows the XRD patterns collected as a function of time-on-stream during this experiment. Within the first hour of reaction, disappearance of the diffraction peaks associated with the Co$_3$O$_4$ phase of the pristine catalyst (31° and 37°) and appearance of peaks associated with CoO (36.5° and 42.4°) and metallic Co (44°) was observed. Although weakly-resolved after 30 minutes on stream (see Figure 10), the peak associated with metallic cobalt phase was well-resolved after an hour on stream.
The inset to Figure 12 shows a comparison of the intensities of peaks associated with CoO (42.4°) and metallic Co (44°) after one hour and 12 hours-on-stream.

**Figure 11** In-situ XRD patterns collected as a function of temperature during ethanol steam reforming over Co/CeO$_2$(O).

Comparison of the peak intensities clearly show a decrease in the intensity of the CoO peak and a concomitant increase in the metallic Co peak,
which suggests an increase in the extent of reduction of cobalt species with time-on-stream during ethanol steam reforming under these conditions.

Figure 12 In-situ XRD patterns collected as function of time-on-stream during ethanol steam reforming over Co/CeO2(O) at 500°C. (Inset shows a comparison of patterns after 1 hour and 12 hours on-stream.)
3.3.2 X-Ray Absorption Spectroscopy (XAFS)

The transformation of cobalt coordination environment during ethanol steam reforming over Co/CeO$_2$ catalysts that underwent different pretreatments was investigated using X-ray absorption fine structure spectroscopy. Controlled-atmosphere XAFS data were collected at the Co K-edge (7709 eV) at room temperature under helium over Co/CeO$_2$(O) and Co/CeO$_2$(R) following catalyst pretreatment and subsequent ethanol steam reforming over the catalysts in the 350-500°C range. Figure 13 presents the Co K-edge X-ray absorption near edge spectra (XANES) collected over Co/CeO$_2$(R) following ESR over this catalyst together with the XANES spectra of the reference compounds, i.e. CoO and Co, used in linear combination fitting of the XANES region. Also included in Figure 13 is the linear combination XANES fitting results to estimate the relative contribution of each cobalt state. Following the reduction pretreatment step, CoO and metallic cobalt were observed to co-exist over the catalyst with metallic Co component having a larger contribution. In line with the in situ XRD results, re-oxidation of some portion of metallic cobalt species to CoO was observed during ethanol steam reforming at 350°C and the XANES analysis showed a larger fraction of CoO. Although the XRD patterns showed the presence of Co$^0$ and CoO as the only crystalline phases over pre-reduced Co/CeO$_2$ and Co/CeO$_2$(R) after ESR, respectively, the XANES results showing the presence of more than one cobalt phase in each case are not contradictory with the XRD results. Both of the techniques indicate the same major cobalt phase, Co$^0$ for pre-reduced
Co/CeO$_2$ and CoO for CO/CeO$_2$(R) after reaction at 350°C, and XRD technique has lower resolution. Further increase in the reaction temperature, resulted in a gradual reduction of CoO to metallic cobalt moieties.

Figure 13 Normalized XANES spectra and results of linear combination XANES fitting with reference compounds of Co/CeO$_2$(R) following ethanol steam reforming in the 350-500°C range

Figure 14 presents the Co K-edge XANES spectra collected during a similar experiment over Co/CeO$_2$(O) together with linear combination fitting of the collected spectra with reference compounds. The XANES region of the oxidation pretreated Co/CeO$_2$ catalyst was fitted by Co$_3$O$_4$ only. With the introduction of reaction feed at 350°C, the reduction Co$_3$O$_4$ species on the Co/CeO$_2$(O) catalyst was observed and at 400°C, all Co$_3$O$_4$ was completely converted to CoO. Further increase in the reaction temperature led to further reduction of CoO to metallic Co. Such a reduction scheme is in agreement with the previously reported two-
step reduction process for unsupported \( \text{Co}_3\text{O}_4 \) and supported cobalt catalysts where, \( \text{Co}_3\text{O}_4 \) is converted to \( \text{CoO} \), before reduction of \( \text{CoO} \) to \( \text{Co}^0 \) takes place \cite{20, 52, 54, 80}. Below 500°C, the extent of cobalt reduction over the \( \text{Co/\text{CeO}_2(O)} \) catalyst was lower than \( \text{Co/\text{CeO}_2(R)} \) however, the contributions from \( \text{CoO} \) and \( \text{Co}^0 \) phases for both \( \text{Co/\text{CeO}_2(O)} \) and \( \text{Co/\text{CeO}_2(R)} \) were, within experimental error, similar after reaction at 500°C. This observation indicates that same extent of reduction of cobalt species over the \( \text{Co/\text{CeO}_2} \) catalysts is achieved under reaction conditions regardless of the initial state of cobalt. These results are in agreement with literature \cite{53, 81} and clearly show that reduction/oxidation of cobalt species over ceria can take place under these reaction conditions.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure14}
\caption{Normalized XANES spectra and results of linear combination XANES fitting with reference compounds of \( \text{Co/\text{CeO}_2(O)} \) following ethanol steam reforming in the 350-500°C range.}
\end{figure}
The magnitude of $k^2$-weighted Fourier transforms of the Co K-edge EXAFS spectra collected over the Co/CeO$_2$(R) catalyst following ESR at the designated temperatures are given in Figure 15a. Following ESR over the Co/CeO$_2$ at 350°C, the Co-Co coordination region in the EXAFS shows a peak at 2.5Å (peak at 2.14Å in the uncorrected FT) with a shoulder in the high R region (at c.a. 2.5Å in the uncorrected FT). The former peak is consistent with Co-Co coordination in metallic Co and the latter is due to scattering from bridging Co-O-Co atoms in CoO environment. The EXAFS spectrum collected following ESR at 400°C over the same catalyst showed similar features. Above 400°C, a single Co-Co coordination peak at 2.5Å, which is consistent with Co$^0$ was observed. The contributions of Co-O-Co and Co-Co shells to the EXAFS were evaluated by isolation of the respective coordination shell from the inverse Fourier transform. The reference compounds, CoO and Co-foil, were analyzed by the same procedure. The coordination parameters obtained through fitting the EXAFS data for Co/CeO$_2$(R) are given in Table 2. As suggested by the XANES data, cobalt atoms exist in the form of both Co$^0$ and CoO therefore, the true coordination numbers were calculated by the fit value of coordination number divided by the fraction of the particular component. The coordination parameters suggest the presence of large cobalt particles over this catalyst.

Figure 15 b shows the magnitude of $k^2$-weighted Fourier transforms of the Co K-edge EXAFS spectra of Co/CeO$_2$(O) catalyst following ESR reaction in the 350-500°C range. Following ESR at 350°C, the magnitude of the Fourier
transform shows a peak at about 1.5 Å due to Co-O and another peak at about 2.5 Å due to scattering from bridging Co-O-Co atoms at 3.0Å. Increasing reaction temperature gives another peak at 2.14 Å and the peak arising from Co-O scatter from CoO was observed to disappear. This observation is in good agreement with the XRD results indicating the reduction of CoO to metallic cobalt with reaction above 400°C. The coordination parameters, obtained through isolation of the respective coordination shells, are given in Table 3. These parameters are also in-line with large cobalt particles in each stage of reaction.

3.3.3 X-ray photoelectron spectroscopy

Figure 16 shows the X-ray photoelectron spectra in the Co 2p region for pristine Co/CeO₂ and a Co/CeO₂(O) sample that went through the ethanol reaction in the 350-500°C range. The sample was transferred to the XPS analysis chamber without exposure to air using a special controlled-atmosphere transfer arm. For direct comparability of results from this XPS experiment with the XAFS results, the post-reaction catalyst sample was taken through the same reaction steps as in the XAFS experiment prior to collection of the XPS spectrum.
Figure 15 Magnitude of $k^2$-weighted Fourier transforms of cobalt K-edge EXAFS spectra collected following ethanol steam reforming in the 350-500°C range over (a)Co/CeO$_2$(R) and (b)Co/CeO$_2$(O)
### Table 2 Results of EXAFS fitting of Co/CeO$_2$(R) at the Co K-edge

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Scatter</th>
<th>CN</th>
<th>R (Å)</th>
<th>$\Delta \sigma, \text{Å}^2$</th>
<th>$\Delta E_0, \text{eV}$</th>
</tr>
</thead>
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<td>-1.45</td>
</tr>
</tbody>
</table>

### Table 3 Results of EXAFS fitting of Co/CeO$_2$(O) at the Co K-edge

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Scatter</th>
<th>CN</th>
<th>R (Å)</th>
<th>$\Delta \sigma, \text{Å}^2$</th>
<th>$\Delta E_0, \text{eV}$</th>
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<td>500°C</td>
<td>Co-Co</td>
<td>11.9</td>
<td>2.49</td>
<td>0.0006</td>
<td>-2.11</td>
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</table>
Figure 16 X-ray photoelectron spectra of a) CoCeO$_2$ pristine b) following steam reforming under ethanol

The curve fitting of the X-ray photoelectron spectrum of the Co 2p$_{3/2}$ region of the pristine catalyst suggests that this envelope is composed of two components located at 779.3 eV and 781.1 eV. In agreement with the assignments in the literature [53, 82], the lower binding energy component is assigned to Co$^{3+}$, while the higher binding energy component was assigned to
Co$^{2+}$. The assignments were further verified by calculating the ratio of the areas under the fitted components. The area ratio of the lower binding energy component to the higher binding energy component was calculated to be ~2 which is consistent with the stoichiometry of Co$^{3+}$ and Co$^{2+}$ species in Co$_3$O$_4$.

Over the post-reaction Co/CeO$_2$(O) catalyst, curve fitting in the Co 2p$_{3/2}$ region suggested the presence of three features assigned to Co$^0$ (779 eV), Co$^{2+}$ (781.4 eV) and a shake-up component associated with paramagnetic Co$^{2+}$ species and is displaced by 4.1 eV relative to the Co$^{2+}$ main photopeak. The relative contributions of the Co$^0$ and Co$^{2+}$ components to the main photopeak were calculated from the areas under the curve for the respective components as 70% and 30%, respectively. These values are in agreement with the XANES results and show that the average oxidation state of the cobalt surface species closely resembles that of the bulk.

3.3.4 Steady-state catalytic activity testing

Steady state activity testing was carried out over Co/CeO$_2$(O) and Co/CeO$_2$(R) to investigate the effect of catalyst pretreatment on the ESR activity and to correlate the transformation of cobalt phases observed through the in situ XRD and XAFS experiments with the catalytic activity of Co/CeO$_2$ catalysts in ethanol steam reforming reaction. Figure 17 compares the H$_2$ production rates (TOF) over Co/CeO$_2$(O) and Co/CeO$_2$(R). In the same figure, the inset shows the Arrhenius plots obtained using the TOFs calculated for the two catalysts, as described in Section 3.2.3. The production rates of carbon-containing products
of ethanol steam reforming are presented in Table 3. Below 450°C, Co/CeO$_2$(O) achieved significantly lower H$_2$ and CO$_2$ production rates than Co/CeO$_2$(R) however, as the reaction temperature is increased, Co/CeO$_2$(O) catalyst was activated rapidly and was capable of achieving rates similar to its pre-reduced counterpart (see Figure 17). This behavior is consistent with the XRD and XAFS results where the transformation of cobalt phases under ethanol steam reforming conditions was observed to yield the same composition of CoO and metallic Co phases, regardless of the initial state of cobalt on the catalyst. It seems that both CoO and Co$^0$ exist over the catalyst showing high activity. Furthermore, the Co/CeO$_2$(O) catalyst which was shown to consist of CoO mainly at 400°C through the analysis of the XANES data (See Figure 14) is not capable of achieving similar production rates for H$_2$ and CO$_2$ as Co/CeO$_2$(R), indicating that the presence of CoO alone is not enough for achieving high steam reforming activity, although Co$^{+2}$ sites appear to have some intrinsic activity themselves. The take-off of the steam reforming reaction over the oxidation pretreated catalyst was observed only after cobalt species with metallic character formed over the surface, suggesting the importance of co-existence of CoO and Co phases for achieving high steam reforming activity. Previously, Llorca et al. [51] have reported similar conclusions on the presence of an equilibrium state between CoO and Co$^0$ over supported cobalt catalysts during ethanol steam reforming and Lin et al. [53] showed that such an equilibrium state between CoO and metallic Co is influenced by the water-to-ethanol ratio in the feed.
Figure 17 Effect of oxidation (triangles) and reduction (circles) pretreatment on $\text{H}_2$ production rate as a function of temperature over Co/CeO$_2$. WHSV = 2.7 g EtOH (g cat)$^{-1}$ h$^{-1}$, $C_{\text{EtOH}} = 0.8\%$ and $\text{H}_2\text{O}:\text{EtOH} = 10:1$ (molar ratio). (Inset shows the Arrhenius plots obtained using TOFs based on total surface Co atoms)

The activation energies obtained using the Arrhenius plots shown in the inset are 26 and 112 kJ/mole for the Co/CeO$_2$(R) and Co/CeO$_2$(O) catalysts, respectively. It should be noted that these are apparent activation energies and do not take into account the changing nature of the degree of reduction of the catalyst with temperature.
TOFs for the Co$^0$ and Co$^{+2}$ sites were also calculated using the XANES data to obtain the number of Co$^0$ and Co$^{+2}$ sites. The calculation procedure is outlined in Section 3.2.3. It should be noted that these calculations involve some assumptions. For example, at each temperature, it is assumed that each of the Co$^0$ sites have the same TOF, regardless of the catalyst matrix they belong to. A similar assumption is made for the Co$^{2+}$ sites. This is a simplifying assumption and in reality, one would expect that the coordination environment of each site (i.e., whether it is neighboring more of the metallic sites or oxide sites) would change its activity. Another assumption involved in the calculations is that the compositions obtained from XANES, which is a bulk technique, are representative of the surface compositions. The fact that the XPS data obtained from a post-reaction Co/CeO$_2$(O) catalyst that went through the 350-500°C reaction sequence gave compositions not too different from the XANES data may be used to justify this assumption. However, there may be differences in the abundance of the metallic and oxidic sites on the surface versus in the bulk. Finally, including only two type of sites, i.e., of Co$^0$ and Co$^{2+}$, may also be an oversimplification. For example, there is evidence that metallic sites supported on reducible oxides such as ceria may undergo electron transfer with the support and may assume positive charges (Co$^{δ+}$) [83, 84]. The TOFs calculated for the Co$^0$ and Co$^{+2}$ sites are plotted as a function of temperature in Figure 18.
The TOFs for the Co\(^0\) sites change from 2.4 to 4.2 s\(^{-1}\) in the 350-500°C temperature range. These TOFs are comparable to those reported for transition metals, e.g., (2.2-10 s\(^{-1}\) for Ni/MgO catalysts at 650°C\[85\], ~0.1 s\(^{-1}\) for Cu-Ni catalysts at 550 °C \[86\]), or even for precious metals (1-20 s\(^{-1}\) for Rh/MgO at 650°C \[87\]). The TOFs for the Co\(^{2+}\) sites vary from 0.2 to 1.7 s\(^{-1}\) in the same temperature range. As expected, the intrinsic activity of metallic sites is much higher than that of the Co\(^{2+}\) sites. The Arrhenius plots constructed using the TOFs for individual sites are presented in the inset of Figure 18.
energies calculated from these plots for the Co$^0$ and Co$^{2+}$ sites are 15 and 67 kJ/mol, respectively.

Throughout the temperature range, CO$_2$, CO, CH$_4$, C$_2$H$_6$ and liquid by-products such as acetaldehyde and acetone were also observed in varying quantities in addition to, H$_2$. Ethanol steam reforming reaction network over Co-based catalysts is governed by a large number of intermediate steps and side reactions. A comparison of the production rates of carbon-containing species over Co/CeO$_2$(O) and Co/CeO$_2$(R) is given in Table 4. As expected, CO$_2$ is the main carbon-containing product over Co/CeO$_2$(R) at all temperatures. Over Co/CeO$_2$(O), the CO$_2$ production rate slowly increases with temperature, reaching the same level with the pre reduced catalyst at 450°C. Acetaldehyde, which is a product of ethanol dehydrogenation and an intermediate of ethanol steam reforming over cobalt-based catalysts, was observed over both Co/CeO$_2$(O) and Co/CeO$_2$(R). In the literature, both CoO [50] and Co$_3$O$_4$ [52, 54, 79] have been reported to exhibit activity for selective dehydrogenation ethanol to yield acetaldehyde. Acetone, produced through aldol condensation of acetaldehyde, was observed as one of the two liquid by-products at all temperatures. The high acetone production rates observed over the Co/CeO$_2$(O) catalyst at 350°C suggests a propensity for the oxide phases for aldol-condensation type reactions since this catalyst does not have any metallic sites at this temperatures. One of the reason for the higher rates observed for the liquid by-products is the high WHSVs used in these experiments to keep the
conversion levels low. Similar observations on the product distribution over a similar Co/CeO$_2$ catalyst have previously been reported by Song and Ozkan [20].

**Table 4** Effect of pretreatment conditions on the rates of production of C-containing products (mmol.min$^{-1}$.g cat$^{-1}$) WHSV = 0.27 g EtOH (g cat)$^{-1}$ hr$^{-1}$, C$_{EtOH}$ = 0.8% and H$_2$O:EtOH = 10:1 (molar ratio).

<table>
<thead>
<tr>
<th></th>
<th>350°C</th>
<th></th>
<th>400°C</th>
<th></th>
<th>450°C</th>
<th></th>
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<td>(R)</td>
<td>(O)</td>
<td>(R)</td>
<td>(O)</td>
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<td>4.0</td>
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</tbody>
</table>

Ethane, methane and CO are the other products produced in small quantities, with CO giving the lowest yields. Despite the differences in product distribution at lower temperatures, above 400°C, the rates of formation of all the reaction products were very similar within experimental error. This observation is in agreement with the catalyst characterization studies aiming at identifying the state of cobalt under reaction conditions. The differences in the state of cobalt tend to diminish under reaction conditions with increasing temperature which is fully aligned with the observed rates of the reaction products that converge to similar values as reduction of cobalt to the metallic form takes place during reaction. It should be noted that the ethanol steam reforming reaction is

57
governed by a complex network of reactions, as reported previously[64, 88], but there was no attempt at elucidating the complexities of the reaction network in this study.

