Anti-coking Materials for Steam Crackers

A Dissertation

Presented to

the faculty of the School of Engineering and Applied Science

University of Virginia

in partial fulfillment
of the requirements for the degree

Doctor of Philosophy

by

Kehua Yin

December 2016

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is submitted in partial fulfillment of the requirements
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Abstract

Steam cracking is one of the most important chemical processes in the world, which provides olefin monomers ethylene and propylene for the chemical industry. The boom of shale gas in the past decade has spurred the investment in steam cracking, with construction of new crackers and expansions of existing crackers planned. There has been growing interest in improving the operational profits of steam crackers by applying a catalytic coating on the internal wall of cracker tubes to reduce coke formation and increase the on-line production time. Ceria-based oxides have been widely used in the three way catalysts for gasoline car emission control and have shown excellent activity in carbon oxidation due to their redox property. The addition of cerium oxide has also been shown to reduce the coke formation over catalysts used for steam reforming of hydrocarbons. Therefore, ceria-based oxides are promising anti-coking coating materials for steam crackers. Moreover, a methodology for reaction of carbon needs to be developed to obtain reproducible kinetics.

In this study, a methodology has been developed by using coke oxidation with dioxygen over cerium-zirconium mixed oxides as a model reaction and was validated with classic gas phase CO oxidation. The surface-area-based reaction rates were obtained by evaluating the active catalyst surface area in the mixture of catalyst and coke, which correlated with the reaction rates of CO oxidation. The composition $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ was found to be the most active catalyst for coke oxidation. Detailed kinetic studies of both coke and CO oxidation revealed the important role of lattice oxygen.

The developed method was then used to study coke gasification with dioxygen and steam over alkaline-earth-metal-doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$. The alkaline earth metal compounds were highly

dispersed on the surface of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$. The presence of alkaline earth metals promoted the catalytic activity of coke gasification with steam but decreased the rate of coke gasification with dioxygen.

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Chapter 1. Introduction

Adapted from Industry Engineering & Chemistry Research, Shilpa Mahamulkar,^[+] Kehua Yin,^[+] Pradeep K. Agrawal, Robert J. Davis, Christopher W. Jones, Andrzej Malek and Hirohazu Shibata, “Formation and oxidation/gasification of carbonaceous deposits: A review”, 2016, 55 (37), 9760-9818, with permission from ACS Publisher. ^[+] Equal contribution

1.1 Coke formation during steam cracking

Ethylene is one of the most important building blocks for the chemical industry, with its production exceeding any other organic compound. The global ethylene production was about 167 million tons in 2014, while the production in the US was about 36 million tons. Around 60% of the ethylene produced is utilized in the production of polyethylene. Other important ethylene derivatives are ethylene oxide (13%), ethylene dichloride (13%) and ethylbenzene (7%). At these high temperatures, radical reactions play an important role in the formation of a wide range of hydrocarbons. The major reaction for cracking of ethane involves dehydrogenation as shown in the following equation:

The cracking units are typically made of alloys containing Ni, Fe, Cr, that are capable of withstanding very high temperatures.¹ The residence time for these reactions is around 0.5 – 1 s. At these high temperatures, radical reactions play an important role in the formation of a wide range of hydrocarbons. One of the major by-products of the steam cracking process is the formation of carbonaceous deposits (coke) on the walls of the reactor. The amount and type of coke formed depends on the operating conditions, nature of the feed, and nature of the reactor surface. Steam dilution of the feed has been observed to reduce coke formation.² Coke formation affects the production efficiency in a number of ways, as mentioned below:^{3,4}

- Increases pressure drop in the reactor⁵
- Reduces the reactor volume
- Increases the temperature of the reactor tube by affecting heat transfer from tube to gas
- Leads to expensive shutdowns
- Causes carburization of steel
- Influences the flow in the reactor
- Decreases the production capacity⁶

Coke formed in the cracking reactor is typically combusted by passing a mixture of steam and air at very high temperatures through the reactor in regeneration mode. The plant typically requires a shutdown for decoking every 20-60 days, depending on the type of feed used.⁷ These shutdowns are usually expensive and efforts are directed towards increasing the run length of steam crackers.

Coke deposition in steam cracking reactions is a combination of the following mechanisms namely: radical reactions in the gas phase, droplet condensation and coke formed on metallic particles.

Figure 1.1 Catalytic coke formation schematic,¹¹ Copyright The Society of Chemical Engineers, Japan.

1.1.1 Catalytic coking mechanism

In a steam cracker, catalytic coke formation takes place in the presence of catalytic sites, which can be the metallic walls of the reactor, more likely at grain boundaries.^{3,8} Since most industrial cracking units are made of alloys of Ni, Fe, and Cr, many types of metallic sites are present on the reactor surface. These sites can catalyze coke formation at temperatures as low as 500 °C. Although the catalytic coking rate increases significantly with increasing reaction temperatures, the coking rate is also highly dependent on the reactor surface used. Due to the presence of metallic sites, coking rates are higher in reactors made of materials like stainless steels or Incoloy (superalloys made of iron-nickel-chromium having good corrosion resistance and stability at high temperatures), compared to more inert oxide materials such as quartz.^{3,4,9,10} Figure 1.1¹¹ shows a schematic of the catalytic coking process taking place on a reactor wall. Hydrocarbons adsorb on the metallic surface and form coke. This coke further dissolves and diffuses through the metallic particle. With time, carbon deposits at the end of the metal particle,

raising the metal from the reactor surface. This mechanism is most important after the decoking step when the reactor wall is clean, devoid of any coke exposing the metallic sites on the surface for reaction.¹²

Figure 1.2 Radical mechanism for coke formation,⁸ Copyright The Society of Chemical Engineers, Japan.

1.1.2 Radical coking mechanism

At very high temperatures in the steam cracker, radicals are formed in the gas phase producing pyrolytic coke, which deposits on the reactor surface.^{3,8} These endothermic reactions require significant energy input to form the radical intermediates and hence take place only at high temperatures. Figure 1.2 shows a pathway for the formation of coke by the radical mechanism.⁸ Coke radicals in the gas phase react with the hydrogen present in unsaturated hydrocarbons. Decomposition of the aliphatic chain gives rise to new radicals. Further dehydrogenation of such molecules results in increase in the aromatic nature of the coke and also regeneration of radicals. Coke formed by this mechanism has very low hydrogen content because

of the dehydrogenation of molecules during the coking reactions. The coke formed is typically very hard (graphitic) due to the cross-linking of aromatic molecules under the reaction conditions.

The rate of coke formation is highest for acetylene and lowest for paraffins and follows

Figure 1.3 Droplet condensation mechanism,⁸ Copyright The Society of Chemical Engineers, Japan.

the order: acetylene > olefins > aromatics > paraffins.

1.1.3 Droplet condensation coke

Aromatics with one or two rings act as coke precursors and condense by dehydrogenation to form tar-like particles after striking the reactor surface.¹³ This condensation takes place downstream of the cracking reactor where the temperature is lower than that in the reactor furnace.

A schematic of the droplet condensation mechanism is shown in Figure 1.3. At elevated temperatures, molecules undergo dehydrogenation, aided by radicals. This mechanism helps in

further growth of the coke layer. Some molecules undergo hydrogen abstraction in the gas phase itself and are deposited on the reactor surface. The coke formed in the transfer line exchanger results from the condensation of polyaromatics.¹⁰ Since the mechanism involves condensation of aromatic molecules at lower temperature, the coking rate is independent of the chemical characteristics of the reactor surface.¹⁰

Figure 1.4 Rate of coke formation and weight content on a metallic cylinder.⁷

Figure 1.4 shows the rate of coke formation on a stainless steel surface as a function of time. The rate is initially high and decreases with time.⁷ Coke formation takes place both by catalytic and radical mechanism in the region where the coking rate changes with time. Deposition of coke on the metal surface decreases the rate of catalytic coke formation until all of the sites are blocked. At this point, the rate of coke formation becomes approximately constant and only radical coke is formed.

