INVESTIGATION OF REACTION NETWORKS AND ACTIVE SITES IN BIO-ETHANOL STEAM REFORMING OVER COBALT BASED CATALYSTS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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ABSTRACT

Hydrogen is likely to play an important role in the energy portfolio of the future. Especially when it is used in fuel cells, it is an ideal energy carrier that can offer clean and efficient power generation. In the United States, ~95% of hydrogen is produced using a steam reforming process [1]. Over 50% of world’s hydrogen production relies on natural gas as the feedstock [2]. As the concern for a sustainable energy strategy grows, replacing natural gas and other fossil fuels with renewable sources is gaining new urgency. In this context, producing hydrogen from bio-derived liquids such as bio-ethanol has emerged as a promising technology due to the low toxicity, ease of handling and the availability from many different renewable sources (e.g., sugar cane, algae) that ethanol has to offer. An added advantage of producing hydrogen from bio-derived liquids is that it is quite suitable for a distributed production strategy.

In this study, the effects of metal loading, preparation methods, synthesis parameters, cobalt precursors, impregnation medium, promoters and supports as well as reaction conditions are investigated for steam reforming of bioethanol and other bio-derived liquids over Co-based catalysts. In addition to these effects, the reaction networks and catalytic active sites are evaluated through steady state reaction using Gas Chromatography (GC)-Mass Spectrometer (MS) as analytical tools. Characterization studies have been performed by employing versatile
characterization techniques such as Temperature Programmed Reaction (TPRxn), Temperature Programmed Reduction (TPR), Temperature Programmed Desorption (TPD), Temperature Programmed Oxidation (TPO), N₂ Physisorption, Pulsed Chemisorption, X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), Laser Raman Spectroscopy (LRS), Thermogravimetric Analysis-Differential Scanning Calorimetry (TGA-DSC), Isotopic Labeling, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) to gain insights to the catalyst structure and its variations at different life stages on a microscopic level, leading to the proposal of possible reaction pathways and identification of the probable catalytic active sites. Integrated with the experimental results obtained, the predictions from molecular simulation are expected to theoretically guide the catalyst formulation with improved catalytic properties. In addition, the work also involves the deactivation mechanism exploration and strategy for sample regeneration in order to extend the catalyst lifetime. Furthermore, the economic analysis of this technique is performed from feedstock to final product ready for distributed usage, which will be beneficial for industrial applications.

According to the results acquired in this research, the relationship between surface and structural properties (e.g., cobalt dispersion and oxygen availability) and activity has been initially established to facilitate rational design of catalyst systems for the steam reforming reactions studied. H₂ yields over 90 % have been achieved at relatively lower temperatures (<450 °C) in bioethanol steam
reforming. In addition, the deactivation mechanism has been determined to be closely related with carbon deposition due to insufficient supply of oxygen and cobalt sintering. Catalysts with modified formulations have been developed to achieve long-term stability while keeping high activity. The H\(_2\) selling price of $4.27 /kg has been estimated from the simulated process at 1,500 kg H\(_2\)/day scale with ~70 % energy efficiency, where $1.78 /kg is attributed to feedstock cost, mainly ethanol charge. Through the sensitivity analysis over various influencing parameters, the H\(_2\) yield and catalyst cost have been found to play a significant role on the final H\(_2\) price, which verifies the importance of the development of non-precious catalyst system with excellent performance.

Combined with the estimated economic analysis of this process simulated at industrial scale, the outcomes originating from this study will eventually lead to the commercialization of the developed catalyst system specially tailored for central and distributed hydrogen production from steam reforming of bio-derived liquids suitable for fuel cell application.
DEDICATION

Dedicated to my mother and beautiful fiancee
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I am eager to appreciate my advisor, Umit S. Ozkan, for her selfless intellectual support and valuable recommendations which make the thesis possible, and for her precious time and efforts spent on correcting both my grammar and scientific errors.

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**PUBLICATIONS**

Research Publications


9. Song, H., Chen, F.M., Zhongguo Youzhi (2005), 30(2), 41-43;

Patents
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FIELDS OF STUDY

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CHAPTER 1

INTRODUCTION

Along with the development of science and technology, the demand for energy has been increasing dramatically, especially in the last several decades (raised by almost three times since 1965 [3]). More importantly, more than 85% of the energy consumption relies on fossil fuels. [4], the use of which poses many problems.

According to the current proven reserves and production rates [3], oil, natural gas, and coal, the main constituents of fossil fuels, will be depleted within 40, 63, and 147 years, respectively, as shown in Fig.1. Moreover, the fossil fuel reserves are concentrated in only a few regions of the world. For instance, the proven oil reserves are mostly located (61.5%) around the Middle East region.

In addition, the combustion of fossil fuels causes a lot of environmental issues, among which the release of green house gases (CO$_2$, CH$_4$, and NO$_x$) is the main concern for global warming. Besides, the emission of NO$_x$, SO$_2$, and
fine particulates that accompanies the combustion of fossil fuels induces the formation of acid rain, which will result in the serious damages to both natural area and human architecture. The environment (specifically water and air) can also be polluted during the processes of harvesting, refining, and distributing fossil fuels. More importantly, some of the emissions from fossil fuel combustion create insalubrious influence on human body, especially on the respiratory system. Therefore, it is imperative to find a substitute for fossil fuels as the energy carrier for the next generation, particularly in view of the escalating world oil prices.

Hydrogen offers many advantages as a clean energy carrier for the sustainable development of the future. First of all, the storage of hydrogen on earth is abundant and hydrogen can be produced through various pathways including thermochemical production from many different fuels such as natural gas, coal, and renewable sources, electrolytic production from water, photobiological production by microorganisms, and photocatalytic splitting of water. Secondly, the implementation of hydrogen is environmentally friendly, because the only emission from the combustion of hydrogen is water. More attractively, hydrogen is

![Figure 2. The gravimetric energy density of various fuels](image)
especially applicable as a fuel for fuel cells, which have much higher efficiencies than internal combustion engine. Among the energy sources commonly used today, hydrogen has the highest gravimetric energy density as shown in Fig.2. Overall, hydrogen deserves extra attention.

Currently, ~95 % hydrogen is manufactured using steam reforming in the United States. Especially, over 50 % hydrogen production relies on the feedstock of natural gas throughout the world. As one of the fossil fuels mentioned above, the employment of CH₄ can still not meet the requirement from the viewpoint of sustainable development. Therefore, it is important to search for an energy carrier which is renewable and environmentally benign. Bio-ethanol obtained from the fermentation of biomass (e.g. sugar canes, celluloses, corn) seems desirable to be studied as the reactant for steam reforming to produce hydrogen, for several reasons. First, compared with other chemicals studied for steam reforming, ethanol has no negative impact on the surroundings and is not harmful to human body when handled. Moreover, higher hydrogen yield can be obtained from steam reforming when ethanol is charged as the reactant rather than methane and methanol. Simultaneously, ethanol is much easier to be reformed than other high carbon containing hydrocarbons and alcohols such as propanol, butanol, and naphtha. Second, since ethanol is present in liquid form, there is no high pressure hazard during storage and transportation. Thus this technique lends itself very well to on-board or distributed hydrogen production. In other words, instead of hydrogen refilling, ethanol is stored and the hydrogen produced either from on-board steam reformer or from distributed small-scale reformers
without involving intermediate hydrogen storage steps, hence eliminating the safety and space limitation concerns. Finally, the CO₂ gas concomitantly released from steam reforming with hydrogen can be recycled back into the process of plant growth through photosynthesis, theoretically leading to zero CO₂ emission. Although from the viewpoint of commercialization, ethanol steam reforming has higher cost than methane steam reforming mainly due to the cost from ethanol feedstock, the environmental benefits can compensate this issue and the ethanol generation from cellulose rather than corn can even lower the cost facilitating the realization of this technology in the near future.

1.1 Ethanol Reforming Reactions

Hydrogen can be produced from ethanol through a seemingly straightforward steam reforming reaction (ESR)

\[
\text{C}_2\text{H}_5\text{OH}(l) + 3 \text{H}_2\text{O}(l) \rightarrow 2 \text{CO}_2 + 6 \text{H}_2 \quad (\Delta H_r = 348 \text{ kJ/mol})
\]

This reaction is endothermic and would require energy input. An alternative reaction involving ethanol is partial oxidation (POE) shown below [6]

\[
\text{C}_2\text{H}_5\text{OH}(l) + 1.5 \text{O}_2 \rightarrow 2 \text{CO}_2 + 3 \text{H}_2 \quad (\Delta H_r = -509 \text{ kJ/mol})
\]

Although POE is exothermic and does not need additional energy input, the stoichiometric ratio of H₂ to ethanol is much lower than steam reforming. Steam reforming carried out in the presence of a limited amount of oxygen can combine both of these reactions. If the relative extent of the two reactions is such that it leads to an enthalpy-neutral reaction, the overall reaction can be represented as autothermal ethanol reforming (AER), which is theoretically the most efficient route from ethanol to CO₂ and H₂ [7].
C₂H₅OH(l) + 0.608 O₂ + 1.784 H₂O(l) ⇌ 2 CO₂ + 4.784 H₂  \ (ΔH_r = 0)

Although the products from the desired reactions are only CO₂ and H₂, in reality, depending on the reaction conditions and catalysts used, the product distribution can be governed by a very complex reaction network. Possible reactions involved can be as follows.

\[ \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_4 + \text{CO} + \text{H}_2 \] (ethanol decomposition)

\[ \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2 \] (ethanol dehydrogenation)

\[ \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2\text{O} \] (ethanol dehydration)

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightleftharpoons 2 \text{ CO} + 4\text{H}_2 \] (ethanol incomplete reforming)

\[ 2 \text{ CH}_3\text{CH}_2\text{OH} \rightleftharpoons (\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O} \] (ethanol dehydrative coupling)

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + 2 \text{H}_2 \] (acetic acid formation)

\[ \text{CH}_3\text{CHO} \rightleftharpoons \text{CH}_4 + \text{CO} \] (acetaldehyde decomposition)

\[ 2\text{CH}_3\text{CHO} \rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{CO} + \text{H}_2 \] (acetone formation)

\[ \text{CO} + 3 \text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \] (methanation)

\[ \text{C}_2\text{H}_4 \rightleftharpoons \text{coke} \] (polymerization)

\[ \text{CH}_4 + 2 \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 4 \text{H}_2 \] (methane steam reforming)

\[ \text{CH}_4 \rightleftharpoons \text{C} + 2 \text{H}_2 \] (methane cracking)

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \] (water-gas shift)

\[ 2 \text{ CO} \rightleftharpoons \text{CO}_2 + \text{C} \] (Boudouard reaction)

There are many side reactions that might take place during ethanol steam reforming, complicating the product distribution. To get the highest possible H₂
yield for industrial applications, it is essential to investigate the effects of temperature, reactants ratio, pressure, space velocity as well the catalytic parameters. A thermodynamic analysis was performed using the software HSC®5.1. All possible products, including solid carbon were included among the possible species that could exist in the equilibrium state. In the thermodynamic analysis, the following definitions are used.

\[
\text{H}_2 \text{ Yield}\% \ = \ \frac{\text{moles of } \text{H}_2 \text{ produced}}{6 \times (\text{moles of ethanol fed})} \times 100
\]

\[
\text{Selectivity}\% \ = \ \frac{\text{mol of a certain product}}{\text{mol of total products}} \times 100
\]

\[
\text{EtOH Conv.}\% \ = \ \frac{\text{moles of ethanol converted}}{\text{moles of ethanol fed}} \times 100
\]

The thermodynamic analysis in Fig.3 shows ethanol conversion, yield and selectivity of main products starting from a reactant composition similar to a bio-ethanol stream from biomass fermentation (ethanol-to-water ratio of 1:10). Ethanol conversion is not thermodynamically limited at any temperature. The methanation reaction, which is exothermic, is thermodynamically favored at lower temperatures (below 400 °C). At higher temperatures (above 500 °C) the reverse of this reaction, i.e., steam reforming of methane to CO\(_2\) and H\(_2\) becomes favorable. This would suggest that, if operated in a thermodynamically controlled regime, in order to minimize CH\(_4\) concentration in the product stream, the reaction temperature should be kept as high as possible. However, as shown in Fig.3, once the temperature is increased above 550 °C, the reverse-water-gas shift reaction takes off, i.e., CO formation becomes significant and hydrogen yield
decreases. At this ethanol-to-water ratio, there is no solid carbon at the equilibrium state.

**Figure 3.** Product distribution from ethanol steam reforming at thermodynamic equilibrium with EtOH:Water = 1:10 (molar), $C_{\text{EtOH}}=2.8 \%$, and atmospheric pressure

**Figure 4.** Effect of EtOH-to-water molar ratio on equilibrium $H_2$ yield and C selectivity at (no dilution)

Fig.4 shows the effect of ethanol-to-water molar ratio on $H_2$ yield. Lower molar ratios of ethanol-to-water can increase the hydrogen yield, since both water gas shift reaction and $CH_4$ reforming reactions would shift to the left with increased water concentration. In Fig.4, solid carbon selectivities for the lowest water concentrations are also included. At high ethanol-to-water ratios, solid carbon deposition becomes thermodynamically favorable, especially at lower temperatures.

The effect of dilution with an inert gas on the equilibrium $H_2$ yield is shown in Fig.5. The addition of inert gas increases the equilibrium hydrogen yield at low temperatures and has no effect at high temperatures. At low temperatures, the dominant reaction is the methanation/methane steam reforming. Diluting the system favors the methane steam reforming, and hence we see a difference at
low temperatures. At high temperatures, the main reaction is the reverse water gas shift reaction, which is not affected by dilution, since there is no change in the number of moles with the extent of this reaction. Increased pressure has a negative influence on hydrogen yield at lower temperatures and no effect at higher temperatures (Fig.6).

![Figure 5. Effect of dilution on equilibrium hydrogen yield (Dilution ratio used: Inert:EtOH:H₂O = 25:1:10)](image)

![Figure 6. Effect of pressure on equilibrium hydrogen yield (EtOH:Water=1:10 (molar ratio), no dilution)](image)

Although it is important to be aware of the thermodynamic limitations, these analyses do not provide any information about the product distribution that would be obtained under kinetically controlled regimes. However, the study is still meaningful for guiding the choice of the desirable reaction parameters such that reaction is always controlled by kinetics under thermodynamically favorable conditions.

### 1.2 Catalytic Systems

In order to achieve equilibrated or even higher hydrogen yield especially at lower temperatures, catalytic bio-ethanol steam reforming (BESR) has been studied increasingly in recent years. More than two hundreds papers have been
devoted to this field within the last two decades. The catalyst systems developed in these studies can be generally classified into two categories, i.e., supported noble and non-noble metal catalysts [8, 9]. However, based on the results reported in the literature, there is no commonly accepted optimal catalyst system which has excellent performance as well as low cost.

The noble metal catalysts such as Rh, Ru, Pd, Pt, Re, Au, and Ir [10-15] have been extensively investigated for BESR, which exhibit promising catalytic activity within a wide range of temperatures (350 °C~800 °C) and gas hourly space velocities (GHSV: 5,000~300,000 h⁻¹). The outstanding catalytic performance experienced by noble metal catalysts might be closely related to its remarkable capability in C-C bond cleavage [16]. Among the noble metal catalysts reported so far, it is evidenced [17-20] that Rh is generally more effective than other noble metals in terms of ethanol conversion and hydrogen production. Diagne et al. [21] claimed that up to 5.7 mol H₂ can be produced per mol ethanol (equal to 95 % H₂ yield) at 350 °C–450 °C over CeO₂–ZrO₂ supported Rh catalyst. However, although the metal loading is relatively low (1~5 wt.%) compared with its non-noble counterparts (10~15 wt.%), the extremely high unit price still limits its wide-scale industrial applications.

As a less expensive alternative way to address the cost issue, increasing attention has been focused on the development of non-noble metal catalysts. According to the publications documented so far, the efforts are mainly focused on the Cu, Ni, and Co based catalyst systems, especially supported Ni catalysts. As typical transition metals, the active outer layer electrons and associated
valence states determine their identities as the candidates for BESR. Similar with noble metals, Ni also works well as it favors C-C rupture. Based on the observations reported by several authors [14, 19, 22], the non-precious metals are less reactive than noble metal supported samples. Specifically, Rh sites resulted to be 3.7 and 5.8 times more active than Co and Ni, respectively, supported by MgO under the reaction conditions used in [19]. For obtaining the same reactivity (H\textsubscript{2} yield > 95 \%), much higher temperatures (650 °C) have to be employed [19, 23] over Ni catalysts. Furthermore, the non-noble metals are more prone to be deactivated due to sintering and coking compared with Rh. In order to achieve the comparable catalytic performance with noble metals, the formulation modifications of non-noble metal catalyst systems are worth studying for future commercialization. After summarizing the papers dedicated to investigation of various supports, ZnO and La\textsubscript{2}O\textsubscript{3} seem more promising than MgO, Y\textsubscript{2}O\textsubscript{3}, and Al\textsubscript{2}O\textsubscript{3} in terms of activity and stability [24, 25]. The basicity of sample surface has been evidenced crucial to improve its stability by adding La\textsubscript{2}O\textsubscript{3} into the Al\textsubscript{2}O\textsubscript{3} support aiming to neutralize the acidic sites present on the Al\textsubscript{2}O\textsubscript{3} surface [26]. The addition of alkali metals (e.g., Na, K) to Ni/MgO has been observed to depress the deactivation occurrence by preventing Ni sintering [27]. It is worth noting that the recent interests on Ni catalysts seem to be transferred to CeO\textsubscript{2} and ZrO\textsubscript{2} supported samples, which could be ascribed to its well-known oxygen mobility, oxygen storage capability (OSC), and thermal stability [28-31], in turn improving coke-resistance. In addition, the synergetic effects become notable leading to better catalytic performance (activity, selectivity, and stability)
when the second component (Cu) is incorporated into the Ni catalysts indicated by the work performed by Fierro et al., Marino et al., and Velu et al. [32-34]. They believe that the introduction of Cu might favor the dehydrogenation of ethanol to acetaldehyde, one of the important surface reaction intermediates during BESR. Compared with Ni based catalysts, cobalt samples have been less studied as catalysts for BESR. However, recent years have witnessed a significant increase in publications focusing on the development of Co-based catalysts, among which is the pioneering work by Haga et al. [35, 36]. Then Llorca et al. reported the promising results that 5.1 mol of H₂ can be produced per mol of reacted ethanol over Co/ZnO sample [37]. Although the reaction condition is slightly unrealistic for industrial applications, this study proved that cobalt is also efficient in C-C bond breakage [38]. Neither copper nor nickel alone supported on zinc oxide appears to have as good reactivity and stability as that of its Co counterpart for hydrogen production under the same reaction conditions [39, 40]. After thorough investigation of the product distribution at various temperatures, it was indicated that the copper sample prefers dehydrogenation of ethanol into acetaldehyde but the reforming reaction does not further progress significantly into H₂ and COₓ. On the other hand, the nickel sample favors the decomposition reaction of ethanol to CH₄ and COₓ, accounting for the lower H₂ yield at lower temperatures. Only at high temperatures can the methane production be lowered through steam-reforming. Moreover, Co catalysts have been applied in the Fischer-Tropsch to generate liquid hydrocarbons for more than 80 years. The knowledge accumulated during the study of Co based catalyst systems provides a good
starting point. With these encouraging initial data, cobalt catalysts merit to be studied extensively as an alternative solution for reducing the cost from usage of noble metals.

1.3 Optimization of Cobalt Catalyst Systems

In order to acquire competitive catalytic performance with noble metals, a series of optimization procedures need to be carried out over cobalt based catalysts. The significance of support was first explored by Haga et al. [35] indicating that Co/Al₂O₃ shows more promising activity than SiO₂, C, ZrO₂, and MgO. A relatively systematic investigation of the effect of supports was performed by Llorca and his coworkers [41]. Among the supports of CeO₂, Sm₂O₃, MgO, Al₂O₃, SiO₂, TiO₂, ZnO, La₂O₃, V₂O₅ reported in this study, ZnO was ranked the best.

Recently mixed metal oxides have been employed as the support to improve the behavior of single metal oxides by doping one or more additional components into the original support lattice. For instance, in the implementation of Ce₁₋ₓZrxO₂, as the washcoat material in three-way catalysts, support combines the oxygen mobility of CeO₂ and thermal tolerance of ZrO₂ [42-45]. The introduction of Ca creates oxygen vacancies, which is beneficial for the enhancement of oxygen mobility [46, 47]. Besides, the perovskite-type oxides such as LaAlO₃, SrTiO₃, and BaTiO₃ have been used as the support for BESR catalysts due to their highly labile lattice oxygen [48, 49].

The cobalt precursor was proved by several authors [36, 50, 51] to have prominent effect on catalytic performance, which was proposed to be related to
the cobalt dispersion. From the comparison between several precursor candidates, the one complexed with organic functional groups gave higher dispersion, which could be attributed to its isolation effect on the nearby Co atoms from agglomeration. It has been accepted that the active site during bio-ethanol steam reforming is related to the metal cobalt [52], that is, the higher the percentage of the cobalt that is available, the better the catalytic performance for BESR. Therefore, the improvement of cobalt dispersion will benefit the enhancement of corresponding catalytic activity.

It is expectable that cobalt loading has direct impact on the cobalt dispersion in the final catalyst. From the studies performed over Ni-based catalysts [29, 53], there exists an optimal loading, which can obtain the highest metal dispersion, through increasing the metal loading while avoiding metal sintering occurring at high loading due to the agglomeration of nearby metal atoms during thermal treatment. To the best of our knowledge, there is no systematic research of the effect of cobalt loading on its catalytic performance during BESR. Therefore, executing such a study can provide us better control of the catalyst optimization.

The impregnation medium is expected to have influence on the diffusion of cobalt precursor during impregnation and redistribution of cobalt atoms during the subsequent thermal treatment, which is shown by the experimental observations over Co/SiO₂ [54]. The smaller Co₃O₄ crystallite size obtained for samples using ethanol rather than water as impregnation solvent is attributed to the formation of ethoxyl groups on silica and/or Co₃O₄ surface during impregnation which hindered the sintering of Co₃O₄ by physically interfering
during the thermal decomposition of nitrates. As a result, a higher percentage dispersion of cobalt metal was achieved from reduction of smaller crystallites of Co$_3$O$_4$. In addition, further sintering of cobalt metal during reduction might be hindered by ethoxyl groups as well. Since the cobalt dispersion is closely correlated to the activity during BESR as described above, this effect needs to be further investigated.

It was reported by Enache et al. [55] and Ruckenstein [56] in their studies of cobalt-based catalysts for Fischer-Tropsch reaction that the parameters used in the sample heat treatment before being charged for reaction play a significant role on the cobalt dispersion and in turn catalytic activity. Thus the synthesis parameters during calcination and reduction need to be explored to optimize the catalytic performance.

The promotion effect of alkali metal addition has been observed separately by Llorca et al., and Galetti et al. [39, 40, 57]. The hydrogen yield enhancement and carbon deposition inhibition showed the improvement of catalytic performance even when a small amount of Na and K (~0.7 wt.%) was introduced. As an inexpensive additive, this promising modification should be included in the future work plan.

Similar to Ni catalysts, promotion effect has also been evidenced over the samples with the formation of metallic alloy. According to the results published so far, the second active metal in addition to Co can be generally categorized as noble metals (e.g., Rh [58] and Ru [59-61]) and non-noble metals (e.g., Ni, Cu [39, 62], Fe, and Mn [63]). The integration of each metal specialized in different
functions might be responsible for the synergetic interaction on the improvement of catalytic performance. The non-noble metal additives also merit further investigation.

Not only the modifications to the formulation of catalyst system, but also the preparation methods can impact the catalytic performance. Versatile synthesis strategies have been developed for obtaining catalysts with high performance during BESR. Incipient wetness impregnation (IWI) [64-67], wet impregnation [60, 68, 69], sol-gel (SG) [70, 71], and co-precipitation (CP) [39, 40, 62, 63] are the most commonly utilized methods, each of which has its own advantages and disadvantages. Impregnation is the most convenient method to be scaled up, for manufacturing. However, nonhomogeneous distribution of the metal precursor is the biggest issue associated with the impregnation method, leading to metal agglomeration, one of the reasons which contribute to catalyst deactivation. On the contrary, it is easier for SG and CP to achieve homogeneous dispersion of active metal. However, the synthesis procedure of SG and CP is more complicated compared with that of impregnation, leading to poor reproducibility between various batches. Also, since most of the active metal atoms are embedded in the matrix of support, resulting in less exposure of active metal on the sample surface, SG and CP prepared samples are more stable but less active than those prepared by impregnation. In addition, several novel preparation protocols such as hydrothermal [72], solvothermal [73], and microemulsion [74] have been developed to control the sample particle size and morphology which have been shown to be highly relevant to catalytic activity. On
the other hand, most of the newly developed methods mentioned involve the employment of organic solvents, which could be harmful to the surroundings. Although all the preparation techniques documented up to now supply abundant resources to start with, the establishment of an appropriate method balancing low cost, easy operation, and environmental benignancy is important to be included in the proposed work plan.

1.4 Investigation of Reaction Mechanisms for Ethanol Reforming

As can be seen in Section 1.1, the reaction network which would possibly occur during BESR is fairly complicated and heavily dependent on the catalyst system employed. In order to obtain maximum amount of hydrogen out of ethanol used, the side reactions should be effectively suppressed, leading to the minimization of byproducts such as methane, carbon monoxide, acetaldehyde, acetone, acetic acid and so on. For controlling the reaction proceeding along the desired pathway which will give us the highest hydrogen yield, it is critical to gain a comprehensive understanding of the reaction mechanisms involved, which will in turn guide the rational design of catalyst system. There are two approaches we can follow to achieve our final goal, that is, theoretical and experimental directions. The theoretical approach (reaction mechanism study through computational chemistry) is still at its initial stage referring to the papers published in this area and will be covered in detail in Chapter 14. However, the experimental route has been widely adopted to study the catalytic behaviors present during BESR.

As an interfacial phenomenon, any heterogeneous catalytic reaction takes
place involving three basic steps: reactants adsorption, surface reaction, and products desorption. To be a gas-solid reaction, catalytic BESR must embroil gas composition variation and catalyst surface evolution. Therefore, in order to attain a complete view of the reaction, systematical investigation should be performed on both gas and solid phases. Gas chromatography (GC) and mass spectrometer (MS) are the two popular instruments used to monitor the gas phase composition and fourier transform infrared spectroscopy (FTIR) can detect the surface species and their evolutions during BESR. In addition, using other characterization techniques including nuclear magnetic resonance (NMR) and laser Raman spectroscopy (LRS) can provide an alternative way to get better insight into the reaction mechanisms.

Based on the results reported in the literature, the dehydrogenation and dehydration reactions are the two pathways ethanol can go through first, the choice of which depends on the catalysts charged. If the catalyst has high acidity (e.g., Al₂O₃ and SiO₂ [75, 76] supported samples), dehydration reaction is favored, resulting in the formation of C₂H₄, a precursor of coking through polymerization. If the catalyst present basic features (e.g., MgO and ZnO [77, 78] supported sample) instead, dehydrogenation reaction is preferred, leading to the production of acetaldehyde, an important reaction intermediate related to higher H₂ yield. Acetaldehyde can then be decomposed into CH₄ and CO [79] or undergoes steam reforming to generate CO and H₂ relying on the catalyst employed. These single carbon containing products (CH₄ and CO) can be further reformed to CO₂ and H₂ through methane steam reforming and water-gas shift
reaction if sufficient water is supplied. Besides, two acetaldehyde molecules can react with each other to form acetone through aldol condensation reaction [15] or be oxidized to acetic acid [80]. Carbon can be formed at various stages from carbon-containing species via either cracking or Boudouard reaction [81].

Ethanol adsorption and subsequent surface reaction have been extensively studied over many different catalyst systems employing FTIR technique. Although the exact locations of the ethanol adsorption bands vary with catalysts tested, the identifications of surface species and its evolutions are well established. Ethanol can be adsorbed on the sample surface dissociatively and molecularly [82-84]. The ethoxide species is the result of ethanol dissociative adsorption. Then the surface acetate species is obtained from the oxidation of ethoxide by the lattice oxygen coming from the sample surface [85, 86]. The acetate species can then experience C-C breakage leading to the formation of single carbon fragments. Whether these fragments will be released directly from the surface or undergo further oxidation to carbonate species is closely linked to the sufficiency of oxygen stored in the sample. The adequate oxygen supplies benefit the formation of carbonate species. Finally CO₂ originates from the decomposition of carbonate species. However, compared with ethanol, water adsorption and its role in the subsequent surface reaction remain unclear for BESR. Therefore, the surface features need to be investigated during water adsorption and co-adsorption of water and ethanol.

¹³C NMR technique has been applied into the study of ethanol adsorption behavior to track the evolution of carbon containing species over Cu/ZnO [87].
Different oxygenate species have been identified after integrating with the results obtained from MS. Unfortunately, just 1-C was labeled in the ethanol molecule, in order to get a comprehensive picture of the surface species and its evolution after ethanol adsorption, 2-C, even H and O labeled ethanol is also worth being considered. A similar approach is also applicable for water adsorption and co-adsorption of ethanol and water by choosing suitable isotopic labeled elements.

Based on the observations obtained from both gas phase and sample surface, several kinetic models have been proposed to simulate the mechanistic behaviors of various catalyst systems [88-92], which will facilitate better understanding of the reaction mechanisms. If the estimated values are in good consistency with the reported experimental results, the assumed reaction pathways and rate-determining step (RDS) will uncover the actual reaction mechanisms to a certain level. Furthermore, the activation energy measured from this study provides the reference for molecular simulation. In addition, the outcomes from this kinetic analysis will benefit the reactor design which can promote mass and heat transfer during reaction.
CHAPTER 2

REACTOR SYSTEM

A reactor system (shown in Fig.7) has been designed for BESR and oxidative ethanol steam reforming (OESR), for catalytic performance evaluation and kinetic studies. Various gases can be sent into the system at desired flow rates controlled through several mass flow controllers. Solenoid valves are installed right after each mass flow controller for remote control. The addition of pressure relief valve will prevent system from operating under high pressure. Furthermore, the pressure is monitored by both a pressure gauge and a pressure transducer right before the inlet of the reactor. The synthesized feed with desired molar ratio of water-to-ethanol or the crude ethanol solution obtained from the fermentation of biomass can be sent into the system either through bubblers or through the combination of a HPLC pump and an evaporator. The temperatures of the bubblers are separately controlled for achieving desired ratio of ethanol-to-water. The evaporator is heated above 200 °C for rapid evaporation of all the liquid mixture fed. The liquid vapor generated is then carried out by a carrier gas and subsequently fed into the reactor for reaction. In order to prevent re-condensation of the liquid vapor, all the gas lines after the bubblers and the evaporator are heated by the heating tapes slightly above 100 °C. The
Figure 7. Schematic diagram of the reactor system for the bio-ethanol steam reforming
thermocouples are distributed throughout the reactor system to ensure that the temperatures be maintained at appropriate ranges. The sample pretreatment, reaction, and regeneration steps have been integrated into one system. The reactant and product streams can be analyzed online by either being directly injected into a GC or first passing through a condenser and then being sent into the GC separately. Analysis methods have been developed to identify and quantify the reaction products. An on-line mass spectrometer has also been included for additional product analysis or for isotopic labeling studies.

The analysis of the reactants and all the reaction products is carried out online by gas chromatography (Shimadzu Scientific 2010). Analysis is done using two different detectors and the separation is achieved using two different sample injection loops/valves and two analysis lines: The first line consists of a Carboxen column and a 5-Å molecular sieve column connected in series in a column isolation scheme. This combined column arrangement is used in conjunction with a Pulse DischargeHelium Ionization Detector (PDHID). The second line is a separate 30m-long Q-Plot column used with a Methanizer and a Flame Ionization Detector (FID) to allow detection of CO down to 10 ppm. Helium is used as the carrier gas for both analysis lines. All the carbon containing products can be separated by the Q-Plot column and detected by FID. PDHID can detect all the products in the stream, including CO, CO₂, and H₂. Feed stream analysis is performed before each catalytic test. Response factors for all products are obtained and the system is calibrated with appropriate standards periodically.
In order to improve the system safety and provide automatic shutdown capability in case of emergencies, Labview® is installed and programmed specifically for communication between the instruments and the computer terminals. NI SCC-TC02, SCC-SG24, and SCC-DO01 which were boxed into the SC-2345 signal conditioning connector block were chosen as modules for temperature, pressure, solenoid valve monitor and control. The NI PCI-6220 board was inserted into the slot of the mainboard of the dedicated computer for data transferring. The user interface shown in Fig.8 has been developed through Labview programming. All the components including the plumbing of the reactor system are displayed in the front panel of the interface according to the actual layout. The solenoid valves and all the two-way valves are represented as the red blocks. All the temperature indicators are located beside the components whose temperature should be monitored. The system pressure is displayed by the pressure gauge indicated by the dial. The flow rates of all the mass flow controllers can be input into the controls located at the bottom right of the front panel. In addition, all the control buttons have been concentrated at the bottom left corner. All the real manual operations to the reactor system have been simulated in the software by just pressing corresponding buttons. The actual gas flow within each line is indicated in the panel through changing of the color to blue (shown in Fig.9). The identity of each gas in each line is also indicated on the panel when the cursor is moved near the point of interest. The liquid level of each bubbler can be indicated by the scale beside them. Furthermore, the liquid level can change according to the saturated vapor pressure calculation at the
Figure 8. The user interface of the reactor system
Figure 9. The user interface of the reactor system while running
specific temperature and the time and the flow rate of the carrier passing through the respective bubbler. Moreover, when the liquid level is low, then a prompter appears to remind the user. The subsequent manual refilling of the liquid can be simulated by clicking the corresponding button located within the control sub-panel. A similar prompter is also established for the liquid feed “tanks”. The stop button within the same area can stop the system when an emergency happens or the operator wants to halt the operation on purpose. While exiting, the solenoid valve will be closed automatically and the whole system will be restored to the initial status. Simultaneously, all the important operation parameters, such as the flow rate of each mass flow controller and the pump, and the liquid level of each bubbler and the raw material tank, will be saved into a file, through which all the information can be restored to each corresponding component when the system is restarted the next time. In addition, the abnormal temperature and pressure of the system can trigger an alarm by setting the range of such parameters and all the solenoid valves will be automatically shut down to prevent pressure buildup. In case of an emergency, the flow can be shut down by closing the solenoid valves. Furthermore, the reactor system can be remotely monitored and controlled through visiting the website of http://cbe-p102.chbmeng.ohio-state.edu/Bio-ethanol Steam Reforming Reactor System.html.

A safety review focusing on the reactor system and associated equipment have been performed by the safety committee consisting of experienced personnel. A detailed hazard analysis/risk mitigation plan has been developed prior to reactor installation and has been revised as needed. The plan identifies
safety vulnerabilities and a detailed process hazard analysis. A detailed SOP has been compiled and is revised as needed depending on the modifications to the reactor system. The schematic diagram, normal start-up, shutdown, and emergency shutdown procedures are also attached nearby the system for daily reference.
CHAPTER 3

EFFECT OF SUPPORT

In this study, we examined Co catalysts on different supports including alumina, titania and zirconia. Our research is focused on interactions between metal and supports, nature of active sites, and surface intermediates during reaction. An incipient wetness impregnation method was used for catalyst preparation. Catalysts were tested for their activity in ethanol steam reforming using an in-house-built reactor system. Characterization was performed using TGA, H₂ chemisorption, temperature-programmed reaction (TPRxn), laser Raman spectroscopy, and DRIFTS. It was found that zirconia supported cobalt catalysts gave the best cobalt dispersion. Zirconia was chosen as the support for further studies. DRIFTS was used to investigate surface interactions with reactant molecules during reaction.

3.1 Experimental

3.1.1 Catalysts preparation

Supported cobalt catalysts with different weight loadings were prepared in the air by incipient wetness impregnation from cobalt (II) nitrate hexahydrate (Aldrich 99.999%) aqueous solutions. The supports used and their corresponding surface areas and pore volumes were γ–Al₂O₃ (199 m²/g, 0.44 cm³/g), TiO₂ (59
m²/g, 0.11 cm³/g), ZrO₂ (31 m²/g, 0.21 cm³/g), all of which were purchased from Saint Gobain. The support pellets were ground and then sifted through a 100–150 mesh. The sifted supports were then calcined for 3 h under air at 500 °C prior to impregnation. After repeating impregnation and drying in an oven overnight at approximately 95 °C as many times as determined by the pore volume of each support, some of the resulting samples were calcined at 400 °C for 3 h under air and stored for use, the rest were kept uncalcined for thermogravimetric analysis.

3.1.2 Catalysts characterization

The TGA experiments were performed on a Perkin-Elmer TGA7 instrument. The system is capable of quantitatively measuring the change in mass of a sample as a function of temperature up to 1000 °C. The change in mass is then related to the changes taking place in the catalyst during calcination. For each sample prepared, air was flown through the TGA at 25 mL/min as the temperature was ramped at 10 °C/min.

The volumetric measurement of H₂ chemisorption was conducted using a Micromeritics ASAP 2010 Chemisorption system. Prior to adsorption measurements, calcined samples were reduced in situ under 5% H₂/He at the desired reduction temperature (in this case 400 °C) for 3 h followed by evacuation to 10–5 mmHg and cooling down to 35 °C. The adsorption isotherms were measured at equilibrium pressures between 50 and 500 mmHg. The first adsorption isotherm was established by measuring the amount of H₂ adsorbed as a function of pressure. After completing the first adsorption isotherm, the
system was evacuated for 1 h at 10–5 mm Hg. Then a second adsorption isotherm was obtained. The amount of probe molecule chemisorbed was calculated by taking the difference between the two isothermal adsorption amounts.

TPRxn experiments were performed using the Cirrus MS (MKS Instruments, 1–300 amu) to monitor reactor outlet composition. The samples were pre-reduced (5 % H₂/He, 30 mL/min) at 350 °C and cooled to room temperature under helium. The feed for the TPRxn experiments was provided by saturating helium steams with water and ethanol in a doublebubbler arrangement to provide an ethanol:water molar ratio of 1:10. After stabilization of water and ethanol signals, the temperature was ramped at 10 °C/min.

The Raman spectroscopy was performed using a 514.5 nm argon ion laser on a Laser Raman spectrometer (Kaiser) with a 1000 X microprobe. The three catalysts tested were zirconia supported Co catalysts with different Co loadings: 5, 10 and 15 wt%. The spectra of ZrO₂ and Co₃O₄ were also taken as the standards for crystal phase identification.