3.3.5 In situ DRIFTS during Ethanol Steam Reforming

The effect of pretreatment on the evolution of surface intermediates during steam reforming of ethanol over Co/CeO$_2$ was further investigated using DRIFTS. In situ DRIFT spectra were collected while ethanol steam reforming reaction is progressing over the catalyst and after flushing reactants from the DRIFTS chamber with helium. Figures 19a and 20a present the in-situ DRIFT spectra collected as a function of temperature in the 25°C-500°C range during such experiments over Co/CeO$_2$(O) and Co/CeO$_2$(R), respectively. Figures 19b and 20b show the spectra after the DRIFTS chamber was flushed with He. Over Co/CeO$_2$(R), the formation of a broad band is observed in the 3600-3200 cm$^{-1}$ region was observed upon introduction of the ethanol steam reforming reaction feed to the in situ DRIFTS chamber (Figure 19a). This peak was observed to decrease in intensity with increasing temperature, disappearing completely at 200°C. This band is associated with surface hydroxyls and adsorbed water on the surface. In the low wavenumber region, another weakly-resolved feature was observed around 1650 cm$^{-1}$, which disappears above 100°C. This peak is associated with molecularly adsorbed water [24].
Figure 19 DRIFT spectra collected as a function of temperature during ethanol steam reforming over Co/CeO$_2$(R) (a) spectra acquired in situ and (b) spectra acquired after flushing with He
Figure 20 DRIFT spectra collected as a function of temperature during ethanol steam reforming over Co/CeO$_2$(O) (a) spectra acquired in situ and (b) spectra acquired after flushing with He
A similar control experiment was performed over the same sample, where ethanol was eliminated from the feed stream and only water vapor was fed to the reaction chamber (data not shown). During this experiment, the 1650 cm\(^{-1}\) feature was observed to exhibit the same behavior as in the in situ DRIFTS ethanol steam reforming temperature programmed reaction experiment. It should be noted that water vapor was being fed to the DRIFTS controlled-atmosphere chamber during the collection of the spectra presented in Figures 19a and 20a and therefore, bands arising from the rotational modes of the water molecule in the gas phase are observed in the 3600-3500 cm\(^{-1}\) and 1800-1300 cm\(^{-1}\) regions. A significant decrease in the intensity of these bands, as presented in Figure 19b and 20b was observed upon flushing the chamber with helium.

Along with the aforementioned absorption bands arising from the interaction of water vapor with the catalyst surface, several other bands at 2964, 2931, 1049 and 844 cm\(^{-1}\) were observed at 25°C under the ethanol steam reforming reaction feed. These bands arise from interaction of ethanol with the catalyst surface and have been associated with \(\nu_{\text{as}}(\text{CH}_3)\) at 2964 cm\(^{-1}\), \(\nu_{\text{s}}(\text{CH}_3)\) at 2931 cm\(^{-1}\), \(\nu\) (CO) at 1049 cm\(^{-1}\) and \(\nu\) (COO) at 844 cm\(^{-1}\) modes of surface ethoxy species. Formation of ethoxy species is indicative of associative adsorption of ethanol onto the catalyst, yielding surface ethoxy and hydroxy species [24, 59-63]. Ethoxy species were not stable during helium flush (Figure 19b). Over Co/CeO\(_2\)(R), the intensity of the ethoxy species decreased with increasing temperature (see Figure 19a). Above 100°C concomitant appearance
of absorption bands at 1577 cm\(^{-1}\) and 1465 cm\(^{-1}\) in the C=O vibration fingerprint region was observed. Especially at 100\(^\circ\)C, these bands are not readily observed in the spectrum collected during in situ reaction due to the presence of bands in the C=O fingerprint region arising from the presence of water vapor. However, flushing the chamber with helium allows for better resolution in this region (see Figure 19b). These bands are associated with asymmetric and symmetric vibrations of acetate species, respectively [3-6]. It is also possible to associate 1537 cm\(^{-1}\) band with \(v_{\text{asym}}(\text{COO})\) vibrations of carbonate or formate species. Formation of these species suggests the conversion of ethoxy species to surface acetate and, possibly carbonate species with increasing temperature. Along with the disappearance of ethoxy species and formation of acetate species at 100\(^\circ\)C, formation of CO\(_2\) (2354 cm\(^{-1}\) and 2323 cm\(^{-1}\)) was also observed signaling the kick-off of ethanol steam reforming reaction. Above 250\(^\circ\)C, acetate species were not stable after helium flush.

The transformation of ethoxide species to acetate has been associated with the presence of CoO moieties on the surface, that produce acetaldehyde through dehydrogenation [50] and acetaldehyde was further oxidized to acetate species on the surface [89, 90]. The 3014cm\(^{-1}\) band observed in the DRIFT spectrum collected during ethanol steam reforming at 200\(^\circ\)C and then again at 500\(^\circ\)C, is characteristic of methane. Co/CeO\(_2\) catalysts are extensively studied for preferential oxidation of carbon monoxide and have been reported to exhibit methanation activity above 250\(^\circ\)C [91]. In agreement with literature, the low
temperature evolution of methane can be associated with methanation reaction although, decomposition of acetaldehyde cannot be ruled out. At higher temperatures, on the other hand, ethanol decomposition to yield methane, carbon monoxide and hydrogen takes off and the methane band observed at higher temperatures was associated with this reaction.

Figure 20a presents DRIFT spectra collected under reactant flow during a similar ethanol steam reforming temperature programmed reaction experiment over Co/CeO$_2$(O) where, the formation of similar surface species to Co/CeO$_2$(R) was observed. Consistent with the foregoing discussion, formation of ethoxy (2964 cm$^{-1}$, 2931 cm$^{-1}$, 1049 cm$^{-1}$ and 844 cm$^{-1}$) species and hydroxy groups (3600-3200 cm$^{-1}$) was observed with the introduction of the reaction feed at room temperature. In agreement with the previous discussion on the surface species over Co/CeO$_2$(R), after flushing the reactant gas mixture from the DRIFTS chamber, formation of surface acetate species was observed at 100$^\circ$C (Figure 20b). Above 200$^\circ$C, formation of acetate species was coupled with decrease in the intensity of the ethoxy bands. It is worth noting that although the formation of acetate species was observed at the same temperature over both Co/CeO$_2$(O) and Co/CeO$_2$(R), the ethoxy species persisted until higher temperatures over the Co/CeO$_2$(O) while complete disappearance of the ethoxy bands was observed at 250$^\circ$C over Co/CeO$_2$(R). This observation is in agreement with the steady-state activity tests, where lower rates of acetaldehyde formation were observed over the oxidation pretreated catalyst (see Table 3). Similar observations on the
stability of ethoxy species on Co$_3$O$_4$ were also reported by Hyman and Vohs [50]. Similarly, formation of CO$_2$ (2354 cm$^{-1}$ and 2323 cm$^{-1}$), which signals the onset of steam reforming reaction, was observed at 200°C over both Co/CeO$_2$(O) and Co/CeO$_2$(R), however the intensity of the CO$_2$ bands were significantly lower over Co/CeO$_2$(O). These observations suggest that conversion of adsorbed ethoxy species on the pre-reduced Co/CeO$_2$ catalyst proceeds at a faster rate than its pre-oxidized counterpart. As the temperature is increased, the intensity of CO$_2$ bands increase over Co/CeO$_2$(O), indicating the take-off of steam reforming reaction. The DRIFTS results are aligned with the steady-state activity evaluation and in situ characterization results discussed above and show that similar reaction intermediates are formed on the catalyst surface. However, the transformation of surface intermediates to reaction products are shifted to higher temperatures over Co/CeO$_2$(O) compared to its pre-reduced counterpart.

3.4 Conclusions

*In-situ* X-ray diffraction and controlled-atmosphere X-ray absorption and X-ray photoelectron spectroscopy studies together with steady-state activity measurements were used to examine the transformation of cobalt species during ethanol steam reforming and to correlate the catalytic activity with the observed cobalt phases. The effect of the initial state of cobalt on the steady-state catalytic activity and the state of cobalt over the Co/CeO$_2$ catalyst under reaction conditions was investigated by pretreating the catalyst under an oxidizing or a reducing atmosphere. The catalyst that underwent an oxidation pretreatment was
initially comprised of Co$_3$O$_4$ and went through a gradual reduction under reaction conditions. The reduction of Co$_3$O$_4$ species coincided with the activation the oxidized catalyst. Similarly, partial re-oxidation of metallic cobalt over the catalyst that was pretreated with reduction took place under reaction medium at lower temperatures. Regardless of the initial state of cobalt, co-existence of CoO and metallic Co in similar proportions was observed over both of the catalysts when a reaction temperature of 450°C was reached. While Co$_3$O$_4$ was inactive for steam reforming of ethanol, the active catalyst had both CoO and Co$^0$ species. It is possible that depending on the feed conditions, the phase composition of the catalysts at steady state may converge at different temperatures. The DRIFTS results were in good agreement with the characterization and steady-state reaction results showing that reduction of Co$_3$O$_4$ was necessary for further conversion of ethoxy species.
Chapter 4: Effect of Ceria Morphology

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4.1 Introduction

Co catalysts supported on ceria supports with different morphologies such as nano-rods (NR) and nano-cubes (NC) were investigated in regard to their activity for ethanol steam reforming. Ceria supports were prepared using the hydrothermal method where the particle shape is manipulated by controlling the pH and pressure of the precipitation environment. Structural characterization with TEM and XRD showed the two morphologies to be similar in particle size, but different in the exposure of different crystal planes. The nano-cubes had a higher exposure of the (110) plane, which is known to have a higher affinity for creating anion vacancies and surface defects. Controlled atmosphere X-ray absorption fine structure analysis, temperature programmed reduction/oxidation, dispersion measurements and steady-state reaction performance tests showed significant differences between the two catalysts. Co catalysts supported on nanocubes showed higher reducibility compared to those supported on nanorods or commercial supports of similar particle size. These catalysts also showed high H₂ and CO₂ yields in the 400-500°C range whereas Co/CeO₂(NR) had limited
carbon cleavage activity and were only active for dehydrogenation and dehydration. The superior performance of Co/\text{CeO}_2(\text{NC}) catalysts is thought to be due to a combination of factors, including improved metal dispersion, increased reducibility and higher oxygen mobility.

4.2 Experimental

4.2.1 Catalyst preparation

The support morphologies were prepared via the hydrothermal method [21, 92] where 1.5 g Ce(NO$_3$)$_3$·6H$_2$O (Sigma Aldrich 99.9%) was dissolved in 9.4 ml water and combined with 25 ml of 11 wt% NaOH. The resulting suspension was stirred for 15 min under room temperature. It was transferred to a 50-ml stainless steel autoclave and was heated at 110 °C for 24 hours in the oven. Following the precipitation step, the autoclave was cooled to room temperature and the suspension was filtered, where the remaining solids were rinsed with approximately 2 liters of deionized and distilled water until a pH value of 7 was reached. Following the neutralization step, the solids were dried in air at 90°C overnight. The dried Ce(OH)$_3$ precursors were calcined at 450 °C for 3 h under air to yield CeO$_2$ nanorods with a light yellow color. CeO$_2$ nanocubes were prepared in the same manner with the autoclave being heated to 200 °C for 24 hours. The two supports with nano-rod and nano-cube morphologies are denoted by CeO$_2$-NR and CeO$_2$-NC. Impregnation of 10% (by weight, metallic) cobalt on the support was carried out with incipient wetness impregnation method with Co(NO$_3$)$_2$ (Aldrich, 99.999%) dissolved in 200 proof ethanol (Decon Labs) and
applied onto the support in five consecutive steps by drying the impregnated catalyst at 110°C overnight in between each step to improve the homogeneity of the resulting catalyst. Following the final impregnation and drying step, the catalysts were calcined at 450°C for 3 hours under air flow.

4.2.2 Catalyst characterization

4.2.2.1 Surface area and metal dispersion

The BET surface area and pore volume measurements were done on a Micromeritics ASAP 2020 accelerated surface area and porosimetry instrument, using nitrogen adsorption/desorption isotherms collected at liquid nitrogen temperature. The desorption branch of the isotherm was used to determine the BJH pore size distributions with pore sizes around 15 Å. Before measurement, the catalyst was degassed for 12 hours at 130°C under a vacuum better than 2 μm Hg.

The dispersion measurements were performed using N₂O chemisorption technique outlined earlier by Jensen et al. [73]. For these measurements, 100mg of the sample 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% H₂ in He for 2 hours, which are the same parameters used for reduction pre-treatment prior to reaction experiments. The reactor was then flushed with He at the same temperature and cooled under flow. N₂O chemisorption was performed by introducing a stream of 3%N₂O/He to the reactor at 40°C. Species in the m/z=12 to m/z=46 range were
monitored via an on-line mass spectrometer (MKS – Cirrus II). The mass spectrometer was calibrated for instrumental sensitivity factors. The contribution of N$_2$O fragment to the m/z=28 trace has been subtracted to quantify the N$_2$ amount desorbing from the sample surface. Throughout the experiment, N$_2$O 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 a 1:1 Co:O ratio.

4.2.2.2 TEM

A Phillips Tecnai F20 instrument equipped with a field emission gun operated at 200 kV was used for transmission electron microscopy (TEM). All images are collected in the brightfield. Samples were suspended in n-hexane and were sonicated for 15 minutes for high dispersion. The resulting emulsion was deposited immediately after sonication to prevent agglomeration of the particles. A Tedpella, Inc 200 mesh copper grid coated with lacey carbon was used as the TEM sampleholder. ImageJ processing software is used for analysis of the TEM digital micrographs. Energy-dispersive X-ray spectroscopy (EDAX) under scanning transmission electron microscopy mode (STEM) was incorporated to the instrument for elemental analysis of the samples.

4.2.2.3 X-ray Diffraction

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X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku X-ray diffractometer (X-ray source: Cu Kα radiation, λ = 1.5418 Å) operated at 40 kV and 25 mA. The diffraction patterns were collected in the 2θ range of 20–65°. The identification of the crystalline phases through the collected diffraction patterns was done using the International Center for Diffraction Data (ICDD) database.

4.2.2.4 XAFS

Time-on-stream reduction data using controlled-atmosphere X-ray absorption fine structure (XAFS) technique were collected for the Co K-edge (7709 eV) at the bending magnet beamline (5BM-D) of the Dow-Northwestern-DuPont Collaborative Access Team (DND-CAT) of the Advanced Photon Source, Argonne National Laboratories. The measurements were made in transmission mode with the Si(111) monochromator detuned by 30% to eliminate the higher order harmonics in the beam. The sample thickness was chosen to give an absorption edge jump of about 0.3 at the Co K-edge. The 10% Co/CeO₂ catalysts were mixed with SiO₂ at a ratio of 1:4 and finely ground (<150 mesh) to obtain a homogeneous mixture. Approximately 8 mg of the mixture was then pelletized using a 6-mm polished steel die and placed inside a 5cm long quartz tube (6.5 mm ID) and supported with quartz wool plugs. The sample was then centered in a 45×2 cm controlled-atmosphere XAFS chamber that was fitted with Kapton® windows. The XAFS reactor set-up allowed continuous flow of the reactants as well as the isolation of the catalyst sample.
The catalyst in the controlled-atmosphere XAFS cell was heated to 400°C under nitrogen and kept at that temperature for 15 minutes. After the introduction of 3.6% H₂ in balance helium, XAFS spectra were collected every 12 minutes for a total reduction time of 60 minutes. WinXAS data analysis software package was used for analysis of the collected XAFS data following standard procedures outlined by Ressler [77]. Phase shifts and backscattering amplitudes used for the analysis of the data were obtained from the experimental reference spectra collected on reference compounds, i.e., CoO and Co-foil. XANES spectra were obtained by linear combination fitting of the Co₃O₄, CoO and Co foil profiles. The coordination parameters for Co-Co and Co-O-Co shells were obtained by isolation of the respective shells from the EXAFS spectrum using the difference method outlined earlier by Miller et al. [78]. The coordination numbers obtained through fitting the isolated shells are then divided by the fraction of that component obtained from XANES analysis for calculating the corrected coordination numbers.

4.2.2.5. Temperature-programmed re-oxidation

The oxidation/reduction characteristics of the samples were examined via temperature programmed re-oxidation (TPO) studies. 100 mg of the sample was packed in a ¼ “ OD quartz tube and loaded into a Carbolite MTF 10/15/130 furnace. Prior to the oxidation step, both catalysts went through an in-situ temperature-programmed reduction (TPR) procedure with 5% H₂/He until both of the reduction features, that correspond to Co₃O₄-to-CoO and CoO-to-Co
reduction steps \([20, 52, 54, 58, 93]\) were observed. Following the reduction step, the samples were kept under helium for water removal at the same temperature for 30 minutes and then cooled down to room temperature. The reactor effluents during reduction were monitored via a residual gas analyzer (MKS - Cirrus II) operated in scanning ion mode. A 100x multiplier detector was used to monitor the m/z signals of 2, 4, 17, 18, 32 and 44. The gas lines from the reactor outlet to the mass spectrometer were heated to prevent condensation in the lines during the procedure. The mass traces were allowed to stabilize at room temperature for 30 minutes while the sample was kept under a helium atmosphere. The sample is ramped with varying heating rates of 10, 13, 16 and 19 °C/min up to 700 °C under the flow of 5% \(\text{O}_2/\text{He}\) and the reactor effluent is monitored throughout the temperature ramp. Kissinger’s method \([94]\) was used for estimating the re-oxidation activation energies where the activation energies are correlated with the temperature \((T_m)\) at which the maximum rate of oxygen consumption at different heating rates occurs. The activation energy \(E_a\) can be calculated by plotting \(1/T_m\) against \(\ln (\Phi/T_m^2)\) which gives a straight line with its slope being equal to \(-E_a/R\), where \(R\) is the universal gas constant in J/K mol and \(\Phi\) stands for the heating rate in °C/min.