1.2 Inhibition of coke formation in steam cracking

Various researchers have undertaken different routes to reduce the coke formed due to the catalytic mechanism. The main approach to reduce the coke formed by this method is to create a barrier between the metallic reactor surface and the gas phase in the reactor.

For example, an aluminum coating has been used to passivate the cracking reactor surface before the reaction began, which reduced the amount of catalytic coking.^{6,14} Addition of magnesium to aluminum further reduced the coking rate. It was observed that the coke deposition reduced significantly due to these coatings, as the metal reactor surface sites were blocked. Zinc coatings were found to be effective in the oxidation of the coke formed on the reactor surface.⁶ Thermal spraying,¹⁴ plasma spraying,⁶ packed cementation^{6,14} and chemical vapor deposition (CVD) techniques have been used for coating of ceramic powders on the cracking furnace.¹ TiC and SiC coatings proved to be effective in reducing the rate of coke formation for n-hexane cracking.¹

A coating of sulfur or phosphorous on the cracking furnace has also been shown to passivate the reactor surface, leading to decreased coke formation. This involved formation of metallic sulfides or metal phosphorous complexes that coordinated with the metal sites and reduced their catalytic activity. Addition of SiO₂/S to the S/P coating further enhanced the coke reduction.^{15–17} Dimethyl disulfide and carbon disulfide are other sulfur compounds used as coke inhibitors.⁶ Annealing of the cracking furnace in the presence of a H₂/H₂O mixture has been applied at higher temperatures to reduce the presence of metallic sites (Ni, Fe) and enrich the surface with chromia.¹⁸

Westaim Surface Engineered Products Inc. developed a coating called CoatAlloy™ for use in ethylene pyrolysis furnaces. The coating consists of three layers: to prevent catalytic coking, gasify radical coke and stop carbon deposits from penetrating the metal surface to cause

carburization. After one year of service, no carburization was observed on the surface of the coating.¹⁹ SK Corporation developed a coating called PY-Coat that serves similar purposes.²⁰ The coating formulation is immediately injected into the hot furnace after the decoking step. The formulation vaporizes and deposits on the reactor inner surface and acts as a barrier. The basic components of the coating are Si, Cr, Al, Ti, and alkali and alkaline-earth. In a pilot plant set-up for ethane cracking at 65% conversion, the coating showed no pressure drop and temperature drop. The uncoated reactor showed a pressure drop of 27 psi and temperature difference of 26 °C higher than the start of the operation.

Another furnace coil coating technology called catalyzed assisted manufacture of olefins (CAMOL) by BASF aims to have a coke-free environment in cracking furnaces.^{21–23} This technology proposed to increase the run-length of the reactor and has been undergoing commercial trials since 2006. These coatings have the ability to be used in high temperature furnaces above 1130 °C, and they can potentially reduce the amount of steam required for dilution to keep coke formation to an optimum. The coatings act as a barrier between the metal sites from the reactor and the hydrocarbon gases and usually exist as an oxide layer < 10 µm in thickness. The coating also has a catalytic layer that can gasify the coke formed on the surface of the coating. Around 1 – 2 furnace run-lengths have been achieved with this technology for lighter feedstocks and around 100 days for higher feedstocks. The coating was reported to have no impact on the product distribution and a positive impact on the yield of products, by mitigating the formation of filamentous and amorphous coke. Two types of coatings have been developed, including one for low-level catalytic gasification for lighter feeds and another for high-level catalytic gasification coating for heavier feeds.

The Alcroplex® diffusion coating from Alon Surface Technologies Inc., which is a surface modified HP material (heat resistant alloy made of iron-nickel-chromium), has been reported to reduce the coke formation rate up to 90% in the cracking of ethane.²⁴ It is a technology that uses a CVD mechanism for creating a stable coating on the surface of the reactor. Commercially, it has performed well by reducing the carburization of the steel and also the surface-induced catalytic coking.

NOVA Chemicals developed a technology called ANK 400 over the past 10 years.^{25,26} They claim to have increased run lengths in the crackers around 10 fold with the help of an inert, nanocrystalline spinel coating that reduces both catalytic and radical coke. They also have various pretreatments that could be carried out on stainless steel reactors that can help passivate the reactor surface and reduce coke formation.²⁷

Schietekat et al. recently developed a coating called YieldUp based on a perovskite catalyst system for reducing coke formation during steam cracking.²⁵ These coatings reduced the coke formed on Incoloy 800HT drastically by aiding the reaction of coke with steam. A reduction of 76% in the coke deposition on Incoloy was reported. Performance of the coating in an industrial reactor was checked by a simulation of the reactor. It was estimated that a 525% increase in the run length could be achieved by application of the coating.

In other work, an H_2PtCl_6 additive lowered the rate of coke formation during steam cracking of ethane or propane, both on a quartz and a stainless steel reactor.⁴ Quartz is inert in nature due to the absence of metallic sites on its surface. The coke formed on quartz surfaces is mainly gas phase coke. Stainless steel has presence of metallic sites which can catalyze coke formation. Both pyrolytic and catalytic coke species are formed on stainless steel surfaces. The addition of H_2PtCl_6 was able to reduce both pyrolytic and catalytic coke.

The coatings of materials on cracking furnaces develop cracks after prolonged use at higher operating temperatures. These cracks might then serve as the sites for catalytic coke formation. Thus, efforts are underway to increase the stability of the coatings used to passivate the surface, thus further increasing run lengths.

1.3 Cerium-based oxides: Promising anti-coking coating materials for steam crackers

Ceria-based materials have received a lot of interest because of their demonstrated catalytic activity in several reactions, such as CO oxidation and soot oxidation, which can be attributed to the redox property of cerium.^{28–31} Ceria-based materials have been widely used in the Three Way Catalysts (TWC) for the emission control of gasoline cars since the mid-1980s.^{32–}

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1.3.1 Ceria-based materials for soot oxidation with dioxygen

Ceria-based materials have been extensively studied for soot abatement of diesel engines. Early studies used cerium salts as fuel additives in diesel engines. Cerium oxides were formed in the combustion process and entered the soot particles, which significantly lowered the ignition temperature of the soot and increased the oxidation rates by 20 fold.^{35,36} However, the exhaust of cerium nanoparticles poses potential environmental, health and ecological effects, which need to be taken into consideration, disfavoring use of these species as fuel additives.³⁷

Bueno-López et al. studied the CeO₂ catalyzed soot oxidation reaction with labelled oxygen in an advanced TAP reactor.³⁸ They found that the oxygen from CeO₂ reacted with soot, and the direct reaction of the gas-phase oxygen with soot did not occur under the conditions used. They defined such oxygen as “active oxygen”, which was induced from the chemisorption of

gas-phase dioxygen on CeO_2 . Such “active oxygen” may be oxygen superoxide ions (O_2^-), which were detected by ESR³⁹ and FTIR experiments.^{40,41}

Figure 1.5 Scheme of active oxygen mechanism for CeO_2 catalyzed carbon oxidation,²⁸ Copyright Elsevier.

However, these measurements were not performed under *in-situ* soot oxidation reactions. DFT calculations have also confirmed the formation of superoxide and peroxide ions on ceria-based catalysts.^{42,43} Machida et al. concluded that active oxygen could be formed by either the lattice oxygen at the CeO_2 /soot interface or gas-phase oxygen adsorbed at the boundary of soot + reduced CeO_2 + the gas phase, with the former being much more important.³⁹ The active oxygen was not only localized at the CeO_2 /soot interface, but also transferred to the soot surface by spillover through surface diffusion.⁴⁴ However, the distance of spillover for active oxygen

species was still not clear. The active oxygen species then reacted with soot to form surface oxygen species, followed by their decomposition to form CO and CO₂. Figure 1.5 shows a scheme of the proposed active oxygen mechanism for CeO₂ catalyzed carbon oxidation.