The DRIFTS experiments were performed on a Bruker IFS66 DRIFT spectrometer equipped with a MCT detector. The catalyst used for the DRIFTS experiment was the 10 % Co/ZrO₂ calcined at 400 °C for 3 h. The catalyst was pre-reduced in situ at 350 °C while flowing 5 % H₂/He for 2 h. An ethanol and water mixture (1:10 ratio) was then allowed to adsorb onto the catalyst surface for one hour. The system was then flushed with helium. The spectra were taken after stabilization at each temperature.
3.1.3 Catalytic tests

All catalysts were first pretreated at 300 °C for 30 min under He and then reduced in situ at 400 °C for 2 h under 5 % H₂/He. Subsequently the catalytic performances were tested in the temperature range of 300–550 °C, in 50 °C increments. The catalyst was held at each temperature for at least 2 h. At the end of the catalytic test, the flow of EtOH + H₂O was stopped and the catalyst was cooled under He stream.

The H₂ yield and ethanol conversion were defined the same as those used for thermodynamic analysis given in the 1.1 section.

3.2 Results and Discussion

3.2.1 TGA

The changes occurring during the calcination of catalysts were studied through TGA. Fig.10 shows the derivative of the mass (DTG) profile obtained during calcinations. The TGA profiles for the cobalt catalysts supported on titania and alumina are very similar. They each have only one sharp peak corresponding to the weight loss associated with decomposition/oxidation of nitrates and precursor materials from the catalyst. However, TGA results over the zirconia-supported sample show that there is greater interaction between the
support and the metal as seen through additional mass change features at higher temperatures.

3.2.2 Raman

Fig. 11 shows the Raman spectra of Co/ZrO₂ with different Co loadings after calcination. Compared with ZrO₂ (monoclinic) spectra, it is evident that the surface of ZrO₂ in all the samples has been covered by cobalt particles even if the cobalt loading is as low as 5 wt%, resulting in the absence of ZrO₂ characteristic peaks in the sample spectra. The only Raman features visible are those of CO₃O₄ as identified by the Co₃O₄ standard spectrum.

3.2.3 H₂ Chemisorption

As suggested by the TGA results, interactions between the cobalt metal and the support varied significantly, depending on the support material. The support effects are likely to result

![Figure 11](attachment:raman_spectra.png)

**Figure 11.** Raman spectra of ZrO₂ support, CO₃O₄ and Co/ZrO₂ with different Co loading levels

![Figure 12](attachment:chemisorption.png)

**Figure 12.** Cobalt dispersion measured through H₂ chemisorption over different supports
in differences in cobalt crystal size and dispersion on the surface after reduction. H$_2$ chemisorption was used to determine the ratio of exposed metal atoms to total metal atoms (dispersion (%)). The dispersion calculation is based on a stoichiometry of 1 H atom per metal atom. As shown in Fig.12, ZrO$_2$ supported catalysts gave the highest metal dispersion compared with the alumina and titania supports. The lowest cobalt dispersion was observed for the titania-supported catalyst.

3.2.4 DRIFTS

![Figure 13. In-Situ DRIFT Spectra of 10 %Co/ZrO$_2$ after adsorbing ethanol and water vapor (1:10, molar ratio) at room temperature](image)

The reaction intermediates on the surface of 10 % Co/ZrO$_2$ were investigated through DRIFTS. The evolution of surface species along with the
increase of reaction temperature is shown by DRIFT spectra shown in Fig. 13. At room temperature, the band located at 1653 cm\(^{-1}\) [107] is due to the O–H scissoring coming from adsorbed water. The monodentate and bidentate ethoxide (drawn on the top left in Fig. 13) is formed on the sample surface, as identified by the CH\(_3\) bending (1458, 1385 cm\(^{-1}\)) and CCO stretching (1169, 1105, 1063 cm\(^{-1}\)) vibrations due to ethanol adsorption [10,66]. Initial temperature increase favors the ethoxide adsorbed in bidentate form. The bands characteristic of ethoxy species subsequently disappeared with the further increase in temperature due to the BESR reaction happening. The presence of surface acetate species has been identified at 1569 cm\(^{-1}\) (\(\nu_{\text{assym}}(\text{COO})\)), 1429 cm\(^{-1}\) (\(\nu_{\text{sym}}(\text{COO})\)), and 1380 cm\(^{-1}\) (\(\delta(\text{CH}_3)\)) [85]. As seen in Fig. 13, these species could first evolve to monodentate carbonate [64,108] as an intermediate, then dissociate into gas molecules, such as CO, CO\(_2\) and CH\(_4\).

3.2.5 Activity tests

Fig. 14 shows some of the preliminary results presented in terms of ethanol conversion and hydrogen yields.

**Figure 14.** Steady state reaction results for 10%Co catalysts on different supports. Reaction conditions: H\(_2\)O:EtOH:Inert = 3:1:6 (molar ratio), GHSV=150,000 h\(^{-1}\) (a) Ethanol conversion rates (b) H\(_2\) yields.
conversion rates per catalyst surface area. The H$_2$O:EtOH:inert ratio is 3:1:6 and the GHSV is 150,000 h$^{-1}$. The results are interesting in showing the importance of the support on the performance of the catalyst. As shown, zirconia-supported catalyst has the highest activity based on equal surface area while alumina- and titania-supported cobalt catalysts show much lower activities (Fig.14a). When hydrogen yields are compared (Fig.14b), it is seen that only the zirconia-supported catalyst shows appreciable yields of hydrogen (at 450 and 500 °C) while the yields over the other two catalysts are much lower.

Although data not shown here, the alumina-supported catalyst showed selectivity mainly to ethylene, which is not surprising considering the many reports that show the acidity of alumina contributing to the formation of ethylene and coke. The titania and alumina-supported catalysts also showed selectivity to acetaldehyde while the zirconia-supported catalysts exhibited very low acetaldehyde formation. The cobalt–zirconia system presents itself as promising for hydrogen production from bio-ethanol steam reforming. Later in our work, zirconia supported cobalt catalysts were chosen as the focus of study.

The effect of Co loading on ZrO$_2$ support was also examined. The experimental parameters used for these

![Figure 15. Effect of catalyst loading on H$_2$ yield over Co/ZrO$_2$ catalysts](image)
reactions were 4 % EtOH, EtOH/H₂O ratio = 1:10, and GHSV = 250,000 h⁻¹. A comparison of the H₂ yields is presented in Fig.15. A loading of 10 % is found to give the highest H₂ yield at temperatures above 400 °C. The highest yield obtained over this catalyst is 75 % at 450 °C.

The TPRxn experiments for the 10 % Co/ZrO₂ catalyst calcined at 400 °C and reduced at 350 °C for 2 h have been performed to explore the product distribution under unsteady state. The reaction mixture consisted of 3 % EtOH and a EtOH:H₂O ratio of 1:10. The GHSV was 15000 h⁻¹. The results are shown in Fig.16. The light-off temperature for ethanol conversion is below 300 °C and by 430 °C, 100 % ethanol conversion is achieved. The H₂ signal rises sharply up to 430 °C and shows a slower increase up to 600 °C.

There is a decrease in H₂ signal at higher temperatures. Methane formation is limited to a temperature window between 300 and 430 °C. The CH₃COCH₃ formation is seen between 350 and 400 °C. The CO signal shows multiple maxima, possibly due to different reactions involved in its formation, including ethanol decomposition, CH₄ reforming and reverse water-gas shift reaction. The decrease seen in the CO₂ signal at temperatures above 450 °C is also likely to be due to reverse shift reaction. Other species observed include C₂H₆ or C₂H₄.
(C2) and diethyl ether, both of which are in very small quantities. TPRxn experiments are informative in demonstrating the complex reaction network involved in the ethanol steam reforming and how the product distribution is determined by the many competing reactions that become important at different temperatures.

Fig. 17 shows the steady state reaction results obtained over the 10% Co/ZrO₂ catalyst at a lower GHSV. The most striking result is the high H₂ yields that reach 75% at temperatures as low as 400 °C. At 550 °C, a H₂ yield of 92% is achieved, which is equivalent to 5.5 mol of H₂ produced per mol of ethanol fed. Compared with the equilibrium value obtained from thermodynamic calculation, 400 °C gives much higher experimental hydrogen yield, confirming that the reaction is kinetically controlled at lower temperatures. However, above 450 °C, the H₂ yield is very close to the equilibrium yield, indicating that thermodynamic limitation begins taking control at higher temperatures. In addition, ethanol can be fully converted at temperatures as low as 350 °C. What is also worth noting is that at temperatures above 475 °C, the only other product besides hydrogen and CO₂ is CO, making H₂ the only
H-containing product.

3.3 Conclusions

Initial studies on cobalt-based catalysts supported γ-Al₂O₃, TiO₂, ZrO₂ supports have shown promising results for BESR reaction. As determined by the H₂ chemisorption studies, ethanol conversion is found to correlate closely with metal dispersion and hence, the metallic Co sites. The product distribution, on the other hand, is determined by a complex network of competing reactions, including BESR, methanation, WGS, dehydration, and dehydrogenation. Among the supports studied, zirconia is shown to provide the highest metal dispersion and the highest H₂ yield. H₂ yields as high as 92 % (5.5 mol of H₂ per mole of ethanol fed) are achieved over a 10% Co/ZrO₂ catalyst at 550 °C.
CHAPTER 4

EFFECT OF SYNTHESIS PARAMETERS

In the previous chapter, we have reported the effect of different supports on the activity of Co-based catalysts in ethanol steam reforming. In this study, we report the effect of synthesis parameters on the BESR activity of ZrO₂-supported cobalt catalysts prepared by incipient wetness impregnation method. Effects of calcination temperature, reduction temperature, and reduction time were examined systematically. Characterization was performed using BET surface area measurement, H₂ chemisorption, TPR, temperature programmed oxidation (TPO), XRD, XPS, temperature programmed calcination (TPC), Laser Raman Spectroscopy (LRS), thermogravimetric analysis (TGA), ethanol pulse chemisorption, and temperature programmed reaction (TPRxn) techniques. It was found that under different treatments, physical and chemical properties of the catalyst vary significantly, affecting the catalytic performance in ethanol steam reforming.

4.1 Experimental

4.1.1 Catalyst preparation

Supported cobalt catalysts with 10 wt% metal loading were prepared in air by incipient wetness impregnation from cobalt (II) nitrate hexahydrate (Aldrich
aqueous solution. The support used was ZrO$_2$ (Saint Gobain) with a surface area and pore volume of 55 m$^2$ g$^{-1}$ and 0.21 cm$^3$ g$^{-1}$, respectively. The support pellets were ground and then sifted to obtain a 100–150 mesh particle size. The sifted support was then calcined for 3 h in air at 500 °C prior to impregnation. After repeating the impregnation and drying steps (at 95 °C) as many times as determined by the pore volume of the ZrO$_2$ support, the resulting samples were divided into seven aliquots. Each of them was calcined at a different temperature for 3 h in the air and stored for use.

4.1.2 Catalysts characterization and activity tests

The surface areas of the prepared samples were measured using nitrogen adsorption at 77 K (Micromeritics ASAP 2010).

The volumetric measurement of H$_2$ chemisorption was conducted using a Micromeritics ASAP 2010 chemisorption system. Prior to adsorption measurements, calcined samples were reduced in-situ under 5 % H$_2$–He at the desired reduction temperature for various times, followed by evacuation to 1.33–0.67 KPa and cooling down to 100 °C to maximize activated chemisorption while minimizing H$_2$ spillover.[109] The adsorption isotherms were measured at equilibrium pressures between 6.67–66.7 KPa. The first adsorption isotherm was established by measuring the amount of H$_2$ adsorbed as a function of pressure. After completing the first adsorption isotherm, the system was evacuated for 1 h at 1.33–0.67 KPa. Then a second adsorption isotherm was obtained. The amount of probe molecule chemisorbed was calculated by taking the difference between the two isothermal adsorption amounts. Metallic surface area was
determined by assuming a one-to-one stoichiometry between Co and atomic hydrogen and a crosssectional area of 0.0662 nm$^2$ for a Co atom.

XRD profiles were collected from 20° to 90° at a step width of 0.0144° using a Bruker D8 Advance X-Ray Diffractometer equipped with a CuKa source. In-situ XRD was also performed during calcination and reduction processes under air and 5% H$_2$–N$_2$, respectively, using a linear heating rate of 10°C min$^{-1}$ and holding at different preset temperatures for a given time for stabilizing and data collection.

XPS analysis was performed using an AXIS His, 165 Spectrometer manufactured by Kratos Analytical with a monochromatized Al X-ray source. A voltage of 2.3 V was chosen to balance the charging. A stainless steel holder was employed to support catalysts. The survey scan was performed to identify all the elements within the sample, followed by regional scans for Co 2p, C 1s, O 1s, Zr 3d orbitals in order to achieve the high resolution for elements of interest.

The calcination process was investigated through a TPC technique. The sample was sandwiched within two layers of quartz wool in a stainless steel reactor which was placed in the center of a temperature programmable furnace. A constant air flow rate was maintained over the sample throughout the process and the reactor outlet stream was monitored by a Cirrus Mass Spectrometer (MKS Instruments, 1–300 amu).

Raman spectra were taken with a LabRAM HR-800 spectrometric analyzer integrated with OLYMPUS BX41 microscope (50 X magnification) and CCD detector. The in-situ calcination experiment was performed under air (30 ml/min.)
using an “operando cell”. The sample was first heated to various temperatures and cooled down to room temperature where the spectra were taken using an argon ion green laser (514.5 nm, operated at 3 mW). The similar procedure was followed while performing in-situ reduction experiment under 5 %H₂/He.

H₂ TPR experiments were performed using a laboratory flow system equipped with a thermal conductivity detector. Samples of 100 mg were subjected to an oxidative cleaning step at the samples’ calcination temperature in air, followed by cooling to room temperature under helium. TPR experiments were subsequently performed under 5 % H₂–N₂ (30 ml min⁻¹) with a heating rate of 10 °C min⁻¹.

The TPR–TPO–TPR was performed using an Autochem- 2920 (Micromeritics). The sample was first reduced under 10 % H₂–Ar with a heating rate of 10 °C min⁻¹. After cooling down under helium, the sample was subsequently oxidized under 10 % O₂–He with the same heating rate followed by the second TPR running under the same condition as the first one.

TGA experiments were performed using a TG-DSC 111 (SETARAM). Samples were first pretreated under helium (30 ml min⁻¹) at 400 °C for 30 min and then cooled down to the room temperature under helium. The mass signal was subsequently recorded during the temperature programmed increase with a ramp rate of 5 °C min⁻¹ under 5 % H₂–N₂ (30 ml min⁻¹).

The ethanol pulse chemisorption experiments were performed using an AutochemII 2920 at room temperature to measure the ethanol uptake capability of the catalysts prepared under various conditions. The sample loop was
calibrated by injections of a known volume of argon through the analyzer septum using a syringe. The ambient temperature and pressure corrections were incorporated for each measurement. The effluent from the sample was monitored by a Cirrus mass spectrometer by following the m/z ions of 2, 16, 18, 8, 31, 43, 44, 58, 59, and 60.

TPRxn experiments were performed using a Cirrus MS (MKS Instruments, 1–300 amu) to monitor reactor outlet composition. The H₂ signal was corrected using H₂–He flow of known concentration before each reaction for catalytic activity comparison. The samples of 100 mg were pre-reduced (5 % H₂–He at 30 ml min⁻¹) at pre-designated temperatures and cooled to room temperature under helium. The feed for the TPRxn experiments was provided by saturating helium streams with water and ethanol in a double-bubbler arrangement to provide an ethanol : water molar ratio of 1 : 10. The total flow rate was set at 60 ml min⁻¹. After stabilization of water and ethanol signals, the temperature was ramped at 10 °C min⁻¹ while the product signals were monitored by a mass spectrometer.

4.2 Results and Discussion

4.2.1 BET

The surface areas of the samples calcined at different temperatures were measured using the BET technique. The results are shown in Fig.18. As

![Figure 18. BET surface areas of 10 wt% Co/ZrO₂ calcined at different temperatures]
expected, the surface area decreases from 55 m² g⁻¹ to 48 m² g⁻¹ as the calcinations temperature increases from 250 °C to 550 °C. There are three distinct steps in the surface area decrease, between 250 and 300 °C, between 350 and 400 °C, and between 500 and 550 °C. The first step may signal the decomposition of the nitrate left behind from the synthesis. The second step may be due to the onset of crystallization of the Co oxide species. The final decrease observed at higher temperatures may be due to sintering and/or strong interaction between the support and the metal. The changes in the overall surface area are expected to affect the reducibility of the catalysts as well as their metallic surface areas, as will be discussed in the next sections.

4.2.2 H₂ chemisorption

Using a constant reduction temperature of 350 °C (5% H₂ for 2 h), the metallic surface areas of the samples calcined at different temperatures were measured. The results are shown in Fig. 19 (cobalt dispersion data are incorporated). A gradual increase in Co surface area was observed up to 400 °C followed by a sharper decline at higher calcination temperatures. This indicates that 400 °C is the optimum calcination temperature that will allow for the highest metallic surface area. The sintering of the cobalt oxide particles or the metal-support complex formation may suppress

Figure 19. Metallic surface areas of 10wt% Co/ZrO₂ calcined at different temperatures reduced at 350 °C for 2 h
the reducibility of the sample, which results in a decrease of cobalt dispersion at higher calcination temperatures.

To examine the effect of reduction temperature on the cobalt dispersion of the 10 wt% Co catalysts, several batches of the catalyst calcined at 400 °C but reduced at different temperatures (5 % H₂ for 2 h) were used in hydrogen chemisorption experiments. The results, which are given in Fig.20 (cobalt dispersion data are incorporated), indicate that the highest metallic surface area is obtained at 350 °C, after which a decline is observed. The sintering of the reduced metal cobalt particles could contribute to the decline of the cobalt dispersion at higher reduction temperatures.

The effect of reduction time was also examined by using samples calcined at 400 °C. The reduction temperature was kept constant at 350 °C while the duration of reduction was varied. The results are presented in Fig.21 (cobalt dispersion data are incorporated).

**Figure 20.** Metallic surface areas of 10 wt% Co/ZrO₂ calcined at 400 °C and reduced at different temperatures for 2 h

**Figure 21.** Metallic surface areas of 10 wt% Co/ZrO₂ calcined at 400 °C and reduced at 350 °C for different lengths of time
The metallic surface area was seen to increase up to 2 h and then steadily declined with the increasing reduction time. The maximum in the metallic surface area is likely due to competing effects of increased extent of reduction and increased agglomeration of the metal with increasing reduction time.

4.2.3 XRD

In order to identify the crystalline phases present in the cobalt catalysts after calcination and after reduction, XRD experiments were performed. The X-ray diffraction pattern of a catalyst calcined at 400 °C is presented in Fig.22. The diffraction line at 36.96 ° can be identified as the (311) crystal plane reflection from the cubic Co$_3$O$_4$ phase. The other diffraction lines in Fig.22 can be assigned to the monoclinic ZrO$_2$ crystal phase. The intensity of the Co$_3$O$_4$ pattern is very weak, implying that Co$_3$O$_4$ is well dispersed on ZrO$_2$ surface and not highly crystalline. There are no other phases detected.

The calcination process of the catalyst precursor was investigated using in-situ XRD technique. As shown in Fig.23, the monoclinic ZrO$_2$ support is visible at each temperature. The crystal phase of Co(NO$_3$)$_2$ is observed as the cobalt precursor and gradually disappears until a calcination temperature of 200 °C is
reached. The diffraction line that corresponds to cubic Co$_3$O$_4$ increases with increasing calcination temperature indicating the decomposition of cobalt nitrate to Co$_3$O$_4$. Above a calcination temperature of 400 °C, the area of the Co$_3$O$_4$ peak does not change. The sharpening of the Co$_3$O$_4$ peak at higher temperatures implies the sintering of the Co$_3$O$_4$ particles.

![Figure 23](image1.png)  ![Figure 24](image2.png)

**Figure 23.** In-situ XRD patterns of 10 wt% Co/ZrO$_2$ during calcination in air  
**Figure 24.** In-situ XRD patterns of 10 wt% Co/ZrO$_2$ during reduction under 5 %H$_2$/N$_2$. Catalysts were calcined at 400 °C for 3 h

The evolution of the crystalline phases during the reduction process is also shown through the in-situ XRD patterns acquired during reduction (Fig.24). The disappearance of the Co$_3$O$_4$ phase along with the appearance of the CoO phase coincides at a reduction temperature of 350 °C. The diffraction line that corresponds to the CoO phase disappears above 450 °C and a metallic Co phase appears at 525 °C.

**4.2.4 XPS**
The Co 2p regions of the XPS spectra of the 10% Co–ZrO₂ calcined at different temperatures are shown in Fig.25. At lower calcination temperatures there are very weak and broad features at about 6 eV higher binding energy from the main peaks, which may be due to shake-up lines, suggesting the presence of some Co²⁺ species on the surface. This may be due to nitrate species left behind from the impregnation step or to a CoO phase. At higher calcination temperatures (>400 °C), this feature disappears, indicating that a significant amount of cobalt was in the Co³⁺ oxidation state, consistent with Co₃O₄ in which 2/3 of the cobalt is in the Co³⁺ oxidation state. The absence of clear shake-up peaks on these samples containing 10 % Co is not surprising, since even the shake-up peaks observed from bulk Co₃O₄ were relatively weak.[110–112] Calcination at higher temperatures (> 450 °C) leads to a decrease in intensity. From this observation, it appears that the cobalt oxide particles begin to sinter with the increasing calcination temperature above 450 °C, resulting in a decrease in Co surface concentration.

The reduction process is also monitored by employing XPS technique. Fig.26 shows the XPS Co 2p region spectra collected over 10 %Co/ZrO₂ at three
different reduction stages. The room temperature spectrum indicates the presence of Co$_3$O$_4$ evidenced by the characteristic binding energy of Co 2p$_{3/2}$ at 780.2 eV. After reduction at 350 °C, the whole spectrum is shift up to higher binding energy accompanied by the presence of the shake-up lines nearby the two main peaks, indicating the appearance of Co$^{2+}$. When the reduction temperature is raised up to 600 °C, the whole spectrum shifts back to lower binding energy with Co 2p$_{3/2}$ peak at 778.4 eV synchronized with the disappearance of the shake-up lines, which is the evidence of the metallic cobalt existence. In addition, the intensity decrease of the cobalt 2p XPS spectrum at 600 °C might be associated with the cobalt particle sintering at higher reduction temperature.

4.2.5 TPC

The evolution of the catalyst during the calcination process was also examined by calcining the sample in an air stream using a linear temperature program, while monitoring the gas phase effluents by an on-line mass spectrometer. The products eluting from the sample during the calcination process are shown in Fig.27. As expected, the water and NO$_x$ (determined by
m/z = 30 and 46 ion fragments) result from the decomposition of the cobalt precursor, Co(NO₃)₂•6H₂O. The m/z = 30 signal could be due to fragmentation of NO₂, however formation of NO cannot be ruled out. The elution of NOₓ up to temperatures well above 300 °C supports our earlier assertion that part of the Co may still be in a nitrate matrix when calcined below 400 °C, as seen through the XPS results. The water signal may also have a contribution from adsorbed H₂O. The CO₂ signal is also due to the CO₂ adsorption from the atmosphere during sample handling.

4.2.6 Raman

As a complementary tool to X-ray diffraction technique to study crystal structures, the Raman spectroscopy has been employed here to detect the phase transition of cobalt during calcination and reduction treatment.

Fig. 28 shows the Raman spectra of Co-Zr sample at different calcination temperature and the standard materials as the reference. Because CoO is less Raman active [192], less intensity of CoO in Raman spectra is obtained as a result, compared with Co₃O₄. The phase change is obviously observed during the calcination process, which indicates the existence of CoO as the intermediate oxidation state of Co during the decomposition of cobalt nitrate. The Co₃O₄ is formed when the temperature is above 400°C. Two clues can be concluded from
the evidence that the ZrO$_2$ support is never seen during the whole run when referred to the standard spectra from monoclinic ZrO$_2$. Firstly, the support has been fully covered after the impregnation of cobalt precursor. Secondly, the support never has a chance to expose to the air during the calcination.

Fig. 28. In-situ Raman results over 10 %Co/ZrO$_2$ during calcination

Fig. 29. In-situ Raman results over 10 %Co/ZrO$_2$ during reduction

Fig.29 shows the Raman spectra of Co-Zr sample at different reduction temperatures, along with reference spectra taken of unloaded m-ZrO$_2$, CoO, CO$_3$O$_4$ and metallic Co. Because CoO is less Raman active, spectrum for CoO is less intense compared with Co$_3$O$_4$. The spectrum of the calcined 10 %Co/ZrO$_2$ sample (before any reduction) is almost identical to the one obtained from the bulk Co$_3$O$_4$, while the vibrational bands that correspond to the ZrO$_2$ support are barely visible. This is likely due to the smaller Raman cross-section of m-ZrO$_2$. 
compared to that of $\text{Co}_3\text{O}_4$ [193].

There is no reduction up to 250 °C, resulting in no variation in the spectra. When the temperature is around 300 °C, the $\text{Co}_3\text{O}_4$ begins to be reduced, leading to the appearance of the $\text{ZrO}_2$ support. This could be explained by the size reduction of the cobalt oxide crystallites due to reduction and by the possibility that the larger Raman cross-section of $\text{Co}_3\text{O}_4$ is no longer “masking” the $\text{ZrO}_2$ signal. It is conceivable that there is an intermediate phase (CoO) that the sample goes through between 300 and 400 °C. At 400 °C, the only Raman signal visible is from the support.

4.2.7 TPR

The TPR profiles of the samples calcined at different temperatures are shown in Fig.30a. The first small peak at lower calcination temperature comes from residual nitrate from the catalyst preparation, since, as seen in Fig.27, the cobalt precursor is not completely decomposed until 400 °C. The first major feature is due to $\text{Co}_3\text{O}_4 \rightarrow \text{Co}^{2+}$ reduction and the second main feature results from the $\text{Co}^{2+} \rightarrow \text{Co}$ reduction step. The identification of the reduction steps was verified by measuring the hydrogen consumption through CuO reduction calibration. When the $H_2$ consumption quantified in the first peak is compared to the amount of $H_2$ needed for the $\text{Co}_3\text{O}_4 + H_2 \rightarrow 3\text{CoO} + H_2O$ reduction step, the relative error is found to be around 10 %. When a similar comparison is carried out between the $H_2$ consumed in the second step and $H_2$ needed for the $\text{CoO} + H_2 \rightarrow \text{Co} + H_2O$ reduction, the relative error is about 5 %. The TPR results agree very well with the in-situ XRD data, which showed the disappearance of $\text{Co}_3\text{O}_4$. 
and the formation of CoO around 350 °C and the formation of metallic Co above 450 °C under a linear temperature program.

Figure 30. (a) H₂-TPR profiles of 10 wt%Co/ZrO₂ calcined at different temperatures for 3 h, and (b) correlation of reducibility with H₂ chemisorption results

Fig.30b shows the variation of the second reduction peak temperature with calcination temperature. It is seen that the temperature for this second reduction step goes through a minimum with increasing calcination temperature. When the metallic surface area measured from H₂ chemisorption experiments is plotted on the same graph, the two curves show a mirror image of one another. Initial increase of reducibility may be due to structural changes in the cobalt phase as the nitrate phase decomposes and the Co₃O₄ phase is formed. Much higher calcination temperatures, on the other hand, lead to the sintering of the cobalt oxide particle, which contributes to the final decrease of the reducibility. The sample calcined at 400 °C has the minimum reduction temperature and should thereby be the easiest to reduce. The H₂ chemisorption results indicate that this
sample has also the maximum metallic surface area. The calcination temperature of 400 °C is also the lowest at which residual nitrate from the preparation is not present in the calcined sample. Based on these results, 400 °C is chosen as an optimum calcination temperature for these catalysts.

One of the questions that come to mind is whether a reduction temperature of 350 °C is sufficient to obtain metallic Co sites, since the bulk reduction to metallic Co takes place at a much higher temperature under a linear temperature ramp. To answer this question, a TPR experiment similar to the one described above was performed over a catalyst sample that was calcined at 400 °C and reduced at 350 °C for 2 h. The resulting TPR profile is shown in Fig.31. The TPR profile from a calcined sample is also included for comparison. Very low hydrogen consumption seen over this pre-reduced sample (manifested as a flat TPR profile) indicates that the prereduction treatment at 350 °C is sufficient to reduce most, if not all of the cobalt to metallic Co. Although under a linear temperature program, the reduction is not complete until much higher temperatures are reached, if the temperature is held for a longer time, the reduction process will proceed until the cobalt oxide is fully transformed into metallic cobalt even at lower temperatures. The reduction state of cobalt in the sample after reduction treatment at 350 °C for 2 h has also
been investigated by the XRD technique. As shown in Fig. 32, when the sample is kept at 350 °C for 2 h, the CoO phase disappears and the metallic phase appears, which is consistent with the TPR profile in Fig. 31.

4.2.8 TPR–TPO–TPR

The TPR–TPO–TPR experiment was performed on 10% Co–ZrO\textsubscript{2} calcined at 400 °C, the results of which are shown in Fig. 33. The sample, which went through an initial TPR process was oxidized under a similar temperature profile and then the TPR was repeated. Unlike the H\textsubscript{2} signal, the O\textsubscript{2} consumption signal is very weak since TCD has much less sensitivity for O\textsubscript{2}. Therefore, the O\textsubscript{2} consumption signal in Fig. 33 has been multiplied by 5 for better observation. As can be seen from Fig. 33, two reduction peaks are still observed after the oxidation of cobalt, which indicates that during the TPO step, the metal cobalt has been fully oxidized into Co\textsubscript{3}O\textsubscript{4} rather than to CoO. However, a higher starting point of the reduction and broader second peak
indicate that the sample is harder to reduce. Moreover, after integration, the area under the second TPR curve is seen to be smaller than that of the first H₂ consumption curve, which indicates that part of the sample has been sintered during the first TPR step at higher reduction temperatures. This amount of sample could not be oxidized, and consequently, could not be reduced again. Interaction of cobalt with the support at higher reduction temperatures to form some metal-support complex is also a possibility.

4.2.9 TGA

The reduction process of the sample is also investigated through the TGA technique. As shown in Fig.34, three mass losses in the TG signal and corresponding peaks in DTG curve (first derivative of the TG signal) are readily apparent. The first small peak comes from residual nitrate decomposition from the catalyst preparation. The first reduction peak is due to Co³⁺ → Co²⁺ and the second reduction peak comes from Co²⁺ → Co, which are calculated from the mass change. The results are consistent with the H₂ TPR profile in Fig.30a.

4.2.10 Ethanol pulse chemisorption

Because the catalytic performance of these materials may be directly linked to their ethanol adsorption capacity, pulsed chemisorption experiments were
performed over catalysts that were exposed to different pretreatment parameters. The results from one such series of experiments are presented in Fig.35. In these experiments, samples calcined at 400 °C were prerduced at 350 °C for different time periods, then ethanol vapor was pulsed over the sample at room temperature and each pulse was sent to the TCD detector. In the same Figure, the relationship between metallic Co surface area and reduction time determined by H₂ chemisorption is also presented. It is interesting to note that the reduction time that gives the highest ethanol uptake coincides with the reduction time that gives the highest metallic Co surface area. The similarity of the trends in these two measurements strongly suggests that the metallic Co centers constitute the active sites for ethanol adsorption in BESR.

4.2.11 TPRxn

The TPRxn experiments were performed for samples calcined at 400 °C and reduced at different temperatures for 2 h. The maximum in the hydrogen signal in each run has been plotted as a function of reduction temperature (shown in Fig.36). The variation of metallic Co surface area with the reduction temperature is also plotted in the same Figure for comparison. As can be seen
from Fig.36, the TPRxn results are in agreement with the chemisorption results, showing similar overall trends, especially for reduction temperatures above 200 °C. The reduction temperature which leads to the maximum H₂ formation is also the reduction temperature which gives the highest metallic surface area. The observation that the trend does not continue for the lowest reduction temperature can be explained by the fact that when the catalyst is mostly in an oxide phase there may be other reactions, besides the steam reforming of ethanol, that dominate the reaction network and these reactions may take place on active sites other than the metallic Co sites.

![Figure 36](image1.png) **Figure 36.** Variation of H₂ yield with reduction temperature for 10 wt%Co/ZrO₂ calcined at 400 °C. Variation of metallic Co surface area with reduction temperature is included for comparison

![Figure 37](image2.png) **Figure 37.** Variation of H₂ yield with calcination temperature for 10 wt%Co/ZrO₂ reduced at 350 °C for 2 h. Variation of metallic Co surface area with calcination temperature is included for comparison

A similar comparison was made by performing TPRxn experiments over catalysts calcined at different temperatures, but reduced at 350 °C for 2 h. The maximum in H₂ signal is plotted against calcination temperature as seen in Fig.37. The variation of metallic Co surface area with calcinations temperature is also plotted in the same Figure for comparison. Again, there appears to be a
close correlation between the H$_2$ yield and the metallic Co surface area. The dependence of both ethanol adsorption capacity and H$_2$ yield on the metallic Co surface area strongly suggests that metallic Co centers are the active sites in BESR reaction.

It should be noted that in Fig.36 and Fig.37 although the general trends are similar, there may not be an exact correlation at each temperature point. As described in the introduction section, many side reactions which could affect the H$_2$ yield might take place at different temperature regions besides the BESR reaction, such as ethanol dehydration or dehydrogenation at lower temperature and reverse water–gas shift at higher temperature. Therefore, the accurate correlation of the BESR activity with the metallic Co sites might be difficult, due to the complex networks of reactions governing the H$_2$ production.

4.3 Conclusions

Investigation of the evolution of the Co–ZrO$_2$ catalysts through different stages of the synthesis process showed that catalyst precursors start out with Co existing primarily in a nitrate phase and transforming into a Co$_3$O$_4$ phase in the fully calcined state. The reduction proceeds in two distinct steps as in Co$_3$O$_4$ → CoO and CoO → Co. There is an optimum in each of the synthesis parameters, which gives the highest metallic Co surface area. The maximum in metallic Co area is often determined by a series of competing processes, such as transformation from a nitrate to an oxide phase and onset of crystallinity versus reaction with the support at higher calcination temperatures, reduction to metallic state versus sintering at higher reduction temperatures. The maximum in metallic
Co area was seen to coincide with the maxima in both ethanol adsorption capacity and H₂ yield in the BESR reaction, suggesting a strong correlation between metallic Co sites and BESR activity. The steady-state reaction studies, which will be presented in the next article of this series, provide further evidence that metallic Co centers may be the active sites for the bio-ethanol steam reforming reaction.
CHAPTER 5

EFFECT OF OXYGEN MOBILITY

In the previous chapters, we have reported on the catalytic activity of Co/ZrO\textsubscript{2} catalysts in ethanol steam reforming and the effect of synthesis parameters on catalytic performance. In this study, we focus on the deactivation behavior of these Co-based catalysts and the effect of the oxygen mobility of the support on catalytic activity and stability. Ceria, which is known for its high oxygen storage capacity, has been reported to enhance the catalytic activity and stability in several reactions such as CO oxidation, water gas shift, and steam reforming of methane [108, 113, 114]. In this paper, the role of CeO\textsubscript{2} addition in improving the stability of Co-based catalysts, as examined through characterization studies that included N\textsubscript{2} physisorption, X-ray photoelectron spectroscopy (XPS), temperature-programmed oxidation (TPO), laser Raman spectroscopy (LRS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), O\textsubscript{2} pulse chemisorption, \textsuperscript{16}O\textsubscript{2}/\textsuperscript{18}O\textsubscript{2} exchange, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques, is reported.

5.1 Experimental

5.1.1 Catalysts preparation
Supported cobalt catalysts with 10 wt% metal loading were prepared in air by incipient wetness impregnation from cobalt (II) nitrate hexahydrate (Aldrich 99.999%) aqueous solutions. The pure supports used were ZrO$_2$ (Saint Gobain, surface area: 55 m$^2$/g, pore volume: 0.21 cm$^3$/g) and CeO$_2$ (powder < 5 µm, 99.9% Aldrich, surface area: 71 m$^2$/g, pore volume: 0.34 cm$^3$/g). The 10 wt% CeO$_2$-ZrO$_2$ support was prepared by impregnating the ZrO$_2$ support using an aqueous solution of cerium (III) nitrate (Aldrich 99.999%). All the supports were calcined for 3 h in air at 500 °C prior to metal impregnation. After repeating the impregnation of cobalt precursor and drying steps (at 95 °C) as many times as determined by the pore volume of the corresponding supports, the resulting samples were calcined at 400 °C for 3 h in the air and stored for use. The term “fresh sample” is used to represent the sample after calcination; the “reduced sample” denotes the sample reduced at 400 °C for 2 h; and the “spent sample” refers to the sample after reduction treatment and exposure to reaction atmosphere for various time periods.

5.1.2 Catalysts characterization and reaction performance measurement

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

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

Temperature-programmed oxidation (TPO) experiments were performed using Autochem-2920 (Micromeritics) with an online mass spectrometer (MS) (MKS Instruments, 1-300 amu). The samples were first pretreated at 300 °C with He for 30 min in order to remove adsorbed contaminants during storage. After cooling down to room temperature under Helium, 10 %O₂/He (30 ml/min.) was introduced into the reactor and TPO experiments were subsequently performed with a heating rate of 10 °C/min after the MS signal was stable.

Raman spectra were taken with a LabRAM HR-800 spectrometer equipped with an OLYMPUS BX41 microscope (50 X magnification) and a CCD detector. An argon ion green laser (514.5 nm, operated at 3 mW) was used as the excitation source during spectra collection. The ¹⁶O₂/¹⁸O₂ experiment was performed using an “operando cell”. Following a cleaning step under He at 400 °C for 30 min targeting to remove impurities from sample surface during storage, the reactor was cooled down to 300 °C, at which the ¹⁶O₂/¹⁸O₂ exchange took place where the spectra were taken.

O₂ pulse chemisorption experiments were conducted using AutoChem II 2920 (Micrometrics) connected with a Cirrus Mass Spectrometer (MKS Instruments, 1-300 amu). Catalysts of ~200 mg were sandwiched between two
layers of quartz wool and subjected to an oxidative cleaning step in air for 30 min, at the calcination temperature of the sample, followed by a reduction step at 400 °C for 2 h. After the system was flushed with He to remove any moisture, the O₂ pulses were introduced at 300 °C. The m/z = 32 signal was continuously detected by the MS until there was no variation between two consecutive peaks.