4.2.2.6 Methanol oxidation pulse reaction experiments

Methanol oxidation experiments were conducted using Autochem II 2920. The feed and product analysis were performed with a MKS – Cirrus II on-line mass spectrometer for the mass signals of m/z 30 for formaldehyde, m/z 31 for
methanol and m/z 44 for CO₂. Equal surface area of 4 m² was used for catalyst loading. The samples were pre-reduced as described previously in the section. Following reduction pretreatment, 4% methanol, 10 % oxygen with balance He was fed with a 12 ml sample loop. Methanol conversion; HCHO and CO₂ production were observed on line via MS. The signals were numerically integrated to compare and relate the peak areas to product concentrations.

4.2.2.7 CO₂ pulse chemisorption experiments

CO₂ pulse chemisorption experiments were conducted using a home built flow system utilizing an automated 6 port valve with a 3 ml sample loop. Gow Mac 20 series binary gas analyzer with TCD detector was used to analyze the product stream. He is used as the reference gas and 10% CO₂/He is used for chemisorption at 35 °C. Equal surface area of 2 m² was used for catalyst loading. The samples were pre-reduced as described previously in the section.

4.2.2.8 Post reaction temperature-programmed oxidation

Following steady state reaction experiments, catalysts underwent a temperature programmed oxidation experiment to examine any carbon deposition on the surface. In these experiments, 15 mg of post reaction catalyst is loaded into a 4 mm-ID quartz reactor with a quartz frit and is heated in a Carbolite, MTF 10/15/130 furnace under a 30 cc 10% O₂/He flow using a linear temperature program of 10 °C/min up to 500 °C. The reactor effluent was monitored via an MKS – Cirrus II on-line mass spectrometer for the mass signals
of m/z=32 for oxygen and m/z= 44 for carbon dioxide. CO evolution is not detected.

4.2.3 Steady-state catalytic activity testing

The steady-state ethanol steam reforming activity data were collected in the 350-500°C range using a fixed bed flow reactor system, which consisted of a feed system capable of delivering reactant mixtures of desired flow rate and composition, a 4 mm-ID quartz reactor with a quartz frit, and an on-line gas chromatograph. For each run, a 9-25 mg batch of the Co/CeO$_2$ catalyst or the CeO$_2$ support was packed inside the reactor. The reactor was placed inside a resistively-heated furnace (Carbolite, MTF 10/15/130) and the temperature was controlled by an Omega CSC232 PID temperature controller. Helium was used as the carrier gas and the reactants were introduced to the helium stream using a heated evaporator-syringe pump assembly. The reactants, water and ethanol, at a 10-to-1 molar ratio, were fed to an evaporator maintained at 230°C, using pulse-free syringe pumps (Cole-Parmer). The gas lines in contact with the reactant gas stream were heated to 130°C to prevent condensation. The steady-state reaction experiments were run in the kinetically controlled regime by maintaining the reaction conditions away from equilibrium at all temperatures. The reaction experiments were conducted with a feed stream concentration of 0.8% ethanol and 8% water in balance helium. The weight hour space velocities (WHSV) ranged between with 1.35 and 3.35 g EtOH (g cat)$^{-1}$ hr$^{-1}$ and was varied to allow for equal surface area or equal conversion comparisons. All catalyst
samples were subjected to the reduction pretreatments at 400 °C as explained earlier in the section.

The reported reactant conversion and product yield values are representative of the catalytic activity after steady state was reached at each temperature.

Ethanol conversion, hydrogen yield and selectivity of carbon containing species are defined as follows:

$$\text{Ethanol conversion}(\%) = \frac{\text{moles of ethanol converted}}{\text{moles of ethanol fed}} \times 100$$

$$H_2 \text{ yield}(\%) = \frac{\text{moles of } H_2 \text{ produced}}{6 \times (\text{moles of ethanol fed})} \times 100$$

$$\text{Selectivity of product } i(\%) = \frac{\# C \text{ atoms} \times (\text{moles of } i \text{ produced})}{6 \times (\text{moles of ethanol fed})} \times 100$$

The quantitative analysis of the reactor effluents was carried out by on-line gas chromatography (Shimadzu Scientific 2010) equipped with a Carboxen® column coupled with a pulsed discharge helium ionization detector (PDHID) which was used to separate and detect H₂, CO and CO₂ and a Q-Bond column with a flame ionization detector (FID) to separate and detect the hydrocarbon species. The carbon balances were always better than 95%.
4.3 Results and Discussion

4.3.1 Characterization

3.1.1 Surface Area, Pore volume and Dispersion

Surface areas and pore volumes of bare supports and supported catalysts are presented in Table 5. The rods had a higher surface area and higher pore volume than the cubes. The surface area and pore volume decreased for both supports when impregnated with Co, but the trend remained the same.

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂ - NR</td>
<td>100</td>
<td>0.39</td>
</tr>
<tr>
<td>CeO₂ - NC</td>
<td>60</td>
<td>0.12</td>
</tr>
<tr>
<td>Co/CeO₂ - NR</td>
<td>87</td>
<td>0.35</td>
</tr>
<tr>
<td>Co/CeO₂ - NC</td>
<td>40</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Figures 21a&b show the pore size distribution of ceria supports and Co/CeO₂ catalysts. Both CeO₂-NC and Co/CeO₂-NC showed the highest volume of pores in the 70 Å region whereas CeO₂-NR and Co/CeO₂-NR have a significantly different distribution with most of the pores being around 140 Å. The insets of Figure 21 show a more detailed view of the 20-40 Å range where it is evident that the CeO₂-NC sample shows a higher volume of pores in the 20-40 Å range. Moreover, following cobalt impregnation, the nanocubes sample loses
approximately half of the pores in this range whereas its nanorod counterpart shows no difference before or after the Co impregnation. These findings indicate that Co species have a higher tendency to occupy the small diameter pores on the Co/CeO$_2$-NC sample. The dispersion of metallic cobalt over the ceria morphologies was studied with N$_2$O as the probe molecule with low concentrations in order to have a mildly oxidizing atmosphere which has minimal chance of further oxidation of CoO to Co$_3$O$_4$ at 40 °C. Cobalt dispersion was found to be significantly lower with Co/CeO$_2$-NR with 7% as opposed to 21% with Co/CeO$_2$-NC, indicating either formation of larger Co particles on the nanorods or incomplete reduction of cobalt oxide to metallic Co, as this measurement probes only the metallic sites. In comparison, Co impregnated on commercial 25 nm ceria (Sigma Aldrich 71 m$^2$/g, 0.34g/cm$^3$) via the same method was reported to have 14% dispersion [18]. Another factor that may play a role in the dispersion is the different pore size distribution the nano-cube and nano-rod supports possess. The nano-cubes have a larger fraction of the smaller pores (20-40 Å range). Furthermore, cobalt impregnation of nano-cubes results in loss of these small pores, suggesting filling of these pores with Co species. If this is the case, the small pores may prevent the particles from agglomerating, resulting in a higher Co dispersion for the catalysts supported on ceria with the nano-cube morphology.
Figure 21 Pore size distribution of bare ceria supports and Co/CeO2 catalysts a) nanorods b) nanocube. The insets show the 20-40 Å region in more detail.

4.3.1.2 Transmission electron microscopy (TEM)

CeO₂ particles prepared by controlling the parameters used during the hydrothermal method exhibited two distinctly different morphologies, nano-rods
(CeO$_2$–NR) and nano-cubes (CeO$_2$–NC). The nano-cubes had particle sizes of 21± 7 nm. The average lengths and widths of nano-rods were 22± 6nm and 6± 1.3 nm, respectively. The histograms in Figure 22 show the distribution of particle sizes over a large sampling area through multiple micrographs to ascertain random sampling. Figure 23 shows the digital TEM micrographs of bare ceria supports. The images of cobalt-impregnated catalysts are shown in Figure 24. All micrographs were collected in the absence of the objective aperture, which enables lattice fringe diffraction, which, in turn, allows for the identification of the diffracted planes. Energy-dispersive X-ray spectroscopy (EDAX) was conducted in scanning transmission electron microscopy mode (STEM). Figure 25 shows very low cobalt counts for the Co/CeO$_2$–NR sample on the edges of the ceria nanorod morphologies. Spectra collected from inner regions as shown in Figure 25-II and 25-III show significant cobalt counts indicating higher cobalt content in the bulk of the sample. In comparison Figure 26 shows no such trend for cobalt dispersion, Figure 26-III carries information on the bulk of the sample and shows similar counts as Figure 26-I which is collected on the edge.

3.1.3 X-ray diffraction (XRD)

The X-ray diffraction patterns of the bare supports and supported catalysts are shown in Figure 27 where the most intense diffraction line occurs at a 2θ value of 28.5˚, which corresponds to the (111) plane of the cubic cerianite phase (ICDD 81-792). The diffraction lines at 2θ values of 33°, 47.5° and 56° were identified as (200), (220) and [311] planes of CeO$_2$, respectively. All of the
diffraction lines that correspond to CeO$_2$ were observed in supported catalysts as well. The Co/CeO$_2$ samples, however, also had a peak at $2\theta = 37^\circ$, which was associated with [311] Co$_3$O$_4$ plane (ICDD 42-1467). The peak intensities normalized with respect to the peak intensity of the (111) ceria plane are shown in Table 6 for both of the Co/CeO$_2$ samples. There was no change observed in the relative intensities of the diffraction lines resulting from the support due to Co impregnation. The ceria (200) planes for both samples were found to have similar relative intensities, however the (220) plane showed significantly higher diffraction for ceria nanocubes with 71% compared to 52% for Co/CeO$_2$-NR.

The theoretical work of Sayle et al. has shown that the formation energies for anion vacancies for cerium oxide surfaces are given as (111) > (100) > (110) [36, 95, 96]. Previous work on the subject has shown the importance of oxygen vacancies on the support material in ethanol steam reforming [8, 19], where introduction of oxygen vacancies improved the catalyst performance significantly.

The peak at $2\theta = 37^\circ$ for Co$_3$O$_4$ has a relative intensity of 18% for Co/CeO$_2$-NR as opposed to 5% for Co/CeO$_2$-NC. Higher intensities would suggest higher crystallinity and larger particle size for cobalt oxide on the surface. The results are consistent with the dispersion values reported above. It is also conceivable that anionic vacancies, which may constitute surface defects, may assist in stabilization of the metal oxide species during impregnation steps, thereby providing an increase in metallic dispersion. Previous studies performed over Cu/CeO$_2$ morphologies suggest the capability of ceria supporting finely dispersed
oxides which reduce into finely dispersed metals [35]. Co catalysts supported on similar morphologies appear to exhibit similar characteristics in terms of dispersion.

4.3.1.4 X-ray absorption spectroscopy (XAFS)

The reducibility as well as the coordination environment of the Co catalysts supported on different ceria morphologies was investigated via XAFS technique during time-on-stream reduction of the samples at 400°C under 3.6% H₂/He. Figure 28 presents the Co K-edge X-ray absorption near-edge spectra (XANES) collected over Co/CeO₂-NR and Co/CeO₂-NC catalysts during in-situ reduction. Co₃O₄, CoO and Co were used as reference compounds in linear combination fitting of the XANES region. These reference spectra are shown along with the sample to estimate the relative contribution of each cobalt state. Pristine samples were observed to have fully oxidized cobalt states, i.e. Co₃O₄ for both samples and these spectra were fitted with Co₃O₄ reference only, whereas the latter spectra were fitted with linear combinations of CoO and Co, thereby following the two step reduction scheme discussed previously [20, 52, 54, 58, 93].
Figure 22  Particle size distribution histograms a) CeO$_2$-NR particle length b) CeO$_2$-NR particle width c) CeO$_2$-NC particle size

Figure 23  TEM micrographs a) and b) CeO$_2$-NR c) and d) CeO$_2$-NC
Figure 24 TEM micrographs a) Co/CeO$_2$-NR b) Co/CeO$_2$-NC

Figure 25 STEM/EDAX Analysis for Co/CeO$_2$-NR
Figure 26 STEM/EDAX Analysis for Co/CeO₂-NC

Table 6 XRD intensities for Co/CeO₂ catalysts normalized with respect to CeO₂ (111)

<table>
<thead>
<tr>
<th></th>
<th>2θ</th>
<th>28.53°</th>
<th>33.06°</th>
<th>47.48°</th>
<th>36.85°</th>
<th>56.33°</th>
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<td></td>
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</tr>
<tr>
<td><strong>Respective Planes</strong></td>
<td>CeO₂ (111)</td>
<td>CeO₂ (200)</td>
<td>CeO₂ (220)</td>
<td>Co₃O₄ (311)</td>
<td>CeO₂ (311)</td>
<td></td>
</tr>
<tr>
<td>Co/CeO₂ - NR</td>
<td>100%</td>
<td>32%</td>
<td>52%</td>
<td>18%</td>
<td>39%</td>
<td></td>
</tr>
<tr>
<td>Co/CeO₂ - NC</td>
<td>100%</td>
<td>32%</td>
<td>71%</td>
<td>5%</td>
<td>61%</td>
<td></td>
</tr>
</tbody>
</table>
Figure 27 X-ray diffraction patterns for Co/CeO$_2$-NR and Co/CeO$_2$-NC and the bare supports

The extent of reduction values in Figure 29 showed Co/CeO$_2$-NR sample with 51% metallic Co after 1 hour of reduction as opposed to 79% shown by Co/CeO$_2$-NC. For comparison, Co impregnated on commercial 5 μm commercial ceria with a similar impregnation method yielded 62% metallic Co after reduction with 3.6% H$_2$ in He at 400 °C for 50 minutes [58]. The extent of reduction of the Co/CeO$_2$-NC sample is higher, which could be due to its higher dispersion and
the crystal plane structure of its support, which allows for higher anion vacancies, and hence higher oxygen mobility.

Magnitudes of $k^2$-weighted Fourier transforms (FT) of the cobalt K-edge EXAFS spectra collected over Co/CeO$_2$-NR and Co/CeO$_2$-NC samples are given in Fig 29 a and b. Three regions are observed: the 3.01 Å region (peak is located at 2.5 Å on Figure 29 due to uncorrected Fourier transform) which corresponds to scattering from the Co-O-Co bridging atoms in a CoO environment; the Co-Co coordination around the 2.50 Å region (2.11 Å uncorrected) where the high intensity signals the metallic character of the sample and the 2.11 Å (1.4 Å uncorrected) Co-O region. The Co-O shell as well as the Co-O-Co coordination were visible on both samples in their pristine states, in agreement with the XANES fittings which showed both samples to consist of Co$_3$O$_4$ prior to any reduction. After time-on-stream reduction at 400°C, Co/CeO$_2$-NC was observed to have a high intensity feature in the region of Co-Co shell whereas Co/CeO$_2$-NR sample shows a strong Co-O peak even after 60 minutes of reduction. The results are in agreement with the XANES region where Co/CeO$_2$-NC was shown to have a significantly higher metallic Co content after reduction.
Figure 28 XANES spectra for time-on-stream reduction in I) Co/CeO$_2$-NR II) Co/CeO$_2$-NC
Figure 29 Magnitude of $k^2$-weighted Fourier transforms of cobalt K-edge EXAFS spectra collected following time on stream reduction measurements at 400 °C in a) Co/CeO$_2$-NR b) Co/CeO$_2$-NC

4.3.1.5 Temperature programmed re-oxidation

After the ease of reducibility of the Co/CeO$_2$-NC catalysts was established, ease of re-oxidation of the catalysts was also examined using temperature-programmed re-oxidation experiments. These experiments can also provide a comparison of the oxygen accessibility in these materials. Prior to the oxidation step, both catalysts went through an in-situ temperature-programmed reduction (TPR) procedure until both of the features that correspond to Co$_3$O$_4$-to-CoO and CoO-to-Co reduction steps [20, 52, 54, 58, 93] were observed to ascertain complete reduction to metallic cobalt. Figure 30 shows the temperature programmed oxidation profiles obtained by changing the heating rate. The oxidizing gas was 5% O$_2$/He and the ramp rates used were 10, 13, 16 and 19 °C/min. The maximum oxidant consumption rate shifted from 223 °C to 270 °C for
Co/CeO$_2$-NR and from 196 °C to 278 °C for Co/CeO$_2$-NC as the heating rate was increased from 10°C/min to 19°C/min. The activation energy for re-oxidation can be calculated from the deflection point of the oxygen consumption curve as explained in the experimental section. The inset in Figure 30a shows the Arrhenius plot for re-oxidation for Co/CeO$_2$-NR with a slope of -2.616 which corresponds to an apparent activation energy ($E_a$) of 21.8 kJ/mol. Similarly, the inset in Figure 30b shows a slope of -0.975 and $E_a$= 8.1 kJ/mol for Co/CeO$_2$-NC. Based on the activation energies, re-oxidation of Co/CeO$_2$-NR takes place at a slower rate when compared to Co/CeO$_2$-NC. Co/CeO$_2$-NC catalysts, on the other hand, are easier to reduce and easier to re-oxidize. Both reduction and reoxidation are strongly affected by the oxygen mobility. The CeO$_2$-NC morphology, which preferentially exposes (110) plane is more likely to form anion vacancies, and hence has higher oxygen mobility. The higher dispersion observed over the Co/CeO$_2$-NC catalysts may also contribute to the ease of reduction/oxidation. Although the amount of oxygen vacancies is reported to be inversely proportional to the ceria particle size [49], it is not clear if it is a factor in our case since the dimensions of the particles, i.e., the edge of the cubes and the length of the rods are rather comparable.
Figure 30 Temperature-programmed re-oxidation of reduced Co/CeO2 samples at different ramp rates. Insets show determination of activation energies of re-oxidation using the Kissinger method a) Co/CeO2-NR b) Co/CeO2-NC