Although ceria is active for the soot oxidation reaction, it suffers from sintering under high temperatures and thus a loss of activity. Therefore, modification of ceria with other metal ions has been explored to improve its thermal stability, enhance the reducibility of Ce⁴⁺/Ce³⁺ and improve the bulk oxygen mobility. These elements include La,^{45–47} Zr,^{48–51} Hf,⁵⁰ Co,⁵² Mn,⁵³ Sm,⁵⁴ Tb,⁵⁴ Nd,⁵⁵ Fe,⁵⁶ Gd,⁵⁷ and Lu. Among those parameters, surface reducibility is thought to be the most important. Mixed oxides can be prepared by various methods: coprecipitation,⁵¹ sol-gel,^{58–60} thermal decomposition of mixed salts,⁴⁸ solid combustion,⁶¹ formation of inverse micromulsion,⁶¹ and with poly(methyl methacrylate) (PMMA) colloidal crystal templates.⁶² The carbon oxidation reaction mechanism of carbon oxidation is thought to remain the same after the doping of rare-earth metals, while the reaction mechanism may change after modifications with alkali metals, transition metals and noble metals. These mechanisms are discussed in a recent review by Liu et al.⁶³

It is well established that the doping of cerium oxide with Zr⁴⁺ leads to the formation of solid solutions, which increases the thermal stability, reducibility and enhances the oxygen storage capacity of the oxide.⁶⁴ Aneggi et al. investigated the roles of lattice/surface oxygen in cerium-zirconium oxide catalysts for soot oxidation. They found that there was an inverse correlation of total available surface oxygen and T₅₀. Furthermore, the oxygen storage capacity was only important in the absence of gaseous oxygen.⁵¹ Hurtado et al. found that the cerium zirconium mixed oxides prepared from (NH₄)₂Ce(NO₃)₆ showed higher activity than those made from Ce(NO₃)₆·6H₂O.⁶⁵ The cubic structure of the cerium zirconium mixed oxides gradually

turned into a tetragonal structure with an increased amount of zirconium. The ceria-rich mixed oxides showed higher catalytic activity than the corresponding zirconium-rich mixed oxides. The optimal molar fraction of Ce in the mixed oxides was between 0.7 and 0.8.^{51,66,65} The morphology of cerium zirconium mixed oxides was found to affect the soot oxidation activity.⁶⁷ Hierarchically porous cerium zirconium mixed oxides were synthesized with a biotemplate method: pine sawdust was impregnated with a solution of cerium and zirconium nitrates and the dried sample was calcined at 600 °C to give a mixed oxide with predictable porosity. The resulting mixed oxides showed higher soot oxidation activity than the corresponding ones made from a co-precipitation method, which was attributed to higher amount of mobile lattice oxygen, as characterized by the lower temperature peak in H₂-TPR and the higher oxygen storage capacity.

1.3.2 Effect of cerium addition during steam reforming reactions: Inhibition of coke formation

To the best of my knowledge, there is no study about the application of cerium-based materials for steam gasification of coke. However, the presence of cerium in the catalysts has been shown to inhibit coke formation during the steam reforming of hydrocarbons^{68–71}. Zhuang et al. investigated the effect of cerium oxide in MgAlO₃ supported Ni catalyst for methane steam reforming⁶⁸. Cerium oxide not only decreased the rate of coke deposition, but also increased the catalytic activity of steam reforming. Natesakhawat et al. reported the beneficial effects of cerium promoter in a Ni/Al₂O₃ catalyst for propane steam reforming by both inhibiting coke formation and improving catalytic activity⁶⁹. Wang et al. compared the steam reforming rates of methane, ethane, n-butane, n-hexane on a Pd/ceria catalyst and a Pd/alumina catalyst⁷¹. The Pd/ceria catalyst had much higher reaction rates than the Pd/alumina catalyst, as well as higher

resistance to coke formation. The improved resistance to coke deposition has been attributed to the high oxygen mobility over CeO_2 , which facilitates the gasification of coke.^{72,73} Thus, the ceria-based materials may also present high activity for steam gasification of coke, which can reduce coke formation in steam crackers.

1.4 Objectives of this work

The overall goal of this work is to explore the utilization of ceria-based materials for anti-coking coating materials for steam crackers. In particular, this dissertation aims to develop a quantitative method to obtain the reproducible kinetics of reactions involving coke and compare the reaction rates of coke gasification with different ceria-based materials to obtain the best catalyst composition. The specific objectives of this dissertation are outlined below:

1. Synthesize coke at elevated temperature to mimic coke formation during steam cracking and characterize the physical properties of the obtained coke.
2. Synthesize cerium-zirconium mixed oxides of varying chemical compositions and investigate the effect of composition on structure, oxygen storage capacity and reducibility, as well as the catalytic behavior during gasification of coke.
3. Develop a quantitative method to study reactions involving coke, which makes the comparison of coke gasification catalysts more accurate.
4. Explore the effect of alkaline earth metals addition to cerium-zirconium mixed oxides on the catalytic behavior of coke gasification with dioxygen and steam.

The prepared coke and catalysts were extensively characterized by a variety of techniques, including X-ray diffraction (XRD), Raman spectroscopy, elemental analysis, surface area analysis, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM),

transmission electron microscopy (TEM) and temperature-programmed reduction (TPR). The coke gasification with dioxygen was carried out in a thermogravimetric analyzer (SDT Q600, TA instruments). The coke gasification with steam was carried out in a customized thermogravimetric analyzer (STA449F3 Jupiter, NETSCH). Coke gasification with dioxygen and steam were evaluated both with temperature-programmed oxidation and isothermal reactions. The tight contact samples of coke and catalyst mixture were prepared by extensive grinding of the mixture. The CO oxidation was conducted in a fix-bed stainless steel reactor to confirm the method we developed for study of coke gasification.

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Chapter 2. Catalytic Oxidation of Solid Carbon and Carbon Monoxide over Cerium-Zirconium Mixed Oxides

Abstract:

A series of cerium-zirconium mixed oxides was prepared by coprecipitation and evaluated in the catalytic oxidation of solid coke under tight contact conditions with 10 vol.% O₂ in He at 673 K using a thermogravimetric analyzer. The measured first order rate constant for coke oxidation was proportional to the catalyst loading when the mass ratio of catalyst to coke was low, which enabled the calculation of a surface area specific reaction rate. The validity of the normalization method was confirmed by performing CO oxidation over the cerium-zirconium mixed oxides in a fixed bed reactor at 573 K with 2 vol.% of CO and 2 vol.% of O₂ in He at ambient total pressure. Although there was no correlation between the coke oxidation rate and the oxygen storage capacity or the reducibility of the catalysts, there was an excellent correlation to the CO oxidation rate. Kinetic studies of both coke and CO oxidation suggested an important role of surface lattice oxygen from the catalyst in the two reactions.