^{16}O_2/^{18}O_2 exchange experiments were performed using a Thermo Finnegan Trace Ultra DQC GC/MS. ~50 mg samples were placed in a U-tube quartz reactor. Following a cleaning step under He at 400 °C for 30 min to remove impurities adsorbed during storage, the reactor was cooled down to 300 °C, at which temperature the ^{16}O_2/^{18}O_2 exchange took place. The m/z = 32, 34, and 36 (mass-to-charge ratio) signals were monitored by the mass spectrometer during the exchange process. 10 % Ar was included in the 2 % ^{16}O_2/He stream to account for the gas-phase hold-up time, as described previously [115-117]. In addition, blank experiments were also performed and showed no exchange in the gas phase when no catalyst was present.

The spent sample morphology was obtained from Philips XL-30 ESEM instrument equipped with an X-ray analyzer for energy-dispersive X-ray spectroscopy (EDS). The engaged samples were dispersed onto the surface of carbon tabs before being mounted into the vacuum chamber for SEM image capture.

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

The XRD patterns applied for particle size estimation at various sample lifetime were collected from 20 ° to 90 ° at a step width of 0.002 ° using Rigaku Ultima III X-Ray Diffractometer equipped with a CuKα source (λ=1.5406 Å).

Diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS) was performed with a Thermo NICOLET 6700 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a KBr beam splitter. The in-situ experiments were performed using a Smart collector DRIFT environmental chamber with ZnSe windows. Following the pretreatment under He at 400 °C for 30 min and reduction under 5 % H2/He at 400 °C for 2 h, the environmental chamber was heated to 450 °C for 1 h under He for removing moisture generated from the reduction step. The reactant vapors generated from a two-bubbler system were then flowed over the sample for 1 h at room temperature using He as a carrier gas. The sample was then flushed with He for 10 min. Spectra were taken at pre-set intervals while the sample temperature was ramped from 25 °C to 500 °C. For oxygen isotopic exchange experiment, the background spectra were taken at 300 °C. The sample charged subsequently underwent re-oxidation at 550 °C for 1 h. Finally, sample spectra were taken periodically at 300 °C under He after 2 % 18O2/He flows through the sample chamber for 5 minutes. When there was no variation observed from the comparison between two consecutive sample spectra, 2 % 16O2/He begins to be introduced into the sample chamber.
Sample spectra were again taken periodically at 300 °C under He after 2 % $^{16}$O$_2$/He flows through the sample chamber for 5 minutes. For sample basic sites calibration, after background spectra were taken, 10 % CO$_2$/He was introduced into the chamber at 50 °C for 1 h. He was used to flush the gas phase and weakly adsorbed CO$_2$ on the surface after the adsorption step. A temperature programmed desorption was conducted. DRIFTS spectra were collected from 50 °C to 400 °C with 50 °C interval. After these measurements, the environmental chamber was cooled down to room temperature under He.

The catalytic performance measurement and analysis methods used were reported elsewhere [45]. Briefly, all catalysts were first pretreated at 400 °C for 30 min. under He and then reduced in-situ at 400 °C for 2 h under 5 % H$_2$/He. The reactant liquid consisting of ethanol and water at 1:10 molar ratio was delivered into an evaporator. The generated reactant vapor was carried by He and introduced into the reactor. The dilution ratio varied between 40 and 75 (inert-to-ethanol molar ratio). For neat experiments, gas phase reactants were directly fed to the reactor without dilution with an inert gas. Subsequently the catalytic performances were tested in the temperature range of 300 °C to 550 °C, in 50 °C increments. The catalyst was held at each temperature for at least 2 h. At the end of the catalytic test, the flow of EtOH + H$_2$O was stopped and the catalyst was cooled under He stream. The hydrogen yield is defined as

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

The time-on-stream (TOS) tests were performed at 450 °C for different time periods depending on the deactivation rate.
of various samples. The spent samples after TOS experiments were cooled down to room temperature under helium before characterization.

The turnover frequency (TOF) reported in the paper is calculated based on the ethanol conversion rate divided by the total available metallic cobalt active sites contained over the samples charged in the reactor. The cobalt dispersion is estimated using a H\textsubscript{2} chemisorption technique, which is described in detail previously [45].

5.2 Results and Discussion

5.2.1 The deactivation behavior of Co/ZrO\textsubscript{2} catalysts in BESR

As we have reported previously, Co/ZrO\textsubscript{2} catalysts with a 10\%Co loading gave high H\textsubscript{2} yields, at temperatures as low as 450 °C. The H\textsubscript{2} yield at this temperature is 77 \% and reaches 92 \% at 550 °C, which is equivalent to 5.5 mols of H\textsubscript{2} produced per mol of ethanol fed. What is also worth noting in Fig.38 is that at or above 450 °C, there are no liquid products remaining in the system. At 450 °C and above, the only by products are CO (less than 2 \%) and CH\textsubscript{4} (less than 7 \%). At 550 °C, the only H-containing product is H\textsubscript{2}, giving it a 100 \% selectivity. The only other

![Figure 38](image-url)
product observed at this temperature besides H\textsubscript{2} and CO\textsubscript{2} is CO. At lower temperatures, in addition to the main products which are expected to be formed during BESR reaction, (i.e., H\textsubscript{2} and CO\textsubscript{2}), small quantities of acetone, CO, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, and acetaldehyde were also observed at different levels. As seen in the figure, above 350 °C, the ethanol conversion is complete, hence the yield of H\textsubscript{2} is determined by the competing reactions, including ethanol decomposition, dehydration, dehydrogenation, methanation, WGS and reverse WGS reactions.

Although the activity and H\textsubscript{2} yield over these Co/ZrO\textsubscript{2} catalysts were quite promising, the TOS experiments showed that after about 25 h on stream at 450 °C, the activity declined rapidly. There was also significant pressure build-up in the reactor.

Post-reaction characterization of the spent 10 % Co/ZrO\textsubscript{2} catalysts provided information as to the nature of catalyst deactivation. Fig.39 shows the results of TPO experiment performed over a deactivated catalyst. As the temperature is raised under an oxygen flow, significant levels of CO\textsubscript{2} formation were observed over the catalyst, indicating that carbon was deposited over the surface during reaction. The maximum in the CO\textsubscript{2} signal, which takes place at 520 °C is accompanied by a minimum in the O\textsubscript{2} signal,
showing the oxygen depletion during the oxidation of the carbon deposited on the surface.

The XPS spectra of 10 % Co/ZrO$_2$ were taken at different life stages, i.e., fresh, reduced and spent, which are shown in Fig.40. The Co 2p$_{3/2}$ peak centered at 780.3 eV over fresh sample could be assigned to Co$_3$O$_4$. The peak shift to 778.4 eV was observed when the reduced sample was analyzed, indicating the existence of metallic Co [118-121]. Moreover, the absence of the shake-up lines nearby the two main Co 2p peaks characteristic of Co$^{2+}$ [110-112] implied the full reduction of cobalt oxide under these reduction conditions. The spectrum of the spent sample showed a very weak signal in the Co 2p region, suggesting that most of the Co sites were covered by (or encased in) carbon. Fig.40b shows C 1s region of the XPS spectra of 10 % Co/ZrO$_2$ catalyst taken at different life stages, i.e., fresh, reduced and spent. Compared to the fresh and reduced samples, there was a very strong signal observed over the spent catalyst,
indicating carbon deposition on the surface. Zr 2p and O 1s regions of the spectra (not shown) also showed reduced intensities compared to the fresh and reduced samples. However, this was especially severe for the Co 2p signal.

Raman spectroscopy was used to characterize the carbon deposited on the post-reaction catalysts. Fig. 41 shows the Raman spectra taken over 10 % Co/ZrO₂ sample, before reaction (reduced) (Fig. 41a) and after 45 h on stream at 450 °C (Fig. 41b). The two broad bands observed over the spent catalyst that are centered at 1340 and 1590 cm⁻¹ are characteristic of disordered carbonaceous and ordered graphitic species [57] and are referred as D band and G band, respectively. The G band is known to be very sensitive to the extent of two-dimensional graphitic ordering. The degree of the disordering of the carbonaceous materials can be roughly estimated quantitatively based on the integrated intensity of D and G bands. The larger the microcrystalline planar size Lₐ defined as 44(I_G/I_D) is [112], the higher the degree of ordering is in the carbonaceous materials. In our case, Lₐ is estimated to be 2.5 nm after peak fitting by using two Gaussian type bands, which is higher than the reported value obtained from carbon deposits over Co-based catalysts [41], indicating the higher degree of ordering.

![Figure 41. Raman spectra of 10 % Co/ZrO₂ (a) fresh, (b) spent](image)
The fresh and spent sample morphologies are investigated using SEM technique. According to Fig. 42, for the fresh Co/ZrO$_2$ sample cobalt particle is evenly distributed throughout ZrO$_2$ support and decorated within the porous structure of ZrO$_2$. The carbon filaments are obviously observed outside the surface of the spent catalyst. Whereas, the carbon deposition is not clearly detected when the ceria modified sample is engaged (not shown), further verifying as a straightforward way that the surface coverage by carbon leads to the inaccessibility of the active sites during the BESR, thus results in the deactivation of the sample.

**Figure 42.** SEM images of (a, b) fresh and (c, d) spent 10 %Co/ZrO$_2$ at different resolutions

Fig.43 shows TEM and STEM images of the Co/ZrO$_2$ samples at three
different life stages – calcined (a), reduced (b) and spent (c-f). The Co$_3$O$_4$ crystallites are represented as darker particles (a), while the ZrO$_2$ supports are seen as lighter particles. The lattice fringes are visible for both phases (i.e., Co$_3$O$_4$ and ZrO$_2$). The average particle size decreased from 24 nm for the Co$_3$O$_4$ to 12 nm for Co particles, following a reduction treatment. The decrease in size was confirmed by in situ-XRD results as well [113]. For spent samples, in addition to amorphous carbon, carbon nanofibers are also observed over 10 % Co/ZrO$_2$ with varying diameters. The cobalt particles appear to be encased at the tip of the fibers. Fig.43 (d) and (f) are the STEM images of the same sample area represented in Fig.43 (c) and (e), respectively. Superimposed on the STEM images are the EDS analysis results from the highlighted areas. The area highlighted in Fig.43 (d) is at the tip of a fiber and the analysis shows a very strong Co signal. The area highlighted in Fig.43 (f) is on a fiber and EDS analysis shows a very strong C signal. The Cu signal observed in both cases is due to the copper grid used to support the samples. The carbon fibers are seen to vary in diameter substantially, depending on the size of the Co particle that catalyses its growth. While most of the fibers are shorter with diameters around 20 nm, there are some fibers with much larger diameters (~150 nm). Compared to the average size of the Co particles of freshly reduced samples, some of the Co particles encased in carbon fibers appear to be much larger, suggesting that there may have been sintering of Co particles during reaction, resulting in larger particle sizes.

5.2.2 The effect of support modification with CeO$_2$ on catalytic performance
Figure 43. Electron microscopy of 10 % Co/ZrO₂: (a) TEM image after calcination, (b) TEM image after reduction, (c and d) TEM images of spent catalysts, (e and f) STEM images of the same sample areas shown in (c) and (d), respectively. EDS analyses of the highlighted areas are superimposed.
While the Co/ZrO$_2$ catalysts deactivated rapidly due to carbon deposition on the surface, addition of ceria to the support showed significant improvement in catalyst stability. Fig. 44 shows a comparison of the TOS performance of 10 % Co/ZrO$_2$ and 10 % Co/10 % CeO$_2$-ZrO$_2$ catalysts at 450 °C. While the initial activity and hydrogen yields observed over these two catalysts are comparable at 450 °C (~76 %), Co/ZrO$_2$ catalyst shows rapid deactivation after about 30 h of TOS. There was not much change in selectivity during the rapid deactivation. The catalyst that contains 10 % CeO$_2$ in the support maintains its activity even after 110 h TOS. Ceria addition also imparts the catalysts with a higher reforming activity, especially at lower temperatures, as seen in the inset.

The surface areas and pore volume of these two catalysts are compared in fresh and spent form and the results obtained through N$_2$ physisorption are presented in Table 1. The Co/ZrO$_2$ catalysts show increased surface area and pore volume after TOS, while ceria-containing sample does not show much change. The increase in surface area and pore volume may be due to carbon deposition on the surface of the Co/ZrO$_2$ catalyst.

**Figure 44.** (a) Product yields obtained over 10 % Co/ZrO$_2$ and 10 % Co/10 % CeO$_2$-ZrO$_2$ during ethanol steam reforming collected at 450 °C (EtOH:H$_2$O = 1:10 (molar ratio), GHSV = 5,000 h$^{-1}$ and Ce$_{EtOH}$ = 1.2 %)
Table 1. Surface area, pore volume and pore size of fresh and spent 10 %Co/ZrO₂ and 10%Co/10%CeO₂-ZrO₂ catalysts measured using N₂ physisorption

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/ZrO₂ Fresh</td>
<td>49.5</td>
<td>0.202</td>
<td>158.0</td>
</tr>
<tr>
<td>Co/ZrO₂ Spent</td>
<td>56.4</td>
<td>0.251</td>
<td>170.7</td>
</tr>
<tr>
<td>Co/CeO₂-ZrO₂ Fresh</td>
<td>38.2</td>
<td>0.160</td>
<td>160.3</td>
</tr>
<tr>
<td>Co/CeO₂-ZrO₂ Spent</td>
<td>38.6</td>
<td>0.163</td>
<td>164.8</td>
</tr>
</tbody>
</table>

When Co/CeO₂-ZrO₂ catalysts were characterized with LRS after being kept on stream for 110 h, there was no Raman signal that corresponded to carbon (data not shown), indicating that there was either no carbon deposition or the carbon on the surface was below the detection limits of the Raman spectrometer.

Post-reaction TEM characterization of the Co/CeO₂-ZrO₂ catalysts was also performed (Fig.45). Surface was found to be mostly free of any carbon deposition with very few carbon fibers detected. Co particles appeared to remain intact on the surface. EDS analysis also verified that there was not much carbon deposited on the surface. Since incorporation of CeO₂ into the zirconia support demonstrated significantly better catalytic performance, Co catalysts supported on CeO₂-only were tested under more demanding reaction conditions (i.e., higher ethanol concentrations and higher GHSV). Fig.46 shows a comparison of the H₂ yields...
achieved over 10  %Co/10CeO$_2$-ZrO$_2$ and 10  %Co/CeO$_2$ catalysts. Under these reaction conditions, Co/ZrO$_2$ catalysts showed very rapid deactivation and pressure build-up, not allowing data collection at steady-state. As shown in Fig.46, Co catalysts supported on ceria gave substantially higher yields for H$_2$ than the ones supported on CeO$_2$-ZrO$_2$ supports in the entire temperature range studied.

The three catalysts (Co/ZrO$_2$, Co/CeO$_2$-ZrO$_2$ and Co/CeO$_2$) were also compared using TOFs calculated from ethanol conversion data at 450 °C. For these measurements, neat reaction conditions were used. The TOF data, which are presented in Table 2, show that the intrinsic activities of the three catalysts increase in the order of Co/ZrO$_2$ < Co/CeO$_2$-ZrO$_2$ < Co/CeO$_2$.

Table 2. The TOFs (s$^{-1}$) based on ethanol conversion collected under neat reaction conditions at 450 °C: EtOH:H$_2$O=1:10 (molar ratio), GHSV=5000 h$^{-1}$ and $C_{EtOH}=7.5$ %

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/ZrO$_2$</td>
<td>0.054</td>
</tr>
<tr>
<td>Co/CeO$_2$-ZrO$_2$</td>
<td>0.214</td>
</tr>
<tr>
<td>Co/CeO$_2$</td>
<td>0.476</td>
</tr>
</tbody>
</table>

The long term stability of the three catalysts were tested under neat reaction conditions (without the dilution of an inert gas) with EtOH:H$_2$O = 1:10 (molar ratio), GHSV = 5,000 h$^{-1}$ and $C_{EtOH} = \sim 7.5$ %. The Co/CeO$_2$ catalyst was kept on-
line at 450 °C for 45 h and showed no change in activity or product distribution. The H$_2$ yield under these conditions was slightly higher than 60 %. The Co/ZrO$_2$ deactivated within the 1st hour and showed severe pressure build-up. Co/CeO$_2$-ZrO$_2$ catalyst showed deactivation starting after ~15 h. These experiments showed that the stability also increased in the order of Co/ZrO$_2$<Co/CeO$_2$-ZrO$_2$<Co/CeO$_2$.

Since Co catalysts supported on ceria or ceria-modified zirconia gave much higher yields and showed much better stability and resistance to coking, the differences between the ceria-containing and ceria-free catalytic systems were examined using different techniques.

Co crystal sizes were determined using X-ray diffraction. Table 3 summarizes the evolution of cobalt crystal sizes at different life stages for all three catalysts calculated using Scherrer equation. The diffraction lines used for these calculations are (311) and (111) for the Co$_3$O$_4$ and Co phases, respectively.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fresh*</th>
<th>Reduced**</th>
<th>Spent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/ZrO$_2$</td>
<td>27</td>
<td>15</td>
<td>24</td>
</tr>
<tr>
<td>Co/CeO$_2$-ZrO$_2$</td>
<td>29</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>Co/CeO$_2$</td>
<td>31</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>

* Calculations are based on (311) diffraction line for Co$_3$O$_4$;
** Calculations are based on (111) diffraction line for Co;

All three catalysts show a decrease in crystal size upon reduction. The percent increase in crystal size upon exposure to reaction medium is the largest for Co/ZrO$_2$ catalyst. Co/CeO$_2$ catalyst shows no increase in crystal size during
reaction.

DRIFTS technique was used to monitor the surface species during BESR reaction over 10 %Co/ZrO₂. Fig.47a and b show the in-situ DRIFT spectra taken during ethanol TPD over 10 % Co/ZrO₂ and 10 % Co/CeO₂, respectively. At room temperature, in the region between 3600-3800 cm⁻¹, the negative features originate from the molecularly adsorbed ethanol through the formation of hydrogen bridge bonding with the OH groups of the support. Furthermore, the molecularly adsorbed ethanol produces the vibrational bands located at 1323 (δ(CH₃)) and 1280 cm⁻¹ (δ(OH)) [10]. Ethanol adsorption also leads to the formation of monodentate and bidentate ethoxy species through disassociation as identified by the CH₃ bending (1443, 1381 cm⁻¹) and CCO stretching (1161, 1110, 1066 cm⁻¹) vibrations [66]. The C-H stretching located within 3000-2700 cm⁻¹ (2970, 2928, 2867, 2710 cm⁻¹) comes from the CH₃- and CH₃CH₂- groups. Initial temperature increase favors the ethoxide species adsorbed in bidentate form (stronger 1161 cm⁻¹ peak). The bands characteristic of ethoxy species disappeared with further temperature increase due to oxidation with the lattice oxygen from the support. Surface acetate species were observed to form subsequently at 1552 cm⁻¹ (νassym(COO)), 1441 cm⁻¹(νsym(COO)), and 1346 cm⁻¹ (δ(CH₃)) [85]. These species could first evolve to monodentate carbonate [10, 108] as an intermediate, then dissociate into CO₂, which is seen through the bands at 2361 and 2338 cm⁻¹. It was noted that in the region from 2200 to 2000 cm⁻¹ where adsorbed CO bands would be [56] there were no peaks during the entire run. Interestingly, over the CeO₂-supported catalyst, the appearance and
disappearance of each surface species mentioned above occur at much lower temperatures (shown in Fig. 47b). For instance, even at room temperature, the vibration peaks characteristic for acetate species are present, implying the abundance of oxygen on the surface available for oxidation of adsorbed ethanol species. The fact that almost no species remain on the surface of ceria-supported sample at 400 °C while very strong acetate bands are still visible even at 500 °C over the ZrO$_2$-supported catalyst is an indication that the oxidation of surface species is easily facilitated due to the oxygen mobility of the ceria support. This observation is consistent with the resistance to coking seen over the ceria-containing catalysts.

The in-situ DRIFT spectra obtained during ethanol/water TPD over 10 % Co/ZrO$_2$ and 10 % Co/10 % CeO$_2$-ZrO$_2$ are shown in Fig. 48. Compared to Fig. 47a, the spectra collected during ethanol/water TPD spectra over Co-ZrO$_2$ at room temperature shows much stronger adsorption bands around 3600-3800 cm$^{-1}$.
due to adsorbed water. The peak located around 1653 cm\(^{-1}\) [107] is also due to the O-H scissoring resulting from adsorbed water. As a result of water dilution, the vibration peaks corresponding to the molecular or dissociative adsorption of ethanol are much weaker than the ethanol TPD spectra taken at the same temperature. Many of the same features are observed as those seen in Fig. 47a, except for slight shifts. The effect of water addition to facilitate ethanol conversion can be seen from the disappearance of the surface acetate species peaks at lower temperatures. It is worth noting that similar phenomena are observed over CeO\(_2\) containing catalyst, however, the increased accessibility of oxygen and hence the ease of oxidation is apparent through the disappearance of acetate species at lower temperatures (Fig. 48b).

The oxygen storage characteristics of Co catalysts supported on ceria or zirconia and the bare supports were examined through O\(_2\) pulse chemisorption. The samples were pre-reduced in-situ prior to pulsing oxygen and monitoring
oxygen uptake at 300 °C. The results are presented in Fig. 49. ZrO$_2$ support has no reducibility and shows no oxygen uptake. Ceria without any Co loading shows, although small, a non-negligible oxygen uptake, indicating modest reducibility. Partial reducibility of ceria near the surface at lower temperatures has been previously observed by other researchers [123, 124]. Compared to blank supports, cobalt-loaded samples display much higher oxygen uptakes, however ceria-supported samples have a higher oxygen uptake compared to ZrO$_2$-supported ones, suggesting a greater accessibility of oxygen from the ceria lattice compared to zirconia. The difference between the oxygen uptake values is more pronounced when the Co-loaded samples are compared, suggesting a role for Co in facilitating oxygen mobility within the support. A similar phenomenon has been previously reported over noble-metal samples [123, 125-127]. In fact, the quantification of the results shows that part of the oxygen uptake for the ceria-supported samples is attributable to the support.

Isotopic oxygen exchange technique has been widely accepted as a useful tool for investigating oxygen mobility in oxides [115-117]. The inset of Fig. 50a shows the typical profiles collected during $^{16}$O$_2$-to-$^{18}$O$_2$ and $^{18}$O$_2$-to-$^{16}$O$_2$ switches. All the signals are normalized by the total counts. During the first switch, $^{16}$O$^{16}$O
signal (m/z=32) decreases, accompanied by a rise of $^{18}$O$^{18}$O signal (m/z=36). The $^{16}$O$^{18}$O signal (m/z=34) is shown to go through a maximum. The $^{16}$O$^{18}$O formation is derived from the dissociative adsorption of $^{18}$O$_2$ and subsequent recombination of the $^{18}$O atom created and $^{16}$O atom originally attached to the sample. This mechanism has been referred as going through a “three-atom complex” by Winter [128]. The doubly labeled oxygen results from a “four-atom” complex on the surface. Following the $^{18}$O$_2$-to-$^{16}$O$_2$ switch, relaxation and rise curves are essentially identical as well as the signal for the cross-labeled oxygen. After integrating the peak areas of corresponding oxygen species and subtracting the gas-phase holdup contribution determined from the Ar signal as described previously [107, 123, 124], the amount of exchanged oxygen atoms was calculated using a technique described previously in the literature [129] for the two bare supports and ceria- and zirconia-supported catalysts. As seen in the Fig.50a, not only the CeO$_2$ support, but also the CeO$_2$-supported Co sample presents notably higher oxygen mobility than their zirconia counterparts. The effect of the exchange temperature was further examined over Co-CeO$_2$ sample

Figure 50. (a) Oxygen exchange over ZrO$_2$, CeO$_2$, 10%Co/ZrO$_2$, and 10 %Co/CeO$_2$ measured using $^{16}$O$_2$/$^{18}$O$_2$ switch and (b) Effect of temperature on oxygen exchange over 10 %Co/CeO$_2$
and shown in Fig.50b. As expected, higher temperatures facilitate the lattice diffusion of oxygen atom, resulting in higher oxygen mobility. When the temperature reaches 550 °C, almost all of the oxygen atoms stored in the sample become accessible to participate in the exchange process.

As a powerful tool for investigating surface species and their corresponding evolutions under reaction conditions, DRIFTS has been used to monitor the isotopic exchanges happening at the sample surfaces.

Since the sample after reduction is taken as the background, all the peaks shown in Fig.51 collected over Co/CeO₂ can be assigned to the M-O bond vibrations. According to the peak assignments interpreted in [130], the region where we observe band shifts due to isotope effect located between 1050-950 cm⁻¹ region can be attributed to the surface superoxide species evolution during oxygen isotopic exchange. Therefore, 1030 cm⁻¹ peak occurring at initial $^{18}$O₂ flowing stage is associated with $(^{16}\text{O}-^{16}\text{O})\cdot$. The sequential appearance and disappearance of band 1010 and 996 cm⁻¹ can be correspondingly related with $(^{16}\text{O}-^{18}\text{O})\cdot$ and $(^{18}\text{O}-^{18}\text{O})\cdot$. The peak located at 976 cm⁻¹ might also be due to the vibration of $(^{18}\text{O}-^{18}\text{O})\cdot$ species. The wavelength discrepancy could be ascribed to their respective chemical environment [130]. 1523 cm⁻¹ peak decrease accompanied by simultaneous increase of 1494 cm⁻¹ band is likely to reflect the isotopic effect on the Co-O bond stretching. In addition, the gradual peak shift from 1223 cm⁻¹ to 1207 cm⁻¹ might originate from the molecularly adsorbed O₂ species. Because there is no chemical bonding involved, the isotopic effect seems not so prominent compared with the other two band regions mentioned.
Figure 51. DRIFTS spectra collected during (a) $^{18}$O$_2$ flowing and (b) $^{16}$O$_2$ flowing over 10 % Co/CeO$_2$ (H$_2$O) above. Besides, no transformation is observed over 1352 cm$^{-1}$ band area, which could be linked with strong Co-O bonding less intervened by the surroundings.

When the sample is saturated with $^{18}$O$_2$, $^{16}$O$_2$ is introduced into the sample chamber. As evidenced by the Fig.51b, all the peaks are traced back to the initial locations. Finally, the original state is almost retrieved, suggesting excellent reversibility of the Co/CeO$_2$ for oxygen mobility.

The same experiment is run again over blank support to further confirm the peak assignments described above. Multiple peaks present in Fig.52 reveal various sites existing in CeO$_2$ surface available for oxidation. However, isotopic
effect is not observed throughout the whole exchange process. Neither the peak positions nor the peak intensity vary within the detected time period, indicating that remarkable isotopic effect depends on the dissociative adsorption of oxygen species, which is favored by cobalt addition. The results obtained correlate very well with the information collected during the same experiment monitored by MS.

Additional experiments were performed over 10 % Co/ZrO$_2$ sample. Judged from Fig.53, similar spectra with those exhibited in Fig.51 display themselves again except for the absence of the bands ranging from 1050 to 950 cm$^{-1}$. As explained before, this region is associated with superoxide species formation, which is closely related with Ce$^{3+}$/Ce$^{4+}$ redox pair. When oxygen molecules are adsorbed on the surface of Ceria, one electron can be transferred from Ce atom to oxygen molecule, leading to the formation of superoxide species and oxidation of Ce from +3 to +4 state [129, 131]. However, this capability is missing for zirconia, resulting in the absence of the special vibration region. The blue shift of the twin peaks region due to the Co-O stretching might be derived from the different interaction with
Figure 53. DRIFTS spectra collected during (a) $^{18}$O$_2$ flowing and (b) $^{16}$O$_2$ flowing over 10 %Co/ZrO$_2$ support between two samples. Similarly, the restoration of the peaks due to oxidation after an isotopic exchange cycle also supplies a clue for the acceptable reversibility of the Co/ZrO$_2$ for oxygen mobility.

As a complementary technique to IR spectroscopy data presented above, Raman spectra were collected during $^{16}$O$_2$/$^{18}$O$_2$ exchange to provide useful information about the isotopic effect. Fig.54 shows the spectra evolution 30 min after flowing labeled oxygen over ZrO$_2$, CeO$_2$, 10 % Co/CeO$_2$, and 10 % Co/ZrO$_2$. No variations are observed for blank supports. The isotopic effect is more prominent over Co/CeO$_2$ than over Co/ZrO$_2$, leading to peak shift to a lower position. Similar phenomena have been reported by other authors over different
samples [130, 132]. In addition, it is worth noting that the lower the Raman shift where the peak is located, the smaller the distance the peak shifts, which is predicted following the formula:

\[
\Delta \omega = \omega_m \left(1 - \frac{m}{M}\right),
\]

where \(\omega_m\) is the original vibration frequency with the element mass \(m\); \(\Delta \omega\) is the isotopic Raman shift due to the mass variation from the isotope substitution. \(M\) is the mass of the substitution element. Referring to the \(\text{Co}_3\text{O}_4\) standard (not shown), the 694, 623, 527, 484, 194 cm\(^{-1}\) peaks are due to \(\text{Co-O}\) stretching, but shift to higher positions, which might come from interaction with the ceria support. However, the 464 cm\(^{-1}\) peak can certainly be assigned to the \(\text{Ce-O}\) stretching without any shift when cited to the ceria standard. Although there is no shift for pure ceria support, the peak shift is still observed when cobalt is impregnated during isotopic exchange. Therefore, the interaction between cobalt and support contributes significantly to the oxygen
exchange behavior. When the results from different characterization results are combined, the emerging picture suggests that the availability of oxygen plays a key role in determining both the H₂ yield and the stability of the Co-based catalysts. Ethanol steam reforming can be considered as a redox reaction, where ethanol is oxidized by the oxygen species originating from water. If there is sufficient oxygen available/accessible, ethanol can be fully oxidized to CO₂. However, if replenishment of oxygen on the surface is slower compared to its depletion, other byproducts with intermediate oxidation states will be formed, including CH₄, carbon and CO. Hydrogen yield will be maximized when carbon in ethanol is oxidized all the way to CO₂. Therefore, effective delivery of oxygen to the oxidation sites plays a key role in determining the hydrogen yield and maintaining catalyst stability. Ethanol adsorbs preferentially on the Co sites and water molecules tend to adsorb onto support surface. The ethanol oxidation seems to take place at the interface of cobalt particles and the support. The higher oxygen mobility benefits the oxygen transfer across entire sample surface, resulting in complete oxidation of ethanol and in turn maximization of hydrogen production.

5.3 Conclusions

Steady-state reaction experiments coupled with post-reaction characterization experiments showed significant deactivation of Co/ZrO₂ catalysts through deposition of carbon on the surface, mostly in the form of carbon fibers, the growth of which is catalyzed by the Co particles. The addition of ceria appears to improve the catalyst stability due to its high OSC and high
oxygen mobility, allowing gasification/oxidation of deposited carbon as soon as it forms. Although Co sintering is also observed, especially over the ZrO$_2$-supported catalysts, it does not appear to be the main mode of deactivation. The high oxygen mobility of the catalyst not only suppresses carbon deposition and helps maintain the active surface area, but it also allows delivery of oxygen to close proximity of ethoxy species, promoting complete oxidation of carbon to CO$_2$, resulting in higher hydrogen yields. Overall, oxygen accessibility of the catalyst plays a significant role on catalytic performance during BESR.
CHAPTER 6

INVESTIGATION OF SURFACE REACTION MECHANISM

In this paper, the surface reaction mechanism was traced by employing DRIFTS technique incorporated with Mass Spectrometer (MS) during temperature programmed desorption (TPD) process, combined with isotopic labeling technique aiming to track the pathway of the reactants during BESR. TGA-DSC is implemented as a complementary technique to further verify the results obtained from TPD duration in addition to the disquisition of corresponding thermal features. The respective roles of active metal and support can thus be identified, which will guide us the rational design of supported catalysts suitable for BESR with excellent activity and stability.

6.1 Experimental

6.1.1 Catalysts preparation

Supported cobalt catalysts with 10 wt.% weight loading were prepared in air by Incipient Wetness Impregnation (IWI) technique from cobalt (II) nitrate hexahydrate (Aldrich 99.999 %) aqueous solutions. The support pellets of ZrO₂ (31 m²/g, 0.21 cm³/g) purchased from Saint Gobain were ground and then sifted through a 100-150 mesh. CeO₂ (Aldrich, 71 m²/g, 0.34 cm³/g) was used as received. All the supports were then calcined for 3 h under air at 500 °C prior to
impregnation. After repeating impregnation and drying in an oven overnight at approximately 95 °C as many times as determined by the pore volume of each support, the resulting samples were calcined at 450 °C under air for 3 h and stored for use.

6.1.2 Catalysts characterization

TPD experiments were performed using AutoChem II 2920. Samples were first pretreated under helium (30 ml/min.) at 450 °C for 30 min and then reduced at 400 °C under 5 %H₂/He (30 ml/min) for 2 h. The samples were subsequently cooled down to room temperature under He. The reactant vapor generated from the bubbler was then allowed to flow through the sample bed for 1 h. Following the purging step with helium, the sample was subjected to a linear temperature program at a rate of 10 °C/min. The effluent was monitored by a Cirrus MKS Mass Spectrometer.

TGA/DSC experiments were performed using TG-DSC 111 (SETARAM). Samples were first pretreated under helium (30 ml/min.) at 450 °C for 30 min and then reduced with 5%H₂ at 400 °C for 2 h. The samples were subsequently cooled down to room temperature under He. TPD experiments were performed using a linear temperature program of 5 °C/min. as ramping rate under helium following the room-temperature adsorption of the reactant for 1 h.

DRIFTS was performed with a Thermo NICOLET 6700 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a KBr beam splitter. The in-situ experiments were performed using a Smart collector DRIFT environmental chamber with ZnSe windows. Following the pretreatment under
He at 450 °C for 30 min and reduction under 5 %H₂/He at 400 °C for 2 h, the background spectra were collected at various temperatures under He flowing before the introduction of reactant vapor. The reactant vapors were then flowed over the sample for 1 h at room temperature using He as a carrier gas. The sample was then flushed with He for 10 min. Spectra were taken at pre-set intervals while the sample temperature was ramped from 25 °C to 500 °C.

Experiments that involved isotopically labeled water (D₂O, H₂¹⁸O) were performed using the same procedures used for unlabeled species.

6.2 Results and Discussion

6.2.1 Ethanol Adsorption on bare ZrO₂ and Co/ZrO₂

The role of Co was examined by ethanol TPD over bare ZrO₂ support and Co-ZrO₂ catalysts, both of which were exposed to the same reduction step used for catalyst samples. As shown in Fig. 55a, at room temperature, the molecularly adsorbed ethanol produces the vibration bands located at 1380, 1330 (δ(CH₃)) and 1292 cm⁻¹ (δ(OH)) [10]. Ethanol adsorption also leads to the formation of monodentate and bidentate ethoxy species through disassociation as identified by the CH₃ bending (1425, 1380 cm⁻¹) and CCO stretching (1076 cm⁻¹) vibrations [133]. The C-H stretching located within 3000~2800 cm⁻¹ (2966, 2933, 2873 cm⁻¹) comes from the CH₃- and CH₃CH₂- groups. The IR band at 1167 cm⁻¹ is attributed to the vibration of C-C bond [66]. The peaks characteristic of molecularly or dissociatively adsorbed ethanol disappear with increasing temperature due to oxidation reactions with the lattice oxygen from the catalyst. Although abstraction of a second hydrogen atom would be expected to lead to
acetaldehyde species, there is no indication of a carbonyl group on the surface. The absence of acetaldehyde species can be explained by its rapid decompositon or rapid oxidation to acetate species as soon as they are formed, as suggested earlier by Yee et al. [113]. The presence of subsequently formed surface acetate species [66] can be seen through the bands at 1563 cm⁻¹, 1442 cm⁻¹, and 1348 cm⁻¹. These species could be further oxidized to produce CO₂, which is seen through the adsorbed CO₂ bands at 2373 and 2350 cm⁻¹ bands. Compared with the ethanol DRIFTS-TPD results over 10 %Co/ZrO₂ shown in Fig.55b, much stronger C-C vibration band intensity and disappearance at much higher temperatures over blank support indicate that the Co is active in catalyzing the C-C breakage. Furthermore, compared with Fig.55b, the appearance and disappearance of each surface intermediate at higher temperatures over bare ZrO₂ support implies that the metal/support interface can favor the ethanol oxidation process, resulting in higher ethanol conversion ability.

![Figure 55. In-situ DRIFTS during ethanol TPD over (a) ZrO₂ (b) Co/ZrO₂](image)

6.2.2. Role of H₂O
To examine the role of water and its interaction with ethanol on the surface, a sequential adsorption step was used in a TDP-DRIFTS experiment, similar to the one described in section 6.2.1, where ethanol adsorption was followed by water adsorption before spectral acquisition started. The results are presented in Fig.56a. The water adsorption is evident from the broad band around 3700~3200 cm\(^{-1}\) due to the OH group stretching and the peak located around 1653 cm\(^{-1}\) due to O-H scissoring [107]. The surface species formed following ethanol adsorption go through similar transformations with increasing temperature as seen in Fig.55b. However, when water is adsorbed following ethanol, these transformations take place more readily (at lower temperatures) showing the role of water in facilitating ethanol conversion.

Fig.56b shows the DRIFT spectra acquired during a similar experiment where H\(_2\)O was replaced with D\(_2\)O in the water adsorption step. The rationale behind this experiment was to identify the source of the surface hydroxyl groups by making use of the isotopic shift that would be expected in the IR bands when hydroxyl groups are replaced by deuteroxyl groups. Fig.56b shows the OH band that appeared in 3700-3200 cm\(^{-1}\) region to shift to lower frequencies by about 1000 cm\(^{-1}\) when D\(_2\)O is used, exhibiting the isotopic shift one would expect to see between OH and OD groups in the IR spectra [129]. Simultaneously the peak due to the molecularly adsorbed D\(_2\)O has been observed to shift from 1653 cm\(^{-1}\) in the H\(_2\)O adsorption to 1581 cm\(^{-1}\). When the temperature is above 100 °C, the band due to molecularly adsorbed D\(_2\)O disappears. A similar phenomenon is observed for the H\(_2\)O adsorption. In addition, the OH group derived from
dissociative adsorption of ethanol (the broad band ranging from 3600 cm\(^{-1}\) to 3200 cm\(^{-1}\)) is almost gone. However, the OD group is still present until most of the adsorbed surface species are desorbed completely, implying that the OD group participates throughout the ESR reaction.