4.3.1.6 Methanol oxidation pulse reaction experiments

In order to probe the surface of both catalysts, pulse reaction experiments were performed using methanol oxidation as a probe reaction as demonstrated by Wachs and co-workers [97, 98] for several catalytic systems. A stream of 4% methanol, 10 % oxygen with balance He, was pulsed over the catalyst bed at
150°C, where the reaction products were monitored by an on-line mass spectrometer. CO$_2$ and HCHO were the only products resulting from the pulses. The quantification of the signals was done by integrating the respective peaks. A relatively large sample loop of 12 ml was used to keep the methanol conversions at a minimum. Methanol conversion was negligible in most pulses. Co/CeO$_2$-NR sample has shown very low CO$_2$ in the product stream where significant CO$_2$ peaks were present in Co/CeO$_2$-NC catalyst throughout the experiment. For the HCHO signal Co/CeO$_2$-NR sample has shown a significantly higher peak area in the first pulse. The following pulses have also shown higher peak areas compared to Co/CeO$_2$-NC. The HCHO signals were compared by the following equation, and were reported in Table 7.

\[
\frac{\left(\text{Area for m/z 30} \right)_{\text{rods}}}{\left(\text{Area for m/z 31} \right)_{\text{rods}}} / \frac{\left(\text{Area for m/z 30} \right)_{\text{cubes}}}{\left(\text{Area for m/z 31} \right)_{\text{cubes}}}
\]

\[(\text{m/z:30 peak area/ m/z: 31 peak area})_{\text{rods}} / (\text{m/z:30 peak area/ m/z: 31 peak area})_{\text{cubes}}.\]
Table 7 Methanol pulse oxidation results

<table>
<thead>
<tr>
<th></th>
<th>Relative Activity for HCHO NR/NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse 1</td>
<td>1.73</td>
</tr>
<tr>
<td>Pulse 2</td>
<td>1.07</td>
</tr>
<tr>
<td>Pulse 3</td>
<td>1.11</td>
</tr>
<tr>
<td>Pulse 4</td>
<td>1.06</td>
</tr>
</tbody>
</table>

The CO$_2$ data do not allow such quantification due to the lack of CO$_2$ in the NR sample. However, the calculated areas for the CO$_2$ in the pulses were between 4-5% of the methanol peaks in the feed. Since CO$_2$ formation over oxides is associated with basic sites, these results suggest a higher density of surface basic sites with the Co/CeO$_2$-NC sample.

4.3.1.7 CO$_2$ pulse chemisorption experiments

CO$_2$ uptake of reduced samples was investigated at 35 °C. CO$_2$ is an acidic molecule which is used to probe the surface basic sites. In Table 8, Co/CeO$_2$-NR sample has shown significantly lower CO$_2$ uptake with 1.1 $\mu$mol/m$^2$ as opposed to 7.4 $\mu$mol/m$^2$ in the Co/CeO$_2$-NC catalyst. Similar to the pulse oxidation experiments nanorods were found to have less basic sites as opposed to the nanocubes. Bare ceria supports have also shown a similar trend with CeO$_2$-NC having significantly higher CO$_2$ uptake. For both samples cobalt impregnated samples have shown around 1.3 times more CO$_2$ uptake than the ceria counterparts.
Table 8 CO₂ uptake rates of the samples at 35 °C for 2m² equal surface area basis

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO₂ Uptake (μmol/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/CeO₂-NR</td>
<td>1.1</td>
</tr>
<tr>
<td>CeO₂-NR</td>
<td>0.9</td>
</tr>
<tr>
<td>Co/CeO₂-NC</td>
<td>7.4</td>
</tr>
<tr>
<td>CeO₂-NC</td>
<td>5.5</td>
</tr>
</tbody>
</table>

4.3.2 Catalytic performance: Steady state catalytic activity testing

Steady state activity testing over Co/CeO₂-NR, Co/CeO₂-NC catalysts was performed to investigate the effect of different morphologies on ESR catalytic activity. Reaction experiments with blank reactors with the same feed conditions showed no discernible ethanol conversion within the temperature range 350-500 °C (data not shown), thereby it was assumed that gas phase ethanol reforming was negligible.

The products formed over both catalysts included H₂, CO₂, CO, CH₄, C₂H₄ and liquid products such as CH₃CHO, acetone, acetic acid, with the latter two observed only in trace amounts. The product distribution was seen to change significantly with temperature and support morphology. Reaction parameters were chosen to remain in the kinetically controlled region for all reaction experiments. The catalyst loadings were varied in order to enable equal surface area or equal conversion measurements, when needed.
A comparison of ethanol conversion levels, H\textsubscript{2} yields and selectivities for C-containing products is shown in Table 9 for Co/CeO\textsubscript{2}-NR and Co/CeO\textsubscript{2}-NC catalysts. These experiments were conducted keeping the total surface area of the catalyst in the reactor constant. Co/CeO\textsubscript{2}-NR was observed to have significantly lower conversions and lower H\textsubscript{2} yields than its counterpart in the entire temperature range. Even a more striking difference between these two catalysts is in the product distribution. For the Co/CeO\textsubscript{2}-NC catalyst, CO\textsubscript{x} is always the major C-containing product. Although CH\textsubscript{3}CHO is produced at lower temperatures over this catalyst, its selectivity rapidly declines and at 500°C, there is no acetaldehyde in the product stream. At this temperature, the only other C-

**Table 9** Steady state catalytic activity data for ESR catalysts WHSV = 2.90 (Co/CeO\textsubscript{2}-NR), 1.35 (Co/CeO\textsubscript{2}-NC) g EtOH (g cat)\textsuperscript{-1} hr\textsuperscript{-1}, C\textsubscript{EtOH} = 0.8% and H\textsubscript{2}O:EtOH = 10:1 (molar ratio)

<table>
<thead>
<tr>
<th>Products</th>
<th>350 °C (NR)</th>
<th>350 °C (NC)</th>
<th>400 °C (NR)</th>
<th>400 °C (NC)</th>
<th>450 °C (NR)</th>
<th>450 °C (NC)</th>
<th>500 °C (NR)</th>
<th>500 °C (NC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% C\textsubscript{2}H\textsubscript{5}OH Conversion</td>
<td>4.2</td>
<td>32.6</td>
<td>9.0</td>
<td>59.0</td>
<td>30.1</td>
<td>74.0</td>
<td>55.2</td>
<td>84.4</td>
</tr>
<tr>
<td>%H\textsubscript{2} Yield</td>
<td>0.7</td>
<td>25.0</td>
<td>2.9</td>
<td>53.8</td>
<td>8.8</td>
<td>68.7</td>
<td>17.8</td>
<td>80.0</td>
</tr>
<tr>
<td>% Selectivity</td>
<td>CO\textsubscript{2}</td>
<td>-</td>
<td>36.4</td>
<td>-</td>
<td>74.0</td>
<td>-</td>
<td>84.9</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>-</td>
<td>13.1</td>
<td>-</td>
<td>8.0</td>
<td>-</td>
<td>7.1</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{4}</td>
<td>-</td>
<td>4.8</td>
<td>-</td>
<td>2.3</td>
<td>-</td>
<td>3.0</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{2}H\textsubscript{4}</td>
<td>2.1</td>
<td>0.3</td>
<td>3.9</td>
<td>0.4</td>
<td>3.5</td>
<td>1.5</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{3}CHO</td>
<td>97.9</td>
<td>45.4</td>
<td>95.1</td>
<td>15.3</td>
<td>96.2</td>
<td>4.7</td>
<td>82.4</td>
</tr>
</tbody>
</table>
containing product is CH₄, with a selectivity of 1.9%. Ethylene, which is a product that signals dehydration activity, shows a very low selectivity, ranging between 0 and 1.5% over Co/CeO₂-NC. Co/CeO₂-NR catalyst, on the other hand, exhibits a very different behavior, with acetaldehyde being the major product at all temperatures. Over this catalyst, there is no discernible COₓ formation until a temperature of 500°C is reached. The other prominent product over this catalyst is C₂H₄. Considering that in ethanol steam reforming, the first step in the reaction network is the ethoxy formation, and acetaldehyde is the first stable intermediate to be formed [64, 65], product distribution over this catalyst indicates a reaction pathway that cannot proceed beyond the first hydrogen abstraction steps. This product distribution indicates a lack of C-C bond cleavage activity and an affinity for dehydration over the Co/CeO₂-NR catalyst.

**Table 10** Comparison of product distributions at equal ethanol conversion WHSV = 1.93 (Co/CeO₂-NR) and 3.34 (Co/CeO₂-NC) g EtOH (g cat)⁻¹ hr⁻¹, CEtOH= 0.8%

<table>
<thead>
<tr>
<th>Products</th>
<th>450 °C</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>405°C (NR)</td>
<td>405°C (NC)</td>
<td></td>
</tr>
<tr>
<td>% C₂H₅OH Conversion</td>
<td>50.9</td>
<td>51.9</td>
<td></td>
</tr>
<tr>
<td>%H₂ Yield</td>
<td>8.5</td>
<td>40.5</td>
<td></td>
</tr>
<tr>
<td>% Selectivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>-</td>
<td>78.0</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>0.3</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>C₂H₄</td>
<td>3.5</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>96.2</td>
<td>7.4</td>
<td></td>
</tr>
</tbody>
</table>
Table 11 Steady state catalytic activity for bare ceria supports WHSV = 3.33 (CeO2-NR) 2.03 (CeO2-NC) g EtOH (g cat)^{-1} hr^{-1}, C_{EtOH}= 0.8\% and H_{2}O:EtOH = 10:1 (molar ratio) 1, C_{EtOH}= 0.8\% and H_{2}O:EtOH = 10:1 (molar ratio)

<table>
<thead>
<tr>
<th>Products</th>
<th>350 °C</th>
<th>400 °C</th>
<th>450 °C</th>
<th>500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(NR)</td>
<td>(NC)</td>
<td>(NR)</td>
<td>(NC)</td>
</tr>
<tr>
<td>% C_{2}H_{5}OH Conversion</td>
<td>3.2</td>
<td>1.5</td>
<td>3.7</td>
<td>7.4</td>
</tr>
<tr>
<td>% H_{2} yield</td>
<td>0.2</td>
<td>0.7</td>
<td>0.4</td>
<td>3.8</td>
</tr>
<tr>
<td>% Selectivity</td>
<td>83.8</td>
<td>-</td>
<td>59.0</td>
<td>-</td>
</tr>
<tr>
<td>CO_{2}</td>
<td>-</td>
<td>3.3</td>
<td>3.6</td>
<td>2.2</td>
</tr>
<tr>
<td>CO</td>
<td>1.7</td>
<td>-</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>CH_{4}</td>
<td>1.0</td>
<td>1.0</td>
<td>4.5</td>
<td>35.0</td>
</tr>
<tr>
<td>C_{2}H_{4}</td>
<td>1.0</td>
<td>1.0</td>
<td>4.5</td>
<td>35.0</td>
</tr>
<tr>
<td>C_{2}H_{6}</td>
<td>11.9</td>
<td>0.5</td>
<td>2.5</td>
<td>0.9</td>
</tr>
<tr>
<td>CH_{3}CHO</td>
<td>97.2</td>
<td>-</td>
<td>89.7</td>
<td>-</td>
</tr>
</tbody>
</table>

Since the comparison presented above was made on an “equal surface area basis”, reaction experiments were repeated in such a way that equal conversion levels were achieved over both of the catalysts, keeping temperature and feed composition the same, but varying the WHSV. Table 10 presents the data obtained at 450°C. The conversion levels were equal within experimental error, around 51.2\%. The product distribution reiterated previous observations that Co/CeO_{2}-NR catalyst was unable to provide any activity for C-C bond cleavage, not progressing beyond the formation of acetaldehyde. The second major product produced over this catalyst was ethylene, suggesting some dehydration activity. CoO and Co_{3}O_{4} both are reported to exhibit activity for
selective dehydrogenation of ethanol into acetaldehyde [50, 52, 54, 79]. Also, the work of Martono and Vohs [56] shows that both Co and CoO were active for ethanol dehydrogenation.

In addition to the steady-state reaction experiments run over Co/CeO$_2$ catalysts, activity of bare CeO$_2$ morphologies was also examined using the same reaction parameters. The reactions were run using new reactors, which were not exposed to Co-containing species to prevent cross contamination. Table 7 shows ethanol conversion, H$_2$ yield and selectivity for carbon-containing products obtained over the two supports. Reaction runs show significant ethanol conversions over both samples, with CeO$_2$-NC sample being more active at every temperature tested. CeO$_2$-NC support also shows some reforming activity. The product distribution is seen to be very different over the CeO$_2$-NR, with acetaldehyde being the main product at all temperatures, whereas CeO$_2$-NC shows C-C cleavage activity, albeit at significantly lower rates than the cobalt catalyst. CeO$_2$-NC sample was also observed to produce more C$_2$ products at 400 and 450 °C, signaling dehydration activity.

There may be several reasons for the pronounced differences observed in the catalytic performances of the two supported catalysts. One possible explanation is the difference in dispersion. Since the dispersion over the Co/CeO$_2$-NC catalyst is three times higher than that of its counterpart, the number of accessible cobalt sites per surface area would be expected to be higher over this catalyst, resulting in higher conversions and H$_2$ yields. The
dispersion may also be linked to the different pore distribution exhibited by the two supports. The differences may also be due to differing extents of reduction of the two catalysts. The XAFS data show that at the end of a 1-hour reduction period, the percentages of the metallic sites for the Co/CeO$_2$-NC and Co/CeO$_2$-NR catalysts were 79% and 51%, respectively. The reduction trend shows that at the end of a two-hour reduction period, which is what is used as a pre-treatment procedure, the degrees of reduction for the two catalysts may be closer, but still not 100%. Our previous work [58] suggested that both Co$^0$ and Co$^{2+}$ sites have catalytic activity for ESR, however the intrinsic activity of the metallic sites, especially for complete reforming, was higher. The apparent activation energies calculated from TOF data shows a higher activation energy for the Co/CeO$_2$-NR. A third explanation for the pronounced differences in activity may be related to the preferred exposure of different crystal planes over the two supports. It is to be expected that the orientation of Co species on different crystal planes of ceria would be different. Since CeO$_2$-NC support preferentially exposes the (110) plane, it is conceivable that this support offers an orientation favorable to Co species. Since this plane is more likely to create anion vacancies and defects, increased oxygen mobility of the support may be another factor affecting activity and product distribution. It is also possible that the intrinsic activity of the supports may be contributing to the overall conversion and product distribution. It is likely that more than one of these factors may be contributing to the superior performance observed over the Co-CeO$_2$-NC
catalysts and molecular simulation studies, which are currently underway, can provide some answers, as reported in several related articles [45-47, 99].

In order to examine possible carbon deposition on the catalysts during ethanol steam reforming, post-reaction characterization experiments were performed. Catalysts that were kept on stream for a reaction experiment explained in the previous sections, underwent a temperature programmed oxidation process, where CO\textsubscript{x} species evolving from the surface were monitored by mass spectrometry as a function of temperature Figure 31 shows the m/z= 32, 44 and 28 signals that are traced for O\textsubscript{2}, CO\textsubscript{2} and CO. CO evolution was found to be negligible. In Figure 31 a\&b, both profiles are reported on the same scale. Co/CeO\textsubscript{2}-NC catalyst shows significantly higher CO\textsubscript{2} evolution compared to Co/CeO\textsubscript{2}(NR), with two peaks at 185 °C and 210 °C. Co/CeO\textsubscript{2}-NR sample shows a wide peak centered at 260 °C. The limited C-C cleavage activity in nanorods shows that there is a significantly lower amount of carbon on the catalyst surface. For the Co/CeO\textsubscript{2}-NC sample, a recent review by Mattos et al. has shown that carbon deposition does not necessarily lead to deactivation and many catalysts operate despite some carbon deposition for extended periods of time [69]. It should be noted that although the ethanol feed is relatively dilute with 0.8% and may act as a deterrent to coking, the gas hourly space velocities used for this studies are significant with ~100000 hr\textsuperscript{-1}. In our previous work, neat conditions (no diluents) were used for ethanol steam reforming and catalysts were found to be stable for 70 hours time-on stream [18]. Figure 32 shows TEM
images of post-reaction samples and show no apparent signs of sintering or loss of morphology following the reaction.

Figure 31 Post-reaction TPO a) Co/CeO$_2$-NR b) Co/CeO$_2$-NC
Figure 32 Post reaction TEM micrographs a) CeO$_2$-NR b) CeO$_2$-NC
4.4 Conclusions

Co catalysts supported on ceria with two different morphologies, nano-rods and nano-cubes, were examined for their performance in ethanol steam reforming. TEM images showed nano-rods and nano-cubes to have average particle sizes of 20x6 nm and 23x23 nm, respectively. XRD technique showed nano-cubes preferentially exposing the (110) crystal plane, which are more likely to form oxygen vacancies and surface defects. Co catalysts supported on ceria nano-cubes had a higher metallic dispersion and were easier to reduce and to reoxidize, as shown by dispersion measurements and XAFS and TPR/TPD analyses. These catalysts also were better reforming catalysts for ethanol, showing high yields for H₂ and CO₂. The catalysts supported on nano-rods, on the other hand, showed very little activity for C-C bond cleavage, yielding only dehydrogenation and dehydration products. The superior performance of the catalysts supported on nano-cubes may be due to a combination of factors, including higher Co dispersion, ease of reducibility, higher occurrence of surface basic sites, higher oxygen mobility of the support as well as intrinsic activity of the supports themselves.
5.1 Introduction

Co catalysts supported on ceria supports with two different particle sizes, one in the micro- and the other in the nano-range, were investigated for their ethanol and ethylene steam reforming performance. Pre- and post-reaction characterization techniques, including high resolution transmission electron microscopy, temperature-programmed oxidation, dispersion and pore size measurements. In-situ XRD and XAFS studies were performed to examine the reducibility of the catalysts. Steady-state-activity testing has shown nano-particles to have a higher reforming activity for ethanol, but also high ethylene yields. In spite of the high ethylene yields, catalysts supported on nano-particles proved to be highly resistant to coking while the catalysts supported on larger ceria particles suffered from coke formation. Reforming experiments performed with ethylene showed significant differences in activity and stability. Bare supports were also tested for activity and the nano-particle support showed high dehydration activity. Operando DRIFTS experiments performed during ESR showed differences in surface species. Pulse experiments performed to use methanol oxidation as a probe reaction suggested differences in the relative abundance of redox cites and basic sites. The superior performance of the
catalysts supported on nano-particles is thought to be due to a combination of factors including increased reducibility, improved metal dispersion and a difference in relative abundance of redox sites on the surface.