2.1 Introduction

Carbon formation reactions are common in chemical processes involving hydrocarbons, such as coke buildup on catalysts in hydrocarbon cracking reactors,^{1,2} deposition of solid carbon on the walls of steam cracking reactors,^{3,4} and production of soot in diesel engines.^{5,6} While carbon rejection via coke may be desirable in some processes for upgrading petroleum residue (e.g. FCC),⁷ it often leads to catalyst deactivation, poor heat transfer through reactor walls and even damage to the reactor.^{2,8} Emission of soot particle from diesel engines also poses a threat to the environment and human health because of the small particle sizes and residual volatile organic compounds.⁹ Thus, mitigation of solid carbon by catalytic oxidation reactions can be an important remediation step in these processes, either in-situ or after its formation. Ceria-based materials are recognized as promising catalysts for carbon oxidation because of their excellent redox behavior and oxygen storage capacity.¹⁰ Indeed, ceria compounds have been an important component of the automotive three-way catalyst for decades.¹¹ Ceria-based catalysts have also demonstrated activity in soot oxidation, especially after doping with other elements, such as La^{12–14} and Zr.^{15–18}

Although there is an abundance of literature on the study of catalysts for carbon oxidation, three important problems remain unsolved. First, there is not a well-defined method to quantitatively assess the catalyst performance since the reaction involves the reactivity of a solid-solid interface together with a gas. Most studies utilize temperature-programmed oxidation (TPO) reactions, from which specific temperatures of carbon oxidation in the presence of catalysts are reported and compared. The most common characteristic temperatures used to compare catalyst performance are T_{50} (temperature at which 50% of the carbon is oxidized) and $T_{\max}$ (peak temperature of the TPO curve). Although some researchers evaluate catalyst activity by

calculating carbon oxidation rates under isothermal conditions,^{19,20} these rates are normalized to the total surface area of catalyst in the sample, which may not be strictly proportional to observed rate. In fact, the catalyst/carbon mass ratio is an important parameter for reporting carbon oxidation activity. Neeft et al. found that the carbon oxidation temperature in the presence of a V_2O_5 catalyst decreased with increasing catalyst/carbon mass ratio, but remained constant at a mass ratio greater than 4.²¹ A similar relationship was observed with a K/CeO_2 catalyst, with a constant carbon oxidation temperature being observed at catalyst/carbon mass ratio greater than 5.²² These reports clearly indicate how rates of oxidation do not always scale linearly with total catalyst surface area and may lead to improper comparison of catalyst performance. Therefore, a method that gives reproducible specific reaction rates is desired. Second, the doping of cerium oxide with other metal ions often leads to changes in physical and chemical properties of the solid, such as specific surface area, surface reducibility of cerium, oxygen storage capacity and oxygen mobility throughout the bulk of the solid.²³ There is still no consensus regarding which property changes are responsible for the variation in carbon oxidation activity of ceria catalysts after doping. Third, detailed kinetic studies of carbon oxidation catalyzed by ceria-based oxides are still lacking.

In this work, a series of cerium-zirconium mixed oxides was prepared and used for solid carbon oxidation. A methodology was developed to obtain reproducible rates of carbon oxidation. The physical and chemical properties of different mixed oxides were characterized with various techniques and compared with carbon oxidation activity to determine which properties were the most important for oxidation catalysis. A classic catalytic oxidation reaction, CO oxidation, was also performed to validate the results from the carbon oxidation studies.

2.2 Experimental methods

2.2.1 Catalyst preparation

A series of cerium-zirconium mixed oxides (Ce/Zr atomic ratio = 4, 1, 0.25), cerium oxide and zirconium oxide were prepared using a controlled precipitation method. First, an aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Sigma Aldrich) and ZrONO_3 (99.99%, Sigma Aldrich) was prepared with a total metal ion concentration of 0.2 M. The metal precursor solution was added dropwise to 100 cm³ of distilled deionized water (DDI) at 298 K while a solution of 15 wt.% aqueous ammonia was added continuously during precipitation to maintain a pH of 10. The resulting suspension was stirred for 20 h at 298 K. The precipitate was recovered by vacuum filtration, washed 3 times with DDI water, dried in air at 400 K overnight. The samples were then heated to 1073 K in air at a rate of 5 K min⁻¹ and held at 1073 K for 6 h. To obtain a cerium oxide sample with higher surface area (closer to that of the Ce-Zr mixed oxides), the calcination temperature for cerium oxide was decreased to 873 K.

2.2.2 Coke formation from thermal reaction of ethylene

Solid carbon, otherwise known as coke, was formed by passing a mixture of ethylene and He through a quartz tube placed in a high temperature furnace (GSL 1100X, MTI Corporation). The quartz tube was heated to 1150 K at a rate of 10 K min⁻¹ in 20 cm³ min⁻¹ He. Upon reaching 1150 K, a mixture of 20 cm³ min⁻¹ ethylene and 20 cm³ min⁻¹ He was fed to the quartz tube for 4 hours, followed by cooling to the room temperature in 20 cm³ min⁻¹ flowing He. Three types of coke were formed: solid coke, soft coke and liquid coke. Liquid coke was removed by rinsing the quartz tube with toluene and solid coke was collected by scraping the tube. Soft coke could not be isolated. The collected solid coke was dried in air at 400 K to remove the remaining volatile organic compounds, followed by milling with zirconium beads in a plastic bottle on a jar mill (US Stoneware) for 64 hours. The recovered solid coke was used as a model carbon in this study.

2.2.3 Characterization of catalyst and coke

Powder X-ray diffraction (XRD) patterns of the catalysts and coke were obtained on a PANalytical X'Pert Pro MPD Diffractometer with Cu K α radiation. Each sample was scanned at a rate of 0.2° s⁻¹, over a range of 2 θ from 10° to 90°. For coke, the mean size of crystal in the c-direction, L_c, and mean size of crystal in the a-direction (layer diameter), L_a, were calculated using the Scherrer equation.

$$L = \frac{K \cdot \lambda}{B_{2\theta} \cos \theta}$$

where λ is the wavelength of X-rays used (0.15418 nm), B_{2 θ} is the full width at the half height and K is a constant, which was 0.91 and 1.84 for calculation of L_c and L_a, respectively.²⁴

Specific surface area of the catalysts and coke was obtained by N₂ adsorption measured at 77 K using the BET method on a Micromeritics ASAP 2020 automated analyzer.

Elemental analyses of the catalysts and coke were performed at Galbraith Laboratories (Knoxville, TN). The contents of cerium and zirconium in the oxide catalysts were determined by inductively coupled plasma atomic emission spectroscopy while the contents of carbon and hydrogen in the coke were determined by combustion analysis.

Raman spectra of the oxide catalysts and coke were recorded with a Renishaw InVia Raman Microscope with an Ar laser (514 nm) and a 3000 g mm⁻¹ grating. The Raman scope was calibrated using a silicon wafer.

Scanning electron microscopy was performed on an FEI Quanta 650 FEG-SEM with a working distance of 10 mm under the secondary electron imaging mode. The sample was prepared by adhering the catalyst powders to a copper conductive tape on a sample stage.

The high-resolution transmission electron microscopy (HR-TEM) was performed on an FEI Titan 80-300 operating at 300 kV that is equipped with a Gatan 794 Multi-scan Camera (EFTEM). To prepare a sample, ~ 1 mg of catalyst was suspended in 10 cm^3 of ethanol by agitating the mixture for 30 min in a sonication bath. A copper grid with a holey carbon film was dipped into the solution to capture the particles and the ethanol was thoroughly evaporated before microscopy.