![Figure 56. In-situ DRIFT spectra over Co/ZrO\(_2\) during (a) EtOH+H\(_2\)O TPD (b) EtOH+D\(_2\)O TPD](image)

The role of water was further examined by monitoring the gas phase species by mass spectrometry during the EtOH+D\(_2\)O TPD experiment. As shown in Fig.57, in addition to the D\(_2\)O peak due to the removal of physically adsorbed D\(_2\)O, the simultaneous HDO formation suggests that there may be OD groups may be combining with H atoms resulting from dissociative adsorption of ethanol. Similar to the H\(_2\) signal observed when normal water is charged [134], two HD peaks are also seen, indicating contribution from water and ethanol molecules to the formation of the hydrogen molecule. The first peak is likely due to the H atom abstracted from ethanol reacting with D or OD from water dissociation. The fact that there is almost no carbon-containing species such as CH\(_4\) or CO (over ZrO\(_2\)-supported catalyst, there is a very small CO peak) in the low-temperature regions.
suggests that the extent of decomposition of ethanol at this temperature is small. The second HD peak at the higher temperature coincides with the formation of carbon containing products such as CH₃D, CO₂, and small amounts of CO. Water gas shift conversion of CO with H₂O is also a possible reaction at this temperature. Referring to the surface intermediates observed by DRIFTS in Fig.55, these compounds are derived from the C-C bond breakage of surface acetate species. The CH₃D product observed in the same temperature window might be the result of the reaction taking place between CH₃ fragment coming from the C-C bond breakage of the acetate and a nearby OD or D species left on the surface from the D₂O dissociation. The second HD peak also shows the involvement of water in the formation of hydrogen molecule at this temperature. Interestingly, there is no D₂ species observed within the temperature range tested, which excludes the possibility of the adjacent OD species reacting with each other. There is also a small signal corresponding to acetone, appearing around 340°C, which may be due to an aldol-condensation-type reaction between two acetaldehyde species.

When a similar experiment was performed over ceria-supported catalyst (Fig.57b), the trends observed were very similar to those obtained over Co-ZrO₂ catalyst. There were, however, differences in relative intensities. The smaller amount of CH₃D formation and larger amounts of CO₂ and CO could be an indication of the ease of oxidation of the carbonaceous species over Co/CeO₂ catalyst. This, in turn, is likely a result of the higher oxygen mobility of the ceria-supported catalyst, as was discussed previously [194].
In order to trace the oxygen atom contained in the water molecule during ethanol steam reforming reaction, water with labeled oxygen ($H_2^{18}O$) was used in the ethanol-water TPD experiment, where the gas phase species were monitored by mass spectrometry. As shown in Fig.58, the desorption peaks from ethanol and $H_2^{18}O$ are observed at the low temperature region (30-230°C). The hydrogen formation peak occurring at lower temperatures (230-330°C) is again due to combination of H atoms abstracted from ethanol and water molecules. Small amounts of CO and CH$_4$ around 280 °C show that, decomposition of ethanol ($C_2H_5OH\rightarrow CO+H_2+CH_4$) can...
take place, but is not a predominant step. The $\text{H}_2^{18}\text{O}$ formation peak present between two neighboring hydrogen formation peaks is possibly evolved from the recombination of adjacent labeled hydroxyl groups derived from the dissociative adsorption of $\text{H}_2^{18}\text{O}$. The second $\text{CH}_4$ peak is accompanied by a strong unlabeled CO peak which may be due to decomposition of acetaldehyde. The strong signal from cross-labeled CO$_2$ ($\text{C}^{16}\text{O}^{18}\text{O}$) shows direct involvement of water in the formation of acetate species by providing an oxygen atom to the acetaldehyde and further oxidation of carbonaceous fragments. The $\text{C}^{16}\text{O}^{18}\text{O}$ species may also be a product of the water gas shift reaction ($\text{CO}+\text{H}_2^{18}\text{O} \rightarrow \text{C}^{16}\text{O}^{18}\text{O}+\text{H}_2$).

The role of water in the ethanol steam reforming mechanism was further investigated combining isotopic labeling with DRIFT spectroscopy. Fig.59a and 59b compare the in-situ DRIFT spectra taken during ethanol-water TPD over Co/CeO$_2$ catalyst using $\text{H}_2^{16}\text{O}$ and $\text{H}_2^{18}\text{O}$, respectively. Similar to what was observed over CO/ZrO$_2$ catalyst (Fig.56a), water and ethanol molecules are first dissociatively adsorbed onto the catalyst surface, leading to the formation of OH group (the broad band ranging from 2800-3800 cm$^{-1}$) and ethoxide species (2966, 2954, 2867, 1110, 1070, and 890 cm$^{-1}$). Over the Co/CeO$_2$ catalyst, the ethoxide species are oxidized much more readily (compared to Co/ZrO$_2$), forming acetate species (1558, 1433, and 1346 cm$^{-1}$) even at room temperature. Furthermore, the CO peak centered at 1944 cm$^{-1}$ appears, possibly as the result of the decomposition of acetaldehyde surface acetate. With increasing temperature, acetate species are further oxidized to carbonates evidenced by the presence of
1508 cm\(^{-1}\) in addition to 1558, 1433, and 1346 cm\(^{-1}\) bands. The decomposition of carbonate species leads to the formation of CO\(_2\) (2364 and 2356 cm\(^{-1}\)).

![Figure 59. The DRIFT spectra collected during (a) EtOH+H\(_2\)\(^{16}\)O (b) EtOH+H\(_2\)\(^{18}\)O TPD over 10 \%Co/CeO\(_2\).](image)

When Fig.59a and b are compared, it is seen that there is no shift in the position of the bands due to the C-C (1110 cm\(^{-1}\)) and C-H (2966, 2954, 2867, 1346, 1070, and 890 cm\(^{-1}\)) bond vibrations. However, isotopic shifts are seen in the bands that result from C-O and H-O vibrations. The broad band due to OH groups is seen to become broader, but the shift, as expected, is small. Another observation to make is that, while the bands at 1508, 1433, and 1346 cm\(^{-1}\) do not show any major shifts, the band due to C-O vibration is shifted from 1558 cm\(^{-1}\) to 1525 cm\(^{-1}\). This suggests that the oxygen in the acetate and carbonate species come from two different sources. Moreover, the presence of three CO\(_2\) vibration peaks (2360, 2345, and 2337 cm\(^{-1}\)) rather than the doublet peaks (2364 and 2356 cm\(^{-1}\)) is another evidence that the oxygen in the ethanol oxidation products comes from both ethanol and water. As expected, the peak originating
from the molecular adsorption of water is shifted from 1650 cm\(^{-1}\) to 1643 cm\(^{-1}\).

6.2.3 Possible Reaction Intermediates

6.2.3.1 Acetaldehyde

Since acetaldehyde is observed as a side product in the steady-state ethanol steam reforming reaction at lower temperatures, its adsorption/desorption characteristics and interactions with the catalyst surface were examined using the TPD technique. The gas phase species observed through the mass spectrometry during the TPD experiment following room-temperature adsorption of acetaldehyde are shown in Fig. 60.

The desorption of physically adsorbed CH\(_3\)CHO and CO\(_2\) are observed at low temperatures (~100 °C) in Fig. 60. At higher temperatures, the chemisorbed CH\(_3\)CHO appears to undergo decomposition and possibly oxidation reactions, forming CO\(_2\), H\(_2\) and CH\(_4\). Most of these transformations take place in a relatively narrow temperature window between 300 and 350 °C, implying that ethanol could be reformed easily if acetaldehyde is formed as intermediate through dehydrogenation reaction (C\(_2\)H\(_5\)OH→CH\(_3\)CHO+H\(_2\)). Simultaneously, a small amount of acetone is also formed from 300 °C to 350 °C, which may be due to an aldol condensation-type

![Figure 60. Gas phase species monitored with mass spectrometry during acetaldehyde TPD over Co/ZrO\(_2\).](image)
The transformation of acetaldehyde during its temperature-programmed desorption was also examined by monitoring the gravimetric and calorimetric changes through TGA-DSC experiments. In this experiment, acetaldehyde is adsorbed at room temperature and the mass change (TG), the first derivative of the mass change (DTG), as well as endothermic or exothermic heat effects (DSC) are recorded as a function of temperature (Fig.61). From the first derivative of TG (DTG) signal, two main mass losses are observed, corresponding to the two endothermic peaks from the DSC signal. The first mass loss is due to the desorption of adsorbed acetaldehyde at room temperature, which is an endothermic process. The second mass loss could be attributed to the reaction(s) taking place on the catalyst surface. The narrow window where most of the heat effects take place is similar to what was observed in the corresponding MS traces (Fig.60). The net heat release indicates that the surface transformations taking place in that temperature window add up to an endothermic reaction. Considering that most of the reactions in this window involve reforming reactions between surface OH groups and acetaldehyde derivatives, an endothermic reaction is to be expected. At higher temperatures, a
gradual mass loss continues, possibly due to slow desorption of surface species.

The evolution of surface species during the same desorption procedure has also been monitored using the DRIFTS technique. The DRIFT spectra taken over Co/ZrO$_2$ during acetaldehyde TPD are shown in Fig. 62. The peaks centered at 2736, 1267, and 1025 cm$^{-1}$ are characteristic for acetaldehyde molecularly adsorbed as η$^2$ configuration [57, 86]. The 1745 cm$^{-1}$ band is due to C=O stretching, which can be observed at lower temperature and disappears with increasing temperature, indicating either a rapid decarbonylation step or transformation to acetate species. The 1556, 1442 cm$^{-1}$ peaks along with the small shoulder located at 1360 cm$^{-1}$ indicate the presence of acetate species, similar to those seen in ethanol TPD (Fig. 55b). The formation of surface acetate species and the evolution of adsorbed CO$_2$ bands at 2366 and 2355 cm$^{-1}$ indicates the relative ease of transformation of acetaldehyde to acetate and its subsequent conversion to CO$_2$ and CH$_4$, using the OH groups left on the surface from the reduction step. The presence of the acetaldehyde could form CO$_2$ and CH$_4$ using the residual water present on the surface of catalyst generated from reduction step, since the C-H stretching peak can still be seen
even at 400 °C indicating the formation of CH₄. These observations are in agreement with the acetaldehyde TPD experiments monitored with MS in Fig.60, which showed the formation of CO₂ and CH₄. The similarity of the surface species seen in acetaldehyde and ethanol TPD-DRIFT spectra suggests a common pathway in the reaction of these two species in the presence of water.

6.2.3.2 Acetone

Interaction of acetone with the catalyst surface was also examined through TPD experiments, since acetone is one of the liquid byproducts observed during ethanol steam reforming. Gas phase species evolving during TPD, the gravimetric and calorimetric changes and evolution of the surface species are monitored using MS (Fig.63), TGA/DSC (Fig.64) and DRIFTS (Fig.65), respectively. Compared to acetaldehyde desorption behavior, acetone exhibits a much broader conversion region up to 550 °C in Fig.63, which indicates a stronger interaction with the surface and a higher degree of difficulty for reformation. In addition, there may be multiple sites involved in acetone transformations, with different energetics, leading to multiple CO₂ and H₂ formation peaks. Three major peaks in MS signal correspond to the three significant mass changes in DTG signal (Fig.64). As seen in Fig.63, the first
negative peak in DTG curve comes from the desorption of acetone and is accompanied by an endothermic DSC signal. The other two peaks are derived from a two-step surface reaction between catalyst and adsorbed acetone molecules, giving products of CO₂ and H₂. The MS signals coincide with the DTG features indicating mass loss and are accompanied by endothermic heat effects.

There is an additional exothermic feature in the DSC profile seen around 550°C, which cannot be explained by the gas phase species alone. However, the DRIFT spectra presented in Fig.65 provide additional clues. The 1712 cm⁻¹ band is due to C=O stretching vibration, which can be observed at lower temperatures and disappears with increasing temperature. The 1456 and 1371 cm⁻¹ bands are due to the “umbrella” CH₃ vibrations [135]. The 1232 cm⁻¹ peak present at room temperature due to the C-C-C stretching [135] begins to disappear with increasing temperature, indicating cracking of the C-C-C chain.
1170 cm\(^{-1}\) peak can be seen to evolve with temperature, first increasing in intensity and then decreasing, which indicates that there is a C-C-O-intermediate. The two peaks centered around 1580 and 1440 cm\(^{-1}\) and the one at 1310 cm\(^{-1}\) indicate the formation of surface acetate species as a possible reaction intermediate. The formation of acetate species suggests demethylation. Although methane signal was very weak in the gas phase, the exothermic DSC feature seen at 550 °C can be due to CH\(_x\) decomposition and carbon deposition on the surface, which has been confirmed by the subsequent TPO experiment (data not shown).

6.2.3.3 Acetic acid

Since the surface acetate has been observed as a reaction intermediate during TPD of reactants (i.e., ethanol and water) using DRIFTS technique, the surface evolution of acetic acid following its room-temperature adsorption was also examined through TPD and DRIFTS. As shown in Fig.66a, water is generated around 150 °C, which could possibly come from the reaction between adsorbed acetic acid and the surface hydroxyl groups: M-OH+CH\(_3\)COOH→M-OOCCH\(_3\)+H\(_2\)O [136]. The hydroxyl groups can be left behind from the pre-reduction step. The desorption of molecularly adsorbed acetic acid is observed following water release. The decomposition of adsorbed acetic acid begins to occur above 200 °C, resulting in the formation of CH\(_4\), CO, CO\(_2\) and H\(_2\) as the major products. In addition, acetone is also produced around 280 °C possibly due to the dehydrative coupling of two molecules of acetic acid (2CH\(_3\)COOH→CH\(_3\)COCH\(_3\)+H\(_2\)O+CO\(_2\)) [113]. The subsequent formation of C\(_3\)H\(_6\)
at a slightly higher temperature, combined with the corresponding dip in the hydrogen peak suggests a reduction reaction: $\text{CH}_3\text{COCH}_3 + \text{H}_2 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}$. The increase of the CO accompanied with the consumption of H$_2$ and CO$_2$ at even higher temperatures indicates the presence of reverse water gas shift reaction [62].

**Figure 66.** Acetic acid TPD over Co/ZrO$_2$ (a) Gas phase species monitored with mass spectrometry (b) DRIFT spectra

Fig.66b shows the in-situ DRIFT spectra taken during acetic acid TPD. Following adsorption at room temperature, molecularly adsorbed acetic acid is observed at 1728 cm$^{-1}$ ($\nu$(C=O)) and 1297 cm$^{-1}$ ($\delta$(OH)). In addition, some of acetic acid molecules are converted to surface acetate species through dissociation ($\text{CH}_3\text{COOH}_{(a)} \rightarrow \text{CH}_3\text{COO}_{(a)} + \text{H}_{(a)}$) [137]. The increasing temperature facilitates the formation of bidentate surface acetate (1558, 1465, 1446, 1350 cm$^{-1}$) [84] and the disappearance of molecularly adsorbed acetic acid. Furthermore, presence of adsorbed CO$_2$ (2366, 2345 cm$^{-1}$) above 200 °C is consistent with the TPD results in Fig.66a, indicating the decomposition of surface acetate species.
In addition, the location of the surface acetate confirms the assignment of our previous DRIFT spectra collected during ethanol or ethanol + water TPD.

6.2.3.4 Methane

As it is one of the major byproducts observed during the steady-state and transient reaction experiments of ethanol steam reforming, interaction of methane with the catalyst surface was examined through TPD and DRIFTS experiments. Fig.67a shows the in-situ DRIFT spectra taken during methane TPD. Methane is dissociatively adsorbed onto the Co/ZrO₂ surface at room temperature through C-H bond cleavage, resulting in the formation of CHₓ and H radicals. The hydrogen abstracted from methane is combined with the surface oxygen originating from ZrO₂ support to form hydroxyl groups, evidenced by the broad band ranging from 3600 cm⁻¹ to 2500 cm⁻¹ and the peak located at 3691 cm⁻¹ due to the existence of tri-bridging OH groups [195]. The adjacent OH groups formed will then react with each other to produce water, which is seen through the strong band located at 1668 cm⁻¹ due to the molecularly adsorbed water. The formation of water from OH groups and abstracted H radicals is also a possibility. The CHₓ fragments formed from the dissociative adsorption of methane present themselves at various oxidized forms. For instance, the methyl groups are attached to the surface through the formation of CH₃O-M indicated by the small peak centered at 2835 cm⁻¹ [196]. The oxidation of methylene groups lead to the formation of formaldehyde species, which is discerned from the band at 1668 cm⁻¹ (overlapped with molecular water adsorption peak) together with the relatively weaker shoulder peak located at 1500 cm⁻¹ (δCH₂) [195, 197]. Part of
the resulting formaldehyde species will be further oxidized to formate even at room temperature, which is evidenced from the presence of 1523 cm\(^{-1}\) (\(\nu_{\text{co}}\)) and 1317 cm\(^{-1}\) (\(\delta_{\text{CH}}\)) bands [198]. Furthermore, the formaldehyde or formate species can decompose to generate CO as the band at 2085 cm\(^{-1}\) can be assigned to linearly adsorbed CO to metallic Co. Along with increasing temperature, the surface formate species is oxidized further to form carbonate species, as seen through the characteristic vibrations at 1446 cm\(^{-1}\) [199, 200]. Carbonates can decompose to CO\(_2\) (2364 and 2356 cm\(^{-1}\)) at higher temperatures. The concurrent existence of the bands located at 1581 and 1348 cm\(^{-1}\) together with 2867 cm\(^{-1}\) band due to the stretching of C-H bond suggests that part of the formate species still remains on the surface without undergoing oxidation to carbonates [201, 202]. When temperature is at 300 °C, the catalyst surface is almost clean except for residual formate, carbonate and CO\(_2\) species attached. It should also be noted that there is a negative feature observed at 3685 cm\(^{-1}\), which may indicate the consumption of surface OH groups, which were originally on the surface from the reduction step, by reacting with adsorbed methane. Surface OH groups may be involved in formation of H\(_2\)O or oxidation of CH\(_x\) fragments [200]. A similar experiment was performed over CeO\(_2\)-supported sample (data not shown). The species observed were very similar, except for the appearance and disappearance of the aforementioned surface intermediates at much lower temperatures, resulting from the high oxygen mobility of the ceria support.

Fig.67b shows the gas phase products evolving from the Co/ZrO\(_2\) catalyst surface during methane TPD, as monitored by mass spectrometry. Significant
amounts of water formation is seen in 50 °C to 300 °C temperature region, which may be due to interaction of H abstracted from CH₄ reacting with surface OH groups, and which coincides very well with our DRIFTS observations. The three consecutive CO₂ formation peaks might originate from different sources. Considering the surface species observed through DRIFTS (Fig.67a), the first peak may be the result of further oxidation of the adsorbed CO species, since no CO formation has been detected from the m/z=28 signal. The last two CO₂ peaks may be from the sequential decomposition of formate and carbonate species.

Figure 67. Methane TPD over Co/ZrO₂ (a) DRIFT spectra (b) Gas phase species monitored with mass spectrometry

6.3 Proposed Reaction Mechanism

Based on the TPD and DRIFTS results presented in the previous sections and the surface acidity characteristics, which will be discussed in a separate paper, a possible reaction pathway for ethanol steam reforming over Co-based catalysts is proposed in Fig.68. In Scheme 1, the reactant molecules (EtOH and
water) diffuse from gas phase to the surface of the catalyst. The ethanol molecules adsorb dissociatively on the Co sites, forming ethoxide species. Water, on the other hand, adsorbs on the support, forming hydroxyl groups. The first H abstracted from ethanol can either form OH groups with the surface oxygen species or combine with hydrogen from H₂O and form H₂ (Scheme 3). Ethoxide species move to the interface of metal and oxide support and be oxidized by an additional hydrogen abstraction forming aceteldehyde (Scheme 4). Acetaldehyde molecules may lead to the formation of acetone through an aldol-condensation type reaction and acetone molecules are observed only in the gas phase. Acetaldehyde species have a short surface residence time, converting readily to acetate species through further oxidation with surface oxygen or OH groups (Scheme 5). There are multiple routes for the acetate species once they are formed. In one of the routes, the metal may be involved in C-C bond cleavage leading to the formation of single carbon species (Scheme 7), leading to the formation of CH₄. The carbon-oxygen surface species may desorb or further oxidize to give carbonate species, especially on supports with high oxygen storage capacity (Scheme 8), which can desorb as CO₂ (Scheme 9). In a second route, especially, if oxygen accessibility is high, the CH₃ fragment will undergo oxidation through H subtraction and O addition (Scheme 10) to form formate, possibly through a formaldehyde intermediate (Scheme 11), and carbonate (Scheme 12). The catalyst surface is then regenerated through CO₂ desorption (Scheme 13) and ready for the next catalysis cycle regardless of the route followed.
If the surface is highly acidic, ethanol dehydration may dominate the reaction pathway and result in the formation of H$_2$O and C$_2$H$_4$ which is the major precursor to coke due to polymerization, as described in Scheme 2 and 6. If the oxygen mobility in the catalyst is not high enough, the acetate species may remain on the surface and lead to coke formation, as reported earlier [10, 203].

**Figure 68.** Proposed Reaction Mechanism for Ethanol Steam Reforming over supported Co catalysts

### 6.4 Conclusions

Based on the results acquired in this paper, a tentative reaction pathway for ESR over Co-based catalysts is proposed. Dissociative adsorption of ethanol and water leads to ethoxide species and hydroxyl groups, respectively. The active metal catalyzes the C-C bond cleavage and formation of single carbon species. ESR reaction could happen at the interface of the active metal and the oxide support, which could participate by providing oxygen from the lattice to facilitate the oxidation of carbon species. The resulting oxygen vacancies can be filled by
the oxygen in the hydroxyl species formed from water adsorption. Therefore, it is necessary to have rapid oxygen delivery mechanism throughout the oxide support to prevent carbon deposition on the surface due to deficient oxidation of carbon species. High metal dispersion will favor the ethanol adsorption and formation of more accessible metal/oxide interfaces as well as C-C cleavage. High oxygen storage capability and mobility will facilitate the oxygen delivery through the support and suppress coke deposition. The Co-based systems that incorporate oxides with high oxygen storage and oxygen mobility could deliver the required characteristics needed for active and stable ESR catalysts.
CHAPTER 7

INVESTIGATION OF REACTION NETWORKS

In this study, the complicated reaction networks involved in the BESR mentioned in Section 1.1 have been systematically investigated using the Temperature Programmed Reaction (TPRxn) and isotopic labeling techniques monitored by Mass Spectrometer (MS). The results obtained from this study will benefit clarification of the reactions taking place during BESR over specific model catalysts, which will be valuable to guide the minimization of side reactions for maximizing hydrogen production.

7.1 Experimental

7.1.1 Catalysts preparation

Supported cobalt catalysts with 10 wt.% weight loading were prepared in air by Incipient Wetness Impregnation (IWI) technique from cobalt (II) nitrate hexahydrate (Aldrich 99.999 %) aqueous solutions. The support pellets of ZrO$_2$ (31 m$^2$/g, 0.21 cm$^3$/g) purchased from Saint Gobain were ground and then sifted through a 100-150 mesh. CeO$_2$ (Aldrich, 71 m$^2$/g, 0.34 cm$^3$/g) was used as received. All the supports were then calcined for 3 h under air at 500 °C prior to impregnation. After repeating impregnation and drying in an oven overnight at approximately 95 °C as many times as determined by the pore volume of each
support, the resulting samples were calcined at 450 °C under air for 3 h and stored for use.

7.1.2 Catalysts characterization

TPRxn experiments were performed using AutoChem II 2920. Samples were first pretreated under helium (30 ml/min.) at 450 °C for 30 min and then reduced at 400 °C under 5 %H₂/He (30 ml/min) for 2 h. The reactor was then heated to 450 °C under He for 1 h to eliminate moisture generated during reduction. The samples were subsequently cooled down to room temperature under He. The ethanol and labeled water vapors generated from a two-bubbler setting or other gas reactants at desired flow rates were then allowed to flow through the sample bed. The effluent was monitored by a Cirrus MKS Mass Spectrometer. When the MS signals were stable, the sample was subjected to a linear temperature program at a rate of 10 °C/min while the reactant vapors were flowing.

7.2 Results and Discussion

From the results predicted from thermodynamic analysis and obtained from steady state reaction, methane steam reforming (MSR) is a significant reaction pathway within the complex BESR reaction network. Therefore, the MSR over 10 %Co/ZrO₂ was investigated by using TPRxn technique, the results of which are shown in Fig.69-71. Four distinct reaction stages have been observed in Fig.69. In stage I, there is no reaction happening except for the CO₂ desorption due to the adsorption of CO₂ from the atmosphere during sample storage. However, in stage II, methane activation begins to take place resulting in the
production of H₂, CO and CO₂ as well as small amounts of acetone and propylene, suggesting coupling reactions for methane. The increased H₂O signal could come from associative desorption of OH groups from the surface. The reaction between CH₄ and oxygen from the catalyst crystal lattice is also a possibility. In stage III, reverse MSR (methanation) leads to the formation of CH₄ while consuming CO₂ and H₂. A significant increase of H₂ signal is observed in stage IV, accompanied by a pronounced decrease in the CH₄ signal. The prominent reaction in this region is likely to be the methane cracking reaction. A qualitative consideration of the carbon balance in this section suggests coke formation, which is considered to happen in this region due to the small amount of C₃H₆. To further examine this possibility, we have performed another TPRxn experiments, this time using only methane as the reactant. The profiles obtained from this experiment are shown in Fig.70. The sharp decrease in CH₄ signal is accompanied by an increase of H₂. Obviously, the small amount of C₃H₆ formation could not account for all the carbon consumption from the decomposition of methane. The only way to account for the carbon balance is the cracking of methane, i.e., CH₄ ⇌ C+2H₂. The deposition of the carbon on the
surface of the sample is confirmed by the subsequent TPO experiment where a stream of \( \text{O}_2/\text{He} \) was sent over the catalyst after the methane-H\(_2\)O TPRxn was completed. The \( \text{O}_2 \) consumption and \( \text{CO}_2 \) formation profiles, which mirror each other, are shown in Fig.71.

![Figure 70. Methane TPRxn results over 10 %Co/ZrO\(_2\)](image)

![Figure 71. TPO results over 10 %Co/ZrO\(_2\) after MSR experiment](image)

Water gas shift (WGS) reaction also plays an important role in the BESR network. It is also important in determining the CO/CO\(_2\) selectivity. Therefore, the performance of 10 %Co/ZrO\(_2\) in the WGS was studied using the TPRxn technique, the result of which is shown in Fig.72. The WGS reaction begins to take place when the temperature is between 150 and 200 °C, leading to the production of CO\(_2\) and H\(_2\). Methanation reaction

![Figure 72. WGS TPRxn results over 10 %Co/ZrO\(_2\). Reaction conditions: CO:H\(_2\)O=1:8 and total flow rate=51 ml/min.](image)
starts to occur around 300 °C. Above 350-400 °C, reverse water gas shift (RWGS) becomes dominant. H₂ production at higher temperatures may be due to methane steam reforming. A small amount of acetone is also observed around 350-450 °C.

The reverse WGS (RWGS) reaction was also studied in a similar way except for using H₂ and CO₂ as the reactants instead of CO and H₂O. As seen in Fig.73, the whole temperature range can be separated into four regions characterized by different reactions. There is no reaction happening in stage I. In stage II, two reactions contribute to the increase of the CH₄, H₂O, and CO as well as the decrease of H₂ and CO₂, i.e., Methanation: CO₂+4H₂ ⇌ CH₄+2H₂O and RWGS: CO₂+H₂ ⇌ CO+H₂O. In stage III, in addition to RWGS, MSR reaction takes place to account for the decrease of CH₄ and increase of H₂. The MSR reaction continues to play a role in stage IV, but the main reaction has switched to RWGS.

From the BESR steady state reaction, acetone is one of the byproducts occurring at lower temperatures. Examining the acetone reaction behavior is important to understand the reaction network involved in BESR. The results from the acetone-water TPRxn are presented in Fig.74. The temperature range can be divided into five different stages. In stage I, there is no reaction happening. Initial
acetone steam reforming (ASR) takes place in stage II, generating CO, CO$_2$ and H$_2$ as products. In stage III, a notable amount of propylene was formed, possibly as a result of a hydrogenation reaction, such as $\text{CH}_3\text{COCH}_3 + \text{H}_2 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}$. Decarbonylation of acetone to C$_2$H$_6$ and CO is also possible. CH$_4$ may result from a decomposition as well as a methanation reaction. In stage IV, propane steam reforming may be important. At higher temperatures (stage V), methane steam reforming and RWGS reactions may be becoming more important.

In order to get a better picture of the overall reaction network occurring during BESR reaction, combined with isotopic labeling technique, TPRxn experiments have been revisited. By employing H$_2^{18}$O as one of the reactants, any reaction involving the participation of water can be further clarified. As
shown in Fig.75, no reaction takes place before 280 °C, approximately. The rapid drops of H$_2^{18}$O and ethanol signals, accompanied with the formations of H$_2$, CH$_4$, CO, C$^{16}$O, C$^{16}$O$^{18}$O, C$^{18}$O$_2$, and CO$_2$, indicate the steam reforming and decomposition of ethanol. The gradual decrease of CH$_4$ signal after the maximum point at around 310 °C is due to the steam reforming of methane at higher temperatures. The acetone formation peak located within the temperature window between 300-500 °C may result from the competition of aldol condensation reaction of two acetaldehyde molecules to form acetone and steam reforming of acetone thereafter generated. The decrease of CO$_2$ signal along with the simultaneous increase of CO and C$^{18}$O after 380 °C is an indication of reverse water-gas shift reaction taking place, which has been evidenced again by the decline of C$^{16}$O$^{18}$O at higher temperature (after 480 °C) coinciding with the raise of CO and C$^{18}$O signals. The fact that the appearance of the CO$_2$ formation (centered at 380 °C) is earlier than that of the C$^{16}$O$^{18}$O formation peak indicates that the oxidation of ethanol takes place at catalyst surface rather than in the gas phase and the surface oxygen is mobilized during BESR reaction. CO$_2$ formation results from the oxidation of ethanol by the OH group left on the sample surface from the reduction step and C$^{16}$O$^{18}$O production is derived from the oxidation of ethanol by the surface $^{18}$OH group obtained from the H$_2^{18}$O dissociative adsorption. Since the surface originally has an abundance of OH groups before exposing to the H$_2^{18}$O atmosphere and it will take certain time to completely replace the OH group with $^{18}$OH group indicated from the H$_2^{16}$O/H$_2^{18}$O exchange experiment, the adsorbed ethanol will first react with surface OH group before
getting access to $^{18}\text{OH}$ groups, resulting in earlier presence of CO$_2$ instead of C$^{16}$O$^{18}$O. As time goes on, the consumption of surface OH groups will leave equal amount of oxygen vacancies behind, which will accelerate the exchange of OH/$^{18}$OH. Therefore, when the oxygen vacancies are occupied by the $^{18}$OH groups and the adsorbed $^{18}$OH groups are transported to the location nearby where ethanol is adsorbed, the oxidation of ethanol by $^{18}$OH group will occur, leading to the formation of C$^{16}$O$^{18}$O.

The reaction network is further investigated employing D$_2$O as water source instead of H$_2$O$^{18}$O. As shown in Fig.76, the general trends of all the products displayed are very similar with what have been observed in Fig.75. Again, in addition to the D$_2$O signal, the simultaneous HDO formation implies that ethanol and labeled water are dissociatively adsorbed onto sample surface, respectively. This results in the formations of OH and OD groups and these groups undergo a recombination to produce HDO. There is a HDO formation peak centered around 300 °C, which is absent in the D$_2$O curve. This feature further proves that the HDO species is evolved from the surface reaction rather than gas phase exchanging reaction. The HD and CH$_3$D formation peaks further verify the involvement of hydrogen
atom coming from water molecule in the final production of hydrogen molecules and methane formation if not sufficient oxygen is provided to oxidize ethanol all the way up to CO₂.

### 7.3 Conclusions

From the reaction networks investigated during BESR, it has been observed that dehydrogenation and decomposition of ethanol dominate the reactions taking place at lower temperature (<400 °C), leading to the formation of acetaldehyde, H₂ and small amounts of CO and CH₄. The acetaldehyde produced can then either be decomposed to form CO and CH₄ or form acetone through aldol condensation reaction. Steam reforming reaction begins to dominate when temperature is higher than 400 °C, leading to large amounts of CO₂ and H₂ formation and decrease of the concentrations of methane and other liquid intermediates. Further increase of temperature (>500 °C) will result in the drop of hydrogen and CO₂ production due to reverse water-gas shift reaction. The catalyst with higher oxygen mobility favors oxidation of ethanol up to CO₂, leading to maximization of hydrogen production.
CHAPTER 8

EFFECT OF IMPREGNATION MEDIUM

In this study, the effect of impregnation medium (deionized water, ethanol, and ethylene glycol) on the activity of Co/CeO$_2$ catalysts was systematically investigated under the environment of BESR. The supported catalysts were prepared by Incipient Wetness Impregnation (IWI) and characterized through Temperature Programmed Calcination (TPC), Temperature Programmed Reduction (TPR), X-Ray Diffraction (XRD), Laser Raman Spectroscopy (LRS), X-ray Photoelectron Spectroscopy (XPS), and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). The activity variations aware from steady state reaction over the sample prepared using different solvents were interpreted through incorporating with the observations released from characterization experiments.

8.1 Experimental

8.1.1 Catalysts preparation

Supported cobalt catalysts with 10 wt.% weight loading were prepared in air by Incipient Wetness Impregnation (IWI) technique. Cerium (IV) oxide (nanopowder, <25 nm, Aldrich) was calcined at 550 °C for 4 h, resulting in the support with surface area and pore volume of 71 m$^2$/g and 0.34 cm$^3$/g.
respectively. Then the cobalt (II) nitrate hexahydrate (Aldrich 99.999 %) was chosen as the cobalt precursor to be dissolved into ethanol, ethylene glycol, or deionized water and then impregnated onto the surface of the previously calcined support. After repeating impregnation and drying in an oven overnight at approximately 95 °C as many times as determined by the pore volume of the CeO₂ support, the as-prepared samples were calcined at 450 °C under air for 3 h and stored for use. For abbreviation, the letter located in the parenthesis right after the catalyst formulation represents the solvent used during the cobalt precursor impregnation, i.e., A for DI water, G for ethylene glycol, and E for ethanol.

### 8.1.2 Catalysts characterization

Cobalt dispersion was determined through a H₂ chemisorption technique using a Micromeritics ASAP 2010 Chemisorption system. Prior to adsorption measurements, calcined samples were pretreated at 450 °C and then reduced in-situ under 5 % H₂/He at 400 °C for 2 h followed by evacuation to 1.33-0.67 KPa and cooling down to 50°C to maximize activated chemisorption while minimizing H₂ spillover [109]. The adsorption isotherms were measured at equilibrium pressures between 6.67-66.7 KPa. The first adsorption isotherm was established by measuring the amount of H₂ adsorbed as a function of pressure. After completing the first adsorption isotherm, the system was evacuated for 1 h at 1.33-0.67 KPa. Then a second adsorption isotherm was obtained. The amount of probe molecule chemisorbed was calculated by taking the difference between the two isothermal adsorption amounts. Metallic surface area was determined by
assuming a one-to-one stoichiometry between Co and atomic hydrogen and a cross-sectional area of 0.0662 nm$^2$ for a Co atom.

The calcination process was investigated through TPC experiment. The sample was sandwiched within two layers of quartz wool in a stainless steel reactor which was placed in the center of a temperature programmable furnace. A constant air flow rate was maintained over the sample throughout the process and the reactor outlet stream was monitored by a Cirrus Mass Spectrometer (MKS Instruments, 1-300 amu).

H$_2$ TPR experiments were performed using a laboratory flow system equipped with a thermal conductivity detector (TCD). Samples of 50 mg were loaded into the U-tube and then subjected to an oxidative cleaning step at the samples’ calcination temperature in air, followed by cooling to room temperature under helium. TPR experiments were subsequently performed under 5 %H$_2$/N$_2$ (30 ml/min) with a heating rate of 10 °C/min. The exit gas from the reactor was sent to a column filled with silica gel for water trap before being sent to TCD for analysis.

XRD profiles were collected from 20 ° to 90 ° at a step width of 0.0144 ° using Bruker D8 Advance X-Ray Diffractometer. In-situ XRD was also performed during calcination process under air (30 ml/min.) and reduction process under 5 % H$_2$/N$_2$ (30 ml/min.) using a linear heating rate of 0.3 °C/min and holding at different preset temperatures for a given time for stabilizing and data collection. The XRD patterns applied for particle size estimation at various sample life-time were collected from 20 ° to 90 ° at a step width of 0.002 ° using Rigaku Ultima III
X-Ray Diffractometer equipped with a CuKα source (λ = 1.5406 Å).

Raman spectra were taken with a LabRAM HR-800 spectrometric analyzer integrated with OLYMPUS BX41 microscope (50 X magnification) and CCD detector. The in-situ calcination experiment was performed under air (30 ml/min.) using an “operando cell”. The sample was first heated to various temperatures and cooled down to room temperature where the spectra were taken using an argon ion green laser (514.5 nm, operated at 3 mW). The similar procedure was followed while performing in-situ reduction experiment under 5 %H₂/He (30 ml/min.).

XPS analysis was performed using an AXIS His, 165 Spectrometer manufactured by Kratos Analytical with a monochromatized Al X-ray source. 2.3 V voltage was chosen to make the charge balance. The sample was pressed into a stainless steel cup before loading into the instrument. The survey scan was performed to identify all the elements within the sample, followed by regional scans for Co 2p, C 1s, O 1s, Ce 3d orbitals in order to achieve the high resolution for these elements of interest. A controlled-atmosphere transfer chamber was used for transferring the sample to the XPS instrument in order to prevent the reduced samples from being re-oxidized again.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed with a Thermo NICOLET 6700 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a KBr beam splitter. The experiments were performed using a Smart collector DRIFT environmental chamber with ZnSe windows. For room temperature measurement, following a cleaning step
under He at 450 °C for 30 min targeting to remove impurities from sample surface during storage, the chamber was cooled down to room temperature under He and sample spectra were thus collected by taking DI water impregnated sample as the background after undergoing cleaning pretreatment. However, for temperature programmed test, following the pretreatment under He at 450 °C for 30 min and reduction under 5 %H₂/He at 400 °C for 2 h, the reactant vapors generated from a two-bubbler system were flowed over the sample for 1 h at room temperature using He as a carrier gas. The sample was then flushed with He for 10 min. Spectra were taken at pre-set intervals while the sample temperature was ramped from 25 °C to 500 °C.