5.2 Experimental

5.2.1 Catalyst preparation

Two ceria supports with different particle sizes were prepared. The support with a particle size in the 0.1-0.2 micrometer range (denoted as CeO$_2$-MP) was prepared by calcining Sigma Aldrich 99.999% $<$5µm CeO$_2$ at 450 °C for 3 hours in air. The support with a particle size in the 5-8 nanometer range (CeO$_2$-NP) was prepared via the hydrothermal method [92] where 1.5 g Ce(NO$_3$)$_3$·6H$_2$O (Sigma Aldrich 99.9%) was dissolved in 9.4 ml water and combined with 25 ml of 11 wt% NaOH. The resulting suspension was stirred for 15min under room temperature where Ce(OH)$_3$ particles precipitated. The solution was kept at room temperature for 24 hours before filtration of the solids. Remaining solids were rinsed with approximately 2 liters of deionized and distilled water until a pH value of 7 was reached. Following the neutralization step, the solids were dried in air at 90°C overnight. The dried Ce(OH)$_3$ precursors were calcined at 450 °C for 3 h under air. Impregnation of 10% (by weight, metallic) cobalt on both MP and NP supports was carried out via the incipient wetness impregnation method with Co(NO$_3$)$_2$ (Aldrich, 99.999%) dissolved in 200 proof ethanol (Decon Labs) and applied onto the support in five consecutive steps by drying the impregnated catalyst at 110°C overnight in between each step to improve the homogeneity of
the resulting catalyst. Following the final impregnation and drying step, the catalyst was calcined at 450°C for 3 hours under air flow.

5.2.2 Catalyst characterization

5.2.2.1 Surface area, pore volume and metal dispersion

The BET surface area and pore volume of the samples were measured by a Micromeritics ASAP 2020 (accelerated surface area and porosimetry) instrument, using nitrogen adsorption/desorption isotherms collected at liquid nitrogen temperature. The desorption branch of the isotherm was used to determine the BJH pore size distributions with pore sizes around 18 Å and 8.5 Å for Co/CeO₂(MP) and Co/CeO₂(NP) catalysts, respectively. Before measurement, the catalyst was degassed for 12 hours at 130°C under a vacuum better than 2 μm Hg.

The dispersion measurements were performed using N₂O chemisorption technique outlined earlier by Jensen et al. [73] For these measurements, 100mg of the sample 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% H₂ in He for 2 hours, which are the same parameters used for reduction pre-treatment prior to reaction experiments. The reactor was then flushed with He at the same temperature and cooled under He flow. N₂O chemisorption was performed by introducing a stream of 3%N₂O/He to the reactor at 40°C. Species in the m/z=12 to m/z=46 range were monitored via an MKS – Cirrus II on-line mass spectrometer. The mass
spectrometer was calibrated for instrumental sensitivity factors. The contribution of N$_2$O fragment to the m/z=28 trace has been subtracted to quantify the N$_2$ amount desorbing from the sample surface. Throughout the experiment, N$_2$O 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-microliter-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 a 1:1 Co:O ratio.

5.2.2.2 TEM

A Phillips Tecnai F20 instrument equipped with a field emission gun and operated at 200 kV was used for transmission electron microscopy (TEM). All images are collected in the brightfield. Samples were suspended in ethanol and were sonicated for 10 minutes for high dispersion. The resulting emulsion was deposited immediately after sonication on a 200 mesh copper grid coated with lacey carbon to prevent agglomeration of the particles. ImageJ processing software is used for analysis of the TEM digital micrographs. Particle histograms are obtained by using the “Measure function” of the ImageJ software by using a minimum of 30 particles. For post-reaction characterization, samples that were kept on-line for a minimum of 12 hours were used without further processing.
5.2.2.3 Operando XRD

The operando XRD patterns during reduction of Co/CeO$_2$(MP) and NP samples were collected on a Bruker D8 Advance X-ray diffractometer with monochromatic Cu Kα radiation (λ=1.5418 Å) through a tube operated at 40 kV and 50 mA and equipped with an Anton Paar HTK1200 controlled-atmosphere oven. A linear heating rate of 7°C/min was used and the temperature was held constant at each temperature step for at least 30 minutes prior to the collection of the diffraction patterns. Both samples were reduced stepwise under 30 cc/min 5% H$_2$/He starting from room temperature in 50 °C increments up to 500 °C. The sample was then cooled under hydrogen flow to room temperature. After flushing the in-situ chamber with an inert, temperature programmed reoxidation of the sample was performed with 5% O$_2$/He following the same temperature steps.

5.2.2.4 In-situ XAFS

Catalyst samples oxidized or reduced in situ were investigated in terms of their Co coordination environment using controlled-atmosphere X-ray absorption fine structure (XAFS) technique. The spectra were collected for the Co K-edge (7709 eV) at the bending magnet beamline (5BM-D) of the Dow-Northwestern-DuPont Collaborative Access Team (DND-CAT) of the Advanced Photon Source, Argonne National Laboratories. The measurements were made in transmission mode with the Si(111) monochromator detuned by 30% to eliminate the higher order harmonics in the beam. The sample thickness was chosen to give an absorption edge jump of about 0.3 at the Co K-edge. The 10% Co/CeO$_2$
catalysts were mixed with SiO₂ at a ratio of 1:4 and finely ground (<150 mesh) to obtain a homogeneous mixture. Approximately 8 mg of the mixture was then pelletized using a 6-mm polished steel die and placed inside a 5cm-long quartz tube (6.5 mm ID) and supported with quartz wool plugs. The sample was then centered in a 45×2 cm controlled-atmosphere XAFS chamber that was fitted with Kapton® windows. The XAFS reactor set-up allowed continuous flow of the reactants as well as the isolation of the catalyst sample.

For both samples the XAFS cell was heated to 400 °C under helium and the XAFS spectra for the oxidized catalyst was collected. The catalyst was then reduced in-situ under 3.6% H₂/He for 1 hour after which spectra collection was started. Phase shifts and backscattering amplitudes used for the analysis of the data were obtained from the experimental reference spectra collected on reference compounds, i.e., Co₃O₄, CoO and Co-foil. XANES spectra were obtained by linear combination fitting of the Co₃O₄, CoO and Co foil profiles. The coordination parameters for Co-Co and Co-O-Co shells were obtained by isolation of the respective shells from the EXAFS spectrum using the difference method outlined earlier by Miller et al. [78]. The coordination numbers obtained through fitting the isolated shells are then divided by the fraction of that component obtained from XANES analysis for calculating the corrected coordination numbers.
5.2.2.5 Diffuse reflectance infrared spectroscopy (DRIFTS)

Operando diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) experiments were performed using a Thermo NICOLET 6700 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a KBr beam splitter. The DRIFTS cell consisted of a Smart Collector™ controlled-atmosphere chamber with ZnSe windows. Prior to the introduction of the steam reforming feed to the controlled-atmosphere chamber, there was a pre-reduction step, which consisted of heating the catalyst to 400 °C under a flow of He (30 ccm) for 30 minutes, followed by reduction for 2 hours in 5% H₂/He (30 ccm) at the same temperature and purging with He (30 ccm) for 1 hour at 450°C. Following the aforementioned treatment step, the temperature was raised to 500°C under helium flow and the background spectra were collected every 50°C, during cooling. At 25°C, another background spectrum was collected and the ethanol steam reforming feed with a water-to-ethanol molar ratio of 10:1 and 0.3% ethanol concentration was introduced to the DRIFTS chamber. The feed stream was obtained by flowing helium through two separate bubblers containing water and ethanol kept at room temperature. At each temperature, the reaction was allowed to progress for 30 minutes before collecting sample spectra while reactants are still flowing through the DRIFTS chamber. After the collection of the sample spectrum, the DRIFTS chamber was flushed with helium for 8 minutes and another sample spectrum was collected at the same temperature. Following the collection of this second spectrum, the temperature was increased under the
reaction feed and the procedure was repeated at 50°C intervals up to 500 °C. Any oxygen impurity in helium was removed by an O\textsubscript{2} trap (VICI VALCO Instruments, HP2 He purifier) prior to feeding the gas to the DRIFTS chamber.

5.2.3 Catalytic performance

5.2.3.1 Steady state catalytic activity testing

The steady-state ethanol steam reforming activity data were collected in the 350-500°C range using a fixed bed flow reactor system, which consisted of a feed system capable of delivering reactant mixtures of desired flow rates and compositions, a 4 mm-ID quartz reactor with a quartz frit, and an on-line gas chromatograph. For each run, a 9-50 mg batch of the Co/CeO\textsubscript{2} catalyst or the bare CeO\textsubscript{2} support was packed inside the reactor. The reactor was placed inside a resistively-heated furnace (Carbolite, MTF 10/15/130) and the temperature was controlled by an Omega CSC232 PID temperature controller. Helium was used as the carrier gas and the reactants were introduced to the helium stream using a heated evaporator-syringe pump assembly. The reactants, water and ethanol, at a 10-to-1 molar ratio, were fed to an evaporator maintained at 230°C, using pulse-free syringe pumps (Cole-Parmer). The gas lines for the reactant gas stream were heated to 130°C to prevent condensation. The steady-state reaction experiments were run in the kinetically controlled regime by maintaining the reaction conditions away from equilibrium at all temperatures. The Weisz-Prater
criterion for internal diffusion effects and Mear’s Criterion for external diffusion effects, were used to verify that there were no transport limitations in the system.

The reaction experiments were conducted with a feed stream concentration of 0.8% ethanol with 8% water in balance helium. The bed volumes in each experiment were fixed using silica as an inert diluent. The gas hour space velocity (GHSV) was kept constant at 72,000 h\(^{-1}\). The catalyst comparisons were based on equal surface area in the reactor. Co/CeO\(_2\) samples were run with 0.4 m\(^2\), whereas the ceria supports were run with 0.8 m\(^2\) surface area. All catalyst and support samples were subjected to the reduction pretreatments at 400 °C as described earlier in the section.

For reactions with ethylene as the reactant, all parameters were kept identical, except replacing 0.8% ethanol with 0.8% ethylene.

The reported reactant conversion and product yield values are representative of the catalytic activity after steady state was reached at each temperature.

Ethanol conversion, hydrogen yield and selectivity of carbon containing species are defined as follows:

\[
\text{EtOH conversion(\%)} = \frac{\text{moles of EtOH converted}}{\text{moles of EtOH fed}} \times 100
\]

\[
\text{H\textsubscript{2} yield(\%)} = \frac{\text{moles of H\textsubscript{2} produced}}{6 \times (\text{moles of EtOH fed})} \times 100
\]

\[
\text{Yield of C-containing product } i(\%) = \frac{\# \text{ C atoms} \times (\text{moles of } i \text{ produced})}{2 \times (\text{moles of EtOH fed})} \times 100
\]
Similar definitions were used for conversion and product yields in ethylene reforming reactions.

The quantitative analysis of the reactor effluents was performed by on-line gas chromatography (Shimadzu Scientific 2010) equipped with a Carboxen® column coupled with a pulsed discharge helium ionization detector (PDHID) which was used to separate and detect H₂, CO and CO₂ and a Q-Bond column with a flame ionization detector (FID) to separate and detect the hydrocarbon species. The detectors were calibrated using samples of known concentrations and the responses of the detector were recorded. The procedure was repeated at different concentrations to obtain a calibration curve. Calibration was repeated periodically. The carbon balances were always better than 95%.

5.2.3.2 Post-reaction temperature-programmed oxidation

Following stability and steady state reaction experiments, catalysts underwent a temperature programmed oxidation experiment to examine any carbon deposition on the surface. In these experiments, 15 mg of post reaction catalyst is loaded into a 4 mm-ID quartz reactor with a quartz frit and is heated in a Carbolite, MTF 10/15/130 furnace under a 30 cc 10% O₂/He flow using a linear temperature program of 10 °C/min up to 500 °C. The reactor effluent was monitored via an MKS – Cirrus II on-line mass spectrometer for the mass signals of m/z=32 for oxygen, m/z= 44 for carbon dioxide and m/z=28 for carbon monoxide. CO signal was corrected for contribution from the CO₂ fragmentation.
5.2.3.3 Methanol oxidation pulse reaction experiments

Methanol oxidation experiments were conducted using Autochem II 2920. The feed and product analysis were performed with a MKS – Cirrus II on-line mass spectrometer for the mass signals of m/z 30 for formaldehyde, m/z 31 for methanol and m/z 44 for CO$_2$. Equal surface area of 2.24 m$^2$ was used for catalyst loading. The samples were pre-reduced as described in the previous section. Following reduction pretreatment, pulses of 4% methanol, 10 % oxygen with balance He were fed to the reactor with a 1ml sample loop. Feed and product pulses were analyzed by mass spectrometry. The signal for HCHO was corrected for contribution from the fragmentation of methanol. The signals were numerically integrated to compare and relate the peak areas to relative product concentrations.

5.3 Results and Discussion

5.3.1 Characterization

3.1.1 Surface Area, Pore volume and Dispersion

Surface areas and pore volumes of the supported catalysts and bare supports are shown in Table 12. The commercial support as well as the Co/CeO$_2$(MP) catalyst was found to have significantly lower pore volume than the nano-particles prepared by the hydrothermal method.
Table 12 Surface area and pore volume of bare supports and Co/CeO2 catalysts measured using N2 physisorption

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂ - MP</td>
<td>10</td>
<td>0.04</td>
</tr>
<tr>
<td>CeO₂ - NP</td>
<td>100</td>
<td>0.17</td>
</tr>
<tr>
<td>Co/CeO₂ - MP</td>
<td>9</td>
<td>0.03</td>
</tr>
<tr>
<td>Co/CeO₂ – NP</td>
<td>56</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Dispersion of metallic cobalt over both samples (shown in Table 13) was studied with the Jensen’s [73] method using N₂O as a probe molecule for chemisorption onto the reduced surface. 3% N₂O was fed to the sample following a reduction pre-treatment, outlined in the previous section, thereby creating a mildly oxidizing atmosphere which has minimal chance of further oxidizing CoO species to Co₃O₄. Cobalt dispersion was found to be significantly higher with the Co/CeO₂(NP) with 24% as opposed to 2% with Co/CeO₂(MP) sample, indicating formation of smaller Co clusters on the nanoparticles. Since this technique probes only the metallic sites, it is also possible that the higher degree of reduction observed over the Co/CeO₂(NP) gives a higher dispersion value. It is more likely, however, that the observed difference is the culmination of both effects, i.e., smaller particles and easier reducibility, as discussed in the following sections.
Table 13 Co dispersion of Co/CeO2 catalysts determined using N2O chemisorption.

<table>
<thead>
<tr>
<th></th>
<th>Co dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/CeO2 – MP</td>
<td>2</td>
</tr>
<tr>
<td>Co/CeO2 - NP</td>
<td>24</td>
</tr>
</tbody>
</table>

5.3.1.2 Transmission electron spectroscopy (TEM)

A histogram of the particle size distribution for ceria supports with nano- and micro-sized particles is shown in Figure 33. The average particle sizes for CeO2(MP) and CeO2(NP) are 95 nm and 6.5nm, respectively.

The digital micrographs of the bare ceria supports and the supported catalysts for the nano- and micro-particle samples are shown in Figures 34 and 35, respectively. Figure 34a shows large particles of the support, with various sizes, ranging from 20 nm to 0.2μm. Figure 34b shows Co/CeO2(MP) particles where cobalt oxide particles were located on bulk ceria with limited dispersion. The same figure shows a Co3O4 particle positioned on a larger ceria particle, which allows for lattice fringe identification with 0.14 nm d-spacing, associated with the (220) Co3O4 plane (ICDD 42-1467). Figure 35a&b show CeO2(NP) and Co/CeO2(NP) micrographs where the particle size range is smaller, between 5-8 nanometers. Both ceria and Co3O4 particles were identified with lattice fringe diffractions with d-spacings of 0.31nm for the (111) ceria plane (ICDD 81-792) and 0.29nm for the (220) Co3O4 plane (ICDD 42-1467).
5.3.1.3 Operando X-ray diffraction (XRD)

Operando XRD technique was used to investigate the reduction and re-oxidation characteristics of Co/CeO$_2$(MP) and Co/CeO$_2$(NP) (Figures 36 and 37, respectively). Diffraction patterns were acquired during reduction at 50°C intervals (Figure 36a and 37a). After the temperature was brought to room temperature and the reducing gas mixture was flushed from the operando cell, an oxidizing gas mixture was introduced and diffraction patterns were taken during re-oxidation at 50°C intervals (Figure 36b and 37b). In all of the XRD patterns obtained, a well-resolved ceria peak was observed at 2θ value of 33° which corresponds to the (200) plane in the face-centered cubic cerianite structure (ICDD #34-394). The ceria peaks persisted through reduction and oxidation and were the most prominent feature in the patterns.
**Figure 34** TEM images of (a) CeO$_2$(MP) support and (b) Co/CeO$_2$(MP) catalyst
Figure 35 TEM images of (a) CeO$_2$(NP) support and (b) Co/CeO$_2$(NP) catalyst
Cobalt was observed in fully oxidized form prior to reduction as seen through the diffraction lines at $2\Theta=31^\circ$ and $37^\circ$, which correspond to the (220) and (311) planes of $\text{Co}_3\text{O}_4$ planes, respectively (ICDD #42-1467). Additional diffraction lines corresponding to different Co species emerged at different stages of reduction and oxidation processes and included a peak at $2\Theta =44^\circ$ associated with the (111) plane of metallic cobalt (ICDD #15-806) and the weakly resolved peaks at $2\Theta$ values of $36.5^\circ$ and $42.4^\circ$ signifying the (111) and (200) planes of $\text{CoO}$ (ICDD #43-1004).