The X-ray photoelectron spectroscopy (XPS) was carried out at the Nanomaterials Core Characterization Facility of the Virginia Commonwealth University (Richmond, VA), utilizing a Thermo Scientific ESCALAB 250 spectrometer equipped with a focused monochromatic Al K α X-ray radiation source (1486.6 eV) and a hemispherical analyzer with a 6-element multichannel detector. The incident X-ray beam was 45° off normal to the sample while the X-ray photoelectron detector was normal to the sample. A large area magnetic lens with a $500\text{ }\mu\text{m}$ spot size in constant analyzer energy mode was utilized with a pass energy of 20 eV for region scans. Charge compensation was employed during data collection with an internal electron flood gun (2 eV) and a low energy external Ar ion flood gun. The Ce 3d core level spectra were deconvoluted into 10 peaks using a combination of Lorentzian and Gaussian peaks. The percent of Ce³⁺ (V_0 , V' , U_0 and U') and Ce⁴⁺ (V , V'' , V''' , U , U'' and U''') was calculated from the peak assignments proposed by Burroughs et al.²⁵

The measurement of oxygen storage capacity (OSC) and H₂-temperature programmed reduction (H₂-TPR) were performed on a Micromeritics Autochem II 2920 equipped with a thermal conductivity detector (TCD) using 0.20 g of sample. For OSC measurement, the catalyst was heated to 673 K in a 10 vol.% O₂/He mixture at a rate of 5 K min^{-1} and held at 673 K for 30 min, followed by a He purge at 673 K for 30 min. The gas was then switched to 5 vol.% H₂/Ar

and reduced for 6 h at 673 K, followed by a He purge at 673 K for 30 min. The catalyst was then pulsed with 10 vol.% O₂/He at 673 K until saturation was reached. For H₂-TPR, the catalyst was heated to 673 K in a 10 vol.% O₂/He at a rate of 5 K min⁻¹ and held at 673 K for 30 min, followed by a He purge at 673 K for 30 min prior to cooling to room temperature in He. The catalyst was then heated to 1273 K in 5 vol% H₂/Ar using a rate of 5 K min⁻¹.

2.2.4 Coke oxidation by O₂

The coke oxidation rate was measured in an O₂/He mixture in both temperature-programmed oxidation (TPO) experiments and isothermal reactions in a thermogravimetric analyzer (SDT Q600, TA instruments). Approximately 5 mg of sample (coke mixed with catalyst) was placed in a small, flat Al₂O₃ sample cup. For TPO experiments, the sample was heated at a ramp rate of 1 K min⁻¹ up to 1273 K. For isothermal reactions, samples were heated to the target isothermal temperature at a rate of 20 K min⁻¹, then held at the temperature for a specified time. The samples were prepared in tight contact conditions by grinding the catalyst with the coke using a mortar and pestle for an extensive time (about 70 min).

2.2.5 CO oxidation by O₂

The CO oxidation rate was evaluated in a fixed-bed stainless steel reactor (BTRS Jr., Autoclave Engineers) in the temperature range from 473 K to 573 K at ambient total pressure. Typical feed conditions were CO (2 vol.%), O₂ (2 vol.%), and He as diluent. The CO was purified by passing it through a silica trap immersed in a dry ice-acetone mixture (195 K) to remove any trace iron carbonyls before introduction to the reactor. The product and reactant gases were analyzed by a Hewlett-Packard 5890 series II gas chromatograph equipped with a

TCD and a 6-ft long Alltech-8700 packed column. All of the activity results were obtained at the steady state. Reactant gas flow rates were adjusted to attain ~ 5% CO conversion.

2.3 Results

2.3.1 Characterization of CeO₂, ZrO₂ and Ce-Zr mixed oxides

Table 2.1 Physical properties of CeO₂, ZrO₂ and Ce-Zr mixed oxides

Composition of oxides	BET surface area (m ² g ⁻¹)	Internal surface area (m ² g ⁻¹) ^a	External surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹) ^b	Average pore diameter (Å) ^c
CeO ₂	62	2.4	60	0.08	49
Ce _{0.8} Zr _{0.2} O ₂	25	1.6	23	0.07	102
Ce _{0.5} Zr _{0.5} O ₂	13	1.1	12	0.04	107
Ce _{0.2} Zr _{0.8} O ₂	15	1.1	14	0.08	197
ZrO ₂	7.6	1.1	6.5	0.06	324

^a Calculated from t-plot

^b BJH cumulative pore volume

^c Calculated by BJH adsorption method

The results from N₂ physisorption are summarized in Table 2.1. The internal surface area, calculated from the t-plot method, provides an estimate of the surface area inside of micropores. Because micropore surface area is very small compared with the BET surface area, the samples are considered to be non-porous. The external surface area obtained by subtracting the internal surface area from the BET surface area includes the surface area inside mesopores and the area on the external surface of particles. Since it may be possible for coke to enter the mesopores between 2 nm and 50 nm in width, the surface area of mesopores was estimated. The pore volume of the oxides was calculated by the BJH adsorption method and revealed very low values (< 0.1 cm³ g⁻¹), indicating the oxides are essentially non-porous. To further assess any possible contribution of mesopores to surface area of the oxides, the average particle diameter of Ce_{0.8}Zr_{0.2}O₂ was calculated from the BET surface area assuming the oxide particles are spherical

and the value was compared with the surface-weighted particle diameter measured by TEM (Figure 2.1). The particle diameter calculated from BET surface area (36 nm) was larger than that estimated from TEM (19 nm), which indicates $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ is virtually non-porous. Thus, the average pore diameter measured by N_2 physisorption is not associated with intracrystalline mesopores, but apparently results from the voids between primary particles present in aggregates.

Figure 2.1 TEM image of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$.

Figure 2.2 X-ray diffraction patterns of CeO_2 and ZrO_2 , and Ce-Zr mixed oxides. C: cubic, m: monoclinic, t: tetragonal.

Figure 2.2 shows the X-ray diffraction patterns of Ce-Zr mixed oxides compared to the pure oxides. Cerium oxide exhibited the main reflections typical of a fluorite-structure material with a face-centered cubic unit cell.²⁶ The incorporation of Zr into the cubic structure of CeO_2 resulted in broader peaks, indicating smaller crystal size of the mixed oxides. No evidence of phase segregation was observed for $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, suggesting the formation of a solid solution. The $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ sample presented the pattern of tetragonal zirconia whereas the ZrO_2 sample revealed the pattern of monoclinic zirconia.^{27,28} The $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample showed the patterns of both cubic and tetragonal phases, with the features associated with the cubic structure being much more intense. The change of crystal structure from cubic to tetragonal with increasing amount of zirconium in Ce-Zr mixed oxides is consistent with prior reports.²⁷

Figure 2.3 Raman spectra of CeO_2 , ZrO_2 and Ce-Zr mixed oxides. C: cubic, t: tetragonal, m: monoclinic.

Raman spectroscopy was used to determine the coordination symmetry of cations in the oxides. The Raman spectra of Ce-Zr mixed oxides as well as pure Ce and Zr oxides are shown in Figure 2.3. The pure CeO_2 presented a band positioned at 464 cm^{-1} , which is the F_{2g} mode of the cubic fluorite structure.²⁹ The ZrO_2 is monoclinic, which presents the main bands at 179, 190,

334, 347, 382, 475, 615 and 637 cm^{-1} .³⁰ The addition of Zr to CeO_2 shifted the Raman features of CeO_2 towards higher wavenumbers while maintaining its fluorite structure, which resulted from a lattice contraction by substitution of Ce^{4+} by the smaller cation Zr^{4+} .³¹ The Raman band associated with $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ was 467 cm^{-1} and 472 cm^{-1} , respectively. The Zr-rich mixed oxide $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ presented bands at 139, 248, 312, 457 and 625 cm^{-1} , which are characteristic of the tetragonal structure.³² The equimolar mixed oxide, $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, also presented very weak bands corresponding to the tetragonal structure, which is evidenced in Figure 3b. However, their intensities were much lower than the feature from the cubic structure, indicating the cubic phase is the main one in $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$. All of the Raman results are consistent with the observed XRD patterns.

Figure 2.4 X-ray photoelectron spectra of Ce 3d core electrons of CeO_2 and Ce-Zr mixed oxides.

Table 2.2 Surface compositions of CeO₂, CeO₂ and Ce-Zr mixed oxides derived from XPS.

Catalysts	Bulk atomic ratio ^a	Ce/Zr Surface atomic ratio	Ce/Zr Surface O/(Ce+Zr) atomic ratio	Ce ⁴⁺ / (Ce ⁴⁺ + Ce ³⁺)
CeO ₂	N.A.	N.A.	3.31	0.65
Ce _{0.8} Zr _{0.2} O ₂	4.95	5.05	2.37	0.51
Ce _{0.5} Zr _{0.5} O ₂	1.23	1.07	2.42	0.55
Ce _{0.2} Zr _{0.8} O ₂	0.30	0.36	2.16	0.58
ZrO ₂	N.A.	N.A.	2.30	N.A.