8.1.3 Activity Test

The catalytic activity studies of the BESR were performed in a tubular reactor (4 mm internal diameter). The catalyst was sandwiched between two layers of quartz wool. The aqueous ethanol solution (EtOH:H₂O = 1:10 at molar ratio) was delivered into the evaporator by an isocratic pump (Eldex MicroPro). The feed vapors thereby generated were carried by helium and sent into reactor after being combined with nitrogen, which was used as internal standard. The delivery lines were heated with heat tapes to prevent condensation.

All catalysts were first pretreated at 450 °C for 30 min under He and then reduced in-situ at 400 °C for 2 h under 5 %H₂/He. Subsequently the catalytic performances were tested in the temperature range of 300 °C to 550 °C, in 50 °C increments. The catalyst was held at each temperature for at least 2 h. At the end of the catalytic test, the flow of EtOH+H₂O was stopped and the catalyst was
cooled under a He stream.

The analysis of the reactants and all the reaction products was carried out online by gas chromatography (Shimadzu Scientific 2010). Analysis was done using two different detectors and the separation was achieved using two different sample injection loops/valves and two analysis lines: The first line consisted of a Carboxen column and a 5-Å molecular sieve column connected in series in a column isolation scheme. This combined column arrangement was used in conjunction with a Pulse Discharge Helium Ionization Detector (PDHID). The second line was a separate 30 m-long Q-Plot column used with a methanizer and a Flame Ionization Detector (FID) to allow detection of CO as low as 10 ppm. Helium was used as the carrier gas for both of the analysis lines. All the carbon containing products can be separated by the Q-Plot column and detected by FID. PDHID can detect all the products in the stream, including CO, CO₂, and H₂. Response factors for all products were obtained and the system was calibrated with appropriate standards before each catalytic test.

The H₂ yield, selectivity and yield of carbon-containing products, and ethanol conversion were defined as follows:

\[ \text{H₂ Yield} \% = \frac{\text{moles of H₂ produced}}{6 \times (\text{moles of ethanol fed})} \times 100 \]

\[ \text{C-containing product Yield} \% = \frac{\# C \times \text{moles of this product}}{2 \times (\text{moles of ethanol fed})} \times 100 \]

\[ \text{Selectivity of C-containing product i} = \frac{\# C \times (\text{moles of i produced})}{2 \times (\text{moles of ethanol converted})} \]

\[ \text{EtOH Conv.} \% = \frac{\text{moles of ethanol converted}}{\text{moles of ethanol fed}} \times 100 \]
The turnover frequency (TOF) reported in the paper is calculated based on the ethanol conversion rate and hydrogen production, respectively, divided by the total metallic cobalt active sites exposed on the surface of the samples charged in the reactor, which was determined from H₂ chemisorption experiment described above.

8.2 Results and Discussion

8.2.1 Effect of ethanol impregnation

8.2.1.1 Catalytic performance comparison

As shown in Fig. 77, the activity of the 10 %Co/CeO₂ prepared using ethanol solution has been tested and compared with its counterpart prepared using aqueous solution. Excellent hydrogen yield as well as ethanol conversion have been presented especially under lower temperature (<450 °C). More than twice increase of hydrogen yield is acquired than that of its counterpart and equilibrium value when the temperature is below 400 °C. As exemplified in Table 4, the TOFs of 10 %Co/CeO₂ (A) and 10 %Co/CeO₂ (E) have been compared at 300 °C and 350 °C. Although both samples exhibit comparable capability in ethanol conversion, 10 %Co/CeO₂ (E) is significant more prone to catalyze hydrogen formation reaction than its counterpart when
similar amount of ethanol is converted in both cases, indicating its superior C-C bond cleavage ability.

**Table 4.** The TOFs (s⁻¹) based on ethanol conversion and hydrogen production collected under the reaction conditions: H₂O:EtOH = 10:1 (molar ratio), WHSV = 0.48 gEtOH/gCat/h, GHSV = ~20,000 h⁻¹, C𝑬𝒕𝑶𝑯 = 2 %

<table>
<thead>
<tr>
<th>Reaction Temperature (°C)</th>
<th>10 %Co/CeO₂ (A)</th>
<th>10 %Co/CeO₂ (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EtOH Conversion</td>
<td>H₂ Production</td>
</tr>
<tr>
<td>300</td>
<td>0.007</td>
<td>0.011</td>
</tr>
<tr>
<td>350</td>
<td>0.012</td>
<td>0.033</td>
</tr>
</tbody>
</table>

When Table 5 is referred, the liquid byproducts such as acetone keep present over 10 %Co/CeO₂ (A) throughout the whole temperature region tested. However, as its counterpart, ethanol impregnated sample does not produce any such species when the temperature is higher than 350 °C. Furthermore, it is clearly noticed that single carbon containing products such as CO, CO₂, and CH₄

**Table 5.** The product distribution (%) over 10 %Co/CeO₂ (A) and 10 %Co/CeO₂ (E) at various temperatures under the reaction conditions: H₂O:EtOH=10:1 (molar ratio), WHSV = 0.48 g EtOH/g Cat/h, GHSV=~20,000 h⁻¹, C𝑬𝒕𝑶𝑯=2%

<table>
<thead>
<tr>
<th>Products*</th>
<th>300 °C (A)</th>
<th>350 °C (A)</th>
<th>400 °C (A)</th>
<th>450 °C (A)</th>
<th>500 °C (A)</th>
<th>550 °C (A)</th>
<th>300 °C (E)</th>
<th>350 °C (E)</th>
<th>400 °C (E)</th>
<th>450 °C (E)</th>
<th>500 °C (E)</th>
<th>550 °C (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>10.9</td>
<td>42.4</td>
<td>32.9</td>
<td>83.3</td>
<td>64.7</td>
<td>88.9</td>
<td>71.4</td>
<td>74.9</td>
<td>79.4</td>
<td>91.4</td>
<td>83.8</td>
<td>90.2</td>
</tr>
<tr>
<td>CO₂</td>
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<td>12.4</td>
<td>80.2</td>
<td>33.0</td>
<td>87.1</td>
<td>37.7</td>
<td>87.8</td>
<td>59.8</td>
<td>86.0</td>
<td>70.6</td>
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<td>5.7</td>
<td>2.9</td>
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<td>69.3</td>
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<tr>
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<td>0</td>
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<td>0</td>
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<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>(C₂H₅)₂O</td>
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<td>2.4</td>
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<tr>
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<td>61.3</td>
<td>74.2</td>
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<td>100</td>
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<td>100</td>
<td>100</td>
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</tr>
</tbody>
</table>

* The values reported in the table are conversion for ethanol and yields for all the other species defined in the 2.3 section
dominate the product stream at all temperatures measured, indicating that the ethanol impregnated sample is significantly more efficient at the C-C bond breakage than its aqueous solution impregnated competitor. In addition, although their amount is relatively small, other undesirable byproducts such as diethyl ether, ethylene, and ethane are also observed over 10 %Co/CeO₂ (A) at various temperatures, which might lead to the coke formation.

The stability performance of the ethanol impregnated sample at 350 °C has been measured and shown in Fig.78. When kept on stream for 40 h, this catalyst has shown no sign of deactivation, maintaining a H₂ yield of ~82 %. The ethanol conversion is remained at around ~85 %. Residual liquid byproducts such as acetone and acetaldehyde have been observed throughout the whole run (<10 %). Moreover, the concentration of gas products (i.e. CO and CH₄) has been held below 4 %, which is beneficial for downstream hydrogen stream purification.

The stability feature of this sample at low temperature with excellent activity shows great promise. However, the rapid deactivation is obviously observed over 10 %Co/CeO₂ (A) within 10 h time-on-stream test. The remaining hydrogen produced during deactivation is
mainly derived from the dehydrogenation of ethanol. The carbon deposition is clearly evidenced over this sample from the calculation of carbon balance and a layer of dark stuff located on the top of the catalyst bed when catalyst was discharged from reactor after stability test.

8.2.1.2 Sample characterizations

The characterizations have been performed intensively over the 10 %Co/CeO₂ (E) in order to provide an answer to its significantly better catalytic performance during BESR. Under most of the circumstances, similar characterizations have also been carried out over its counterpart (i.e., 10 %Co/CeO₂ (A)) as the reference convenient for comparision.

Fig.79 shows the gas phase species coming off from the 10 %Co/CeO₂ (E) during calcination process. Water is seen to desorb at two distinct temperatures. The low-temperature feature indicates the release of the crystal water present in the cobalt precursor. The larger peak at higher temperature might be derived from the OH groups in the sample formed from the ethanol impregnation during sample preparation. The combination of 30 and 46 ion fragments reveals the production of NO₂ from the cobalt nitrate oxidative decomposition, which is accompanied by the
corresponding oxygen consumption. No carbon containing gas products being detected suggests the conservation of oxygenate species in the sample coming from the ethanol impregnation.

The calcination process of the ethanol impregnated sample is further investigated by using XRD technique. Although there is a broad feature from 35 ° to 45 ° due to the fluorescence of Co, the signal can still be discriminated from the background. As shown in Fig.80, the cubic CeO$_2$ support is visible at each temperature. However, the evolution of the cobalt oxide is observed along with the increase of the calcination temperature. When the temperature is above 300 °C, the diffraction peaks corresponding to cubic Co$_3$O$_4$ begin to appear. The gradual increase of the Co$_3$O$_4$ peak along with increasing calcination temperature implies the growth of Co$_3$O$_4$ particles at higher temperatures.

The calcination process over this sample has been also investigated by LRS technique. Fig.81 shows the Raman spectra collected during sample calcination. Two Raman shift regions have been reported corresponding to two distinct sets of species in the sample at various stages during calcination. Lower region (100~800 cm$^{-1}$) tracked the

![Figure 80. XRD patterns of 10%Co/CeO$_2$ (E) collected during calcination process](image)
formation of $\text{Co}_3\text{O}_4$ and higher region ($4500\sim5500\text{ cm}^{-1}$) monitored cobalt nitrate decomposition since cobalt nitrate has been chosen as the cobalt precursor. Normally cobalt nitrate has a major peak centered around $1050\text{ cm}^{-1}$, however, $\text{CeO}_2$ is very Raman active and the signal from cobalt nitrate is shielded when cobalt nitrate is impregnated onto $\text{CeO}_2$. Therefore, the maximum Raman shift collected in lower region is reduced to $800\text{ cm}^{-1}$ to save scanning time. As seen in Fig. 81, $\text{CeO}_2$ peak is observed throughout the process without changing, indicating that $\text{CeO}_2$ did not undergo oxidation state transformation. $\text{Co}_3\text{O}_4$ begins to appear when the temperature is above $300^\circ\text{C}$. The gradual increase of the $\text{Co}_3\text{O}_4$ peak along with increasing calcination temperature implies the growth of $\text{Co}_3\text{O}_4$ particles at higher temperature. The doublet peaks shown in higher region shows the cobalt nitrate decomposition which is completed when the

**Figure 81.** The Raman spectra collected over 10%Co/$\text{CeO}_2$ (E) during calcination process
temperature is above 300 °C when Co$_3$O$_4$ is formed.

Very similar evolution behaviors of 10 %Co/CeO$_2$ (A) have also been observed (data not shown) during calcinations process monitored by the same characterization techniques described above.

The reduction feature of the 10 %Co/CeO$_2$ (E) is studied by using TPR technique and the results are shown in Fig.82. Two reduction peaks have been observed and identified as Co$_3$O$_4$→CoO and CoO→Co, using CuO as H$_2$ consumption calibration reagent and Co$_3$O$_4$ standard as reference. Compared to the 10 %Co/CeO$_2$ (A) which presents the significant shift of reduction peaks to higher temperature, the ethanol impregnated sample shows notably better reducibility, which benefits its capability of catalyzing BESR reaction. Neither surface nor bulk reduction of CeO$_2$ occurs within the reduction region investigated.

The evolution of the crystalline phases during the reduction process over the calcined 10 %Co/CeO$_2$ (E) is also shown through the *in-situ* XRD patterns acquired during reduction (Fig.83a). By referring to the diffraction patterns of the standard sample Co$_3$O$_4$ (Fig.83b) collected during the same reduction procedure, The disappearance of the Co$_3$O$_4$ phase along with the appearance of the CoO phase coincides at a reduction

![Figure 82. H$_2$ TPR profiles collected over a: 10 %Co/CeO$_2$ (A) and b: 10 %Co/CeO$_2$ (E)](image-url)
temperature of 350 °C. The diffraction line that corresponds to CoO phase disappears above 400 °C and a metallic Co phase appears at 450 °C, which is consistent with the TPR profile obtained previously in Fig.82. Compared to the standard Co$_3$O$_4$, the hysteresis phenomena of the crystalline phase transformation occurring over CeO$_2$ supported cobalt sample might be an indication of the metal-support interaction. The crystal phase transformation during 10 %Co/CeO$_2$ (A) reduction process is delayed to even higher temperature (data not shown) implying its worse reducibility, which coincides with what has been observed in Fig.82.

![XRD patterns](image)

**Figure 83.** XRD patterns collected during reduction process over (a) 10%Co/CeO$_2$ (E) (b) Co$_3$O$_4$

Fig.84a depicts the ethanol impregnated sample evolution during reduction process detected by the LRS technique. By referring to the standard Raman spectra, the peaks corresponding to CeO$_2$ and Co$_3$O$_4$ have been shown at room
temperature confirming the chemical composition of the sample. No significant cobalt oxide phase change happens below 400 °C. When the temperature is at 400 °C, several broad peaks connected with CeO₂ peak indicate the formation of CoO because CoO is less Raman active than Co₃O₄. In addition, the increase of CeO₂ peak intensity at the same temperature means that more CeO₂ is exposed to the surface due to the particle size reduction from Co₃O₄ to CoO. Along with further increase of the reduction temperature, cobalt oxide phase completely disappears implying the presence of metal Co since metal Co is totally Raman inactive. Simultaneously, the further temperature increasing is accompanied by the decrease of the CeO₂ peak intensity, which might originate from the better surface coverage of metal Co since high temperature facilitates surface diffusion.

\[ \text{Figure 84. The Raman spectra collected over (a) 10 %Co/CeO}_2 (E) \text{ (b) 10 %Co/CeO}_2 \text{ (A) during reduction process} \]
of metal Co. However, the vibration peak centered at 680 cm\(^{-1}\) corresponding to CoO is still visible up to the reduction temperature of 600 °C, indicating that the DI water impregnated sample is more difficult to be reduced, which is coherent very well with its TPR profile shown in Fig.82.

The sample surface composition evolution during reduction process has been addressed by XPS technique. Fig.85 shows the transformations of the oxidation states of surface Co and Ce elements at various reduction stages of 10 %Co/CeO\(_2\) (E). The oxidation state of Ce keeps at +4 throughout the whole reduction, indicating that surface CeO\(_2\) is not reduced within the tested reduction region [138]. However, changes have been observed at the oxidation state of surface Co element. The presence of shake-up lines in the Co 2p XPS spectra of the sample reduced at 400 °C for 2 h points out the reduction of Co\(_3\)O\(_4\) to CoO since the satellite peaks are characteristic of the Co\(^{2+}\) oxidation phase [110-112]. Besides, the peak centered at 777.8 eV nearby the main peak at 780.2eV reveals the existence of metal Co phase at the sample surface [68], which means that after the reduction treatment at 400 °C for 2 h, the Co\(_3\)O\(_4\) particles have been reduced to a mixture of CoO and metal Co. Another XPS spectrum is also collected over the sample reduced at 600 °C for 2 h as the reference. From the reduction behavior of the sample reported in Fig.82, Co\(_3\)O\(_4\) particles should be fully reduced to metal Co at 600 °C. However, the evidence of Co\(^{2+}\) phase can still be witnessed, which can be interpreted as the re-oxidation of the metal Co by the lattice oxygen in the CeO\(_2\) support because CeO\(_2\) is well known as the high oxygen storage capability (OSC). Very similar reduction features have also been
observed at Co 2p and Ce 3d regions (data not shown) over 10 %Co/CeO₂ (A).

Figure 85. The Ce (3d) and Co (2p) XPS spectra collected over 10 %Co/CeO₂ (E) after (a) calcination at 450 °C for 3 h, (b) reduction at 400 °C for 2h, and (c) reduction at 600 °C for 2 h.

The C and O elements on the sample surface during reduction process are also monitored by XPS technique and shown in Fig.86. No significant change of these elements has been detected at different reduction stages. However, compared with the sample prepared by using water solution, extra peaks

Figure 86. The Ce (3d) and Co (2p) XPS spectra collected over 10 %Co/CeO₂ (E) after (a) calcination at 450 °C for 3 h, (b) reduction at 400 °C for 2 h, and (c) reduction at 600 °C for 2 h.
centered at 287.8 eV in the C 1s and 531.1 eV in the O 1s XPS spectra suggests the presence of oxygenated species on the surface of the sample prepared by using ethanol solution [68]. Therefore, the sample activity improvement shown in Fig.77 might be attributed to the oxygenated carbon species (ethoxyl or acetate species coming from the oxidation of the ethoxyl group) formation from ethanol impregnation. It is conceivable that the oxygenated species on the surface hinder the cobalt particle sintering during pretreatment and reaction processes [54], leading to higher cobalt dispersion which has been proven to proportionally correlate with catalyst activity. In addition, it is worth noting that higher minor to major peak ratio in C 1s spectra and extra small peak centered at 533.5 eV in O 1s spectra over the sample after calcination imply the surface oxygenated species present as a different form.

The presence of oxygenated carbonaceous species was further verified by the DRIFTS experiments performed over the samples prepared in different media. Fig.87 shows the difference spectra plotted by subtracting the spectrum collected over the sample prepared in aqueous media from the ones taken over the Co/CeO$_2$ (E) sample, following three
different pre-treatment steps. The band located at 1787 cm\(^{-1}\) suggests the presence of a carbonyl group (\(\nu (\text{C}=\text{O})\)), possibly in a carboxylate species. However, this band is much weaker compared to the ones located at 1552 and 1450 cm\(^{-1}\). The presence of these bands together with a weaker one around 880 cm\(^{-1}\), suggests an acetate salt, possibly in the form of cobalt acetate. Although there are slight shifts in the band position when the samples are reduced, the main features of the spectra remain the same. Although it is difficult to make definitive band assignments due to the complexity of this region, it appears that there are oxygenated carbonaceous species on the surface and these species are stable enough to withstand calcination and reduction steps, the latter at temperatures even as high as 600 °C.

Co crystal sizes were determined using X-ray diffraction. Table 6 summarizes the evolution of cobalt crystal sizes at different life stages for both samples calculated using Scherrer equation. The diffraction lines used for these calculations are (311) and (111) for the Co3O4 and Co phases, respectively. The fact that both of the samples have the similar particle size of Co3O4 after calcination implies that the ethanol as impregnation solvent has no superior capability to water on controlling the Co3O4 formation and succedent growth during calcination. For ethanol impregnated sample, in addition to the decomposition of cobalt nitrate to form Co3O4, the calcination process is more related with the transformation of adsorbed ethanol during impregnation to surface carbon oxygenated species, based on the observations from the combined results of XPS and DRIFTS. The surface carbon oxygenated species
resulted effectively prevents the cobalt particle agglomeration during reduction, leading to smaller particle size compared to 10 %Co/CeO₂ (A). Furthermore, the carbon oxygenated species remaining on the surface of 10 %Co/CeO₂ (E) after reduction favors the dispersion stability of cobalt particles during reaction evidenced by the unchanged particle size after 40 h time-on-stream test. However, without this protection, the cobalt particles of 10 %Co/CeO₂ (A) are severely sintered, which can be concluded from the comparison of cobalt particle size tabulated in Table 6 before and after 10 h stability test.

| Table 6. Cobalt/cobalt oxide crystal size estimation from XRD (nm) |
|-----------------|----------------|--------|--------|
| Catalyst       | Freshᵃ         | Reducedᵇ | Spentᶜ |
| Co/CeO₂ (A)    | 15             | 12     | 25     |
| Co/CeO₂ (E)    | 14             | 8      | 8      |

ᵃ Calculations are based on (311) diffraction line for Co₃O₄;  
b Samples were reduced at 400°C for 2h. Calculations are based on (111) diffraction line for Co;  
c XRD patterns were collected after time-on-stream for 40h over 10%Co/CeO₂ (E) and 10h over 10%Co/CeO₂ (A). Calculations are based on (111) diffraction line for Co.

The ethanol conversion ability over the sample surface is also studied using DRIFTS technique. As shown in Fig.88a, at room temperature, ethanol is adsorbed on the surface of the DI water impregnated sample molecularly (indicated by ν (OH): broad band located between 3600~3200 cm⁻¹) and ethoxide forms (1103, 1054 cm⁻¹). Because of the high oxygen storage capability of ceria, part of the ethoxide has been oxidized into acetate (1564, 1442, 1368 cm⁻¹) even at room temperature. The appearance of carbonate due to further oxidation of acetate and CO₂ (2364, 2343 cm⁻¹) as its decomposition product testifies to the evolution of the surface species during temperature increase.
To examine the effect of ethanol impregnation, the same experiment was also performed over ethanol impregnated sample. As shown in Fig. 88b, more ethanol has been adsorbed onto the surface of the ethanol impregnated sample, which is evidenced by the strong band centered at 1244 cm\(^{-1}\) due to OH group stretching characteristic for molecularly adsorbed ethanol. As discussed in [139], ethanol adsorption ability of the sample is proportionally related to the metal Co availability, i.e., cobalt dispersion. In addition, the presence of CO\(_2\) peak at temperatures as low as 100 °C rather than 150 °C for its counterpart impregnated by aqueous solution further confirms the improved ethanol conversion capability of the ethanol impregnated sample.

The observation that the presence of such species over the (E) sample is
the only apparent difference between the two catalysts suggests that these oxygenated carbon species may be playing a role in the superior performance of the catalysts prepared in organic media. One possibility is that the presence of these organic ligands may keep the Co particles segregated, ensuring a high level of dispersion throughout their life history. The other possibility is that these species may be blocking the sites that lead to the dehydration and aldol condensation type reactions, which would lead to coking and acetone formation, respectively. A related possibility is that the presence of acetate species on the surface of the catalysts prior to any reactions may make it easier for ethanol to be converted to surface acetate species, by following an “imprint” left on the surface during the impregnation step. However, the current results do not provide sufficient evidence to prove or to refute any of these possibilities.

8.2.2 Effect of ethylene glycol impregnation

As evidenced in the case of ethanol impregnation, the choice of ethanol as impregnation medium favors the segregation of cobalt particles during reduction leading to higher cobalt dispersion and in turn better activity and prevents its sintering during reaction resulting in better stability. Motivated by the paper [140], ethylene glycol has been selected as the candidate to serve for the purpose of

Table 7. The hydrogen yield (%) over 10 %Co/CeO₂(A), 10 %Co/CeO₂(E), and 10 %Co/CeO₂(G) at various temperatures under the reaction conditions: H₂O:EtOH=10:1(molar ratio), WHSV = 0.54 g EtOH/g Cat/h, GHSV=5,000h⁻¹, CEtOH=7.5%.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>300 °C</th>
<th>350 °C</th>
<th>400 °C</th>
<th>450 °C</th>
<th>500 °C</th>
<th>550 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/CeO₂ (A)</td>
<td>2.1</td>
<td>18.2</td>
<td>32.8</td>
<td>47.9</td>
<td>55.1</td>
<td>64.3</td>
</tr>
<tr>
<td>Co/CeO₂ (E)</td>
<td>10.5</td>
<td>50.9</td>
<td>60.3</td>
<td>61.8</td>
<td>64.7</td>
<td>67.2</td>
</tr>
<tr>
<td>Co/CeO₂ (G)</td>
<td>16.8</td>
<td>86.7</td>
<td>90.2</td>
<td>91.8</td>
<td>94.3</td>
<td>96.3</td>
</tr>
</tbody>
</table>
acquiring even smaller cobalt particle size even after calcinations.

For activity comparison, all three catalysts have been tested under neat conditions (without dilution of inert gas). The hydrogen yields of them at various temperatures have been tabulated in Table 7. It is clearly observed that 10 %Co/CeO₂ (G) exhibits significant better activity at each temperature point tested. 100% ethanol conversion is obtained at temperature as low as 350 °C and over 90 % hydrogen yield is achieved when temperature is higher than 350 °C. For better comparison, the product distributions of all three catalysts have been compared at 400 °C and shown in Fig.89. 10 %Co/CeO₂ (G) is the only catalyst of which all the products are single carbon containing species. Notable amount of acetone are still observable for 10 %Co/CeO₂ (A) and 10 %Co/CeO₂ (E). Most of the ethanol has been fully oxidized over 10 %Co/CeO₂ (G), resulting in much higher percentage of CO₂ yield. Its stability has also been measured and over 90 % hydrogen yield is achieved during a 70 h time span without evidence of deactivation (data not shown). Therefore, 10 %Co/CeO₂ (G) will be a very promising catalyst candidate for catalyzing BESR reaction at industrial scale on account of its excellent catalytic performance and relatively easy preparation recipe.
In order to provide an explanation to the superior catalytic performance of 10%Co/CeO₂ (G), its particle size has been estimated again employing XRD technique at various life stages. For convenient comparison, the results are tabulated in Table 8 along with the observations in Table 6. Even after calcinations, the Co₃O₄ particle size of 10%Co/CeO₂ (G) has been reduced into half compared to its counterparts. The reduced particle size after reduction treatment is well maintained even after 70 h time-on-stream stability test under more severe reaction conditions, indicating its extraordinary capability in cobalt segregation throughout the whole life time.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Freshᵃ</th>
<th>Reducedᵇ</th>
<th>Spentᶜ</th>
</tr>
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<tbody>
<tr>
<td>Co/CeO₂ (A)</td>
<td>15</td>
<td>12</td>
<td>25</td>
</tr>
<tr>
<td>Co/CeO₂ (E)</td>
<td>14</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Co/CeO₂ (G)</td>
<td>7</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

ᵃ Calculations are based on (311) diffraction line for Co₃O₄;
ᵇ Samples were reduced at 400°C for 2h. Calculations are based on (111) diffraction line for Co;
ᶜ XRD patterns were collected after time-on-stream for 40 h over 10%Co/CeO₂ (E), 10 h over 10%Co/CeO₂ (A) under the reaction conditions: H₂O:EtOH = 10:1 (molar ratio), WHSV = 0.48gEtOH/gCat/h, GHSV = ~20,000h⁻¹, CₑtOH = 2%, and 70 h over 10%Co/CeO₂ (G) under reaction conditions: H₂O:EtOH = 10:1 (molar ratio), WHSV = 0.54gEtOH/gCat/h, GHSV = ~5,000h⁻¹, CₑtOH = 7.5%. Calculations are based on (111) diffraction line for Co.

8.3. Conclusions

The significant catalytic performance improvement has been observed over ethanol impregnated Co-CeO₂ catalyst, especially at lower temperature (300-400°C), compared with its counterpart with aqueous impregnation. This promotion effect is considered to be closely related to the cobalt dispersion amelioration through cobalt particle segregation under the facilitation of surface carbon oxygenated species derived from ethanol impregnation. Moreover, even better
catalytic performance is achieved using ethylene glycol as impregnation medium, which might be closely related with the achievement of even smaller cobalt particle size due to its superior ability in preventing cobalt agglomeration probably originating from the presence of organic surface species.
CHAPTER 9

EFFECT OF CALCIUM DOPING

In this study, the effect of calcium doping on the activity of Co/CeO₂ catalysts has been systematically investigated under the environment of bio-ethanol steam reforming employing various characterization techniques including CO Temperature Programmed Reduction (TPR), O₂ and CO Pulse Chemisorption, Laser Raman Spectroscopy (LRS), X-Ray Diffraction (XRD), Isotopic Labeling, and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS).

9.1 Experimental

9.1.1 Catalysts preparation

Supported cobalt catalysts with 10 wt.% weight loading were prepared in air by Incipient Wetness Impregnation (IWI) technique from cobalt (II) nitrate hexahydrate (Aldrich 99.999 %) ethanol solutions. The support powders of CeO₂ (Aldrich, 71 m²/g, 0.34 cm³/g) and Ca₀.₁Ce₀.₉O₁.₉ (Aldrich, 105 m²/g, 0.41 cm³/g) were used as received. All the supports were then calcined for 3 h under air at 500 °C prior to impregnation. After repeating impregnation and drying in an oven overnight at approximately 95 °C as many times as determined by the pore volume of each support, the resulting samples were calcined at 450 °C under air
for 3 h and stored for use.

9.1.2 Catalysts characterization and reaction performance measurement

O₂ pulse chemisorption experiments were conducted using AutoChem II 2920 (Micrometrics) connected with a Cirrus Mass Spectrometer (MKS Instruments, 1-300 amu). Samples of ~200 mg were sandwiched between two layers of quartz wools and subjected to an oxidative cleaning step at the samples calcination temperature in air for 30 min, followed by a reduction step at 400 °C for 2 h. After the system was flushed with He to remove any moisture, the pulse O₂ were introduced at 300 °C. The m/z=32 signal was continuously detected by the MS until there was no variation between two consecutive peaks.

¹⁶O₂/¹⁸O₂ exchange experiments were performed using a Thermo Finnegan Trace Ultra DQC GC/MS. ~50 mg samples were placed in a U-tube quartz reactor. Following a cleaning step under He at 400 °C for 30 min to remove impurities adsorbed during storage, the reactor was cooled down to 300 °C, at which temperature the ¹⁶O₂/¹⁸O₂ exchange took place. The m/z = 32, 34, and 36 (mass-to-charge ratio) signals were monitored by the mass spectrometer during the exchange process. 10 % Ar was included in the 2 % ¹⁶O₂/He stream to account for the gas-phase hold-up time, as described previously [115-117]. In addition, blank experiments were also performed and showed no exchange in the gas phase when no catalyst was present.

H₂¹⁶O-H₂¹⁸O exchange experiments were performed using AutoChem II 2920. Samples were first pretreated under helium (30 ml/min.) at 400 °C for 30 min and then reduced at 400 °C under 5 %H₂/He (30 ml/min) for 2 h. The reactor
was thereafter heated to 450 °C under He for 1 h to eliminate moisture generated during reduction. The samples were subsequently cooled down to 300 °C under He, at which temperature the H$_2^{16}$O/H$_2^{18}$O exchange took place. The m/z=18, 20, and 40 (mass-to-charge ratio) signals were monitored by the mass spectrometer during the exchange process. ~14 % Ar was included in the ~2.7 % H$_2^{18}$O/He stream generated from a two-bubbler setting to account for the gas-phase hold-up time. In addition, blank experiments were also performed and showed no exchange in the gas phase when no catalyst was present.

CO pulse chemisorption experiments were conducted using AutoChem II 2920 (Micrometrics) connected with a Cirrus Mass Spectrometer (MKS Instruments, 1-300 amu). Samples of ~100 mg were sandwiched between two layers of quartz wools and subjected to an oxidative cleaning step at the sample’s calcination temperature in 10 %O$_2$/He for 30 min. After the system was flushed with He to remove physically adsorbed O$_2$ molecules, the CO pulses were introduced at 300 °C. The m/z=28 and 44 signals were continuously detected by the MS until there was no variation between two consecutive peaks at m/z=28 channel.

CO TPR experiments were conducted using AutoChem II 2920 (Micrometrics) connected with a Cirrus Mass Spectrometer (MKS Instruments, 1-300 amu). Samples of 100 mg were subjected to an oxidative cleaning step at the samples’ calcination temperature in air, followed by cooling to room temperature under helium. TPR experiments were subsequently performed under 10 %CO/He (30 ml/min) with a heating rate of 10 °C/min.
DRIFTS was performed with a Thermo NICOLET 6700 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a KBr beam splitter. The experiments were performed using a Smart collector DRIFT environmental chamber with ZnSe windows. Following a cleaning step under He at 400 °C for 30 min to remove impurities from sample surface during storage and reduction at 400 °C for 2 h under 5 %H₂/He, the chamber was heated to 450 °C under He for 1 h to eliminate moisture generated during reduction. The ethanol vapor generated from a bubbler was then flowed over the sample for 1 h at room temperature using He as carrier gas. The sample was then flushed with He for 30 min. Spectra were taken at pre-set intervals under helium continuous flow while the sample temperature was ramped from 25 °C to 500 °C.

Raman spectra were taken with a LabRAM HR-800 spectrometric analyzer integrated with OLYMPUS BX41 microscope (50 X magnification) and CCD detector. The spectra were taken using an argon ion green laser (514.5 nm, operated at 3 mW).

XRD profiles were collected from 20 ° to 90 ° at a step width of 0.0144 ° using Rigaku Ultima III X-Ray Diffractometer equipped with a CuKα (λ=1.5406 Å) source. The unit cell constant was estimated over multiple characteristic diffraction peaks on the platform of Jade® 6.1, a professional XRD pattern analysis software.

The catalytic performance measurement and analysis methods used are reported in the experimental section of previous several chapters.

**9.2 Results and Discussion**
9.2.1 $^{16}$O$_2$–$^{18}$O$_2$ exchange experiment

Identical procedures described in section 5.2 were also applied for pure Ca$_{0.1}$Ce$_{0.9}$O$_2$ support and its cobalt impregnated catalyst for oxygen storage capability (OSC) measurement. Interestingly, when Ca is doped into the lattice of CeO$_2$, the sample OSC is improved significantly, which is verified from the comparisons of the $^{16}$O$^{16}$O and $^{18}$O$^{18}$O signals demonstrated in Fig.90. The retardation of 32 signal decreasing and 36 signal increasing advice that more oxygen originally stored in the Ca doped sample is required to be pushed out before external oxygen resource can diffuse into the sample and similarly more external oxygen is needed to fully occupy the sites initially held by normal oxygen, resulting in the response delay of the corresponding signals.

After integrating the peak area of corresponding oxygen

![Figure 90](image)

Figure 90. The comparisons of M/Z=32 and 36 signals collected during $^{16}$O$_2$/$^{18}$O$_2$ exchange over CeO$_2$ and Ca$_{0.1}$Ce$_{0.9}$O$_{1.9}$

![Figure 91](image)

Figure 91. The results of $^{16}$O$_2$/$^{18}$O$_2$ exchange experiments over CeO$_2$, Ca$_{0.1}$Ce$_{0.9}$O$_{1.9}$, Co/CeO$_2$, and Co/CaCeO$_{2}$
species, the amount of exchanged oxygen atoms was calculated according to [112] and depicted in Fig.91 over different samples. When Ca is introduced into the CeO$_2$ support lattice, a great enhancement of oxygen mobility is obviously observed resulting from the creation of oxygen vacancies due to the lower valence state of Ca compared with Ce.

9.2.2 $H_2^{16}O-H_2^{18}O$ Exchange Experiment

Since the oxygen used for ethanol oxidation during BESR reaction is originated from another reactant co-fed with ethanol during the reaction, i.e., water, it will be more realistic and accurate to measure catalyst oxygen mobility using H$_2$O as the oxygen source. Therefore, $H_2^{16}O-H_2^{18}O$ exchange experiments have been designed and implemented over the same samples tested before by using $^{16}O_2-^{18}O_2$ exchange technique for comparison. Fig.92 shows the result coming from one typical such experiment collected over empty reactor. During the first switch, $H_2^{16}O$ signal (m/z=18) decreases, accompanied by a rise of $^{18}O^{18}O$ signal (m/z=20). Following the $H_2^{18}O$-to-$H_2^{16}O$ switch, relaxation and rise curves are essentially identical. For the convenience of comparison, the M/Z=20 signals corresponding to the $H_2^{18}O$ collected over various samples have been drawn in
Fig. 93. The time spent on complete replacement of $\text{H}_2^{16}\text{O}$ with $\text{H}_2^{18}\text{O}$ varies following the order of $\text{CeO}_2 < 10 \%\text{Co/CeO}_2 < \text{Ca}_{0.1}\text{Ce}_{0.9}\text{O}_{1.9} < 10 \%\text{Co/Ca}_{0.1}\text{Ce}_{0.9}\text{O}_{1.9}$, indicating the variations of their oxygen accessibility following the reversed order mentioned above. After integrating the peak areas of corresponding water species and subtracting the gas-phase holdup contribution determined from the Ar signal and the contributions from empty reactor, the amount of exchanged oxygen atoms was calculated and tabulated in Table 9. As can be seen from the comparison of the results between $^{16}\text{O}_2-^{18}\text{O}_2$ exchange and $\text{H}_2^{16}\text{O}-\text{H}_2^{18}\text{O}$ exchange, the oxygen mobility difference between various samples has been magnified. All the oxygen mobility results collected from $\text{H}_2^{16}\text{O}-\text{H}_2^{18}\text{O}$ exchange experiments are notably larger than the results collected from $^{16}\text{O}_2-^{18}\text{O}_2$ exchange experiments, which might be associated with the discrepancy of the corresponding bond energy. In order to exchange the oxygen containing in

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<th>$\text{CeO}_2$</th>
<th>$\text{Ca}<em>{0.1}\text{Ce}</em>{0.9}\text{O}_{1.9}$</th>
<th>$\text{Co/CeO}_2$</th>
<th>$\text{Co/Ca}<em>{0.1}\text{Ce}</em>{0.9}\text{O}_{1.9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2^{16}\text{O}-\text{H}_2^{18}\text{O}$ exchange</td>
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<td>10.85</td>
<td>9.42</td>
<td>16.48</td>
</tr>
<tr>
<td>$^{16}\text{O}_2-^{18}\text{O}_2$ exchange</td>
<td>1.64</td>
<td>1.75</td>
<td>2.52</td>
<td>9.01</td>
</tr>
</tbody>
</table>
O₂, O=O double bond is required to be broken, which demands energy input of 119 kcal/mol. However, only 101 kcal/mol energy is needed for O-H bond breakage for oxygen exchange containing in hydroxyl group after dissociative adsorption of water. Another explanation of this difference might rely on the catalyst’s capability in chemisorption of different species. According to the results, water molecules are much easier to be adsorbed along with chemical bond breakage over all the samples tested than O₂ molecules, which favors the following oxygen exchanging process. Nevertheless, the general trends released from the two sets of oxygen mobility results are consistent with each other, which further proves the reliability of the technique for oxygen mobility measurement. Co impregnation benefits the improvement of oxygen mobility, resulting from its excellent ability in bond cleavage (O=O in water and O-H in water). In addition, the oxygen mobility of CeO₂ is significantly enhanced after Ca doping, beneficial from the creation of oxygen vacancies.