Although both catalysts exhibited these features at some stage of their reduction or oxidation process, there were significant differences between the diffraction patterns corresponding to the two samples. One of the pronounced differences was the significant line broadening exhibited by the $\text{Co/CeO}_2$(NP) catalyst. Scherrer calculations have shown ceria particle sizes to be around 95nm and 8.7 nm, for $\text{Co/CeO}_2$(MP) and $\text{Co/CeO}_2$(NP), respectively. The particle sizes for $\text{Co}_3\text{O}_4$ species were found to be around 25 nm and 5nm for the same two samples. Peak broadening effect was fairly constant through the two temperature programs indicating negligible amount of catalyst or support sintering.

Although both catalysts in their pristine form were fully oxidized and showed $\text{Co}_3\text{O}_4$ and ceria peaks only, they were seen to reduce and re-oxidize at different temperatures. During the reduction process of $\text{Co/CeO}_2$(MP) (Figure 36a), diffraction lines corresponding to $\text{CoO}$ were seen to emerge at $300^\circ\text{C}$ and
both Co$_3$O$_4$ and CoO phases were found to co-exist up to 400 °C. Following the reduction at 400 °C, Co$_3$O$_4$ was no longer visible. Instead, a peak corresponding to metallic cobalt was observed at 44°. This behavior indicates a stepwise reduction of cobalt species from Co$_3$O$_4$ to CoO and finally into Co[22]. It is important to note that three oxidation states of Co were not seen to co-exist at any temperature. The catalyst was fully reduced at 450 °C. After the pattern was collected at 500 °C, the sample temperature was decreased to room temperature and another diffraction pattern was collected (data not shown) and the sample was seen to retain its metallic character. Re-oxidation of the sample in Figure 36b showed a rapid oxidation process, where the Co species were found to be metallic at 200°C and fully oxidized at 250 °C, skipping of the CoO phase altogether. This suggests either a single step re-oxidation of the cobalt species or a very rapid re-oxidation where intermediate phases are short lived.

Over the Co/CeO$_2$(NP) sample, Co$_3$O$_4$ phase was observed to reduce at lower temperatures, indicated by the disappearance of the 2θ = 31° and 37° peaks above 250°C. In comparison, these features were visible even at 350 °C with the Co/CeO$_2$(MP) sample. Metallic cobalt formed between 350 and 400 °C and was seen to co-exist with CoO phases up to 500 °C. The re-oxidation profile in Figure 37b shows rapid re-oxidation of the sample showing CoO species at temperatures as low as 150°C. Co$_3$O$_4$ peaks form in the following temperature steps of 200 and 250 °C. The reduction of Co$_3$O$_4$, as well as re-oxidation of the metallic cobalt into CoO was found to take place at lower temperatures for the
Co/CeO$_2$(NP) sample. The diffraction lines for Co species in this sample had a lower intensity compared to Co/CeO$_2$(MP) sample, which may be due to the lack of long range order in the small particles found in the Co/CeO$_2$(NP) sample.

5.3.1.4 X-ray absorption spectroscopy (XAFS)

The reducibility and the coordination environment of the Co catalysts were investigated via XAFS technique during in-situ reduction of the samples at 400°C under 3.6% H$_2$/He. Figure 38 presents the Co K-edge X-ray absorption near-edge spectra (XANES) collected over Co/CeO$_2$(MP) and Co/CeO$_2$(NP) catalysts before and after reduction pretreatment. Co$_3$O$_4$, CoO and Co were used as reference compounds in linear combination fitting of the XANES region. The reference spectra are shown in Figure 38 together with the sample spectra to indicate the relative contribution of the cobalt states. Both samples have shown fully oxidized states of Co$_3$O$_4$ initially and these spectra were fitted with Co$_3$O$_4$ reference only. The reduced samples were fitted with linear combinations of CoO and Co due to the two-step reduction scheme of cobalt species [20, 52, 54, 58, 93].

Following 1 hour of reduction, the Co/CeO$_2$(NP) catalyst was found to be almost completely reduced to metallic Co within experimental error, whereas Co/CeO$_2$(MP) sample consisted of 88% metallic Co and 12% CoO after the same pretreatment. The extent of reduction was found to be higher with the Co/CeO$_2$(NP) sample which can be attributed to the small particle size and high metallic dispersion of the sample.
Figure 36 Operando X-ray diffraction patterns of Co/CeO2(MP) taken during a) reduction b) reoxidation
Figure 37 Operando X-ray diffraction patterns of Co/CeO$_2$(NP) taken during
a) reduction, b) reoxidation
Magnitudes of $k^2$-weighted Fourier transforms (FT) of the cobalt K-edge EXAFS spectra collected over Co/CeO$_2$(MP) and Co/CeO$_2$(NP) samples are shown in Figure 39. The 3.01 Å region corresponded to Co-O-Co bridging atoms in an oxidized cobalt environment. This region is located at 2.5 Å on the figure due to the uncorrected nature of the Fourier transform. The Co-Co coordination around the 2.50 Å region (2.11 Å uncorrected) and the 2.11 Å (1.4 Å uncorrected) indicated metallic Co-Co shell and Co-O bond, respectively. Both samples have shown large peaks at the 2.11 and 3.01 regions prior to reduction, which is consistent with Co$_3$O$_4$ encountered in XANES. Following reduction, the Co-O region and Co-O-Co bridging region were still visible on the Co/CeO$_2$(MP) sample, indicating a more oxidized cobalt environmental state than Co/CeO$_2$(NP) which is consistent with the oxidation state information gained from the XANES region.

Table 14 summarizes the EXAFS fits on the FT magnitude spectra following the reduction pre-treatment. The contributions of Co-Co were obtained by isolating the respective shell from the inverse FT. Co foil and CoO were used as the reference compounds and were analyzed by the same procedure. The coordination parameters obtained through fitting the EXAFS region for Co/CeO$_2$(MP) and Co/CeO$_2$(NP) were given in Table 14. The XANES data suggests that cobalt species exist in the form of Co and CoO, therefore true coordination numbers were calculated by dividing the calculated fit by the fraction of the respective component from the XANES analysis. The fits suggest bulk-like
particles for the Co species of the Co/CeO$_2$(MP) sample with a calculated coordination number (CN) of 11.0, whereas Co/CeO$_2$(NP) shows a Co-Co shell after reduction with a CN of 8.9, which indicates smaller metallic particle size for the sample. XAFS is a bulk technique, which can provide qualitative particle size comparison under operando conditions. The CN information provides us with true in-situ metallic particle size comparison for both samples.

5.3.1.5 Operando DRIFTS during Ethanol Steam Reforming

The effect of ceria particle size on the evolution of surface intermediates and the reaction pathway during ESR over Co/CeO$_2$(MP) and NP catalysts was investigated in the temperature range of 25°C-500°C using DRIFTS. Operando DRIFT spectra collected while ethanol steam reforming reaction is progressing over the catalysts are presented in Figures 40a and 41a. Following each temperature step, the reaction chamber was flushed with He and spectra were collected under He to identify the species remaining on the surface. These spectra are presented in Figures 40b and 41b.
Figure 38 XANES spectra for oxidized and reduced Co/\text{CeO}_2\text{(MP)} and Co/\text{CeO}_2\text{(NP)}
Figure 39 Magnitude of $k^2$-weighted Fourier transforms of cobalt K-edge EXAFS spectra
Table 14 Results of EXAFS fitting at the Co K-edge for the Co/CeO2 catalysts following in-situ reduction

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scatter</th>
<th>CN</th>
<th>CN fit</th>
<th>R (Å)</th>
<th>Δσ (Å²)</th>
<th>ΔE₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/CeO₂(MP)</td>
<td>Co-Co</td>
<td>11.0</td>
<td>9.7</td>
<td>2.50</td>
<td>0.008</td>
<td>-1.62</td>
</tr>
<tr>
<td>Co/CeO₂(NP)</td>
<td>Co-Co</td>
<td>8.9</td>
<td>8.4</td>
<td>2.49</td>
<td>0.007</td>
<td>-1.65</td>
</tr>
</tbody>
</table>

Spectra collected over the two catalysts have many bands in common, although there are some noticeable differences as well. The 3600-3200 cm⁻¹ broad band observed in all six figures is an indicator of surface hydroxyls and adsorbed water. It was visible upon introduction of the ethanol-steam feed mixture to the chamber at room temperature. Peak intensity is seen to diminish with temperature and the peak disappears at 200 °C. The 1650 cm⁻¹ band is associated with molecularly adsorbed water [24] and is not visible above 100 °C. A control experiment was conducted where pure steam was fed into the chamber (data not shown) and yielded 1650 cm⁻¹ peak as well as the rotational bands seen in the 1800-1300 cm⁻¹ region. It should be noted that these localized bands seen in Fig 8a and 9a are independent of the signal-to-noise ratio and arise from the water vapor in the chamber, which is necessary for the true operando nature of the experiment. Upon flushing the chamber with He, these rotational bands disappear.

Figures 40a and 41a show several other bands which follow the same trends, namely 2967(2931 with NP), 1047 (1049) and 885 cm⁻¹ bands were
observed at 25°C under the ethanol steam reforming reaction feed. These bands arise from interaction of ethanol with the catalyst surface and have been associated with $\nu_s$ (CH$_3$), $\nu$ (CO) and (C-C) stretch of surface ethoxy species, respectively. Formation of ethoxy species is indicative of dissociative adsorption of ethanol on the catalyst, yielding surface ethoxy and hydroxy species [24, 59-63]. Most of the ethoxy species were not stable during helium flush.

Starting from 100°C, both catalysts exhibit 1577 cm$^{-1}$ and 1430 cm$^{-1}$ bands which constitute the fingerprint region for $\nu_{as}$ (OCO) and $\nu_s$ (OCO) vibrations, respectively [23]. Although the water vapor makes it difficult to discern the peaks in Figure 40a and 41a, spectra taken after helium flush (Figures 40b and 41b) show the bands clearly. Presence of 1577 and 1430 cm$^{-1}$ peaks throughout the temperature program suggests conversion of ethoxy species to surface acetate species which may further reform into carbonates [58]. It is difficult to distinguish carbonate species from acetates under actual reforming conditions. Disappearance of ethoxy species as well as the increase in intensity of the 2354 cm$^{-1}$ and 2323 cm$^{-1}$ CO$_2$ bands with increasing temperature suggests steam reforming is taking place on both samples. Spectra collected after He flushing show the surface carbonates to be stable up to 400 °C.

Figure 40a of the Co/CeO$_2$(MP) sample shows a significant 3014 cm$^{-1}$ band at 350 °C and 400 °C accompanied by bands at 1301 cm$^{-1}$, both of which are characteristic of methane. Concurrently with methane, 2152 and 2092 cm$^{-1}$ bands appear, signaling CO formation. These may result from decomposition of
ethanol into hydrogen, CO and methane on the microparticle sample. Figure 41a shows much weaker bands at 3014 cm\(^{-1}\) and 1301 cm\(^{-1}\) even at 500 °C and has no CO bands.

Starting at 150 °C, 1336, 1012 and 933 cm\(^{-1}\) bands start to gain in intensity which indicate symmetric (CH\(_3\)) deformation and (CH\(_3\)) rocking. Along with the earlier discussion of the 1577 and 1430 cm\(^{-1}\) bands, these observations also support eventual reforming of surface species into acetates.[6, 61, 90]

Figure 40a shows formation of acetaldehyde species as identified by the 2680, 2647 and 1731 cm\(^{-1}\) bands, where the first two bands can be attributed to C-H stretching and the latter to the CO stretching of the aldehyde group. The acetaldehyde species indicate ethanol dehydrogenation reaction taking place on the sample starting from 250 °C. In the recent literature highly oxidized Co surfaces have been reported to favor ethanol dehydrogenation [50, 56]. It should be noted that Co/CeO\(_2\)(NP) sample may also show dehydrogenation activity. However, the acetaldehyde species may not be stable at a more reduced surface. Figure 40b shows the acetaldehyde species to desorb easily after He flush at all temperatures. It should also be noted that the appearance of methane and CO peaks seen in Figure 40a coincides with the appearance of acetaldehyde species, suggesting that methane and CO may result from acetaldehyde decomposition as well.

Figure 40a shows additional bands at 2987 and 2898 cm\(^{-1}\), which are in the CH\(_3\) vibration region. An additional broad feature is around 1220 cm\(^{-1}\). This
band, which is not seen in Fig 41a, follows the same trend with the bands associated with ethoxy species and could be due to C-C bonds, and but it is difficult to identify it with certainty. Figure 41a shows, in addition to the 2964 cm\(^{-1}\) band, which is present over both samples, show additional bands at 2856 and 2843 cm\(^{-1}\) in the CH\(_3\) vibration region, The bands increase in their intensity first and then decrease with temperature and disappear at 200 °C. On the low wavenumber end of the spectra, a similar behavior is shown by the following bands: 1375 cm\(^{-1}\) \(\delta_s(CH_3)\), and 1118, 1101 and 900 cm\(^{-1}\). The last three bands do not show on the MP sample. The unambiguous assignment of the bands in this region is difficult. These bands may arise from CO vibrations, but they may also be attributed to the C-C stretching vibration of hydrocarbons. If it is the former, these bands would suggest different oxygenated species on the surface, which are not formed over the MP catalyst. However, the experimental results in the following sections suggest alkyl-type species. 2856 and 2843 cm\(^{-1}\) bands, which show the same trends with the bands in the 900-1100 range, can be attributed to ethyl radicals [100], which would indicate parallel formation of ethoxy and ethyl species at lower temperatures. As the temperature increases, ethoxy species persist through the temperature profile, which can be observed by the behavior of the 1049 and 2967 cm\(^{-1}\) bands. However, 2964, 2856, 2843, 1118, 1101 and 900 cm\(^{-1}\) bands disappear after 200-250 °C, suggesting a rapid conversion. Figure 41b shows the same species after He flush indicating strong surface vibrations. Kondo et al. have reported evolution of ethyl species following
ethanol adsorption onto the catalyst surface [101] at 140 °C. Ethyl species may also be a precursor for ethylene [102], as suggested by the same group. This may indicate an alternative pathway for ethylene production for the NP sample since these species are absent in Figure 40a&b. This observation is also consistent with the steady-state data, which will be discussed in the next section. Although ethyl species may offer an alternative route for ethylene formation, all other species observed in operando DRIFTS experiments are consistent with the reaction mechanism we have postulated earlier [64].

5.3.2 Catalytic performance: Steady state catalytic activity testing

5.3.2.1 Ethanol steam reforming over Co/CeO$_2$ catalysts

Steady-state activity testing over Co/CeO$_2$(MP) and Co/CeO$_2$(NP) catalysts was performed to investigate the effect of cobalt and ceria particle size on ESR catalytic activity. Blank reactor experiments with the same feed conditions showed no detectable ethanol conversion within the tested temperature range of 350-500 °C (data not shown). Gas phase reforming was therefore assumed to be negligible within the experimental parameters.
Figure 40 DRIFT spectra for CoCeO$_2$(MP) a) during ESR, b) after flushing with He
Figure 41 DRIFT spectra for CoCeO$_2$(NP) a) during ESR, b) after flushing with He
The products formed over both catalysts included H\textsubscript{2}, CO\textsubscript{2}, CO, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} and liquid products such as CH\textsubscript{3}CHO and acetone where the latter is observed only in trace amounts. Reaction temperature and particle size was seen to significantly affect the product distribution. The reaction experiments were performed with equal surface areas as the basis, where the catalyst loadings were varied to achieve 0.4 m\textsuperscript{2} surface area, which corresponded to 44.4 and 7.1 mg of Co/CeO\textsubscript{2}(MP) and Co/CeO\textsubscript{2}(NP) catalysts, respectively. Catalyst bed was diluted with an inert (silica) to maintain constant bed volume, and hence, constant gas hour space velocity (GHSV).

Table 15 presents the comparison of ethanol conversion levels, hydrogen yields and selectivities for carbon containing products. The Co/CeO\textsubscript{2}(MP) catalyst is observed to have relatively lower conversion and hydrogen yields compared to its nano-particle counterpart at each temperature. However, the product distribution shows more striking differences between the catalysts. At 350°C, both catalysts show acetaldehyde, which is the product of a dehydrogenation step, to be the main species in the product stream. As temperature increases, acetaldehyde yield decreases. At 400°C, the Co/CeO\textsubscript{2}(NP) sample has a higher reforming activity, and hence, a higher H\textsubscript{2} yield than the Co/CeO\textsubscript{2}(MP). Both catalysts show increasing yields for CO and CH\textsubscript{4} with increasing temperature. These products may form from decomposition of aldehyde. However, the ratio is not one-to-one, suggesting other reaction steps for the production of carbon.
monoxide, including incomplete reforming. Both CO and CH₄ yields are higher over the Co/CeO₂(MP) compared to Co/CeO₂(NP).