^a Measured by ICP-AES

While both XRD and Raman spectroscopy provided information about bulk properties of the oxides, XPS was used to obtain information about the surface composition and cerium oxidation state in the oxides. The Ce 3d spectra of CeO₂ and Ce-Zr mixed oxides are shown in Figure 2.4 and the fitting results are summarized in Table 2.2. The surface Ce/Zr ratios were close to the bulk Ce/Zr ratios determined by elemental analysis, suggesting no surface segregation of either cerium or zirconium had occurred. The O/(Ce+Zr) ratios were slightly above the stoichiometric value 2, which can be attributed to adsorbed water as well as the presence of CO and CO₂.³³ For CeO₂, 65% of the surface cerium was present as Ce⁴⁺. After the addition of Zr, the percent of Ce⁴⁺ was between 51% and 58%, which may suggest more surface oxygen vacancies were present in the mixed oxides relative to CeO₂. However, it is known that photoreduction process of cerium during XPS analysis is possible, which can result in the reduction of 30-40 % of surface cerium in CeO₂.^{34,35} Therefore, we cannot definitely conclude from XPS whether the addition of Zr promotes the formation of oxygen vacancies.

Figure 2.5 H₂-TPR of CeO₂ and Ce-Zr mixed oxide. Surface area of the oxide sample, provided in parentheses, is in m² g⁻¹.

The redox property of the samples was characterized by H₂-TPR and the results are shown in Figure 2.5. Pure ceria showed two reduction peaks at about 720 K and 1080 K. The low temperature peak is assigned to the reduction of surface cerium while the high temperature peak is attributed to the reduction of bulk cerium.³⁶ The low temperature peak of ceria with a surface area of 62 m² g⁻¹ was much larger than that of ceria with a surface area of 5 m² g⁻¹, which is consistent with the peak assignments. The addition of Zr to CeO₂ modified its redox property. For Ce_{0.8}Zr_{0.2}O₂, the surface reduction peak shifted to a higher temperature while the bulk reduction peak shifted to a lower temperature, leading to the overlap of the two peaks. Further addition of Zr resulted in significant decrease in both surface and bulk reduction temperatures, with the lowest reduction temperatures observed on Ce_{0.5}Zr_{0.5}O₂, which had surface and bulk reduction temperatures of about 650 K and 790 K, respectively.

Table 2.3 Oxygen storage capacity of CeO₂ and Ce-Zr mixed oxides.

Oxides	Surface area (m ² g ⁻¹)	OSC (μmol O g ⁻¹)	Theoretical OSC at first layer (100) (μmol O m ⁻²) ^a	Number of reduced layers	Depth of reduction (nm)	Particle radius (nm) ^b
CeO ₂	5	113	5.70	4.0	1.1	84
CeO ₂	62	304	5.70	0.9	0.27	7
Ce _{0.8} Zr _{0.2} O ₂	25	321	4.70	2.7	0.85	17
Ce _{0.5} Zr _{0.5} O ₂	13	750	2.91	20	6.2	36
Ce _{0.2} Zr _{0.8} O ₂	15	527	0.98	36	13	36

^a Assume that Zr atoms do not participate in the storage process and the surface exposed is (100)³⁷

^b Calculated from the BET surface area, assuming spherical, non-porous particles

The oxygen storage capacity (OSC) of the oxides was measured by O₂ pulse chemisorption at 673 K after reduction in H₂ at 673 K for 6 h, and the results are listed in Table 2.3. All of the Ce-Zr mixed oxides revealed larger OSC than the pure CeO₂, with the highest OSC observed on Ce_{0.5}Zr_{0.5}O₂, which had OSC of 750 μmol O g⁻¹. To explore whether or not the bulk oxygen is involved in the oxygen storage process, the number of layers reduced and the depth of reduction were calculated based on the method proposed by Madier et al.³⁷ For the high surface area ceria, only the surface layer participated in the OSC measurement. The number of reduced layers increased to 2.7 for Ce_{0.8}Zr_{0.2}O₂. This number further increased to 20 and 36 for Ce_{0.5}Zr_{0.5}O₂ and Ce_{0.2}Zr_{0.8}O₂, respectively. Considering the fact that a deeper layer consists of fewer oxygen atoms than the outer layer, the actual numbers of layers reduced for Ce_{0.5}Zr_{0.5}O₂ and Ce_{0.2}Zr_{0.8}O₂ are larger than the values reported in Table 2.3. Although the number of layers that could be reduced on low surface area ceria was 4.0, that degree of reduction was still much smaller than that associated with Ce_{0.5}Zr_{0.5}O₂ and Ce_{0.2}Zr_{0.8}O₂, indicating the high OSC in Ce_{0.5}Zr_{0.5}O₂ and Ce_{0.2}Zr_{0.8}O₂ is attributed to the introduction of Zr, not to a difference in surface area. These results support the conclusion that the introduction of Zr into CeO₂ improves oxygen

mobility. In fact, Balducci et al. found that the activation energy for bulk oxygen migration decreased with increasing Zr content in Ce-Zr mixed oxides using atomistic simulation methods.³⁸ Two factors contribute to the OSC of Ce-Zr mixed oxides: the amount of cerium and the oxygen mobility in the oxides. The compromise of these two factors resulted in the highest OSC exhibited by $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$.

2.3.2 Characterization of coke

Figure 2.6 SEM image of synthetic coke after 64 hours milling.

The composition of coke collected and prepared after milling was characterized by the combustion method. The coke had 98 wt.% carbon and less than 0.5 wt.% hydrogen. The N_2 -physisorption of coke provided a BET surface area of $14 \text{ m}^2 \text{ g}^{-1}$, a micropore surface area of $2 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.03 \text{ cm}^3 \text{ g}^{-1}$, suggesting that it is nonporous. The morphology of the coke was characterized by SEM, as shown in Figure 2.6, which revealed a wide size distribution of particles, with the majority being smaller than $1 \mu\text{m}$ and some as large as $10 \mu\text{m}$.

The X-ray diffraction pattern of the coke is shown in Figure 2.7. The peaks at 24.9° and 43.1° are attributed to the (002) and (100) features of graphitic carbon, respectively.²⁴ Both of the peaks are broad, indicating the small sizes of graphitic carbon domains. The peak parameters of the (002) feature were used to obtain the d-spacing between graphitic carbon layers and the crystalline size L_c (perpendicular to the graphitic carbon layer), which are 0.36 and 1.7 nm, respectively. The crystallite size L_a (parallel to the graphitic carbon layer) is 2.2 nm calculated from the peak parameters of the (100) feature.

Figure 2.7 X-ray diffraction pattern of synthetic coke.

Figure 2.8 shows a typical HRTEM image of synthetic coke. Small graphitic carbon domains with crystalline sizes L_c and L_a of several nanometers can be clearly observed. The interlayer spacing determined from microscopy is 0.37 nm, which is consistent with the result obtained from XRD (0.36 nm) and is slightly larger than the spacing in graphene (0.34 nm).³⁹

Figure 2.8 HRTEM image of synthetic coke.

Figure 2.9 Raman spectrum of synthetic coke evaluated with an excitation $\lambda_0=514$ nm. Colors associated with various components can be found in the on-line version of the article.