9.2.3 O₂ Pulse Chemisorption

As shown in Fig.94, oxygen uptake was measured for various samples. The results are arranged in the order of increasing O₂ uptake. CeO₂ can adsorb certain
amount of oxygen due to its partial reducibility near the surface layer at lower temperature [123, 124]. It is obvious that the Ca addition improves the oxygen uptake of CeO$_2$ significantly, which might be ascribed to the introduction of oxygen vacancy due to the lower oxidation state of Ca [46, 47] compared with Ce. Compared to blank supports, cobalt impregnated samples display much higher oxygen uptake. In fact, the quantification of the results shows that part of the oxygen uptake for the ceria-supported samples is attributable to the support.

9.2.4 CO Pulse Chemisorption

As complementary data to the OSC measurements using O$_2$ pulse chemisorption described above, CO adsorption/reaction with lattice oxygen has been performed to evaluate the static oxygen accessibility of various samples. Fig.95 shows the CO conversion (denoted as CO uptake) over these catalyst samples. CO uptake signifies the oxygen consumption since CO depletion and CO$_2$ formation mimicked each other very closely. The trend seen in these experiments is very similar to what was observed in oxygen-uptake experiments over reduced catalysts. The oxygen accessibility changes in the following order: Co/CaCeO$_2$ > Co/CeO$_2$ > CaCeO$_2$ >
CeO$_2$. These results, once again, demonstrate the significant changes achieved in making the oxygen more accessible from the support lattice through modifications we made to the catalyst formulations.

9.2.5 CO TPR

CO has been selected as the probe to evaluate the effect of calcium doping on the reducibility. Fig. 96 shows the TPR profiles collected over the samples with and without Ca addition. The reduction peaks have obviously shifted to the lower temperature about 50 °C when Ca is incorporated, indicating that Ca doping makes the lattice oxygen embedded in the sample support more labile, leading to more active surface oxygen species and, in turn, higher oxygen mobility which might contribute to the catalytic performance improvement with Ca modified sample reported previously.

9.2.6 LRS

The effect of Ca doping has been further researched using LRS technique. As shown in Fig. 97, compared to CeO$_2$, the dominant band ascribed to the F$_{2g}$ mode of fluorite [141, 142] over the Ca doped sample shifts from 465.8 to 458.7 cm$^{-1}$, indicating of the expansion of the unit cell after the introduction of certain amount of Ca into the lattice structure of CeO$_2$ [47], predicted by the atomic
simulation [143]. Moreover, the broadening of this peak also implies the smaller particle size. Besides, the presence of the peak at 605 cm\(^{-1}\) is indicative of oxygen vacancy [144], which is consistent with the results obtained from other characterizations discussed so far. In addition, the appearance of the weak band centered at 268 cm\(^{-1}\) can be attributed to a lowering of the cubic fluorite symmetry to a tetragonal structure originated from the distortion in the anion sublattice [141].

9.2.7 XRD

In order to quantify the CeO\(_2\) unit cell expansion derived from the Ca addition, the XRD technique has been employed. The diffraction patterns of CeO\(_2\) and Ca\(_{0.1}\)Ce\(_{0.9}\)O\(_{1.9}\) have been

![Figure 97. The laser Raman spectra collected over CeO\(_2\) and Ca\(_{0.1}\)Ce\(_{0.9}\)O\(_{1.9}\)](image)

![Figure 98. The diffraction patterns collected over CeO\(_2\) and Ca\(_{0.1}\)Ce\(_{0.9}\)O\(_{1.9}\)](image)
displayed in Fig.98. The peak broadening effect has been observed over Ca$_{0.1}$Ce$_{0.9}$O$_{1.9}$ compared to CeO$_2$, indicating the existence of smaller particle size. Furthermore, the small peak shift has been noticed to higher diffraction angle after scrutinizing the difference between these two samples. For magnifying the difference, the inset in Fig.98 zooms in the region where (111) diffraction peak is located (25-32 °). It is clear to see that the peak has moved from 28.56 ° to 28.89 °. The unit cell dimension estimation was then performed on the platform of Jade® 6.1, based on all the peak shifts present in the measured region. The calculation result shows that the CeO$_2$ unit cell has been expanded from 5.4108 Å to 5.4151 Å due to the 10 wt.% addition of Ca, which is in agreement with the results reported earlier [143, 204, 205].

9.2.8 DRIFTS

The ethanol conversion ability over the sample surface is also studied using DRIFTS technique. As shown in Fig.99a, at room temperature, ethanol is

![Figure 99. DRIFT spectra collected during ethanol TPD over (a) 10%Co/CeO$_2$ and (b) 10%Co/Ca$_{0.1}$Ce$_{0.9}$O$_{1.9}$](image)
adsorbed on the surface of the sample molecularly (indicated by ν (OH): broad band located between 3600~3200 cm⁻¹) and ethoxide form (1116, 1049 cm⁻¹). Because of the high oxygen storage capability of ceria, part of the ethoxide has been oxidized into acetate (1560, 1440, 1349 cm⁻¹) even at room temperature. The appearance of carbonate (1525 cm⁻¹) due to further oxidation of acetate and CO₂ (2364, 2343 cm⁻¹) as its decomposition product testifies to the evolution of the surface species during temperature increase.

To examine the effect of Ca doping, the same spectra has been collected over Ca doped sample and shown in Fig. 99b. The presence of CO₂ peak at temperatures as low as 100 °C rather than 150 °C for its counterpart confirms the improved ethanol conversion capability of the Ca doped sample, which has been further evidenced by the early appearance and disappearance of other surface intermediates involved over Ca doped sample. The activity measurement of this sample through steady state reaction will be performed in the coming section.

9.2.9 Catalytic performance

The activities of the samples with and without Ca addition have been measured and its product distribution at 400 °C has been depicted in Figure 100.

**Figure 100.** The product distribution of 10%Co/CeO₂ and 10%Co/Ca₀.1Ce₀.9O₁.₉ at 400 °C under the reaction conditions: H₂O:EtOH=10:1(molar ratio), WHSV = 0.54 g EtOH/g Cat/h, GHSV=5,000 h⁻¹, C₉EtOH=7.5 %
Fig. 100. In both case, 100 % ethanol conversion has been achieved. However, after Ca doping, the hydrogen yield has been notably improved from 60 % to 86 % along with the disappearance of the two-carbon containing species (i.e., acetone) and rising of the final carbon containing product formation (i.e., CO₂) due to complete oxidation of ethanol, implying that Ca doped catalyst has higher oxygen mobility resulting in higher oxidation degree of ethanol than its counterpart without Ca addition.

9.3 Conclusions

According to the observations obtained from the various characterization techniques employed in this paper, the introduction of calcium into the CeO₂ lattice structure leads to the unit cell expansion and creation of oxygen vacancies due to lower oxidation state of Ca (2+) compared to Ce (4+), which facilitates the improvement of oxygen mobility. As a result, the catalytic performance has been significantly enhanced when Ca is present, leading to larger amount of final product formations (H₂ and CO₂) from BESR reaction.
CHAPTER 10

EFFECT OF COBALT PRECURSOR

In this study, the effect of cobalt precursor on the activity of Co/CeO$_2$ catalysts has been systematically investigated under the environment of bio-ethanol steam reforming employing various characterization techniques including Temperature Programmed Reduction (TPR), H$_2$ Chemisorption, Temperature Programmed Desorption (TPD), X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS).

10.1 Experimental

10.1.1 Catalysts preparation

CeO$_2$ (Aldrich, 71 m$^2$/g, 0.34 cm$^3$/g) supported cobalt catalysts with 10 wt.% weight loading were prepared in air by Incipient Wetness Impregnation (IWI) technique from the ethanol solutions of cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$$\cdot$6H$_2$O, Aldrich 99.999 %), cobalt (II) sulfate heptahydrate (CoSO$_4$$\cdot$7H$_2$O, Sigma, > 99 %), cobalt (II) 2-ethylhexanoate ([CH$_3$(CH$_2$)$_3$CH(C$_2$H$_5$)CO$_2$]$_2$Co, Aldrich, 65 wt.% solution in mineral spirits), trans-Dinitrobis (ethylenediamine)-cobalt (III) nitrate (C$_4$H$_{16}$CoN$_7$O$_7$, Aldrich), cobalt (II) acetate (Co(CH$_3$COO)$_2$, Aldrich, 99.995 %), cobalt chloride hexahydrate
(CoCl₂•6H₂O, Riedel-de Haën, >99 %), octacarbonyldicobalt (Co₂(CO)₈, Alfa Aesar, stabilized with 1-5 % hexane), cobalt (II) carbonate hydrate (CoCO₃•xH₂O, Aldrich), cobalt (II) oxalate dehydrate (CoC₂O₄•2H₂O, Aldrich), and cobalt (II) acetyl acetonate (Co(C₅H₇O₂)₂, Aldrich, 97%). The CeO₂ support was calcined for 3 h under air at 500 °C prior to impregnation. After repeating impregnation and drying in an oven overnight at approximately 95 °C as many times as determined by the pore volume of each support, the resulting samples were calcined at 450 °C under air for 3 h and stored for use.

10.1.2 Catalysts characterization and reaction performance measurement

The volumetric measurement of H₂ chemisorption was conducted using a Micromeritics ASAP 2010 Chemisorption system. Prior to adsorption measurements, calcined samples were reduced in-situ under 5% H₂/He at the desired reduction temperature (in this case 400 °C) for 2 h followed by evacuation to 10-5 mmHg and cooling down to 35 °C. The adsorption isotherms were obtained at equilibrium pressures between 50-500 mmHg. The first adsorption isotherm was established by measuring the amount of H₂ adsorbed as a function of pressure. After completing the first adsorption isotherm, the system was evacuated for 1 h at 10-5 mm Hg. Then a second adsorption isotherm was obtained. The amount of probe molecule chemisorbed was calculated by taking the difference between the two isothermal adsorption amounts. The Co dispersion was then obtained by calculating the ratio of the surface Co sites accessible by the probe molecules to the total amount of Co introduced during impregnation.
DRIFTS was performed with a Thermo Nicolet 6700 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a KBr beam splitter. The experiments were performed using a Smart collector DRIFT environmental chamber with ZnSe windows. Following a cleaning step under He at 400 °C for 30 min to remove impurities from sample surface that might be adsorbed during storage and reduction at 400 °C for 2 h under 5 %H\textsubscript{2}/He, the chamber was heated to 450 °C under He for 1 h to eliminate moisture generated during reduction. The background spectra were collected at each temperature under He flow before the introduction of the reactant vapor. The ethanol vapor generated from a bubbler was then flowed over the sample for 1 h at room temperature using He as carrier gas. The sample was then flushed with He for 30 min. Spectra were taken at pre-set intervals under helium continuous flow while the sample temperature was ramped from 25 °C to 500 °C.

TPD experiments were performed using AutoChem II 2920. Samples were first pretreated under helium (30 ml/min.) at 400 °C for 30 min and then reduced at 400 °C under 5 %H\textsubscript{2}/He (30 ml/min) for 2 h. The reactor was then heated to 450 °C under He for 1 h to eliminate moisture generated during reduction. The samples were subsequently cooled down to room temperature under He. The ethanol vapors generated from a bubbler system were then allowed to flow through the sample bed for 1 h. Following the purging step with helium, the sample was subjected to a linear temperature program at a rate of 10 °C/min. The effluent was monitored by a Cirrus MKS Mass Spectrometer.

H\textsubscript{2} TPR experiments were performed using a laboratory flow system
equipped with a thermal conductivity detector. Samples of 100 mg were subjected to an oxidative cleaning step at the samples’ calcination temperature in air, followed by cooling to room temperature under helium. TPR experiments were subsequently performed under 5 %H₂/N₂ (30 ml/min) with a heating rate of 10 °C/min.

XRD profiles were collected from 15° to 105° at a step width of 0.0144° using Rigaku Ultima III X-Ray Diffractometer equipped with a CuKα source. The average crystalline particle size estimation was performed according to the Scherrer equation over multiple characteristic diffraction peaks on the platform of Jade® 10, a professional XRD pattern analysis software.

The TEM experiments were performed by using Philips Tecnai TF-20 TEM instrument operated at 200 kV. An X-ray analyzer for EDS is incorporated into the instrument for elemental analysis under STEM mode for improving image contrast between CeO₂ and Co phases. The sample was first dispersed in ethanol and supported on lacey-formvar carbon on a 200 mesh Cu grid before the TEM images were recorded.

The catalytic performance measurement and analysis methods used are reported in [45]. Briefly, all catalysts were first pretreated at 400 °C for 30 min. under He and then reduced in-situ at 400 °C for 2 h under 5 %H₂/He. The reactant liquid consisting of ethanol and water at 1:10 molar ratio was delivered by a Waters® 590 HPLC pump into an evaporator heated at ~200 °C for rapid evaporation. The generated reactant vapor was carried by He and introduced into the reactor. Subsequently the catalytic performances were tested in the
temperature range of 300 °C to 550 °C, in 50 °C increments. The catalyst was held at each temperature for at least 2 h. At the end of the catalytic test, the flow of EtOH+H2O was stopped and the catalyst was cooled under He stream. The hydrogen yield is defined as

\[
\text{H}_2 \text{ Yield } \% = \frac{\text{moles of } \text{H}_2 \text{ produced}}{6 \times (\text{moles of ethanol fed})} \times 100.
\]

The ethanol conversion is defined as

\[
\text{EtOH Conv. } \% = \frac{\text{moles of ethanol converted}}{\text{moles of ethanol fed}} \times 100,
\]

and carbon containing product yield is defined as: Selectivity of C – containing product \(i\) = \(
\frac{\# \text{C} \times (\text{moles of } i \text{ produced})}{2 \times (\text{moles of ethanol converted})}
\).

10.2 Results and Discussion

10.2.1 Catalytic performances

Different cobalt precursors were used in synthesis of CeO2-supported catalysts to examine the effect of cobalt precursor on the catalytic performance. Not only inorganic salts such as CoCl2, CoSO4, CoNO3, and CoCO3, but also organic precursors like Co(CH3COO)2, Co2(CO)8, Co(C8H15O2)2, C4H16CoN7O7, and CoC2O4 were examined. The hydrogen yields and C-containing product selectivities for the catalysts were measured.

![Figure 101. Effect of Co precursor on the hydrogen yield over ceria-supported cobalt catalysts Steady-state reaction conditions: H2O:EtOH=10:1 (molar ratio), GHSV=−5,000 h−1, and C_{EtOH}=−7.5 %](image)
prepared using CoCl₂, CoSO₄, CoCO₃, Co(C₈H₁₅O₂)₂, Co(NO₃)₂, Co(C₅H₇O₂)₂ are presented in Fig.101, Table 10 for organic precursors, and Table 11 for inorganic precursors, respectively. All of the samples prepared using inorganic salts show significantly lower hydrogen yields compared to the ones prepared by the organometallic precursors. The product distributions were also quite different depending on the Co-precursor used. The ones prepared by inorganic salts showed significant levels of acetone and acetaldehyde even at elevated temperatures (Table 10 and 11). Other uncommon byproducts observed were C₂H₄ over the catalyst prepared from CoSO₄ (signaling dehydration of ethanol), CH₃COOH and C₂H₅OC₂H₅ over the sample prepared using Co(C₅H₇O₂)₂ at 450 °C.

**Table 10.** Effect of organic Co precursor on the selectivities (%) of C-containing products. H₂O:EtOH=10:1 (molar ratio), GHSV=~5,000 h⁻¹, and Cₑths=~7.5 %

<table>
<thead>
<tr>
<th>Products</th>
<th>300 °C</th>
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<th>400 °C</th>
<th>450 °C</th>
<th>500 °C</th>
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</tr>
<tr>
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Table 11. Effect of inorganic Co precursor on the selectivities (%) of C-containing products. H$_2$O:EtOH=10:1 (molar ratio), GHSV=~5,000 h$^{-1}$, and C$_{\text{EtOH}}$=~7.5 %

<table>
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<tr>
<th>Products</th>
<th>300 °C</th>
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<th>400 °C</th>
<th>450 °C</th>
<th>500 °C</th>
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</table>

Among all the precursors examined including Co$_2$(CO)$_8$ precursor which showed the best performance out of the cobalt precursors chosen in early publications [36, 50], Co(C$_5$H$_7$O$_2$)$_2$ led to the best catalytic performance, as shown in Fig.101. Hydrogen yield was much higher, especially at lower temperatures, compared to other catalysts. There were no side products other than CO and CH$_4$ above 300 °C. The stability of this catalyst, which will be referred as Co/CeO$_2$ (A), was tested by keeping it on-line at 450°C for 70 hours. As seen in Fig.102, there was no sign of deactivation with the H$_2$ yield remaining over 90 %. The product distribution also remained constant with no liquid
byproducts such as acetaldehyde and acetone and with only small amounts of CH₄ (<5 %) and CO (<4 %) as gas for the duration of the experiment. When a similar time-on-stream experiment was performed over the catalyst prepared using a nitrate salt (Co/CeO₂ (N)), rapid deactivation was observed starting within 15 h (data not shown). Once activity loss started, the main products were hydrocarbons, signaling dehydration reaction becoming important. Poor carbon balance during this period suggested coking on the surface, which was verified by post-deactivation examination of the spent catalyst.

10.2.2 Catalyst characterization

Based on its superior catalytic performance, the catalyst prepared using cobalt acetyl acetonate as the precursor, Co/CeO₂ (A), was chosen for further characterization to examine the relationship between its properties and catalytic performance. For comparison, characterization results acquired over the catalyst prepared from Co(NO₃)₂, the most commonly used Co inorganic salt for catalyst preparation, are also presented.

10.2.2.1 Co Dispersion

Figure 102. Time-on-stream data collected over 10 %Co/CeO₂ using cobalt acetyl acetonate as precursor at 450°C under reaction conditions of H₂O:EtOH=10:1 (molar ratio), GHSV=~5,000 h⁻¹, and C_{EtOH}~7.5 %.
H₂ chemisorption experiments were performed to measure the Co dispersion on the surface, assuming a stoichiometry of 2:1 between Co and H₂. The dispersion values were 15.1 % for Co/CeO₂ (N) and 31.7 % for Co/CeO₂ (A) catalyst.

10.2.2.2 EtOH TPD using mass spectrometry

Mass spectrometry signals obtained during ethanol TPD for Co/CeO₂ (N) and Co/CeO₂ (A) catalysts are shown in Fig.103. Generally speaking, surface transformation of the ethanol derivatives takes place at lower temperatures over the Co/CeO₂ (A) catalyst, showing a temperature shift of 30~50 °C compared to the Co/CeO₂ (N) catalyst. In both cases, the formation of first water peak could be due to the combination of the hydroxyl groups and the nearby hydrogen atoms produced from the dissociative adsorption of ethanol. The second water peak might be associated with either the recombination of two neighboring hydroxyl groups or the combination of hydroxyl group with a nearby hydrogen atom formed during further dehydrogenation of acetate intermediate. The absence of any ethylene species suggests that dehydration is not a likely step leading to the formation of water. The low-temperature peaks of methane, hydrogen, and CO occurring around the same temperature can be attributed to the decomposition of ethanol following the equation: C₂H₅OH⇒CH₄+CO+H₂. The second H₂ peak is accompanied with a strong CO₂ peak, suggesting the completion of the surface reaction to give the final products of CO₂ and hydrogen. When the relative intensities of different peaks are compared for the two catalysts, there are pronounced differences. The second H₂ peak over the
Co/CeO₂ (A) is much stronger than the first one, accompanied by a strong CO₂ peak and a much smaller CH₄ peak. Over the Co/CeO₂ (N) catalyst, this trend is reversed, with the second H₂ peak being smaller and the second CH₄ peak being stronger than their low-temperature counterparts. CO₂ peak is also not as strong as observed over the Co/CeO₂ (A) catalyst. These results imply that adsorbed ethanol can be more easily oxidized to the final products (i.e., H₂ and CO₂) with minimized byproducts (i.e., CO and CH₄ in this case) over the Co/CeO₂ (A) catalyst. This could be a function of higher oxygen accessibility, which may result from the creation of more metal-support interfaces originating from higher cobalt dispersion, as seen through H₂ chemisorption experiments. Furthermore, the higher cobalt dispersion leads to completion of surface transformations at much lower temperatures, as seen when the CO and CO₂ signals are compared.

Figure 103. Mass spectrometer signals of species eluting during EtOH TPD over 10 %Co/CeO₂ prepared with (a) cobalt nitrate and (b) cobalt acetyl acetonate

10.2.2.3 EtOH TPD using DRIFTS

Temperature-programmed desorption behavior of the two catalyst systems
were also compared using the DRIFTS technique. As shown in Fig. 104a, at room
temperature, ethanol is adsorbed on the surface of the catalyst dissociatively
(indicated by \( \nu (\text{OH}) \): broad band located between 3600~3200 cm\(^{-1}\)) and ethoxide
species (1116 and 1049 cm\(^{-1}\)) [10, 85, 206]. The ethanol adsorption process is
associated with the consumption of surface hydroxyl groups evidenced by the
negative feature occurring around 3666 cm\(^{-1}\), which has also been observed by
Raskó et al. [133] over TiO\(_2\)-supported samples. Because of the high oxygen
storage capability of ceria, part of the ethoxide has been oxidized into acetate
(1560, 1440, 1349 cm\(^{-1}\)) [66, 207] even at room temperature with residual \( \eta^2 \)-type
adsorbed acetaldehyde species present (1713, 1261, and 1024 cm\(^{-1}\)) [208]. The
appearance of carbonate (1525 cm\(^{-1}\)) [108] due to further oxidation of acetate
and CO\(_2\) (2364, 2343 cm\(^{-1}\)) [65] as its decomposition product testifies to the
evolution of the surface species during temperature increase. Furthermore, the
bands at 2971, 2933, 2883, and 889 cm\(^{-1}\) due to C-H stretching and bending

\[ \text{Figure 104. DRIFT spectra collected during ethanol TPD over 10\%Co/CeO}_2\text{ prepared with (a) cobalt nitrate and (b) cobalt acetyl acetonate} \]
further verify the existence of ethoxy and acetone species at various stages.

Referring to Fig.104b, it is clearly seen that the formation of CO adsorption peak centered at 1943 cm$^{-1}$ takes place over Co/CeO$_2$ (A) even at room temperature, which is barely seen over its counterpart, suggesting a difference in oxygen accessibility. Higher oxygen mobility in the Co/CeO$_2$ (A) catalyst also manifests itself by the appearance of CO$_2$ formation peak (2364, 2343 cm$^{-1}$) and disappearance of acetate and carbonate intermediate species (1556, 1529, 1450, 1346 cm$^{-1}$) at lower temperatures.

10.2.2.4 XRD

In order to obtain quantitative information of cobalt particle size over the samples synthesized with various precursors, XRD technique was employed, the results of which are shown in Fig.105. Green rectangles represent the diffraction lines due to CeO$_2$ cubic phase. The dark triangles point to the formation of Co$_3$O$_4$ cubic phase after the calcination treatment. Since the peak broadening effect can be used to estimate the particle size of different crystalline phases, comparison of the diffraction patterns shows that CeO$_2$ 

![Figure 105. XRD patterns collected over 10 %Co/CeO$_2$ prepared with cobalt nitrate and cobalt acetyl acetonate](image)
support maintains its particle size in the two different synthesis processes. However, \( \text{Co}_3\text{O}_4 \) diffraction lines are much less intense in the \( \text{Co}/\text{CeO}_2 \) (A) sample and significant line broadening effect has been observed compared to the \( \text{Co}/\text{CeO}_2 \) (N) catalyst. By applying Scherrer equation to the multiple diffraction peaks indicated by its corresponding crystal planes, the average cobalt oxide particle size has been estimated to be 13~14 nm and 6~7 nm for the samples synthesized by cobalt nitrate and cobalt acetyl acetonate, respectively. This results are consistent with the \( \text{H}_2 \) chemisorption results. Similarly, Panpranot et al. [51] have reported synthesizing \( \text{Co}_3\text{O}_4 \) particles with sizes smaller than 5 nm supported on MCM-41 using cobalt acetyl acetonate as precursor.

10.2.2.5 TEM

Fig.106 shows typical TEM images taken over the \( \text{Co}/\text{CeO}_2 \) (A) and \( \text{Co}/\text{CeO}_2 \) (N). The areas highlighted by the red circles indicate \( \text{Co}_3\text{O}_4 \) particles. Overall, \( \text{Co}_3\text{O}_4 \) particles are well dispersed throughout the entire \( \text{CeO}_2 \) particle surfaces examined. The cobalt oxide particles are easily discriminated from the \( \text{CeO}_2 \) particles, due to their distinct morphological difference. The \( \text{CeO}_2 \) support has a characteristic rectangular shape, whereas, the \( \text{Co}_3\text{O}_4 \) particles formed after calcination are almost in spherical shape. Moreover, the \( \text{Co}_3\text{O}_4 \) phase identification has also been confirmed through characteristic lattice structure analysis at high resolution which is not discussed here. A comparison of the images shown in Fig.106a and 106b shows cobalt oxide particles sizes of 15 nm and 6 nm for \( \text{Co}/\text{CeO}_2 \) (A) and \( \text{Co}/\text{CeO}_2 \) (N), respectively, which coincides very well with our observations from XRD experiments.
10.2.2.6 H₂ TPR

The reducibility of the two catalysts prepared with cobalt nitrate and cobalt acetyl acetonate has been compared through H₂ TPR technique. As shown in Fig.107, although the general profiles look quite similar, with two maxima due to reduction from Co₃O₄ to CoO and from CoO to metal Co, both peaks are shifted to lower temperatures by about 50 °C over the Co/CeO₂ (A) sample, indicating better reducibility when cobalt acetyl acetonate is used as the precursor. Since the

Figure 106. Typical TEM images taken over (a) Co/CeO₂ (N) and (b) Co/CeO₂ (A)

Figure 107. H₂ reduction profiles collected over Co/CeO₂ catalysts prepared with cobalt nitrate and cobalt acetyl acetonate
sample reducibility is closely related to oxygen availability as well as accessibility of active sites, this result is again consistent with the better performance of the catalysts prepared by Co(AcAc)₂ compared to its counterpart (catalyst made from Co(NO₃)₂).

10.3 Conclusions

In this paper, multiple cobalt precursors including inorganic salts and organometallic compounds were used to prepare Co/CeO₂ catalysts. The steady-state reaction experiments show much higher H₂ yields and fewer side products over the catalysts prepared using organometallic precursors. Among these, the catalyst prepared using cobalt acetyl acetonate has the highest H₂ yield, most favorable product distribution, and best stability. The superior performance is verified by the transient data. Characterization results point to an improved dispersion on the surface. It is possible that the organic ligands surrounding Co ions provide a spatial barrier effect, keeping the particles segregated and leading to better dispersion.
CHAPTER 11

EFFECT OF PREPARATION METHOD

In this study, in addition to conventional Incipient Wetness Impregnation (IWI) method, solvothermal, hydrothermal, colloidal crystal templating, and reverse microemulsion methods have also been employed to prepare CeO\textsubscript{2} support and CeO\textsubscript{2} supported Co catalysts with various morphologies characterized using Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) technique. The Co/CeO\textsubscript{2} catalysts synthesized using novel methods mentioned above exhibit significantly better performance during BESR reaction.

11.1 Experimental

11.1.1 Catalysts preparation

11.1.1.1 Solvothermal

One method employed involved growing the CoO and CeO\textsubscript{2} nanocrystals separately using a solvothermal method, and then mixing them together homogeneously at the desired ratio. 40 mmol Ce(III) chloride heptahydrate and 120 mmol sodium oleate were dissolved in a solution consisting of 30 ml ethanol, 40 ml water, and 70 ml hexane. The resulting solution was then heated for 5 hours under refluxing. The oil phase was thereafter collected and washed.
several times with water and ethanol. The washed oil was dried at 105 °C in an oven for overnight. Finally, a light yellowish, gel-like product was obtained after drying. 11.2 g of this gel-like complex was dissolved in 50 g 1-octadecene (ODE) and heated at 320 °C for 4 h under Ar. When the obtained dark solution was mixed with large quantities of ethanol, an oil phase was formed at the bottom of the container containing oleic acid-covered CeO₂ nanocrystals. A similar procedure was applied for cobalt oxide nanocrystal synthesis with slightly different parameters. For instance, 40 mmol Co(II) chloride hexahydrate and 80 mmol sodium oleate were dissolved in 30 ml ethanol, 40 ml water, and 70 ml hexane in this case. By following exactly the same procedure, purple wax-like product was obtained after drying as a result. 11.2 g gel-like complex was then dissolved in 50 g ODE and heated at 320 °C for 30 minutes under Ar to decompose the cobalt-oleate complex. The final product was collected by precipitating the reacted solution with ethanol or acetone. Eventually, the CeO₂ and CoO nanocrystals acquired from above-mentioned processes were dissolved in hexane. Specific amounts of the two solutions were taken and mixed in a glass vial. The solution was heated gradually to 450 °C and kept at this temperature for 4 h. Consequently, black powder was obtained as the catalyst. Henceforth, the sample prepared by this method is referred to as Co/CeO₂ (O).

11.1.1.2 Colloidal Crystal Templating (CCT)

In addition to the solvothermal methods employed above, a novel synthesis method named colloidal crystal templating was also developed to prepare CeO₂ with three-dimensionally ordered macroporous (3DOM) structure. In principle,
polymethylmethacrylate (PMMA) is taken as the template to load Ce precursor. Then the polymer beads with impregnated Ce ions undergo high temperature calcination to combust all the carbon containing template. The Ce precursor will be left and oxidized into CeO$_2$ with the macroporous skeleton structure the template leaves behind. In order to achieve this, the PMMA beads with certain diameters have to be synthesized first. In a typical procedure [145], the monomer (MMA) aqueous solution ($C_{\text{MMA}}=0.688 \text{ mol/l}$) was bubbled by Ar for 20 min under stirring to remove the inhibitor contained in the MMA bottle. The solution was then heated up to 70 °C where sodium dodecyl sulfate (surfactant, Sigma-Aldrich, 99+ %) with concentration of $8.5 \times 10^{-4}$ M and $K_2S_2O_8$ (initiator) with concentration of $2.1 \times 10^{-3}$ M were added and the temperature was held for 2h to complete the polymerization reaction. After centrifuging and washing repeatedly with deionized water and methanol, the solids were dried at 60 °C overnight and stored for later Ce loading.

In addition to PMMA, polystyrene (PS) was also used as template for CeO$_2$ preparation. The original preparation method has been depicted in details elsewhere [146]. Briefly, 200 ml DI water, 0.0412 g sodium p-styrene sulfonate (Aldrich), and 0.1281 g NaHCO$_3$ (Jenneile Chemical) were poured into the three-neck flask and stirred for 10 min. at 75 °C. 21.62 ml styrene ($\geq 99 \%$, Sigma, 10-15 ppm 4-tert-butylcatechol as inhibitor) after inhibitor removal treatment [147] was then added into the flask under N$_2$ flowing for 30 min. 0.288g $k_2S_2O_8$ (99+, Sigma) as initiator was subsequently added for 28 h at 75 °C and allowed for cooling down naturally under stirring while flowing N$_2$. The resulted white colloids
were filtered under vacuum to remove large agglomerates and then allowed for gravity deposition one day. The colloids obtained were dried at 60 °C overnight to get final template. For pore size control, certain amount (0.049 g used in this paper) of sodium dodecyl sulfate (SDS: 99+ %, Sigma) can be selectively added right after $K_2S_2O_8$ addition.

There are two strategies borrowed to load Ce precursor into the prepared PMMA template. One method is the following [148]: Ce(NO$_3$)$_3$•6H$_2$O (concentration: 2 M) was dissolved with 8 mL of ethylene glycol (EG) by stirring in a 100 mL beaker at room temperature for 2 h, and the produced EG solution was poured into a 25 mL volumetric flask. Methanol (8 mL, 32 vol%) and EG were added in amounts necessary to achieve the desired concentration. Then, PMMA colloidal crystals were soaked in the solution for 2 h. Excess solution was removed from the impregnated PMMA colloidal crystals by vacuum filtration. The crystals were allowed to dry in air at room temperature overnight. Finally, a two-step calcination was performed over the sample at 310 °C for 3 h and 550 °C for 4 h under air.

Another way to load the Ce precursor is dropping Ce precursor solution onto the PMMA beads rather than soaking PMMA beads in Ce precursor solution [149]. 1.085 g Ce(NO$_3$)$_3$•6H$_2$O and 0.525 g citric acid were dissolved in 5 ml ethanol. The dried PMMA beads were deposited on a filtering paper in a Büchner funnel. The solution was added dropwise over the PMMA beads while the funnel was under vacuum. The resulting wet sample was then dried at room temperature for 1 day before calcining. The calcination was carried out at 400 °C.
for 5 h with a heating rate of 1 °C/min.

The cobalt has been loaded on all of the CeO$_2$ supports synthesized above through wet impregnation and stored for catalytic performance test. For abbreviation, the sample prepared by this method is referred to as Co/CeO$_2$ (3DOM).

11.1.1.3 Reverse Microemulsion

In order to control the cobalt particle size more effectively, CeO$_2$-supported Co catalysts were prepared through a reverse microemulsion technique. The metal particle size can be controlled by adding surfactants functioning to encapsulate cobalt precursor within a spatially limited hydrophilic environment to prevent reagglomeration of cobalt particles. The addition of tetrahydrofuran (THF: C$_4$H$_8$O) at very slow rates overcomes the problem of metal being embedded by the support. The silylation of metal oxide support by adding hexamethyldisilazane (HMDS: (CH$_3$)$_3$SiNHSi(CH$_3$)$_3$) aims to enhance chemical compatibility between the surface of the support and the micellar medium, resulting in prevention of metal dispersion loss when the metal nanoparticles are deposited onto the outer surface of the carrier.

The detailed preparation recipe through reverse microemulsion has been described elsewhere [150, 151] except for the employment of different support materials. Briefly, the commercial CeO$_2$ (nanopowder, < 25 nm, Aldrich) support first underwent a cleaning process in air flow at 550 °C for 3 h. The fresh support was then mixed with HMDS (Aldrich, 99.9 %) in toluene (C$_6$H$_5$CH$_3$, Mallinckrodt, > 99.0 %) in a molar ratio of CeO$_2$:HMDS:toluene 1:0.15:10. The slurry was
subsequently refluxed at 120 °C for 2 h under a dry nitrogen flow. It was then filtered and washed with toluene several times and the final product was obtained after drying the washed solid at 60 °C overnight. Reverse microemulsions were achieved by mixing \( n \)-hexanol (Fluka, >99%), polyoxyethylene octylphenyl ether (Triton X114: \((\mathcal{C}_2\mathcal{H}_4\mathcal{O})_n\mathcal{C}_{14}\mathcal{H}_{22}\mathcal{O}, n=7 \text{ or } 8, \text{ Aldrich}\)) and aqueous solution of cobalt nitrate hexahydrate \((\text{Co(NO}_3)_2\cdot6\text{H}_2\text{O}, \text{ Fisher, 98.4 \%})\). The water-to-surfactant molar ratio was set to 8 and the cobalt concentration in the aqueous solution was 0.3 M and the surfactant concentration in the organic phase was 1 M. A reddish transparent and stable microemulsion was obtained through stirring. Hydrazine monohydrate \((\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O, Aldrich, 98 \%})\) was then directly added as a weak reductant to the prepared microemulsion to transform the cobalt phase to nanoparticulates, followed by the immediate addition of the appropriate amount of the silylated CeO\(_2\) support, thus leading to a cobalt nominal loading of 10 wt.%. The THF (Sigma, > 99.5 %) was then injected into the acquired slurry at a flow rate of 0.33 mL/min in an amount of 100 mL per gram of support. The resulting sample was filtered and washed thoroughly with ethanol, followed by drying at room temperature overnight and then at 60 °C for 10 h. The resulting precursor was then calcined at 500 °C for 3 h to remove the residual organic materials introduced during the procedure and the anchored trimethylsilyl groups remaining on the sample surface produced during silylation. In order to remove the surface attached SiO\(_2\) species after calcination, the calcined sample was soaked in 5 M NaOH solution for 4 day. After washing with DI water, drying at 95 °C overnight, and calcining at 450 °C for 3 h, the final product was stored for use. Catalysts
prepared by this method will be denoted as Co/CeO$_2$ (HMDS).

11.1.1.4 Hydrothermal

CeO$_2$ nanoparticles with cubic shapes have been synthesized by following a hydrothermal procedure to the similar one described in [152]. The NaOH solution was dropwise added into pre-made cerium (III) nitrate hexahydrate (99.50 %, ACROS) aqueous solution. The [OH$^-$] of the final solution was adjusted to be 15 M. Then the solution was transferred to a Teflon-lined stainless-steel autoclave and put into the oven at 150 °C for 48 h. The resulting precipitate taken out from the autoclave after cooling down was washed with deionized water several times until the waste liquid was neutral. The cobalt (II) nitrate hexahydrate (Aldrich 99.999 %) ethanol solution was then loaded onto the as-prepared CeO$_2$ support using IWI method.

CeO$_2$ (nano-polyhedron) was prepared following the procedure described in [153]. Briefly, necessary amounts of cerium (III) nitrate hexahydrate (99.50 %, ACROS) and NaOH were dissolved into 5 ml and 35 ml deionized water, respectively and then mixed together to generate a solution with the concentration of NaOH (GFS > 97 %) at 0.01 M and [Ce$^{3+}$] at 0.05 M. This mixture was kept stirring for 30 min resulting in the formation of a milky slurry. The obtained slurry was subsequently transferred into a teflon-lined stainless-steel autoclave and put into the oven at 100 °C for 24 h. After the hydrothermal reaction, the white precipitates were washed by deionized water and ethanol for several times, followed by the drying process at 80 °C overnight. The resulting yellow powders were collected and stored for later use.
CeO$_2$ with cuboid shape was synthesized using the procedure described in [152]. Typically, the NaOH solution was added drop-wise into pre-made cerium (III) nitrate hexahydrate (99.50 %, ACROS) aqueous solution. The [OH$^-$] concentration of the final solution was adjusted to be 15 M. Then the solution was transferred to a teflon-lined stainless-steel autoclave and put into the oven at 150 °C for 10 h. The resulting precipitate taken out from the autoclave after cooling down was washed with deionized water several times until the waste liquid was neutral.

Hydrothermal method was also applied to prepare CeO$_2$ with nanorod structure according to a different procedure described in [154]. Basically, Ce(NO$_3$)$_3$•6H$_2$O solution (16 mM, 5 ml) and NaOH solution (14 M, 35 ml) were mixed together without agitation. The suspension was then transferred into a teflon-lined stainless-steel autoclave with 50 ml capacity and put into an electric oven at 100 °C for 72 h. The product was thereafter washed with deionized water for several times and dried at 60 °C overnight.