An interesting feature of the product distribution is the high ethylene yield, which increases over both catalysts as the temperature is raised from 350°C to 400°C. At higher temperatures, ethylene is no longer observed over the Co/CeO₂(MP), whereas it continues to have the second highest yield among C-containing products over the Co/CeO₂(NP) catalyst. High ethylene yields suggest dehydration activity over both catalysts. Possible reaction steps that stem from ethylene include decomposition, which results in coking on the surface[69, 103-105], and ethylene reforming to H₂ and COₓ[106-109]. Both reactions have been reported on different catalytic systems.

When the catalysts were kept on stream at 500°C, Co/CeO₂(MP) sample showed complete loss of activity within 12 hours (Figure 42). The activity loss was accompanied by pressure build-up in the reactor, suggesting significant carbon deposition over this catalyst. Co/CeO₂(NP) catalyst, on the other hand, showed no activity loss for 36 hours, as seen in Fig 42. This result suggests that over the Co/CeO₂(NP) catalyst, the presence of ethylene does not lead to coke formation. It also suggests that Co/CeO₂(MP) catalysts have activity for both ethanol reforming and ethylene decomposition, which appear to proceed in parallel until the coke build-up becomes significant. This may be a phenomenon similar to the one reported in a recent review paper by Mattos et al. [69], where
cobalt-based catalysts exhibited high ESR activity despite formation of filamentous and amorphous carbon.

Table 15 Steady state catalytic activity data for ESR over Co/CeO$_2$(MP) and Co/CeO$_2$(NP) catalysts$^1$

<table>
<thead>
<tr>
<th>Products</th>
<th>350 °C</th>
<th>400 °C</th>
<th>450 °C</th>
<th>500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MP</td>
<td>NP</td>
<td>MP</td>
<td>NP</td>
</tr>
<tr>
<td>% C$_2$H$_5$OH conversion</td>
<td>7.8</td>
<td>14.9</td>
<td>21.8</td>
<td>34.0</td>
</tr>
<tr>
<td>% H$_2$ Yield</td>
<td>3.4</td>
<td>5.8</td>
<td>17.2</td>
<td>27.6</td>
</tr>
<tr>
<td>% Yield</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2.1</td>
<td>3.2</td>
<td>13.2</td>
<td>20.9</td>
</tr>
<tr>
<td>CO</td>
<td>0.4</td>
<td>0.6</td>
<td>2.1</td>
<td>1.0</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.0</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>0.2</td>
<td>0.3</td>
<td>1.5</td>
<td>2.8</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>CH$_3$CHO</td>
<td>4.6</td>
<td>10.3</td>
<td>4.0</td>
<td>8.5</td>
</tr>
</tbody>
</table>

$^1$ C$_{EtOH}$ = 0.8% and H$_2$O:EtOH = 10:1 (molar ratio) 0.4 m$^2$ total surface area.

GHSV=72000 hr$^{-1}$
3.2.3 Post-reaction characterization of catalysts

In order to examine possible carbon deposition on the catalysts during ethanol steam reforming, post-reaction characterization experiments were performed. Catalysts that were kept on stream for 12 hours were subjected to a temperature programmed oxidation process, where CO\textsubscript{x} species evolving from the surface were monitored by mass spectrometry as a function of temperature. Figure 43 shows the m/z= 32, 44 and 28 signals that are traced for O\textsubscript{2}, CO\textsubscript{2} and CO. CO profile has been corrected for contribution from CO\textsubscript{2} fragmentation. The profiles are compared on the same scale. Co/CeO\textsubscript{2}(MP) catalyst shows significantly higher CO\textsubscript{2} evolution over a wider temperature range compared to Co/CeO\textsubscript{2}(NP), with two smaller peaks at 230 °C and 419 °C and a larger peak at 350 °C. The evolution of CO\textsubscript{2} at three different temperatures suggests different
carbon species on the surface, with the low temperature peak corresponding to amorphous carbon and high temperature peaks corresponding to graphitic carbon[110, 111]. Co/CeO$_2$(NP) catalyst shows much lower CO$_2$ evolution, with one major peak at 238 °C and a wide small peak at 419 °C, suggesting mostly amorphous carbon on this catalyst. When the profiles are deconvoluted using GRAMS AI spectroscopy software, more than 90% of carbon formed over the Co/CeO$_2$(MP) sample is seen to be graphitic whereas the carbon deposition on Co/CeO$_2$(NP) catalyst was primarily amorphous. When the areas under the curve are compared, Co/CeO$_2$(MP) sample shows more than 7 times more carbon deposition during the same length of time on stream.

Figure 44 shows post-reaction TEM images of the Co/CeO$_2$(MP) and Co/CeO$_2$(NP) samples. Carbon deposition is quite apparent on the Co/CeO$_2$(MP) sample mainly in the form of filament growth. Co/CeO$_2$(NP) micrographs show no sign of sintering of the ceria or cobalt particles. A typical metallic cobalt particle in Figure 44 shows a particle size of 4.5 nm. This is in agreement with the EXAFS fits in Table 14, which suggest small metallic particle size after reduction.
Figure 43 Temperature-programmed oxidation profiles after 12 hours time on stream at 500°C in ethanol steam reforming a) Co/CeO$_2$(MP) and b)Co/CeO$_2$(NP)
Figure 44 TEM images taken after ESR a) Co/CeO$_2$(NP) and b) Co/CeO$_2$(NP)
Table 16 Steady state catalytic activity data for ESR over bare ceria supports

<table>
<thead>
<tr>
<th>Products</th>
<th>350 °C</th>
<th>400 °C</th>
<th>450 °C</th>
<th>500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MP</td>
<td>NP</td>
<td>MP</td>
<td>NP</td>
</tr>
<tr>
<td>% C$_2$H$_5$OH conversion</td>
<td>0.8</td>
<td>6.8</td>
<td>4.5</td>
<td>33.3</td>
</tr>
<tr>
<td>% H$_2$ Yield</td>
<td>0.0</td>
<td>2.2</td>
<td>1.3</td>
<td>7.9</td>
</tr>
<tr>
<td>% Yield</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.0</td>
<td>1.7</td>
<td>1.4</td>
<td>7.0</td>
</tr>
<tr>
<td>CO</td>
<td>0.0</td>
<td>0.1</td>
<td>0.0</td>
<td>0.7</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.4</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>0.1</td>
<td>2.3</td>
<td>1.9</td>
<td>18.8</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.0</td>
<td>0.1</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>CH$_3$CHO</td>
<td>0.0</td>
<td>2.2</td>
<td>0.0</td>
<td>3.9</td>
</tr>
</tbody>
</table>

 CEtOH= 0.8% and H$_2$O:EtOH = 10:1 (molar ratio) 0.8 m$^2$ total surface area.

GHSV=72000 hr$^{-1}$

5.3.2.3 Ethanol steam reforming over CeO$_2$ supports

Ethanol steam reforming activity of the bare CeO$_2$ supports were investigated with steady-state reaction experiments using the same parameters except the sample loading, which was increased to 0.8 m$^2$ to achieve conversion levels comparable to those attained over the supported catalysts used in this study. The reaction experiments were run using new reactors, which were not exposed to Co-containing species to eliminate the possibility of any cross contamination. Table 16 shows ethanol conversion, H$_2$ yield and the yield of carbon-containing products obtained over the two supports. Same species as the ones seen over the catalysts were encountered in the product stream with
significantly different product distributions. Both supports were found to have significant activity, especially at higher temperatures. However, the C-C bond cleavage activity was seen to be low. The major product over both supports was ethylene, but the yield of ethylene was much higher over CeO$_2$(NP), suggesting a high activity for ethanol dehydration. Methane was found to be another product which was abundant especially at higher temperatures. These experiments confirmed the active participation of the ceria support in ethanol steam reforming, as was reported for other support materials[112]. These experiments also showed the importance of support particle size, with nano-size particles having higher overall activity for dehydration, but being resistant to coking.

<table>
<thead>
<tr>
<th>Products</th>
<th>MP</th>
<th>NP</th>
<th>MP</th>
<th>NP</th>
<th>MP</th>
<th>NP</th>
<th>MP</th>
<th>NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>% C$_2$H$_4$ conversion</td>
<td>7.5</td>
<td>0.9</td>
<td>16.9</td>
<td>2.0</td>
<td>N/A</td>
<td>4.6</td>
<td>N/A</td>
<td>8.9</td>
</tr>
<tr>
<td>% H$_2$ Yield</td>
<td>6.7</td>
<td>0.8</td>
<td>14.8</td>
<td>2.0</td>
<td>N/A</td>
<td>2.7</td>
<td>N/A</td>
<td>5.1</td>
</tr>
<tr>
<td>% Yield</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>6.2</td>
<td>0.9</td>
<td>13.1</td>
<td>2.1</td>
<td>-</td>
<td>2.8</td>
<td>-</td>
<td>5.0</td>
</tr>
<tr>
<td>CO</td>
<td>1.8</td>
<td>-</td>
<td>3.2</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
<td>2.1</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>0.2</td>
</tr>
</tbody>
</table>

$^1$ C$_{Ethylene}$= 0.8% and H$_2$O:EtOH = 10:1 (molar ratio). GHSV=72000 hr$^{-1}$
Encountering significant ethylene yields, especially over the bare supports, led us to investigate steam reforming of ethylene for Co/CeO\textsubscript{2}(MP) and Co/CeO\textsubscript{2}(NP) samples using the same parameters as ethanol reforming reactions. The conversion and yield data are presented in Table 17. Co/CeO\textsubscript{2}(MP) has shown rapid increase in pressure drop as the reaction continued through the isothermal steps. At 450°C and above, steady state data could not be obtained due to the pressure build-up in the reactor over this catalyst although no pressure build-up problem was encountered over the Co/CeO\textsubscript{2}(NP) sample. The results indicate significant ethylene reforming activity over the Co/CeO\textsubscript{2}(MP) sample, especially at lower temperatures, with CO\textsubscript{x} and H\textsubscript{2} being the only products. At higher temperatures, however, ethylene decomposition becomes more prominent, which eventually leads to catalyst deactivation. Co/CeO\textsubscript{2}(NP), on the other hand, was found to have very low ethylene reforming activity even at high temperatures; but there was not much cracking or decomposition activity, either. Coke formation over the Co/CeO\textsubscript{2}-MP catalyst was verified by post-reaction temperature-programmed oxidation experiments (Figure 45), which showed significant carbon dioxide evolution at 180 °C and 350 °C. Post ethylene reaction TPO over the Co/CeO\textsubscript{2}(NP) sample showed very little carbon deposition with a single CO\textsubscript{2} peak at 180°C. These results help explain the product distribution over the two catalysts in ethanol.
steam reforming. It appears that although Co/CeO$_2$(NP) has dehydration activity, ethylene cracking does not proceed on this catalyst, rendering it highly resistant to coking. It also appears that the differences in product distribution may partially stem from the differences in the support properties.

**Table 18** Methanol pulse oxidation

<table>
<thead>
<tr>
<th></th>
<th>Relative selectivity for HCHO NP/MP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse 1</td>
<td>1.5</td>
</tr>
<tr>
<td>Pulse 2</td>
<td>1.7</td>
</tr>
<tr>
<td>Pulse 3</td>
<td>1.7</td>
</tr>
<tr>
<td>Pulse 4</td>
<td>1.5</td>
</tr>
</tbody>
</table>

In an effort to probe the surfaces of these two catalysts, pulse reaction experiments were performed using methanol oxidation as the probe reaction, as demonstrated for several catalytic systems by Wachs and co-workers[97, 98]. CO$_2$ and HCHO were the only products resulting from the pulses. Table 18 shows the ratios of [relative HCHO selectivity for NP] to [relative HCHO selectivity for MP], which is defined as

\[
\frac{\text{Area for HCHO}_{NP}}{\text{Area for CO}_2_{NP}} / \frac{\text{Area for HCHO}_{MP}}{\text{Area for CO}_2_{MP}}
\]
“Relative HCHO selectivity” was calculated by dividing the area for HCHO by the area for CO₂. This ratio was, on the average, 1.6 times higher for the nano-particle sample than for the micro-particle sample. Since HCHO formation over oxides is associated with the redox sites, these results suggest a higher density of redox sites over the Co/CeO₂(NP) catalyst. Although these preliminary probing experiments provide some evidence of the relative abundance of different sites over the catalysts, the limited data do not allow any real quantification. Studies with probe reactions over the catalyst as well as the supports are in progress.

5.4. Conclusions

Co catalysts supported on two different ceria supports with particle sizes of 0.1-0.2 μm and 5-8 nm were examined for their ethanol steam reforming performance. Operando XRD and in-situ XAFS techniques showed higher reducibility with the Co/CeO₂(NP) catalyst. Steady-state activity tests showed significant differences in product distribution between the two samples, with the nano-particle catalyst showing higher steam reforming performance despite high ethylene yields. Post-reaction studies as well as ethylene steam reforming activity tests showed the Co/CeO₂(MP) sample to have high affinity for ethylene decomposition, and hence for coke formation where its counterpart was found to be highly resistant to coking. Operando DRIFTS studies suggested formation of different surface species on the samples, including some surface species which could be a precursor for ethylene. Pulse methanol oxidation experiments were
performed to probe the surface sites of the catalysts. The results indicated a higher density of redox sites on the Co/CeO$_2$(NP) catalyst. The smaller particle size of the support appears to lead to increased reducibility, improved metal dispersion and a difference in relative abundance of redox sites on the surface, all of which, in turn, result in better performance for ethanol steam reforming. It also appears that some of the differences observed in product distribution may have direct contributions from the activity of the supports themselves.
Figure 45 Temperature-programmed oxidation profiles after ethylene steam reforming reactions a) Co/CeO$_2$(MP) and b) Co/CeO$_2$(NP)
Recommendations for Future Work

- The ethanol dehydrogenation reaction pathway is well established by the year 2013 with our previous work as well as the work of the Vohs group. The ethanol dehydration to ethylene pathway however, is still considered to lead to coking and eventual catalyst deactivation. Coking is a matter of oxygen transfer and should be handled as a challenge rather than as a problem. A catalyst with small enough particle size, with crystal planes favoring high cobalt dispersion may succeed in reforming ethylene into final products of $\text{H}_2$ and $\text{CO}_2$. We should build up on our knowledge of ethylene resistant catalysts.

- The reduction of cobalt species should be characterized mechanistically and kinetically. Preliminary studies put the activation energies for reduction around 35-40 kJ/mol. If a more reducible surface is more active, exactly which factors affect the surface reducibility?

- The steam reforming reaction system is modified extensively to allow for different feed conditions. Bio-derivable liquids such as acetaldehyde and dimethylether should be further tested for activity.

- Throughout the project our primary line of thought was to produce hydrogen for mobile applications which would then go through a fuel
reformer and a fuel cell. However, refineries require a lot of hydrogen for their internal processes and currently this hydrogen is produced by steam methane reforming. Due to the increasing possibility of carbon tax on refineries in 2015, there is extensive research on producing hydrogen from renewable sources. The aim of the project may shift to a comparison with steam methane reforming with refinery streams in mind. It should be also noted that 10% ethanol additive use in gasoline is increasing nationwide. Refineries have to purchase ethanol by regulation and a method to utilize this ethanol in different reactions may offer significant insight to the project.
Appendix A: XAFS Analysis

From Candidacy Exam written portion:

**X-ray absorption fine structure (XAFS)**

**Background**

X-ray absorption fine structure spectroscopy uses the x-ray photoelectric effect and the wave nature of the electron to determine local structures around selected atomic species in metals. Unlike X-ray diffraction, XAFS does not require long range order. It works just as fine with amorphous materials, liquids and gases. XANES is the near–edge structure and can be sensitive to charge transfer, orbital occupancy and symmetry. The following Figure shows the schematic for a typical XAFS experimental setup.

![Figure 46 Schematic for a XAFS experiment](image)

Assuming the edge jump is at $E_0$ for a specific edge, a typical XAFS spectrum will look like Figure 47. The extended range X-ray absorption fine
structure (EXAFS) is an addition of dampened oscillations and provides information about neighboring atoms, where XANES carries information about the targeted metal. XAFS is a universal characterization technique with the exception of H atoms. The physics of XAFS start with the absorption of X-ray photon which causes a transition from \( n=1 \ l=0 \ (1s) \) to unfilled \( p \)-symmetry \( (l=1) \) final state. Absorption probability depends on dipole matrix element between the initial and final states of the electron and is determined by the local structure. If the photon energy exceeds binding energy \( E_0 \) the electron has kinetic energy left and will propagate as a spherical wave which is explained by a quantum wave function.

\[
k = \frac{2\pi}{\lambda} = \sqrt{\frac{2m}{\hbar^2}}(E - E_0)
\]  

(1)
Electron wave emitted by central atom is scattered by neighboring atoms. The outgoing and scattered parts of the final state wave function interfere where the initial state is localized. The interference is constructive or destructive depending on the distances of the neighboring atoms and electron wavelength. Scanning the wavelength records and interferogram of distance distribution. The measured spectrum is a Monte Carlo average snapshot spectra ($\sim 10^{-15}$ sec) of all the atoms of the selected type that are probed by the X-ray beam. In general XAFS determines the statistical properties of the distribution of atoms relative to the central absorbers. In the case of single scattering the pair correlation function is probed. Multiple scattering gives information on higher order correlations. Experimental data fitting is done by using EXAFS software which uses the Stern, Sayers, Lytle equation. The general scattering EXAFS equation is as follows:
The EXAFS equation can be summarized as a sum of damped sine waves. Experimental data can be fit by using the EXAFS equation either by building theoretically calculated scattering functions or empirically measuring possible standards. Precise local structural information in the form of distances, numbers and types of atoms as well as structural disorder can be gained from the XAFS technique in crystalline and non crystalline systems including liquids and amorphous materials. All of the targeted atoms are visible; there are no spectroscopically silent atoms for XAFS. XANES region provides information on the charge state and orbital occupancy. Due to the nature of the XAFS experiment, a single edge (or multiple edges in series) will be targeted during an experiment which allows for a wide range of in-situ studies where the beam and the spectra will not get affected by changes in the system such as high pressure, low temperature, pH or redox state of the sample. High temperatures will have an effect on the Debye-Waller factor which will be discussed in the later sections.
**XAFS analysis**

XAFS spectra have three regions as shown in Figure 49, the pre-edge region is accepted as the 300 to 50 eV region prior to the absorption energy of the targeted sample. This section is used for background subtraction and normalization. The edge region is the sudden rise in the absorption coefficient and carries information about the target atom. Analysis of the edge region is called XANES. Finally the post edge region is considered to be 50 to 1000 eV after the edge and carries information about the neighboring atoms, the analysis of this post edge region is requires complex mathematics and is called EXAFS.