Figure 2.9 presents the Raman spectrum of coke using an excitation source with $\lambda_0=514$ nm. The spectrum revealed two broad peaks with maxima at 1349 cm^{-1} and 1598 cm^{-1} , which result from the overlapping contributions from five different types of carbon structures. The five features are known as the G band (1580 cm^{-1} , ideal graphitic lattice), the D1 band (1350 cm^{-1} , disordered graphitic lattice), the D2 band (1620 cm^{-1} , disordered graphitic lattice), the D3 band (1500 cm^{-1} , amorphous carbon) and the D4 band (1200 cm^{-1} , disordered graphitic lattice).⁴⁰ Sadezky et al. reported that curve fitting of an experimental spectrum with four Lorentzian-shaped bands (G, D1, D2, D4) and one Gaussian-shaped band (D3) was best suited for the decomposition of first-order spectra of carbonaceous materials.⁴⁰ Therefore, the same fitting method was applied here to deconvolute the contributions of different carbon structures in our synthetic coke. The results of the fitting procedure are summarized in Table 2.4 and indicate synthetic coke is composed primarily of disordered graphitic and amorphous carbon, which is generally consistent with the Raman characterization of coke formed by thermal reaction of propylene and ethylene.⁴¹

Table 2.4 Deconvolution of Raman features associated with synthetic coke.

	G(%)	D1(%)	D2(%)	D3(%)	D4(%)
Synthetic Coke	11	32	4	33	20

The combined results from XRD, HRTEM and Raman spectroscopy are consistent with the synthetic coke produced by ethylene decomposition in this work being a mixture of graphitic carbon and amorphous carbon, with the size of graphitic carbon domains being several nanometers.

2.3.3 Kinetics of coke oxidation in the presence of CeO_2 and Ce-Zr mixed oxides

Figure 2.10 Temperature-programmed oxidation of synthetic coke with and without 20 wt.% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$. Reaction conditions: 1 K min^{-1} , $100 \text{ cm}^3 \text{ min}^{-1}$ 10 vol.% O_2/He , tight contact sample.

Temperature-programmed oxidation in the presence and absence of catalyst was performed to determine a reasonable isothermal reaction temperature at which uncatalyzed coke oxidation was insignificant. Typical results from TPO are presented in Figure 2.10. The addition of 20 wt.% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ to the coke sample decreased the peak oxidation temperature to 705 K from 834 K for the uncatalyzed combustion reaction. We chose to use 673 K as the isothermal reaction temperature to ensure the contribution from the uncatalyzed reaction was negligible.

The dashed curve in Figure 2.11 shows the weight loss profile during the isothermal oxidation of coke with 20 wt.% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ at 673 K. The profile clearly represents a first order decay that reacted nearly all of the coke after about 400 min. For the reaction at 673 K in the absence of catalyst, only 4 wt% of the coke was oxidized, confirming that 673 K is an appropriate isothermal reaction temperature to study the catalyzed reaction rate. A first order rate equation was used to fit the weight loss profile and the model is shown in as the solid curve in Figure 2.11. The first order fit matched with the experimental loss curve very well over the entire profile.

$$\frac{m}{m_o} = e^{-kt}$$

where m is the weight of coke at time t , m_o is the initial weight of coke in the sample, t is the isothermal reaction time and k is the first order rate constant.

Figure 2.11 Weight loss profile of coke during coke oxidation catalyzed by $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ at 673 K. Reaction conditions: 20 wt.% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, $100 \text{ cm}^3 \text{ min}^{-1}$ 10 vol.% O_2/He , tight contact sample.

The first order model described well the coke oxidation weight loss profiles in the presence of CeO_2 and other Ce-Zr mixed oxides used in this study. Therefore, the first order rate constant of coke oxidation was used to evaluate the effectiveness of the various catalysts.

For catalyzed coke oxidation, the contact conditions between catalyst and coke can significantly affect the observed rate constant. The effect of grinding time was then investigated to determine the appropriate contact conditions to obtain reproducible results, as shown in Figure 2.12. Grinding the mixture of catalyst and coke with a mortar and pestle for 20 min increased the observed rate constant by an order of magnitude compared to a loose contact sample in which the coke and catalyst were ground for 1 h separately and gently mixed by spatula. Further grinding of the coke-catalyst mixture increased the rate constant until it reached a constant value,

indicating that the sample had achieved an optimal contact condition, which is defined here as a tight contact sample. All of the coke-catalyst samples in this study were ground for an extensive time (about 70 min) to ensure tight contact conditions were achieved.

Figure 2.12 Effect of grinding time on the rate constant of coke oxidation catalyzed by $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$. Reaction conditions: 20 wt.% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, $100 \text{ cm}^3 \text{ min}^{-1}$ 10 vol.% O_2/He .

Figure 2.13 SEM images of a mixture of 20 wt.% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and 80 wt.% synthetic coke at tight contact (a and c) and loose contact (b and d) conditions.

The morphology of tight and loose contact conditions was studied by SEM, with representative micrographs presented in Figure 2.13. The dark spots in the images were coke particles whereas the bright ones were catalyst particles. There were larger catalyst particles (presumably aggregates of primary particles) in the loose contact sample (Figure 2.13b) than in the tight contact sample (Figure 2.13a). At higher magnification, small catalyst particles were observed to be well-distributed on the coke particles in the tight contact sample (Figure 2.13c) relative to the loose contact sample (Figure 2.13d). Evidently, grinding the coke with the catalyst helps disperse the catalyst and enhance the contact area between the catalyst and the coke.

Although the first order rate constant is one quantifiable measure of oxidation rate, a catalytic reaction must be operated under conditions at which the rate is proportional to the number of active sites to properly compare performance among various catalysts. Therefore, coke-catalyst samples with different amounts of catalyst were prepared and evaluated in the oxidation reaction. Figure 2.14 shows the relationship between rate constant and catalyst loading, in which the catalyst loading is presented by the total surface area of catalyst per gram of coke in the sample. For all of the four catalysts tested, the same trend was observed: at low catalyst loadings, the oxidation rate constant was proportional to the total surface area of catalyst whereas at high catalyst loadings, the rate constant was independent of the total surface area of the catalyst. There is a saturation amount of catalyst for coke oxidation, beyond which the excess catalyst present in the sample does not participate in the reaction. To obtain the maximum active surface area of catalyst in the mixture, the rate constants at low catalyst loadings were fitted with a line through the origin and the rate constants beyond saturation were fitted with a line at the average value of rate constants. The intersection of these two lines corresponds to coke-catalyst mixture with the maximum active catalyst surface area. The coke oxidation rates determined

from the slopes of the lines in Figure 2.14 at low catalyst loadings can be used to compare the various catalysts. The coke oxidation rate was actually an initial rate because the values on the x-axis (total catalyst surface area per gram of coke) were calculated from the initial weight percent of coke. It should be noted that even at low catalyst loadings, the conversion of coke during a run will eventually produce condition at which the catalyst area greatly exceeds the remaining coke area in the mixture. Thus, the first order loss of coke as depicted in Figure 2.11 results from an evolving contact condition throughout the reaction.

Figure 2.14 Relationship between measured first order rate constant and normalized catalyst loading for CeO_2 and Ce-Zr mixed oxides. Reaction conditions: 673 K, 100 cm³ min⁻¹ 10 vol.% O_2/He , tight contact samples.

The maximum active catalyst surface area and coke oxidation rate at 673 K for the four oxides are presented in Table 2.5. For Ce-Zr mixed oxides, the maximum active surface area increased and the coke oxidation rate decreased with increasing zirconium content. The coke oxidation rate with CeO₂ was between those with Ce_{0.8}Zr_{0.2}O₂ and Ce_{0.5}Zr_{0.5}O₂.

Table 2.5 Active catalyst surface area and coke oxidation rates at 673 K for CeO₂ and Ce-Zr mixed oxides.