CeO$_2$ with nano-belt structure was achieved through hydrothermal method [155]. In the typical procedure, 8 ml urea (ACROS, 99.5 %) aqueous solution ($C_{\text{urea}}=0.9$ M), 8 ml 0.3 M Ce(NO$_3$)$_3$•6H$_2$O solution, 4 ml H$_2$O$_2$ (30 wt. %, Sigma), and 20 ml distilled water were mixed into a teflon-lined stainless-steel autoclave with 50 ml capacity. The autoclave was sealed and maintained at 230 °C for 10 h. After the autoclave was cooled down naturally to the room temperature, the precipitate was washed with deionized water and ethanol several times before being put into an electrical oven at 80 °C overnight for drying.
CeO$_2$ (nano-plate) was synthesized hydrothermally using hexadecyltrimethylammonium bromide (CTAB, Sigma, >99 %) [156]. Briefly, 3 mmol Ce(NO$_3$)$_3$•6H$_2$O and 1 mmol CTAB were mixed together in a 35ml-beaker under stirring. When the solution turned transparent, 4 ml NH$_3$•H$_2$O was added. The slurry with pinkish color was transferred into a 50 ml teflon-lined stainless-steel autoclave and reacted at 100 °C for 48 h. The products were thereafter washed with deionized water for several times and dried at 80 °C overnight.

CeO$_2$ (nano-octahedron) was prepared using Na$_3$PO$_4$ as the base instead of strong bases such as NaOH and KOH commonly used during hydrothermal process [157], which offers an advantage for the downstream purification. In a typical procedure, 1 mmol Ce(NO$_3$)$_3$•6H$_2$O and 0.01 mmol trisodium phosphate hexahydrate (Sigma, 99+ %) were dissolved in 40 ml deionized water. After being agitated at room temperature for 1h, the mixed solution was transferred into a 50 ml teflon-lined stainless-steel autoclave and reacted at 170 °C for 12 h. After cooling to room temperature, the precipitate was washed with deionized water and ethanol for several times and dried at 80 °C overnight.

11.1.1.5 IWI

For comparison, a reference catalyst was also prepared using IWI method. Cerium (IV) oxide (nanopowder, < 25 nm, Aldrich) was calcined at 550 °C for 4 h, resulting in a support with a surface area and pore volume of 71 m$^2$/g and 0.34 cm$^3$/g, respectively. Cobalt (II) nitrate hexahydrate (Aldrich 99.999 %), which was used as the cobalt precursor, was dissolved in deionized water and then impregnated on the previously calcined support to achieve 10 wt. % nominal Co.
loading. After repeated impregnation and drying steps (overnight at approximately 95 °C) as many times as required by the pore volume of the CeO$_2$ support, the as-prepared samples were calcined at 450 °C under air for 3 h and stored for later use. In the nomenclature used in this paper, this catalyst will be denoted as Co/CeO$_2$ (N).

### 11.1.2 Catalysts characterization and reaction performance measurement

The sample morphology was obtained from Philips XL-30 ESEM instrument equipped with an X-ray analyzer for energy-dispersive X-ray spectroscopy (EDS). The samples were dispersed onto the surface of carbon tabs before being mounted into the vacuum chamber for SEM image capture.

The TEM experiments were performed by employing Philips Tecnai TF-20 TEM instrument operated at 200 kV. An X-ray analyzer for EDS is incorporated into the instrument for elemental analysis. For achieving better contrast, some images were also taken under STEM mode. The sample was first dispersed in ethanol and supported on lacey-formvar carbon on a 200 mesh Cu grid before the TEM images were captured.

The catalytic performance measurement and analysis methods used are reported elsewhere [45]. The hydrogen yield is defined as

$$\text{H}_2 \text{ Yield } \% = \frac{\text{moles of } \text{H}_2 \text{ produced}}{6 \times (\text{moles of ethanol fed})} \times 100,$$

ethanol conversion is defined as

$$\text{EtOH Conv. } \% = \frac{\text{moles of ethanol converted}}{\text{moles of ethanol fed}} \times 100,$$

and carbon containing product yield is defined as: Selectivity of C – containing product i = $\frac{\# C \times (\text{moles of i produced})}{2 \times (\text{moles of ethanol converted})}$. 
11.2 Results and Discussion

11.2.1 Catalyst characterization

11.2.1.1 Solvothermal

Fig.108 shows the TEM images of Co/CeO$_2$ (O) and its precursors at different stages of preparation, namely, CeO$_2$, CoO, and Co incorporated CeO$_2$ samples. Because the ceria with small particle size is oleic acid capped, the contrast in Fig.108a is low. However, it can still be seen that CeO$_2$ nanocrystals may have particle sizes around several nanometers. Cobalt oxide particles with various sizes and shapes are identified in Fig.108b, including triangles, rods, spheres, and cubes. Furthermore, the as-made cobalt oxide has been confirmed to be CoO and the calcined sample to be Co$_3$O$_4$ through XRD patterns (not shown). Fig.108c shows the TEM image for the mixed Co/Ce oxide after calcination. Nanoparticles with sizes of several nanometers are observed. The lack of defined shapes as shown in Fig.108b suggests that the original shapes of CoO have been destroyed during the high temperature calcination. Even individual Co$_3$O$_4$ and CeO$_2$ cannot be identified; we expect that the mixture of Co$_3$O$_4$ and CeO$_2$ should be homogeneous because of the nature of the mixing.

![Fig.108](image-url) The TEM images of (a) CeO$_2$, (b) CoO, and (c) Co/CeO$_2$ samples
11.2.1.2 CCT

Although CeO$_2$ with 3DOM structure is used for the design of photonic crystals, sensors, and power sources, there are very few examples of its application in catalysis and, to the best of our knowledge, none in ethanol steam reforming. Considering the distinct structural features, the 3DOM CeO$_2$ could have potential to be used as a support for cobalt, to improve the catalytic stability during ethanol steam reforming. The well ordered porous structure is expected to help with the cobalt dispersion, and in turn, prevent particle sintering (considered as one of the reasons of catalyst deactivation) during reaction, and facilitate diffusion of reactants through the pores.

Fig. 109 shows the synthesized 3DOM CeO$_2$ using the “soaking” method to load the Ce precursor. It is clearly observed that CeO$_2$ with porous structure has been successfully achieved except for the random pore size distribution. Since the materials with well ordered pores are desired, synthesis parameters optimization has to be performed to finely tune the crystal nucleation process.

![Figure 109. The SEM images of synthesized 3DOM CeO$_2$ using soaking method to load Ce precursor](image)

Encouragingly, if “dropping” method is used to load Ce precursor onto PMMA template, the desirable 3DOM CeO$_2$ was eventually acquired, as shown in Fig. 110. Fig. 110a shows an SEM image of the PMMA beads, which confirms
that mono-dispersed PMMA beads with particle size around 300 nm have been obtained. Figs.110b and 110c clearly show the macroporous structure of CeO\(_2\) that was achieved. The macroporous structure can be further optimized through pore size regulation, wall thickness adjustment, and tuning the pore size distribution.

![Figure 110](image)

**Figure 110.** (a) The SEM image of PMMA beads and (b)-(c) the STEM images of 3DOM CeO\(_2\)

In order to further improve the catalytic performance of the supported cobalt catalyst on CeO\(_2\) with three-dimensional ordered macroporous (3DOM) structure, the morphology of the CeO\(_2\) (3DOM) is required to be fine tuned. More specifically, the pores need to be more orderly and the pore size needs to be smaller for achieving smaller cobalt particle size. For this purpose, the

![Figure 111](image)

**Figure 111.** The TEM images taken from various locations over PS colloids
preparation recipe has been modified and PS has been used as the crystal colloidal template rather than PMMA.

Figure 112. The TEM images taken from various locations over PS colloids after SDS modification

Fig.111 shows the TEM images taken at various locations over PS colloidal particles. It is clearly evidenced that the particles are packed closely and orderly layer by layer. Moreover, the particle sizes are uniformly distributed around 200 nm. After adding certain amount of SDS as surfactant to control the particle size of the PS colloids, its size has been reduced in half (~100 nm) evidenced in Fig.112. Moreover, they are still closely and orderly packed. More SDS is planning to be added in order to achieve even smaller particle size for acquiring CeO₂ with smaller pores after template removal treatment.

11.2.1.3 Reverse Microemulsion

Fig.113 shows three of the typical TEM images of the Co/CeO₂ (HMDS) catalysts taken at various locations of the sample focusing on the Co₃O₄ particles highlighted by the red circles. Using a statistical analysis (not shown), ~90 % Co₃O₄ particles were found to have a size falling into a very narrow range between 6 and 7 nm. In addition, as shown in Fig.113, after the surface
modification by hexamethyldisilazane, the cobalt particles are noticeably embedded into the surface of the CeO$_2$ support, leading to better dispersion, enhancement of the metal-support interaction and increase of the metal-support interphase.

![Figure 113](image.png)

**Figure 113.** The TEM images taken from various locations over 10%Co/CeO$_2$ (HMDS)

11.2.1.4 Hydrothermal

There is much evidence which supports the claim (through theoretical calculation and experimental observations) [158-162] that the crystal plane of CeO$_2$ has the activity in the order of (100) > (110) > (111). Therefore, it will be useful to increase the fraction of most reactive (100) crystal planes while decreasing less reactive (110) and (111) planes of CeO$_2$ nanoparticles. It has been reported [152] that the CeO$_2$ particles with cubic shapes have the greatest opportunity to expose (100) crystal planes to the surface, which is the motivation for the preparation of CeO$_2$ nanocubes. As shown in Fig.114, CeO$_2$ nanocubes are successfully obtained with an average particle size around 40-50 nm after exploring multiple regions in the loaded sample. The (100) crystal plane exposure has been confirmed by measuring the spacing between the lattice
fringes at higher resolutions. The cubic morphology is further confirmed by employing SEM technique.

![TEM images](image1.png)

**Figure 114.** (a)–(e) The TEM images at different resolutions and (f) the SEM image of CeO$_2$ nanocubes

In addition to cubic shape, Fig.115 from (a) to (f) elucidate the distinct shapes of the CeO$_2$ samples mentioned in the 11.1.1.4 section representing a wide variety of shapes and size distribution from several to hundreds of nanometers, including cuboid, plate, polyhedron, rod, belt, and octahedron shapes. These TEM images demonstrate our capability to control the crystal growth process, which might in turn exert significant impact on the catalytic activity when cobalt is incorporated. The exact morphological effect on catalytic performance will be evaluated in the near future.
11.2.2 Catalyst Performance

The catalytic performances of the three catalysts synthesized using solvothermal, CCT, and reverse microemulsion methods that are described in the previous section are compared in Fig. 116, using the H₂ production rates in the temperature range.
300 - 550 °C. The results obtained over the catalyst prepared by a conventional IWI technique are also included for comparison. At first glance, it is quite apparent that the three catalysts prepared by the novel synthesis techniques show much higher H₂ yields compared to the catalysts prepared by IWI. What is more remarkable, however, is the fact that the Co/CeO₂ (HDMS) catalyst has a significantly higher H₂ production rate than any of the other four catalysts.

Table 12, which compares the H₂ yields and C-containing selectivities over

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<th>Catalyst</th>
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<th>300 °C</th>
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<th>400 °C</th>
<th>450 °C</th>
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<tr>
<td>Co/CeO₂ (O)</td>
<td>H₂ yield</td>
<td>32.3</td>
<td>68.0</td>
<td>90.7</td>
<td>89.8</td>
<td>90.0</td>
<td>92.4</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>3.7</td>
<td>19.5</td>
<td>28.5</td>
<td>30.4</td>
<td>55.2</td>
<td>61.1</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>0</td>
<td>6.8</td>
<td>8.3</td>
<td>0</td>
<td>5.4</td>
<td>6.8</td>
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<tr>
<td></td>
<td>CH₄</td>
<td>4.6</td>
<td>10.5</td>
<td>8.0</td>
<td>23.5</td>
<td>37.4</td>
<td>32.1</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>28.6</td>
<td>41.3</td>
<td>48.1</td>
<td>46.1</td>
<td>2.0</td>
<td>0</td>
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<tr>
<td></td>
<td>Acetic acid</td>
<td>5.2</td>
<td>21.8</td>
<td>7.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>CH₃CHO</td>
<td>57.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Co/CeO₂ (3DOM)</td>
<td>H₂ yield</td>
<td>31.0</td>
<td>68.3</td>
<td>84.7</td>
<td>90.5</td>
<td>92.1</td>
<td>94.6</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>22.2</td>
<td>60.3</td>
<td>79.9</td>
<td>90.7</td>
<td>92.7</td>
<td>90.1</td>
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<td></td>
<td>CO</td>
<td>5.5</td>
<td>12.1</td>
<td>5.2</td>
<td>1.4</td>
<td>3.1</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>4.3</td>
<td>27.6</td>
<td>14.9</td>
<td>7.9</td>
<td>4.2</td>
<td>2.0</td>
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<td>Acetone</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>CH₃CHO</td>
<td>58.1</td>
<td>0</td>
<td>0</td>
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<td>0</td>
</tr>
</tbody>
</table>
Co/CeO$_2$ (N), Co/CeO$_2$ (O), and Co/CeO$_2$ (3DOM), shows that the catalysts display major differences in product distributions as well. For example, the Co/CeO$_2$ (O) catalyst exhibits much higher selectivities to liquid byproducts, such as acetone and acetic acid, especially at lower temperatures as well as small amounts of C$_2$H$_4$ and C$_2$H$_6$ hydrocarbons (not listed). These are undesirable by-products, since they signal an ease of dehydration reaction over this catalyst and a propensity for deactivation. This became apparent by the rapid pressure build-up observed when the Co/CeO$_2$ (O) catalyst was kept online at 450 °C and the post-deactivation examination of the spent catalyst which displayed coke formation on the surface (data not shown).

The Co/CeO$_2$ with 3DOM structure showed significant improvement compared to Co/CeO$_2$ (N), especially at low temperatures (<450 °C). Ethanol dehydrogenation and acetaldehyde decomposition are two main reactions taking place in sequence at low temperatures (<400 °C), resulting in the formation of acetaldehyde and methane respectively. When the temperature is further increased, methane steam reforming, ethanol steam reforming, and water-gas shift reaction are the dominant reactions, leading to the increase of the main product yields (H$_2$ and CO$_2$). The notable increase in CO selectivity is due to the reverse water-gas shift reaction when the temperature is above 450 °C. The overall hydrogen yield is higher than 90 % at temperatures as low as 450 °C. The acetone formation is not observed in the temperature region used for Co/CeO$_2$ (3DOM). Compared with the IWI catalyst, the superior catalytic activity of 3DOM CeO$_2$-supported sample might be attributed to the higher cobalt dispersion
achieved through the ordered porous network of the CeO$_2$ skeleton.

The H$_2$ yields and selectivities to C-containing products obtained over the Co/CeO$_2$ (HMDS) catalyst are presented in Table 13. An important point to note about the results presented in Table 13 is that the data over Co/CeO$_2$ (HMDS) were obtained using a WHSV twice those used for the other catalysts. In spite of doubling of the space velocity, the Co/CeO$_2$ (HMDS) shows substantial activity even at 200 °C, a temperature at which none of the other catalysts showed any activity. It also shows higher H$_2$ yields than any of the other catalysts at every temperature tested. Dehydrogenation of ethanol appears to be dominant at temperatures below 300 °C, leading to acetaldehyde and H$_2$. Single carbon containing products become more dominant above 250 °C, indicating the take-off of the steam reforming reaction. The subsequent steam reforming of methane and other liquid intermediates such as acetaldehyde and acetone results in the increase of hydrogen yield along with increasing temperature. Increased selectivity to CO at higher temperatures is a result of the reverse water-gas shift reaction.

Table 13. Steady-state H$_2$ yields and C-containing product selectivities obtained over Co/CeO$_2$ (HDMS) catalysts. Reaction conditions: H$_2$O:EtOH=10:1 (molar ratio) and C$_{EtOH}$=~7.5 % GHSV=10,000h$^{-1}$, and WHSV=1.08 g EtOH/g Cat./h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Products</th>
<th>200 °C</th>
<th>250 °C</th>
<th>300 °C</th>
<th>350 °C</th>
<th>400 °C</th>
<th>450 °C</th>
<th>500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/CeO$_2$ (HDMS)</td>
<td>H$_2$ Yield</td>
<td>19.8</td>
<td>39.8</td>
<td>62.8</td>
<td>86.3</td>
<td>93.3</td>
<td>94.7</td>
<td>95.8</td>
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<td></td>
<td>CO$_2$</td>
<td>17.5</td>
<td>25.6</td>
<td>55.0</td>
<td>90.5</td>
<td>92.7</td>
<td>94.0</td>
<td>93.6</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>1.0</td>
<td>1.6</td>
<td>8.5</td>
<td>0.3</td>
<td>2.9</td>
<td>3.7</td>
<td>4.6</td>
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<td></td>
<td>CH$_4$</td>
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<td>11.7</td>
<td>15.3</td>
<td>9.2</td>
<td>4.4</td>
<td>2.3</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>0</td>
<td>0</td>
<td>10.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CHO</td>
<td>69.1</td>
<td>61.1</td>
<td>10.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The stability of the Co/CeO$_2$ (HMDS) catalyst was tested by a time-on-stream experiment where the catalyst was kept on-line at 400 °C for 120 h (Fig. 117). The catalyst showed no sign of deactivation, by maintaining 100% ethanol conversion and a H$_2$ yield over 90% throughout the run. In addition to H$_2$ and CO$_2$, the main products from BESR, only small amounts of CH$_4$ (< 5%) and CO (< 4%) were observed.

11.3 Conclusions

In this paper, preparation of Co/CeO$_2$ catalysts by three different novel synthesis techniques (solvothermal decomposition, colloidal crystal templating, and reverse microemulsion) has been described. All of the novel preparation techniques led to superior behavior in ethanol steam reforming reaction compared to IWI method. Among the catalysts studied, the one prepared with the reverse microemulsion technique showed the best performance, giving higher H$_2$ yields at much higher space velocities. The catalyst also showed good stability, with no sign of deactivation when it was kept on-line at 400 °C for 120 h. The superior performance is likely to be related to the improved cobalt dispersion, enhanced metal-support interaction and increased metal-support interphase.
facilitated by the reverse microemulsion technique.

In addition, the hydrothermal method has also been employed in this paper to prepare the Co/CeO₂ catalyst. The CeO₂ particles with various shapes and size distribution have been successfully achieved by controlling the parameters during preparation process. The morphological effect on the catalytic performance will be evaluated in the future.
CHAPTER 12

EFFECT OF OXYGEN PRESENCE IN THE FEED STREAM

In this study, the effect of oxygen presence in the feed stream has been evaluated under transient reaction conditions (i.e., Temperature Programmed Desorption (TPD) monitored by Mass Spectrometry (MS) and Diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS)), as an initial step towards of a more detailed investigation of oxidative steam reforming of ethanol and autothermal steam reforming of ethanol.

12.1 Experimental

12.1.1 Catalysts Preparation

Supported cobalt catalysts with 10 wt.% weight loading were prepared in air by Incipient Wetness Impregnation (IWI) technique from cobalt (II) nitrate hexahydrate (Aldrich 99.999 %) aqueous solutions. The support pellets of ZrO$_2$ (31 m$^2$/g, 0.21 cm$^3$/g) purchased from Saint Gobain were ground and then sifted through a 100-150 mesh. CeO$_2$ (Aldrich, 71 m$^2$/g, 0.34 cm$^3$/g) was used as received. All the supports were then calcined for 3 h under air at 500 °C prior to impregnation. After repeating impregnation and drying in an oven overnight at approximately 95 °C as many times as determined by the pore volume of each support, the resulting samples were calcined at 450 °C under air for 3 h and
12.1.2 Catalysts characterization

The effect of O\textsubscript{2} presence on the catalytic performance was evaluated during ethanol TPD using AutoChem II 2920 (Micrometrics) connected with a Cirrus Mass Spectrometer (MKS Instruments, 1-300 amu). Following a cleaning step under He at 400 °C for 30 min to remove impurities from the sample surface during storage and reduction at 400 °C for 2 h under 5 %H\textsubscript{2}/He, the sample chamber was heated to 450 °C under He for 1 h to eliminate moisture generated during reduction. The ethanol vapor generated from a bubbler was then flowed over the sample for 1 h at room temperature using He as a carrier gas. The sample was then flushed with 1 %O\textsubscript{2}/He until the MS signal was stable. The M.S. signals were subsequently recorded during a linear temperature program at a ramping rate of 10 °C/min.

DRIFTS was performed with a Thermo NICOLET 6700 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector and a KBr beam splitter. The experiments were performed using a Smart collector DRIFT environmental chamber with ZnSe windows. Following a cleaning step under He at 400 °C for 30 min to remove impurities from the sample surface during storage and reduction at 400 °C for 2 h under 5 %H\textsubscript{2}/He, the chamber was heated to 450 °C under He for 1 h to eliminate moisture generated during reduction. The background spectra were collected at each temperature under He flow before the introduction of the reactant vapor. The reactant vapors (EtOH and H\textsubscript{2}O) generated from a two-bubbler system were then consecutively flowed over the
sample for 1 h at room temperature using He as a carrier gas. The sample was then flushed with He for 30min. Spectra were taken at pre-set intervals after 1 %O₂/He was introduced into the environmental chamber for 5 min. followed by He flush for another 5 min. at each temperature setting while the sample temperature was ramped from 25 °C to 500 °C.

12.2 Results and Discussion

The effect of the presence of O₂ on catalytic activity has been investigated using the combination of DRIFTS and MS techniques. The results obtained in this study are also likely to provide some initial insight for research on oxidative ethanol steam reforming (OESR) and autothermal ethanol steam reforming (AESR) reactions.

![Figure 118](image_url)

**Figure 118.** In-situ DRIFTS spectra collected during ethanol TPD over 10 %Co/ZrO₂ (b) with and (a) without the presence of oxygen

The Fig.118 shows the comparison of the DRIFTS spectra collected during ethanol TPD with and without the presence of oxygen. It is clearly seen that when oxygen is present, the appearance and disappearance of the surface
intermediates such as ethoxide (2987, 2935, 2881, 1383, 1186, 1103, 1062 cm$^{-1}$), acetate (1558, 1440, 1350 cm$^{-1}$), and surface CO$_2$ (2368, 2362 cm$^{-1}$, evolved from the decomposition of carbonate) species occur at much lower temperatures, implying that the oxygen availability is crucial for ethanol conversion, which supports our previous conclusion that higher oxygen accessibility facilitates oxidation of the carbonaceous fragments, resulting in higher hydrogen yields at

**Figure 119.** In-situ DRIFTS spectra collected during ethanol & water TPD over 10 %Co/CeO$_2$ (b) with and (a) without the presence of oxygen

**Figure 120.** In-situ DRIFTS spectra collected during ethanol & water TPD over 10 %Co/ZrO$_2$ (b) with and (a) without the presence of oxygen
lower temperatures. The same phenomenon was observed over CeO$_2$ based samples as shown Fig.119.

A similar effect of O$_2$ has also been observed during ethanol and water TPD over Co/ZrO$_2$, as shown in Fig.120.

In addition to the surface species detected by the DRIFTS technique, the gas phase product distribution has been monitored simultaneously by mass spectrometry to provide a comprehensive view of surface-gas phase interactions during the ethanol and water TPD experiments. Fig.121 shows the comparison of the MS profiles collected during ethanol TPD with and without the presence of O$_2$. The formation of each product shown in Fig.121a is seen to shift to lower temperatures (more than 100 °C) in the presence of oxygen (Fig 121b). The CO signal is much weaker in the presence of O$_2$ due to its oxidation to CO$_2$, leading to a much larger CO$_2$ peak. The H$_2$O formation takes place in two steps, following the H$_2$ formation in the absence of water, suggesting combustion of H$_2$, which has been reported by Cai, et al. over Ir/CeO$_2$ [127]. It is difficult to draw
direct conclusions from these results since they represent transient data (batch adsorption of ethanol, continuous flow of O₂). However, it is clear that maximizing hydrogen yield in OESR and AESR would require careful optimization of the reaction parameters. Another interesting observation from these experiments is that in the absence of O₂, there is a strong C₂H₄ signal. Of course, we have earlier shown the ZrO₂-supported catalysts to be prone to coking and the formation of ethylene is likely to be the first step in coke formation. When O₂ is present, however, there is no C₂H₄ formation, which implies that coking will be a much less serious concern in the presence of oxygen, not only due to the ease of surface carbon oxidation, but also due to the suppression of the dehydration step, which leads to coke precursors.

A similar effect of O₂ is observed by the MS results comparison collected during ethanol and water TPD, as shown in Fig.122.

![Figure 122. MS profiles collected during ethanol & water TPD over 10%Co/ZrO₂ (b) with and (a) without the presence of oxygen](image)

### 12.3 Conclusions

...
According to the results obtained in this study, the presence of oxygen in the feed stream promotes the oxidization of ethanol, leading to larger amounts of CO₂ formation at lower temperatures and gasification of carbon resulting in effective prevention of catalyst deactivation. However, the positive effect of oxygen addition is countered by the loss of hydrogen produced through oxidation to water. Therefore, the careful choice of oxygen concentration in the feed stream is critical for maximizing the hydrogen production as well as avoiding catalyst deactivation through carbon deposition.
CHAPTER 13

KINETIC MODELING

In this study, a kinetic model over the catalyst systems investigated so far has been proposed including all of the major gas products and surface intermediates based on the experimental observations collected from versatile characterization experiments and extensive reaction data. The model established can be evaluated with experimental data and this is recommended as part of the future work.

13.1 Introduction

Compared with the kinetic studies focused on the steam reforming over single carbon containing reactants such as methanol [163-167] and methane [168-172] (MSR) which have been investigated intensively for tens of years, the kinetic investigations performed over ethanol steam reforming (ESR) reaction are still in their burgeoning stage, which might be due to the relatively complicated reaction networks involved originating from the increase of carbon atom. However, the knowledge accumulated during the systematic explorations of the kinetic mechanisms occurring during MSR provides a valuable starting point for ESR researchers to expand upon. In recent years, the number of kinetic studies on ESR has increased significantly.
Based on the experimental observations obtained from monitoring both gas phase and sample surface during the catalytic reaction of ESR employing versatile characterization techniques, several kinetic models have been proposed to simulate the mechanistic behaviors of various catalyst systems [88-92], which will facilitate better understanding of the reaction mechanisms. If the predicted values generated from the tentative kinetic models are consistent with the experimental results, the assumed reaction pathways and rate-determining step (RDS) proposed in the models may help to elucidate the actual reaction mechanisms to a certain level. Furthermore, the activation energy measured from this study provides the reference for molecular simulation. In addition, the outcomes from this kinetic analysis will benefit reactor design.

According to the experimental procedures used by various authors, prior to conducting kinetic measurements over different catalysts, several preliminary tests have to be performed in order to avoid the mass transfer limitation coming from gas phase and fluids channeling and back-mixing effects. To study the kinetics of solid-catalyzed gas-phase reactions such as ESR, the reaction rates must be measured when the intrinsic chemical reaction rate controls the overall reaction rate. The mass transfer resistance might be derived from two sources, i.e., gas diffusion in the continuous gas phase surrounding the catalyst solid particles and in the confined space trapped within the particles (the pores). The absence of the former phenomena can be verified by varying reactant flow rate while maintaining the W/F (catalyst weight/reactant flow rate), catalyst particle size and the molar ratio of ethanol to water constant. As suggested by Idem and
Bakhshi [173] and Wojciechowski and Rice [174], the region at which reactant conversion does not change with increasing flow rate is the acceptable flow rate range to minimize the influence from diffusion resistance in the external continuous gas phase. Analogously, the pore effect can also be minimized through adjusting catalyst average particle size until stable conversion level is achieved while keeping other reaction parameters unchanged. Furthermore, for acquiring plug flow and isothermal behavior in the reactor, certain empirical rules need to be followed although different authors have different descriptions of the criteria. For instance, ratio of catalyst bed height to catalyst particle size \((L/D_p) > 50\), and ratio of internal diameter of the reactor to the catalyst particle size \((D/D_p) > 10\) were adopted in the paper from Akande and co-workers [88] and Arteaga et al. [175]. Whereas, \((D/D_p) > 30\) was selected when both Patel et al. [165] and Sahoo et al. [91] performed the similar kinetic measurements.

Generally speaking, there are no specific requirements for the geometry and size of the reactor where catalyst bed is installed. In other words, any conventional fixed-bed reactor is applicable for carrying out kinetic studies. Nevertheless, microchannel reactor design is also available in order to achieve superior isothermal behavior and almost ideal plug flow [163, 176, 177]. However, special treatments have to be added to incorporate catalyst into the inner wall of the microchannel reactor.

Aiming to obtain kinetic data available for later data processing, a careful choice of the strategy to collect experimental data is crucial to generate high quality data efficiently which can cover the whole range of interest. The most
convenient way for data collection reported so far is to vary the ratio of W/F at the
designated temperature. The two variables (i.e., W and F) can be controlled
independently to achieve various combinations. The reaction rate is therefore
defined as \( r_a = \frac{dX}{d(W/F_w)} \), where X is the conversion of reactant, which can be
easily determined from the slope of the rigorously fitted curve based on the
diagram showing reactant conversion as a function of W/F. From Arrhenius
equation, we know that \( k = Ae^{-\frac{E_a}{RT}} \). After transformation, \( \ln k = \ln A - \frac{E_a}{RT} \). The
activation energy \( E_a \) can then be easily estimated from the slope of the plot which
shows the \( \ln(k) \) as a function of -1/RT, given that rate constant \( k \) is known at
 corresponding tested temperatures. The determination of \( k \) is relatively
challenging, because the reaction mechanisms should be assumed in advance.
That is, the rate expressions have to be derived from the proposed reaction
mechanisms. Therefore, the accuracy of the \( k \) heavily depends on the
understanding of the reaction mechanisms involved.

The difficulty of the derivation of the rate expression relies on how well the
reaction mechanism is understood. The rate expression can be simply obtained
by following the power-law model without any awareness of the reaction
mechanisms. For example, the rate equation can be expressed as
\( -r_{E_\text{OH}} = kp_{E_\text{OH}}^\alpha p_{H_\text{2}O}^\beta \). For each experiment, ethanol and steam partial pressure
are obtained from effluent gas composition. Each calculated reaction rate using
method described previously and its corresponding effluent partial pressures of
ethanol and steam are used to determine the reaction rate equation. The proper constant $k$, $\alpha$, and $\beta$ can be estimated after strict curve regressions to minimize the deviation from the experimental data. Amazingly, sometimes the rate expression attained after this seemingly simple data processing can represent the mechanistic behavior of certain catalyst system even better when the reaction mechanism is not well understood. Since this approach is relatively straightforward, the initial kinetic work has been concentrated on the utilization of power-law model to simulate the catalytic kinetic performance [89]. Along with the development of catalyst characterization techniques, more sophisticated reaction mechanisms have been explored, leading to the appearance of more realistic kinetic models, including Eley Rideal model [88, 92] assuming that the ethanol molecules adsorbed on the sample surface react with the water molecules in the gas phase and Lagmuir-Hishelwood pattern [91, 175] assuming that both ethanol and water reactant molecules are adsorbed onto the sample surface before reacting with each other. After integrating the experimental observations from various characterization techniques such as IR and MS spectra and the effluent compositions analyzed using GC/MS with several reasonable assumptions, the possible reaction pathway consisting of a series of elementary reaction steps is proposed for rate expression derivation. Transition-state theory is employed to account for the presence of reaction intermediates during surface catalysis. Different assignments of the Rate Determining Step (RDS) will result in the different formulations of the final rate expression, because except for the RDS, rate of other reactions can be assumed to be at equilibrium,
and so the site concentration of various intermediate species formed in the equation are written in terms of measurable quantities, e.g., partial pressure. In addition, in certain situations, Quasi-Steady-State Assumption (QSSA) can also be applied to the surface intermediate species formed during reaction, assuming that the concentrations of these designated species do not change with reaction time. For the estimation of equilibrium constants generated from the equilibrium assumption, heats of adsorption can be taken from the literature and their entropies are determined using non-linear regression. The temperature dependency of these equilibrium constants is calculated referring to Van’t Hoff isothermal equation. Eventually, the achieved rate expressions governing the mechanistic behavior of a certain catalyst system are compared with the experimental data. The agreement within acceptable error tolerance indicates the validity of the hypothesized reaction mechanisms. Contrarily, the failing match requires further study.

To the best of our knowledge, Akande et al. developed the first relatively realistic model composed of a series of elementary reaction steps with the participations of sample surface and surface intermediates based on Eley Rideal mechanism over Ni/Al₂O₃ [88]. The significance of the determination of RDS was evaluated through the comparison with power-law model. Although the results predicted from the model containing the detailed description of the reaction mechanism is not as good as those from the power-law models, the initial tentative model still contributes to the discovery of the catalytic mechanistic behavior. Compared with this work, the model proposed by Vaidya et al. over
Ru/Al₂O₃ [90] appears to be oversimplified. The complicated catalytic surface reactions were truncated into only one step. Although the adsorption of water was considered in the model developed as suggested by the Lagmuir-Hishelwood pattern, the subsequent assumption that water is in a large quantity and is in excess eliminated the influence of water in the successive equations. Later, Mathure et al. [92] performed almost identical work as what has been done by Akande et al.. Therefore, few contributions have been made by them. Commonly, only ESR reaction is investigated in the models described previously. In order to predict the product distributions at various temperature regimes, it is necessary to generate a comprehensive kinetic model containing other side reactions. The efforts spent by Sahoo et al. [91] set a milestone toward this direction. In their paper, water-gas shift and ethanol decomposition were included in addition to ESR. From the comparison between the predicted values and measured data, it seems that their model works fairly well at the temperature at which only single carbon containing products such CO, CO₂, and CH₄ were produced. For simulating the liquid byproduct formations such as acetaldehyde and acetone, a more general model needs to be derived, which can cover the whole temperature range, especially the lower temperature region.

These contributions summarized above provide a meaningful starting point for this project to perform the kinetic analysis over the catalyst systems developed at Ohio State University. Experimental data to evaluate the kinetic model can be acquired with the reactor system described in Section 2. The catalyst treatment and effluent analysis methods can be found in [45]. By
following the similar experimental procedures described previously, the kinetic measurements should be carried out straightforwardly. During the investigation, the effects of ethanol concentration, reaction temperature, GHSV, molar ratio of ethanol to water should be evaluated. These studies are recommended as part of the future work.