**XANES analysis**

The analysis of the XANES region provides information on the charge state and orbital occupancy [113] and is usually handled separately from the EXAFS region. A linear combination fitting of theoretically constructed edge spectra may be for XANES analysis. A more common fitting method would be to run experimental standards and compare the charge state of the sample with that
of the standards. This is mainly due to the fact that theoretical equations for the XANES region are not as developed yet. The exact location of the edge may also carry information about the oxidation state. In catalysis literature the exact location of the edge is accepted as the first inflection point of the spectra in the edge jump. Metals with multiple charge states may show a linear trend by shifting the edge jump which can be seen in Figure 50 with a Mn sample. The challenge in linear combination XANES fitting is the similar shapes of different standard functions. It takes very little experimental error to fit a sample spectrum to some linear combination of 2 or 3 spectra collected by the standards. The experimenter needs to have a good understanding of the sample beforehand since XANES linear combination is a purely mathematical process e.g. an oxide and a sulfide of the same species may look similar. EXAFS fitting is more robust procedure due to the nature of the chi function which allows for more differentiation between elements.
Figure 50 Log-Log plot of formal oxidation states of Mn oxides versus average bond length

EXAFS analysis

The data is generally corrected for background, normalized with respect to the edge height and reduced to a Chi(k) function. Figure 51 shows the transformation of the spectra from energy space into the wave function following equation 1. It is possible to fit the data in k-space or it can be Fourier transformed into an r-space presentation which is a function of half path length for the scatters. In r-space different contributions can be isolated and these fits can be shown in k-space.
There is some work focusing on fitting the data directly into the energy space which is advantageous in terms of simplicity and since there are not many steps involved in the data processing, fewer mistakes can be made and experimental bias may be avoided. The best way to approach data processing would be to do both and check the results. In G. Bunker’s words “take the data apart and put it back together again.” In the k-space the wave functions follow the form of sin waves which interfere with each other and are de-localized. Fourier transform (FT) is a frequency filter which localizes the data. Figure 52 from the lecture notes of S.E. Kelly shows the transformation into R space.

**Figure 51** Transformation of the data to k-space

**Figure 52** Examples of localization through FT into R space
Applications in catalysis research

The XAFS probe utilizes photons both in probing the sample and collects photons via either transmission or fluorescence. Therefore XAFS spectroscopy is one of the few spectroscopic techniques which can provide information about the charge state and structural properties of the catalysts under reaction conditions while the reactants are present. X-ray diffraction (XRD) also probes with and collects photons. However, XRD requires long range order which is not needed for XAFS. X-ray photoelectron spectroscopy (XPS) and similar techniques such as Auger spectroscopy can provide similar information but they need the sample to be under ultra high vacuum conditions. These capabilities make XAFS ideal for collecting realistic in-situ and operando reaction data for catalyst applications [8].

Previous work on ceria morphologies reported in the proposal enabled us to synthesize cobalt particles with relatively small particle sizes of 5 nm. Characterization and analysis of noble metals with low particle sizes were conducted with Au, Pd and Pt among others. To our best knowledge, effect of cobalt particle size on reducibility was not investigated under reaction conditions with XAFS method. Using in-situ capabilities of the XAFS method, actual reaction conditions were mimicked and cobalt charge state was found to be very closely related to ethanol steam reforming activity which is in agreement with the literature. Therefore it is important to understand the mechanistic of cobalt reduction. The reaction order, effect of temperature and the effect of particle size
will be investigated via the following example which would demonstrate the potential of the technique for in-situ characterization.

Figure 53 An example of XANES quantification

**Investigating in-situ reduction of cobalt species**

XANES data will be fit with spectra from the bulk Co$_3$O$_4$, CoO and metallic Co samples. Preliminary data collected on in-situ 10% Co/CeO$_2$ reduction for different ceria morphologies at 400 °C, with 3.6 H$_2$/He is shown in Fig 53 where the extent of reduction is calculated by conversion to metallic cobalt. The data set was collected in a beamline with a bending magnet it is possible to increase the number of data points within the same time frame by working with a greater X-ray flux.
Collecting enough data points (~15-20/hr) would enable for a reaction rate to be fit to experimental data. Repeating the experiment at different temperatures such as 300/350/400/450 °C would enable us to get temperature dependence. Utilizing an Arrhenius equation assuming the activation energy to be constant within the temperature range would result in the $E_a$ of reduction for a particular sample. The effect of temperature needs to be taken into account for accurate fitting of the spectra. Temperature increases structural disorder which is taken into account with the $\sigma^2$ Debye-Waller factor (DWF) in the EXAFS equation. Thus, DWF has to be calibrated for certain particle sizes. Okamoto et al. has investigated the effect of phase change and temperature on SrCl$_2$ sample[14]. Miller et al., has investigated the effect of both particle size and temperature for Au. DWF, which is a correction term, is hypothesized to be linear with temperature and is also affected by particle size (Figure 54). Currently there have been 5 nm and 60 nm cobalt particles synthesized on ceria supports. Additionally, the bulk Co standard used for XANES fitting consisted of 5 μm particles. By comparing the spectra of at least these three samples it is expected to calibrate EXAFS fits accordingly.
Noble metals such as Au have shown bond contraction with small particle sizes such as 30 Å\textsuperscript{15}. Surface atoms have less neighboring atoms than bulk locations which causes them to be energetically more stable at lower bond distances. Since XAFS spectra is technically a snapshot of the whole targeted area which is averaged. This effect starts to dominate the EXAFS region as the
particle size smaller and the percentage of surface atoms increase. Figure 55 shows the hypothesized effect of Co particle sizes on the bond distance. Preliminary data on Co/CeO$_2$-cubes showed smaller bond distances than Co/CeO$_2$-rods. Figure 56 shows a comparison of FT-magnitude spectra of the Co-Co shell for both samples where the reduction values fitted from the XANES region gives 51% Co and 49% CoO. It should be noted that the Co dispersion values for nanorods (NR) was 7% and 21% for nanocubes suggesting larger metallic Co particles for nanorods. Also the particle symmetry is subject to change which may result in smaller BD values. In-situ XRD may be a supporting technique if particle symmetry is subject to change. In the literature, the contraction amount was observed to be more prominent for highly metallic samples as opposed to oxidized samples, which is why such an analysis is challenging for non noble metals.
XAFS technique may give limited information on the sample particle size. However, the information gained would be under actual reaction conditions and an average of all the targeted species. Transmission electron microscopy (TEM) on the other hand needs the sample to be under high vacuum, therefore only the pre-reaction and post reaction steps can be analyzed. Moreover, it would fall on the experimenter to collect exposures from a wide range and create a population of images which is representative of the whole sample. With the help of the calibration techniques explained above it would be possible to gain some insight on the particle size of an unknown sample. Additionally, Co species were observed to reduce in-situ under ethanol steam reforming conditions which may impact the structural properties of Co significantly in a sample with smaller metallic particle size.
Appendix B: Steam reforming system sample calculations

From the ideal gas law, at same pressure and temperature, the 1:10 molar ratio is convertible to 1:10 concentration ratio. Therefore, in total flow rate of 30ml/min

\[
\text{Total Flow Rate} = 30 \, \frac{ml}{min}
\]

0.8 % Ethanol = 0.24 \, \frac{ml}{min} \quad 8 \% \text{ Water} = 2.4 \, \frac{ml}{min} \quad 91.2 \% \text{ Helium}

\[
= 27.36 \, \frac{ml}{min}
\]

Using Ideal Gas Law:

\[
PV = nRT \quad n = \frac{PV}{RT} \quad \dot{N} = \frac{P\dot{V}}{RT}
\]

Therefore,

\[
\dot{N} = \text{Molar Flow Rate} \left( \frac{mol}{min} \right)
\]

\[
\dot{V} = \text{Volumetric Flow Rate} \left( \frac{ml}{min} \right)
\]

\[
P = 1 \, \text{atm} \quad T = 298 \, K \, (\text{Room Temperature})
\]

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\[ \dot{N} = \frac{P \times \dot{V}}{R \times T} \]

\[ \dot{N}_{\text{Ethanol}} = \frac{1 \text{ atm} \times 0.24 \frac{\text{ml}}{\text{min}} \times 10^{-6} \frac{\text{m}^3}{\text{ml}}}{8.205746 \times 10^{-5} \left(\frac{\text{m}^3 \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right) \times 298 \text{ K}} = 0.000009814 \frac{\text{mol}}{\text{min}} \]

\[ \dot{N}_{\text{Water}} = \frac{1 \text{ atm} \times 0.24 \frac{\text{ml}}{\text{min}} \times 10^{-6} \frac{\text{m}^3}{\text{ml}}}{8.205746 \times 10^{-5} \left(\frac{\text{m}^3 \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right) \times 298 \text{ K}} = 0.000009815 \frac{\text{mol}}{\text{min}} \]

Density of Ethanol: 0.789 \frac{\text{g}}{\text{cm}^3} \quad \text{Density of Water (Liquid): 1} \frac{\text{g}}{\text{cm}^3}

Molecular Weight of Ethanol: 46 \frac{\text{g}}{\text{mol}} \quad \text{Molecular Weight of Water (Liquid): 18} \frac{\text{g}}{\text{mol}}

\[ \text{Ethanol Flow Rate} = 0.000009814 \frac{\text{mol}}{\text{min}} \times 46 \frac{\text{g}}{\text{mol}} \times \frac{1}{0.789} \frac{\text{g}}{\text{cm}^3} = 0.000572 \frac{\text{ml}}{\text{min}} \]

\[ \text{Water Flow Rate} = 0.00009815 \frac{\text{mol}}{\text{min}} \times 18 \frac{\text{g}}{\text{mol}} \times \frac{1}{1} \frac{\text{g}}{\text{cm}^3} = 0.0017667 \frac{\text{ml}}{\text{min}} \]

\[ \text{Total Volumetric Flow Rate} = 0.000572 + 0.0017667 = 0.0023387 \frac{\text{ml}}{\text{min}} \]

\[ = 0.1403 \frac{\text{ml}}{\text{hr}} \]
Therefore, the pump volumetric flow rate was determined as $0.1403 \frac{ml}{hr}$.

The total volumetric flow rate of 35ml/min after reactor (feed + propane) cannot be used to calculate the molar flow rate (mol/min) of each substance in the GC. That is because the total volumetric flow rate (ml/min) of the feed may increase during the reaction. Therefore, 7% propane of 5ml/min which was controlled was employed as the internal standard to derive the total volume flow rate. This part involves the sequence of calculation of the molar flow rate for each substance, and hydrogen was used as an example.
**Figure 57** GC Calibration Curve of Hydrogen (PDHID): This figure shows the trend-line for the GC calibration data of hydrogen. The data was collected on February 2010.

**Step 1: Concentration (%)**

Assuming that 15 million response factor was obtained from the GC by integrating the hydrogen peaks, the concentration of hydrogen can be calculated from the calibrated graph function.

\[
Y = 2 \times 10^{-0.9} \times X = 2 \times 10^{-0.9} \times 15 = 3.77 \%
\]
Step 2: Volumetric Flow Rate (ml/min)

Assume that propane concentration was also gained as 0.87%, according to Step 1.

\[
\frac{\text{Concentration of Hydrogen } (C_H)}{\text{Concentration of Propane } (C_P)} = \frac{\text{Volumetric Flow Rate of Hydrogen } (V_H)}{\text{Total Volumetric Flow Rate } (V_T)}
\]

Therefore,

\[
\begin{align*}
V_T &= \frac{V_H}{C_H} = \frac{V_P}{C_P} \\
V_H &= C_H \times \frac{V_P}{C_P}
\end{align*}
\]

The volumetric flow rate of 7% propane was set at 5 ml/min in the experiment.

\[
\dot{V}_p = 5 \ \frac{ml}{min} \times 0.07 = 0.35 \ \frac{ml}{min}
\]

\[
\text{Volumetric Flow Rate of Hydrogen } (V_H) = 3.77\% \times \frac{0.35 \ ml/min}{0.87 \%} = 1.51 \ \frac{ml}{min}
\]

Step 3: Molar Flow Rate (mol/min) – Using Ideal Gas Equation

The produced gases are assumed to follow the ideal gas law in the experiment.

Ideal Gas Law:

\[
PV = nRT
\]
\[
n = \frac{PV}{RT} \quad \dot{N} = \frac{P\dot{V}}{RT}
\]

\[
\dot{N}_H = \frac{P \times \dot{V}_H}{R \times T} \quad (\text{for Hydrogen})
\]

Therefore,

\[
\dot{N}_H = \frac{P \times \dot{V}_H}{R \times T}
\]

\[
\dot{N}_H = \text{Molar Flow Rate of Hydrogen} \left( \frac{\text{mol}}{\text{min}} \right)
\]

\[
\dot{V}_H = \text{Volumetric Flow Rate of Hydrogen} \left( \frac{\text{ml}}{\text{min}} \right)
\]

\[
P = 1 \text{ atm} \quad T = 273 \text{ K (0°C)} - \text{ after condenser}
\]

\[
R \ (\text{Gas Constant}) = 8.205746 \times 10^{-5} \left( \frac{m^3 \cdot \text{atm}}{K \cdot \text{mol}} \right)
\]

\[
\dot{N}_H \left( \frac{\text{umol}}{\text{min}} \right) = \frac{1 \text{ atm} \times \dot{V}_H}{8.205746 \times 10^{-5} \frac{m^3 \cdot \text{atm}}{K \cdot \text{mol}} \times 273 \text{ K}} \times \frac{1 \text{ cm}^3}{1 \text{ ml}} \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \times \frac{10^6 \text{ umol}}{\text{mol}}
\]

\[
= \dot{V}_H \times 44.63949607
\]

This coefficient can be used for unit conversion in this specific BESR system.

Therefore,
\[ \dot{N}_p = \text{Molar Flow Rate of Propane} = 0.350 \frac{ml}{min} \times 44.63949607 \]

\[ = 15.62 \frac{umol}{min} \]

\[ \dot{N}_H = \text{Molar Flow Rate of Hydrogen} = 1.51 \frac{ml}{min} \times 44.63949607 \]

\[ = 67.41 \frac{umol}{min} \]

**Step 3: Molar Flow Rate (mol/min) – Using Propane Gas**

The produced gases are assumed to follow the ideal gas law in the experiment.

Avogadro’s Law

\[ \frac{P_1 \times V_1}{T_1 \times N_1} = \frac{P_2 \times V_2}{P_2 \times N_2} \]

At same pressure and temperature,

\[ \frac{V_1}{N_1} = \frac{V_2}{N_2} \quad \text{or} \quad N_1 = \frac{V_1 \times N_2}{V_2} \]

Therefore,

\[ \dot{N}_H = \frac{V_H \times \dot{N}_P}{V_P} \]

\[ N_H = \text{Molar Flow Rate of Hydrogen} \left( \frac{mol}{min} \right) \]

\[ \dot{N}_p = \text{Molar Flow Rate of Propane} \left( \frac{mol}{min} \right) \]
\[ \dot{V}_H = \text{Volumetric Flow Rate of Hydrogen} \left( \frac{ml}{min} \right) \]
\[ \dot{V}_p = \text{Volumetric Flow Rate of Hydrogen} \left( \frac{ml}{min} \right) \]

\[ \dot{N}_p = \dot{V}_p \left( \frac{ml}{s} \right) \times \rho \left( \frac{kg}{m^3} \right) \times \frac{1}{M} \left( \frac{mol}{g} \right) \times \frac{1}{1000000} \frac{m^3}{cm^3} \times \frac{1000 \text{ g}}{kg} \]

\[ \rho \left( \frac{kg}{m^3} \right) = \text{density of propane (gas)} = 2 \frac{kg}{m^3} \]

\[ M \left( \frac{mol}{g \text{mol}} \right) = \text{Molecular Weight of propane} = 44 \frac{g}{mol} \]

\[ \dot{N}_H = \frac{\dot{V}_H \times \dot{V}_p \times 2 \times \frac{1}{44} \times \frac{1}{1000000} \times 1000}{\dot{V}_p} = \dot{V}_H \times 2 \times \frac{1}{44} \times \frac{1}{1000000} \times 1000 \]

\[ = \dot{V}_H \times \frac{1}{22} \times \frac{1}{1000} \left( \frac{mol}{min} \right) \]

Unit Change to umol/min

\[ \dot{N}_H = \dot{V}_H \times \frac{1}{22} \times \frac{1}{10^3} \frac{mol}{min} \times 10^6 \frac{\text{umol}}{mol} = \dot{V}_H \times \frac{1}{22} \times 10^3 \]

Therefore,

\[ \dot{N}_p = \text{Molar Flow Rate of Propane} = 0.350 \frac{ml}{min} \times \frac{1}{22} \times 10^3 \frac{\text{umol}}{min} \]

\[ = 15.91 \frac{\text{umol}}{min} \]

\[ \dot{N}_H = \text{Molar Flow Rate of Hydrogen} = 1.51 \frac{ml}{min} \times \frac{1}{22} \times 10^3 \frac{\text{umol}}{min} \]

\[ = 68.63 \frac{\text{umol}}{min} \]
References


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