13.2 Methodologies

Since the real reaction occurring during the ESR heavily depends on the catalyst system charged, it is necessary to develop a kinetic model suitable for the catalysts developed in our laboratories. The proposal of a reasonable reaction pathway consisting of a series of elementary reactions including the involvement of the catalyst surface plays a significant role in achieving a more accurate rate expression to simulate the catalytic mechanistic behavior during ESR. After integrating the experimental observations described so far and the relative studies reported in the published articles, the following kinetic model is developed. It accounts for all the gas phase species observed in our experiment over the Co-based catalysts. However, it does not take into account carbon formation on the surface. If coking takes place, it will result in deactivation and affect the measured reaction rate and catalytic activity. In addition to the assumptions which are the basis of Langmuir-Hinshelwood kinetics, the model assumes that all of the surface species are adsorbed on the same type of sites. This is likely to be an oversimplification.

\[
2S_1 + CH_3CH_2OH(g) \leftrightarrow^{k_{+1}} \rightarrow CH_3CH_2O_\omega + H_\omega
\]
\[
\text{Additional steps in acetone formation (AF):}
\]

\[
\text{CH}_2\text{CHO} \ (\text{a}) + S \xrightleftharpoons[k_{12-18}]{k_{12-18}} \text{CH}_3\text{CO} \ (\text{a}) + H \ (\text{a})
\]

\[
2\text{CH}_3\text{CO} \ (\text{a}) \xrightleftharpoons[k_{12-18}]{k_{12-18}} \text{CH}_3\text{COCH} + \text{CO} + 2S
\]

\[
\text{Additional steps in water-gas shift (WGS):}
\]

\[
\text{CO} \ (\text{a}) + \text{OH} \ (\text{a}) \xrightleftharpoons[k_{12-18}]{k_{12-18}} \text{HCOO} \ (\text{a}) + S
\]

\[
S + \text{HCOO} \ (\text{a}) \xrightleftharpoons[k_{12-18}]{k_{12-18}} \text{CO}_2 \ (\text{a}) + H \ (\text{a})
\]

\[
\text{Additional steps in ethanol decomposition (ED):}
\]

\[
S + \text{CH}_3\text{CHO} \ (\text{a}) \xrightleftharpoons[k_{12-18}]{k_{12-18}} \text{CH}_4 \ (\text{a}) + \text{CO} \ (\text{a})
\]

\[
\text{CH}_4 \ (\text{a}) \xrightleftharpoons[k_{12-18}]{k_{12-18}} \text{CH}_4 \ (\text{g}) + S
\]

\[
\text{Additional steps in ethanol dehydration (EDHA):}
\]

\[
\text{CH}_2\text{CH}_2\text{O} \ (\text{a}) + H \ (\text{a}) \xrightleftharpoons[k_{12-18}]{k_{12-18}} \text{C}_2\text{H}_4 \ (\text{g}) + \text{H}_2\text{O} \ (\text{g}) + 2S
\]
Additional steps in ethanol dehydrogenation (EDHO):

\[
\text{CH}_3\text{CHO}_{(a)} \xleftarrow{k_{17-27}} \text{CH}_3\text{CHO(g)} + S_i
\]  

(RDS)

The species with subscript (a) indicates that it is a surface reaction intermediate. The steps labeled RDS are assumed to be the rate-determining steps, in other words, they proceed much slower than other steps. Therefore, except for the RDS, the rates of other reactions can be treated to be at equilibrium. There are totally six overall reactions considered in the pathways described above including all the products at the whole reaction region tested during our experiments.

\[
\text{CH}_3\text{CH}_2\text{OH} + 2\text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{CO}_2 + 5\text{H}_2
\]  

(ESR)

\[
2\text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{CO} + 3\text{H}_2
\]  

(AF)

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2
\]  

(WGS)

\[
\text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_4 + \text{CO} + \text{H}_2
\]  

(ED)

\[
\text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2\text{O}
\]  

(EDHA)

\[
\text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2
\]  

(EDHO)

The site concentrations of various intermediate species formed in the equation were written using Langmuir–Hinshelwood approach. The equilibrium constants are written as following:

\[
K_1 = \frac{[\text{CH}_3\text{CH}_2\text{O}_{(a)}][\text{H}_{(0)}]}{P_{\text{C}_3\text{H}_7\text{OH}}[S_i]^2}
\]

\[
K_2 = \frac{[\text{CH}_3\text{CHO}_{(a)}][\text{H}_{(0)}]}{[\text{CH}_3\text{CH}_2\text{O}_{(a)}][S_i]}
\]
Using above relations, the concentrations of all the intermediate products were derived in the form of measurable partial pressure quantities. The reaction intermediate before RDS can be expressed by the combination of reactant partial pressures. However, the surface intermediate after RDS can only be displayed by the array of final product partial pressures. After complicated transformations, the final results are shown as following:
\[
[\text{CH}_2\text{CH}_2\text{O}] = \frac{K_2}{P_{\text{H}_2}} \frac{P_{\text{C}_2\text{H}_5\text{OH}}}{[S_1]}
\] (1)

\[
[\text{CH}_3\text{CHO}] = \frac{K_2K_9}{P_{\text{H}_2}} [S_1]
\] (2)

\[
[\text{CH}_2\text{CO}] = \frac{K_2K_9^{1.5}K_{10}P_{\text{C}_2\text{H}_5\text{OH}}}{P_{\text{H}_2}} [S_1]
\] (3)

\[
[H_{(a)}] = \frac{P_{\text{H}_2}^{0.5}}{K_9^{0.5}} [S_1]
\] (4)

\[
[\text{OH}_{(a)}] = \frac{K_2K_9^{0.5}P_{\text{H}_2\text{O}}}{P_{\text{H}_2}^{0.5}} [S_1]
\] (5)

\[
[\text{CH}_2\text{COO}] = \frac{K_2K_9K_{10}K_{12}P_{\text{H}_2\text{O}}P_{\text{C}_2\text{H}_5\text{OH}}}{P_{\text{H}_2}^{1.5}} [S_1]
\] (6)

\[
[H\text{COO}_{(a)}] = \frac{P_{\text{CO}_2}P_{\text{H}_2}^{0.5}}{K_9K_9^{0.5}K_{13}} [S_1]
\] (7)

\[
[\text{CH}_4] = \frac{P_{\text{CH}_4}[S_1]}{K_{15}}
\] (8)

\[
[\text{CO}_{2(a)}] = \frac{P_{\text{CO}_2}[S_1]}{K_7}
\] (9)

\[
[\text{CO}_{(a)}] = \frac{P_{\text{CO}}[S_1]}{K_8}
\] (10)

\[
[\text{CH}_3] = \frac{P_{\text{CO}_2}P_{\text{H}_2}^{2.5}}{K_9K_9K_9^{0.5}P_{\text{H}_2\text{O}}} [S_1]
\] (11)

The only unmeasurable quantity, [S_1], in the equations above can be eliminated by using the fact that the total number of active sites S_1 available on the catalyst whether occupied by adsorbed species or not is constant.
\[
\begin{align*}
C^T_i &= [S_i] + [\text{CH}_2\text{CHO}_\text{(aq)}] + [\text{CH}_4\text{CO}_\text{(aq)}] + [\text{H}_\text{C} = \text{O}] + [\text{H}_\text{C} \cdot \text{O}_\text{CO}_\text{(aq)}] + [\text{HCOO}_\text{(aq)}] \\
&+ [\text{CH}_4\text{OH}] + [\text{CO}_2\text{H}_\text{(aq)}] + [\text{CO}_\text{(aq)}] + [\text{CH}_3\text{CO}_\text{(aq)}]
\end{align*}
\]

(12)

Substituting equations (1)-(11) into (12), \([S_i]\) can be written as:

\[
[S_i] = C^T_i / (1 + \frac{K_i K_2 K_3 K_{13} P_{C_{1H_{10}OH}}}{P_{H_2}^{1.5}} + \frac{K_i K_2 K_{13} P_{C_{1H_{10}OH}}}{P_{H_2}^{1.5}} + \frac{K_i K_2 K_{13} P_{H_2}^{1.5}}{P_{H_2}^{1.5}} + \frac{K_i K_2 K_3 K_{13} P_{H_2}^{1.5}}{P_{H_2}^{1.5}} + \frac{K_i K_2 K_3 K_{13} P_{H_2}^{1.5}}{P_{H_2}^{1.5}})
\]

Let us have:

\[
\Phi = 1 + \frac{K_i K_2 K_3 P_{C_{1H_{10}OH}}}{P_{H_2}^{1.5}} + \frac{K_i K_2 K_{13} P_{C_{1H_{10}OH}}}{P_{H_2}^{1.5}} + \frac{K_i K_2 K_{13} P_{H_2}^{1.5}}{P_{H_2}^{1.5}} + \frac{K_i K_2 K_3 K_{13} P_{H_2}^{1.5}}{P_{H_2}^{1.5}} + \frac{K_i K_2 K_3 K_{13} P_{H_2}^{1.5}}{P_{H_2}^{1.5}}
\]

Then \([S_i] = C^T_i / \Phi\) (13)

If \(r_s\), \(r_A\), \(r_W\), \(r_E\), \(r_D\), and \(r_F\) represent the reaction rate of ESR, AF, WGS, ED, EDHA, and EDHO, respectively, the rate equation of each reaction can be expressed as:

\[
r_s = k_s [S_i] [\text{CH}_3\text{COO}_\text{(aq)}] - k_s [\text{CH}_3\text{CO}_\text{(aq)}][\text{CO}_2\text{H}_\text{(aq)}]
\]

\[
= \frac{k_s K_2 K_3 K_{13} P_{H_2}^{1.5}}{P_{H_2}^{1.5}} [S_i] - \frac{k_s P_{CO} P_{CO} P_{H_2}^{1.5}}{K_i K_2 K_3 K_{13} P_{H_2}^{1.5}} [S_i]^2
\]

\[
= k_s K_2 K_3 K_{13} K_{15} \left( \frac{P_{H_2}^{1.5} P_{C_{1H_{10}OH}}}{P_{H_2}^{1.5}} \right) [S_i] - \left( \frac{k_s P_{CO} P_{CO} P_{H_2}^{1.5}}{K_i K_2 K_3 K_{13} P_{H_2}^{1.5}} \right) P_{CO} P_{CO} P_{H_2}^{1.5} [S_i]^2
\]

(14)

\[
r_A = k_1 [\text{CH}_3\text{CO}_\text{(aq)}] - k_{-1} P_{CO} P_{CO} [S_i]
\]
\[
\begin{aligned}
&= k_{11} K_9 K_6 K_5 K_2 K_{10} K_{14} P_{C,H,O}^3 \left[ \frac{P_{C,H,O}^2}{P_{H_2}} \right]^2 \frac{[S_1]}{k_{-11} P_{C,H,O} P_{CH,COCH} [S_1]^2} \\
&= k_{11} K_9 K_6 K_5 K_2 K_{10} P_{C,H,O}^3 \left( \frac{P_{C,H,O}^2}{P_{H_2}} \right)^2 \left[ 1 - \left( \frac{k_{-11}}{k_{11} K_9 K_6 K_5 K_{10}} \right) \frac{P_{C,H,O}^2}{P_{H_2}^2 P_{CH,COCH}^2} \right] C_S^2 \Phi_S^2
\end{aligned}
\]

\[
r_e = k_{12} [CO_\alpha] [OH_\alpha] - k_{-32} [HCOO_\alpha] [S_1]
\]

\[
\begin{aligned}
&= k_{12} K_9 K_6 K_5 K_2 K_{10} \left( \frac{P_{H_2} P_{CO}}{K_4 P_{H_2}^3} \right) [S_1]^2 - k_{-32} P_{CO}^2 \left( \frac{P_{H_2} P_{CO}}{K_4 K_9 K_6 K_5 K_{10}} \right) [S_1]^2 \\
&= k_{12} K_9 K_6 K_5 K_2 K_{10} P_{H_2} P_{CO} \left( \frac{P_{H_2} P_{CO}}{K_4 P_{H_2}^3} \right) \left[ 1 - \left( \frac{k_{-32}}{k_{12} K_9 K_6 K_5 K_{10}} \right) \frac{P_{H_2} P_{CO}}{P_{CO}^2 P_{H_2}^2} \right] C_S^2 \Phi_S^2
\end{aligned}
\]

\[
r_E = k_{14} [S_1] [CH_3CHO_\alpha] - k_{-14} [CH_3CHO_\alpha] [CO_\alpha]
\]

\[
\begin{aligned}
&= k_{14} K_9 K_6 K_5 K_2 K_{10} P_{C,H,O} \left( \frac{P_{C,H,O}}{P_{H_2}} \right)^2 \left[ 1 - \left( \frac{k_{-14}}{k_{14} K_9 K_6 K_5 K_{10}} \right) \frac{P_{C,H,O} P_{CO}}{P_{CO}^2 P_{C,H,O}^2} \right] C_S^2 \Phi_S^2
\end{aligned}
\]

\[
r_D = k_{16} [H_\alpha] [CH_3CH_2O_\alpha] - k_{-16} P_{C,H,O} P_{H_2} [S_1]^2
\]

\[
\begin{aligned}
&= k_{16} K_9 P_{C,H,O} \left[ S_1 \right]^2 - k_{-16} P_{C,H,O} P_{H_2} [S_1]^2 \\
&= k_{16} K_9 P_{C,H,O} \left[ 1 - \left( \frac{k_{-16}}{k_{16} K_9} \right) \frac{P_{C,H,O} P_{H_2}}{P_{H_2}^2 P_{C,H,O}^2} \right] C_S^2 \Phi_S^2
\end{aligned}
\]

\[
r_F = k_{17} [CH_3CHO_\alpha] - k_{-17} P_{CH,CHO} [S_1]
\]

\[
\begin{aligned}
&= k_{17} K_9 K_6 K_5 P_{C,H,O} \left[ S_1 \right] - k_{-17} P_{CH,CHO} [S_1]^2 \\
&= k_{17} K_9 K_6 K_5 P_{C,H,O} \left[ 1 - \left( \frac{k_{-17}}{k_{17} K_9 K_6 K_5} \right) \frac{P_{C,H,O} P_{H_2}}{P_{H_2}^2 P_{C,H,O}^2} \right] C_S^2 \Phi_S^2
\end{aligned}
\]

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The rate expressions for each individual reaction were combined to get an overall rate expression for different species. Since the rates of different species are interrelated by stoichiometry, the rate of each individual species was calculated as following:

\[
\begin{align*}
  r_{H_2} &= 5r_s + 1.5r_A + r_w + r_E + r_F \\
  r_{CO_2} &= r_s + r_w \\
  r_{CO} &= r_s - r_w + 0.5r_A + r_E \\
  r_{CH_4} &= r_E \\
  r_{CH,CHO} &= r_F \\
  r_{CH,COCH_3} &= 0.5r_A \\
  r_{C_2H_4} &= r_D \\
  -r_{C_2H_5OH} &= r_s + r_A + r_E + r_D + r_F \\
  -r_{H_2O} &= r_s + r_w - r_D
\end{align*}
\]

The validity of this hypothesized kinetic model can be tested during the process of the data collection of the products distribution as a function of \( W/F_{AO} \). This kinetic model might be refined by considering different RDS assignments and including more than one type of surface active sites.
In this study, a collaborative effort was initiated to combine the experimental results with computational chemistry. This work was done in collaboration with Professor Christopher Hadad and Dr. Xiaoguang Bao. The computational chemistry work was performed at DFT level on the platform of VASP\textsuperscript{®} to simulate the Co/CeO\textsubscript{2} (111) surface. This work is still in its initial stages and is recommended to continue.

14.1 Experiments and Simulation Approach

14.1.1 Catalysts Preparation

Supported cobalt catalysts with 10 wt.% weight loading were prepared in air by Incipient Wetness Impregnation (IWI) technique from cobalt (II) nitrate hexahydrate (Aldrich 99.999 %) aqueous solutions. The support pellets of ZrO\textsubscript{2} (31 m\textsuperscript{2}/g, 0.21 cm\textsuperscript{3}/g) purchased from Saint Gobain were ground and then sifted through a 100-150 mesh. CeO\textsubscript{2} (Aldrich, 71 m\textsuperscript{2}/g, 0.34 cm\textsuperscript{3}/g) and Ca\textsubscript{0.1}Ce\textsubscript{0.9}O\textsubscript{1.9} (Aldrich, 105 m\textsuperscript{2}/g, 0.41 cm\textsuperscript{3}/g) were used as received. All the supports were then calcined for 3 h under air at 500 °C prior to impregnation. After repeating impregnation and drying in an oven overnight at approximately 95 °C as many times as determined by the pore volume of each support, the resulting samples
were calcined at 450 °C under air for 3 h and stored for use.

14.1.2 Catalysts Characterization

TGA/DSC experiments were performed using TG-DSC 111 (SETARAM). Samples were first pretreated under He (30 ml/min.) at 400 °C for 30 min and then reduced at 400 °C for 2 h under 5 %H₂/He. The reduced sample then underwent a moisture removal step under He at 450 °C for 1 h. The samples were subsequently cooled to room temperature under He. The reactant vapors generated from a two-bubbler system were introduced into the reactor chamber at room temperature using He as a carrier gas after the signal was determined to be stable. The signal was recorded until there was no variation observed.

TPD experiments were performed using AutoChem II 2920. Samples were first pretreated under helium (30 ml/min.) at 400 °C for 30 min and then reduced at 400 °C under 5 %H₂/He (30 ml/min) for 2 h. A high temperature (450 °C and 1 h) heating step under inert gas was added after reduction in order to remove moisture generated during the reduction step. The samples were subsequently cooled down to room temperature under He. The reactant vapor generated from the bubbler was then allowed to flow through the sample bed for 1 h. Following the purging step with He, the sample was subjected to a linear temperature program at various ramping rates. The effluent was monitored by a Cirrus MKS Mass Spectrometer.

14.1.3 Simulation approach

In an effort to initiate the model surface selection for simulating various effects studied so far, the Material Studio® 4.0 software package is chosen to
create the atomic assembly platform.

Fig. 123. The support models of ZrO\textsubscript{2} and CeO\textsubscript{2}

Fig. 123 portrays the representation of ZrO\textsubscript{2} and CeO\textsubscript{2} supports with monoclinic and cubic structure, respectively, which are the same as the structures used in our experimental studies. Later Raman and XRD data can be used to validate these support models.

As described in Chapter 11, different crystal planes are associated with unique reactivities. Therefore, the effect of the crystal plane is also simulated as in Fig. 124. By selecting appropriate substrate with the required surface orientation, the CeO\textsubscript{2} with desired crystal plane can be grown through chemical vapor deposition [93-95]. As a result, the characterization data collected over specially prepared single-crystal surfaces will be useful for validating the simulation.
The active metal environment will also be considered by anchoring cobalt atom at various sites of the support surface (shown in Fig.125). The number and nature of unique atomic sites across the support surface has to be predetermined, because each has characteristic energetic and electronic properties, which will have significant effect on the loaded cobalt atom. Since the interaction between active metal and support is expected, the peak variation occurring in the Raman, XRD, and FTIR spectra can be a valuable tool in accounting for the effect.

![Figure 125. The model of cobalt anchoring on the support of ZrO$_2$ and CeO$_2$.](image)

The different cobalt loadings are investigated at simulation level by varying the number of cobalt atoms, which will also depend on the total available support atoms exposed on the surface (plotted in Fig.126).

![Figure 126. The simulation of the effect of cobalt loading over ZrO$_2$ support.](image)

From our previous experimental observations, catalytic activity is closely related to the cobalt dispersion (i.e., the percentage of available surface cobalt...
atoms). Cobalt dispersion, in return, depends on the particle size. Fig.127 shows simulations of the cobalt clusters with various numbers of cobalt atoms.

![Figure 127. The simulation of the effect of cobalt atom cluster size over CeO$_2$ support](image)

The doping and promotion effects have been found to play an important role on the catalytic activity as presented in our preliminary data. Fig.128 and 129 demonstrate our efforts on simulating these effects. In these cases, Ca is chosen as the dopant into the lattice of CeO$_2$ cell by replacing originally existing Ce atom and Cu is taken as an example to represent the promoter effect, because Ca and Cu additions have experimentally exhibited positive effects on catalytic activity improvement.

![Figure 128. The simulation of the doping effect over CeO$_2$](image)  ![Figure 129. The simulation of promotion effect over CeO$_2$](image)

The adsorption of reaction species is visualized in Fig.130. Reactants can be adsorbed on the top of Co atom singly or together. Furthermore, the
adsorbates can be adsorbed atop either Co atoms or support atoms (Ce or O). The adsorption & desorption experiments can provide the evaluation tool for this model.

Fig. 131 shows examples of the effort for modeling reaction intermediates, guided by the FTIR data, which will facilitate the derivation of the most reasonable reaction pathway. The activation energy calculated from this process can be integrated with the kinetic data obtained experimentally to track the reaction proceeding in the real catalysis environment.

**Figure 130.** The simulation of (a) H₂O, (b) ethanol, and (c) H₂O & ethanol adsorption on Co/CeO₂ surface

**Figure 131.** The simulation of (a) ethoxide, (b) acetaldehyde, and (c) acetate intermediates over Co/CeO₂ surface during BESR

### 14.2 Results and Discussion

#### 14.2.1 Experimental observations

Since adsorption of reactants is the initial step of any catalytic surface reaction, the ethanol adsorption behavior of the catalyst is believed to be closely
correlated with catalytic activity during BESR. Simultaneously, the results acquired from this study are also valuable for supplying reference for evaluating the models generated from molecular simulation. Therefore, adsorption energies of several samples have been measured employing TGA-DSC technique. The results are briefly summarized in Table 14.

<table>
<thead>
<tr>
<th></th>
<th>ZrO₂</th>
<th>CeO₂</th>
<th>Ca₀.₁Ce₀.₉O₁.₉</th>
<th>Co/ZrO₂</th>
<th>Co/CeO₂</th>
<th>Co/ Ca₀.₁Ce₀.₉O₁.₉</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H₂O</strong></td>
<td>-10.50</td>
<td>-11.71</td>
<td>-11.51</td>
<td>-12.84</td>
<td>-14.71</td>
<td>-13.52</td>
</tr>
</tbody>
</table>

Table 14 Ethanol & Water Adsorption Energy Measurement using TGA-DSC (unit: kcal/mol)

The more negative the adsorption energy is, the easier the reactant is adsorbed onto the surface. The results show that Co impregnation facilitates the adsorption of both ethanol and water molecules on the catalyst surface and this promotion effect is more prominent for water adsorption as evidenced by the larger energy difference when water is adsorbed. Moreover, it is worth noting that ethanol adsorbs more easily than water on all samples tested.

The TPD technique has been used to explore the reactants’ desorption behavior. Like the adsorption studies, these results can and will be verified by the proposed molecular simulation model. Plainly speaking, the more strongly the adsorbate is attached to the adsorbent, the more difficult it will be to remove it from the surface, leading to higher activation energy required for desorption. By monitoring ethanol species detaching from the sample surface at different heating rates using MS, the ethanol desorption rate over Co/ZrO₂ is plotted as a function of temperature (see Fig.132a). Obviously, the desorption peak shifts to
the higher temperature along with increasing ramp rate accompanied with gradually incremental peak intensity. According to the method given in [189], the desorption activation energy is estimated by linearly fitting \( \ln \frac{\beta H}{RT_p} \) as a function of 

\[-\frac{1}{RT_p}\]

shown in Fig.132b, where \( T_p \) is the temperature of desorption peak, \( R \) is the gas constant, and \( \beta_H \) is the heating rate. The desorption energy is obtained from the slope, which is 9.69 kcal/mol. Interestingly, a discrepancy between the desorption energy and adsorption energy reported previously was found, which might be attributed to the difference between chemisorption and physisorption. The ethanol species measured during TPD experiment is mainly due to the ethanol adsorbed molecularly. However, the adsorption energy calculated above includes the energy released from both ethanol chemisorption and physisorption. The chemisorption process involves chemical bond breakage and formation and therefore associates with heat variation. From previous DRIFTS experiments, it was found that ethanol molecules can be dissociatively adsorbed onto the
sample surface through dehydrogenation, during which O-H bond is broken to form ethoxide reaction intermediate and the H atom released from this bond cleavage will form a hydroxyl group with nearby O atom attached to the support. Similarly, the desorption energies were also estimated for Co/CeO$_2$, Co/CaCeO$_2$, and pure supports, respectively and tabulated in Table 15. The general trend correlates well with the activity improvement. The higher desorption energy increases the “surface residence time” of ethanol molecules, leading to higher activity.

**Table 15** Estimated ethanol Desorption Energy (kcal/mol) over various samples using TPD technique

<table>
<thead>
<tr>
<th></th>
<th>ZrO$_2$</th>
<th>CeO$_2$</th>
<th>Ca$<em>{0.1}$Ce$</em>{0.9}$O$_{1.9}$</th>
<th>Co/ZrO$_2$</th>
<th>Co/CeO$_2$</th>
<th>Co/ Ca$<em>{0.1}$Ce$</em>{0.9}$O$_{1.9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOH</td>
<td>5.82</td>
<td>7.58</td>
<td>9.37</td>
<td>9.69</td>
<td>14.96</td>
<td>17.63</td>
</tr>
</tbody>
</table>

14.2.2 Comparison between experimental observations and simulation results

For the convenience of comparison, the results collected from experiments and molecular simulation have been tabulated into Table 16. It is clearly indicated from the comparison that the choice of the Co/CeO$_2$ (111) model reasonably represents the actual Co/CeO$_2$ prepared. The acceptable difference between experimental observations and molecular simulation might originate from the fact that the real CeO$_2$ support used for catalyst preparation is a mixture with various crystal planes exposed rather than the case in the molecular simulation situation where only the most stable crystal plane (i.e., (111)) is chosen as the representative of CeO$_2$ for simplified computational study. Based on the promising results, a more thorough reaction pathway simulation should be carried out in the future referring to the experimental observations collected.
Table 16 The measured and simulated adsorption energy (kcal/mol) over Co/CeO$_2$ (111)

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Experimental</th>
<th>Simulation</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>14.71</td>
<td>15.45</td>
<td>5 %</td>
</tr>
<tr>
<td>EtOH</td>
<td>16.63</td>
<td>17.52</td>
<td>5.3 %</td>
</tr>
</tbody>
</table>
CHAPTER 15

HYDROGEN SELLING PRICE ESTIMATION AND SENSITIVITY ANALYSIS

In this study, the hydrogen selling price has been estimated at the levels of central production (150,000 kg H₂/day) and distribution production (1,500 kg H₂/day), respectively, based on the established overall process flowchart generated by Aspen Plus® and economic analysis model templated by U.S Department of Energy (DOE). The influences of many processing parameters as well as catalyst properties on the hydrogen cost have been systematically evaluated. The results obtained from this study will benefit the improvement of process efficiency and the reduction of the overall cost, leading to the final commercialization of this technique.

15.1 Methodologies

Fig.133 demonstrates an overall roadmap of the strategy we have used to develop the economic analysis for hydrogen production from BESR. The whole process is generally divided into three steps. Each step is designed to accomplish specific tasks based on various inputs through the use of different softwares. Aspen Plus® v2004 is used to simulate the BESR process. After inputting the operation parameters, mass and energy balances are performed and the data are used as input for the capital investment evaluation. More
accurate simulation can be achieved by using Aspen Catref® v2004 and the user model given in Aspen Plus® v2004 through Fortran programming, depending on the availability of the catalyst kinetic model and deactivation mechanisms. Before performing investment analysis, pinch study needs to be carried out repeatedly until the most efficient energy flow is achieved within the proposed process. Aspen Icarus Process Evaluator (IPE)® v2004 provides the capability to evaluate the process cost through inputting the price information acquired from built-in quotations or literature consultation. The hydrogen selling price is finally determined by H2A v1.0.11 model released by USDOE [209]. The fixed and variable operation & maintenance (O&M), feedstock, and catalyst costs as well as depreciation predictions needed for price estimation have been obtained through the combination of available H2A model case study and literature reports. A more detailed description of the information flow between different modules of
The system is shown in Fig. 134.

The flowchart shown in Fig. 135 was used to simulate the BESR process at different scales. Streams are labeled as rectangular boxes. The value inside the circle connected with the stream label indicates the temperature of each stream. Ethanol and water is mixed at 1:10 molar ratio before being sent to a series of heat exchangers for preheating to reaction temperature. Alternatively, bio-ethanol solution from fermentation can be directly fed into the series of heat exchangers without pre-mixing. Simultaneously, product streams coming from the high temperature reactor can be cooled down through heat transfer with feed stream. Subsequently, the BESR reaction takes place at 500 °C within the reformer. In the absence of detailed kinetic and deactivation data, as a first approximation,
Figure 135. Bio-ethanol stream reforming process flowchart for economic analysis
the reformer is simulated as a RYield reactor to account for the catalytic effect. After being cooled down to 350 °C, the reformate stream undergoes high temperature water-gas shift (HTS) reaction to minimize the concentration of CO. The HTS reactor is simulated as a stoichiometric reactor with a CO conversion of 90 %. Following several consecutive heat exchangers, the condenser is used to separate liquid water from product stream at 40 °C. The gas fraction of the product stream after condensation is then sent into pressure swing adsorption (PSA) unit for hydrogen purification with 85 % recovery [210]. Compressed hydrogen can then be obtained with a purity of up to 99.999 %. The PSA waste gas stream includes unrecovered hydrogen, CH₄ and CO, which is valuable as a process fuel and is used in the combustion furnace to supply the energy required for endothermic BESR reaction in the reformer. The furnace is simulated as a Gibbs reactor with approaching temperature of 10 °C. The condensed water from knock-out vessels can be recycled back and used as process water.

After performing simulation in Aspen Plus® v2004 and several modifications based on the analysis from Aspen Pinch® 11.1, results obtained are input into Aspen IPE® v2004 for investment evaluation. By combining the built-in price and literature quotations (e.g. $7.164 /thousand standard m³/d as installed capital and $0.184 /thousand standard m³/d as operating cost of a PSA system [211]) as the installed capital and operating costs for various equipment items involved as well as the default investment parameters in the software, the capital and operating costs are incorporated into the H2A spreadsheet for H₂ selling price estimation. H2A model released by USDOE provides the platform where the economic
analysis results for H$_2$ selling price are consistent and comparable between diverse hydrogen production and delivery systems by unifying various evaluation methods. The accessible unit costs of feedstock and utilities make the assessment of the variable O&M costs possible. The fixed O&M costs and financial parameters are achieved as suggested in the model.

15.2 Results and Discussion

Fig.136 shows the estimation of the hydrogen selling price and the contribution of different cost components at central production scale. In this case study, 90 % H$_2$ yield is assumed with ethanol to water molar ratio of 1:10 and without dilution. 90 % capacity factor is implemented and all the other financial parameters utilized as suggested in the H2A model. Natural gas consumption used for reformer and reactants heating is classified into the other variable contribution category with cost at $0.34 /Nm$^3$. Besides, $0.08 /\text{kWh}$ is charged for

![Figure 136](image)

*Figure 136. Hydrogen cost contributions at 150,000 kg/day central production size for bioethanol steam reforming and its comparison with other hydrogen production resources*
utility usage. The catalysts category comes from the contributions from catalyst bed installed in the reformer for bioethanol steam reforming with the performance of 3,000 h⁻¹ GHSV at 1,000 h lifetime and commercial catalyst bed in the high temperature water-gas shift reactor with the performance of 3,000 h⁻¹ GHSV and 5-year lifetime at unit price of $4.67 /lb. According to the results obtained, the energy efficiency is close to 70 % and the hydrogen selling price is $2.69 /kg H₂ for central production at 150,000 kg H₂/day output. Ethanol feedstock contributes significantly to the total hydrogen cost, which is the part we can do nothing to deal with. 6.265 L ethanol is required to produce 1 kg of H₂. However, the catalysts cost input into the additional raw material costs cell is already reduced to a very small amount. Therefore, the significant hydrogen cost reduction has to rely on the decrease of the ethanol supply price. Nevertheless, compared with other hydrogen generation methods at central production scale (shown in the inset), the price for bioethanol steam reforming is very competitive although the technique stays at current stage.

The economic evaluation for forecourt hydrogen production at 1,500 kg/day size is also performed by following the ethanol H2A case study released by DOE very recently, in which 70 % capacity factor is assumed. All the other assumptions described in the central production case are applied into forecourt production case entirely. The results shown in Fig.137 indicate that the hydrogen selling price ($4.2 /kg) has already been successfully lower than the 2006 status ($4.4 /kg) reported by 2007 DOE technical plan. In addition, it is worth noting that the catalyst contribution is not explicitly demonstrated in the H2A excel file of the
ethanol case study. Therefore, zero is used for comparison. As seen in Fig.137b, although catalysts contribution is taken into consideration, the final hydrogen selling price is still promising.

Figure 137. (a) Hydrogen cost contributions at 1,500 kg/day forecourt production size for bioethanol steam reforming and (b) its comparison with 2006 status reported in 2007 DOE technical plan

Fig.138 shows how significantly the hydrogen yield has effect on the final hydrogen selling price. Lower hydrogen cost can be achieved at higher hydrogen yield and the price variation can be mainly attributed to the cost contribution from the feedstock, which is reasonable since less feedstock (especially ethanol) would be consumed in order to produce same amount of hydrogen.

Simultaneously, the slight decrease of the catalysts cost is ascribed to the less
installation of the catalysts accompanying the flow rate reduction of the reactants stream for maintaining the same gas space velocity. Besides, the slight increase of other variable contribution is also noticed, which is due to the more natural gas consumption at higher hydrogen yield since less methane will be produced as byproduct used to supply part of the energy for reformer and reactants heating through combustion resulting in more external natural gas requirement.

The supply cost of the electricity and natural gas which are utilized to operate the equipments and heat the reformer and reactants respectively can also exert impact on the final hydrogen cost as the way to vary the other variable category contribution, which is shown in Fig.139. The hydrogen cost does not change notably along with the cost variations of electricity and natural gas, which is probably due to its small scale in the total cost.

![Figure 139](image). The effect of (a) electricity and (b) natural gas cost variation on the final hydrogen selling price

However, compared with the effect of electricity and natural gas supply cost fluctuations, ethanol feedstock cost variation has a prominent influence on the final hydrogen cost, which is evidenced in Fig.140. As one of the main reactants
required for bioethanol steam reforming, a large amount of ethanol is needed for reaction. Although even larger quantity of water is in demand, the much cheaper cost make it less important compared with ethanol which is the main feedstock cost contributor. Since ethanol is mainly obtained from the fermentation of various biomass (e.g., corn, sugarcane, and cellulosics) nowadays, the ethanol cost is tightly dependent on the supply of the biomass mentioned above. As an alternative resource to corn widely used currently, cellulosics can be quite promising to generate ethanol with much lower price due to its abundant sources. Nevertheless, the cost reduction does not come from our effort.

Fig.141 shows the hydrogen cost variation as a function of dilution ratio. Slight increase of the hydrogen selling price is observed when the dilution is less than 50 %, followed by the exponential escalation when the dilution percentage is even higher. The observation that the cost increase is closely accompanied by the feedstock cost increment indicates that the ascending nitrogen requirement for acquiring higher dilution contributes a lot to the final hydrogen cost rise. As a result of this fact, the nitrogen supply fluctuation will has a great impact on the H₂ cost, which is evidenced by the comparison of Fig.141a and b. Since nitrogen at industrial grade ($0.006 /kg) is much cheaper than that at laboratorial grade.
($0.037 /kg), almost half variation of the final hydrogen cost is witnessed when industrial nitrogen is employed. Besides, the inignorable catalysts cost and utility increases as well as more natural gas consumption have also contributions to the hydrogen cost climbing. In order to keep the same GHSV (3,000 h⁻¹), larger amount of catalysts have to be charged for compensating the raising of total flow rate along with increasing dilution.

Fig. 141 shows the effect of dilution with inert gas on the final hydrogen selling price: in this case study, nitrogen with (a) ultra high purity or (b) industrial purity is used as the inert gas.

Figure 141. The effect of dilution with inert gas on the final hydrogen selling price: in this case study, nitrogen with (a) ultra high purity or (b) industrial purity is used as the inert gas.
used, which has reached the 2012 goal ($3.8 /kg of H₂) set in the 2007 DOE technical plan. The closely concomitant rise of other variable cost with increasing hydrogen cost implies that more energy consumption at higher molar ratio of ethanol to water in order to heat the reformer and reactants accounts for the ascending of hydrogen cost. In addition, slight increment of catalysts cost has also contributions to the hydrogen cost climbing. In order to keep the same GHSV (3,000 h⁻¹), larger amount of catalysts have to be installed for compensating the raising of total flow rate originating from more reactants input.

The influence of reformer temperature on the final hydrogen cost is investigated and shown in Fig.143. Almost no variation has been present indicating that reformer temperature has very small

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**Figure 142.** The effect of molar ratio of EtOH to H₂O on the final hydrogen selling price

**Figure 143.** The effect of reformer temperature on the final hydrogen selling price
impact on the hydrogen cost, which might be due to the recycle of the energy used to heat the reformer and reactants. However, when safety and reformer material issues are taken into consideration, low operation temperature is preferred. Furthermore, since same hydrogen yield is assumed at various reaction temperatures for the sake of simplifying the estimation, low temperature faces a big challenge of obtaining high hydrogen yield in real condition. Therefore, it is very valuable to develop a catalyst system which has excellent catalytic performance especially under lower temperature.

Since the reformer is the key component in the whole flowchart to produce hydrogen for forecourt use from steam reforming of ethanol, the influence from reformer cost fluctuation is also studied, which results are shown in Fig.144. From the capital cost analysis, because reformer cost just occupies around 7.87 % of the total cost, the variation of reformer cost does not change the capital cost significantly, which is verified in Fig.144. Since the reformer cost evaluation is just based on the built in database of the Aspen Icarus Process Evaluator 2004®, the estimation might be not accurate enough. Therefore, manufacturer consultation and literature searching about the reformer cost which is close to the one we used in the analysis will be addressed in the near future.

Fig.145 shows the effect of the unit price variation of the catalyst charged in the reformer at GHSV of 3,000 h\(^{-1}\) and 1,000 h lifetime on the final hydrogen cost. In the analysis, the commercial catalyst is assumed for high-temperature water-gas shift reaction, which has the performance of 3,000 h\(^{-1}\) GHSV and 5-years lifetime at price of $4.67 /lb. Over $22 /kg of H\(_2\) have to be sold if the catalyst unit
price is higher than $1000 /kg which is usually at the level of noble-metal catalyst. However, if transition-metal catalyst (~$10 /kg) is utilized instead, the hydrogen selling price can be as low as $4.2 /kg. Further unit price decrease of the reforming catalyst would not contribute a lot to the final hydrogen cost reduction.

If catalyst unit price keeps at the same (i.e., $4.67 /lb) and the catalyst lifetime maintains at 1,000 h⁻¹, the effect of GHSV is investigated and shown in Fig.146a. The GHSV raising will benefit the hydrogen cost reduction significantly particularly when the GHSV is lower than 10,000 h⁻¹. Nevertheless, further GHSV increase does not seem to have the ability to reduce the hydrogen cost remarkably. Moreover, high GHSV has the risk to deactivate catalyst more quickly than lower one. When WHSV is employed to account for the catalyst toleration for the reactants stream, same trend is acquired and shown in Fig.146b, that is, the hydrogen cost is reduced with increasing WHSV and the reduction effect is not so attractive when WHSV is above 0.5 h⁻¹. In other words, our current WHSV of 0.48 h⁻¹ is appropriate for hydrogen production as a reasonable
Exponential decrease of the final hydrogen cost is observed in Fig. 147 along with increasing catalyst lifetime. Although there is no big difference when the catalyst lifetime is longer than 1,000 h, catalyst with longer stability is still strongly encouraged if the labor, reformer down time, and solid waste disposal cost associated with the replacement of the deactivated catalyst installed in the reformer are taken into account.

In order to demonstrate how significative the substitution of transition metal catalyst for noble-metal catalyst is, the comparisons between these two are shown in Fig. 148a through c. If $4.67 /lb is used as the typical cost for transition
metal catalyst and $1,000 /kg is employed to represent the cost for noble catalyst, hydrogen has to be sold at a much higher price (Fig.148a) when noble metal catalyst is charged, which is far beyond acceptability. Therefore, if hydrogen are desired to be sold at the same price, the reforming reaction has to be operated under almost 100 times higher GHSV if the catalyst has the same lifetime (Fig.148b) or the catalyst has to keep the activity longer than 12 years (Fig.148c), which is absolutely unrealistic.

Figure 148. The comparison between transition metal catalyst and noble metal catalyst: (a) different H₂ cost if they have same GHSV and lifetime; (b) different GHSV if they have same H₂ cost and lifetime; (c) different lifetime if they have same H₂ cost and GHSV.

15.3 Conclusions

By incorporating our reaction data into the RYield model used to simulate the performance of the reformer, the hydrogen selling price for central production at 150,000 kg/day scale and forecourt production at 1500 kg/day scale is evaluated. Sensitivity analyses are also performed examining the effect of utility cost, feed cost, catalyst cost, reaction temperature and WHSV. Among the input
parameters examined, the catalyst cost, feed cost and catalyst performance (i.e., H₂ yield) are found to impact the final selling price significantly. The analysis also shows a major cost difference that may arise if precious metal catalysts instead of transition metal are used. For the cost difference to become negligible, the precious metal catalysts need to show a much superior catalytic performance (activity and life time) than the transition metal catalysts. Although better activity and stability are expected from precious metal catalysts, whether the difference in catalytic performance can be so drastic to compensate for the significantly higher unit catalyst cost is not clear.
RECOMMENDATIONS FOR FUTURE WORK

- Kinetic and mechanistic studies should be coupled with catalyst characterization under reaction conditions to obtain kinetic parameters. Rate expressions should be developed for kinetic modeling.
- Long term time-on-stream experiments should be performed (e.g., >100hrs under neat reaction conditions).
- Accelerated deactivation and regeneration studies (e.g., higher C/S ratio and GHSV) should be performed.
- Economic analysis should be fine-tuned based on updated catalyst system knowledge database and the new H2A model.
- Molecular simulation work using DFT calculations should be continued and used to guide rational catalyst design.
- *In-situ* XAFS experiments should be performed at Argonne National Lab to elucidate the oxidation state and coordination environment of cobalt sites during reaction. This should be a collaborative activity.
- Catalyst synthesis for best performing catalysts should be scaled-up through industrial partnership.
- Oxidative steam reforming and autothermal steam reforming should be performed over the catalyst system developed.
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