	CeO ₂	Ce _{0.8} Zr _{0.2} O ₂	Ce _{0.5} Zr _{0.5} O ₂	Ce _{0.2} Zr _{0.8} O ₂
Average rate constant at high catalyst loading (min ⁻¹)	0.011	0.011	0.0059	0.0040
Ratio of maximum active catalyst surface area to coke mass (m ² _{cat} g ⁻¹ _{carbon})	14	7	19	28
Ratio of maximum active catalyst surface area to coke surface area (m ² _{cat} m ⁻² _{carbon})	1.2	0.58	1.6	2.3
Coke oxidation rate (10 ⁻⁴ g _{carbon} m ⁻² _{cat} min ⁻¹)	7.9	17	3.0	1.4

Table 2.6 Order of reaction with respect to dioxygen during coke oxidation with Ce_{0.8}Zr_{0.2}O₂.^a

Catalyst loading (wt.%)	0	10	20	50	70
Order with respect to O ₂	1.0	0.38	0.36	0.30	0.26

^a Reaction conditions: 2.1-21 vol.% O₂/He, 673 K

The reaction order with respect to dioxygen during coke oxidation was measured by varying the gas phase percentage of dioxygen between 2.1 vol.% and 21 vol.% at 673 K. First order rate constants were used to calculate the apparent reaction order and the results are summarized in Table 2.6. The uncatalyzed coke oxidation reaction was first order in O₂, which is consistent the reported order for diesel soot oxidation.^{42,43} The presence of Ce_{0.8}Zr_{0.2}O₂ decreased the order of reaction in dioxygen to about 0.30, which also varied with the amount of catalyst in the samples (See Table 2.6). The O₂ reaction order in the presence of other Ce-Zr mixed oxides

as well as CeO_2 was determined using 70-90 wt.% catalyst and the results are listed in Table 2.7. The four oxide catalysts exhibited similar reaction order in dioxygen of about 0.3. Issa et al. observed a reaction order in O_2 of 0.2 for carbon black oxidation catalyzed by CeO_2 at 701 K.⁴⁴ Fino et al. proposed that an order in dioxygen lower than 0.50 during catalyzed carbon oxidation indicates that the active oxygen species are oxygen atoms generated by dissociative adsorption of dioxygen on the catalyst surface.⁴⁵

Table 2.7 Order of reaction with respect to O_2 during coke oxidation over Ce-based catalysts.^a

Catalyst	Order in O_2
CeO_2	0.28
$\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	0.26
$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	0.30
$\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$	0.25

^a Reaction conditions: 80-90 wt.% catalyst loading, 673 K, tight contact samples.

Table 2.8 Apparent activation energy of coke oxidation in the presence of Ce-based catalysts.^a

Catalyst	Apparent activation energy (kJ mol^{-1})
None	150
CeO_2	117
$\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	129
$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	123
$\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$	123

^a Reaction temperature varied from 653-693 K while O_2 concentration was maintained at 10 vol.%.

Coke oxidation over Ce-Zr mixed oxides with 10 vol.% O_2 was performed at different reaction temperatures so that an apparent activation energy could be derived from the measured first order rate constants. The apparent activation energies of the catalytic oxidation reactions, which are summarized in Table 2.8, were 20-30 kJ mol^{-1} lower than that of the uncatalyzed reaction.

2.3.4 CO oxidation over CeO_2 and Ce-Zr mixed oxides

To maintain differential conversion and minimize the uncatalyzed CO oxidation reactions, the CO oxidation experiments were conducted at 573 K and the reaction rates were calculated at 5% CO conversion. As revealed in Table 2.9, the incorporation of 20 mol.% Zr into CeO₂ doubled the rate of CO oxidation. However, the reaction rates decreased significantly with additional Zr in the catalyst.

Table 2.9 Rate of CO oxidation at 5% CO conversion over CeO₂ and Ce-Zr mixed oxides.^a

	CeO ₂	Ce _{0.8} Zr _{0.2} O ₂	Ce _{0.5} Zr _{0.5} O ₂	Ce _{0.2} Zr _{0.8} O ₂
CO oxidation rate (10 ⁻⁷ mol _{CO} m ⁻² _{cat} min ⁻¹)	29	68	13	3.8

^a Reaction conditions: 573 K, total pressure 1 atm, 2 vol.% CO and 2 vol.% O₂ in He

Figure 2.15 Influence of (a) O_2 and (b) CO concentration on CO oxidation rate over CeO_2 at 513 K. While varying the concentration of one gas, the other gas was kept at 2 vol.%.

Figure 2.16 Influence of (a) O_2 and (b) CO concentration on CO oxidation rate over $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ at 513 K. While varying the concentration of one gas, the other gas was kept at 2 vol.%.

The influences of CO and O_2 concentration on CO oxidation rates over CeO_2 were studied at 513 K and the results are presented in Figure 2.15. The rates of CO oxidation were unaffected by change in the O_2 concentration, indicating zero order behavior. The influence of CO concentration was more complex and depended on how the experiments were performed. The reaction rates obtained at 5% conversion of CO at different CO concentrations gave an order

of 0.69 for CO, which is similar with those reported in the literature.^{46,47} Since the presence of product CO₂ can inhibit CO oxidation,⁴⁶ a more appropriate method to determine the order in CO is to use rates obtained at the same level of CO₂ concentration in the catalyst bed. Results obtained at constant CO₂ level gave an order in CO of 1.3.

To investigate the effect of Zr addition to CeO₂ on the reaction orders in CO and O₂, the response of CO oxidation rates over Ce_{0.8}Zr_{0.2}O₂ to changing the concentrations of CO and O₂ are presented in Figure 2.16. The reaction orders are similar with those found over CeO₂, with the order in O₂ being 0 and the order in CO (at constant CO₂ level) being 1.1. Evidently, the reaction mechanism over the two catalysts is unaffected by the addition of zirconium.

Table 2.10 Apparent activation energy of CO oxidation over Ce-based catalysts.^a

Catalysts	Apparent activation energy (kJ mol ⁻¹)
CeO ₂	114
Ce _{0.8} Zr _{0.2} O ₂	117
Ce _{0.5} Zr _{0.5} O ₂	113
Ce _{0.2} Zr _{0.8} O ₂	98

^a Reaction conditions: temperature range of 543-573 K, total pressure 1 atm, 2 vol.% CO and 2 vol.% O₂ in He.

Oxidation of CO over CeO₂ and Ce-Zr mixed oxides was performed at different reaction temperatures to determine an apparent activation energy. As presented in Table 2.10, the apparent activation energy for CO oxidation over CeO₂ is 114 kJ mol⁻¹, which is similar to values reported for CO oxidation over CeO₂ under similar conditions.^{47,48} Cerium zirconium mixed oxides exhibited similar apparent activation energies to CeO₂, suggesting that the reaction mechanism is not altered after the addition of zirconium, which is consistent with the observed orders of reaction.

2.4 Discussion

In this study, a methodology to evaluate the performance of catalyst for coke oxidation was developed to obtain reproducible reaction kinetics. Samples with different catalyst/coke mass ratios need to be prepared at the same tight contact conditions, followed by the isothermal oxidation reaction to obtain a first order rate constant. Finally, the amount of active catalyst in the mixture and therefore a normalized coke oxidation rate can be calculated. Although the weight loss of coke during catalyzed coke oxidation in this study showed a simple first order decay, this may not be observed with other types of carbon samples.⁴⁹ Therefore, if a first order rate constant cannot be evaluated, the reaction rate at a specified level of conversion could also be related to the amount of catalyst in the reaction. A constant reaction rate per catalyst mass (area) can be determined regardless of the oxidation kinetics. The importance of proper normalization is revealed in Table 5. For example, the average rate constant at high catalyst loading for CeO₂ and Ce_{0.8}Zr_{0.2}O₂ was 0.011 min⁻¹, which might suggest the catalysts exhibit identical catalytic activity. However, once proper normalization of the rates is performed, the rate with Ce_{0.8}Zr_{0.2}O₂ ($17 \times 10^{-4} \text{ g}_{\text{carbon}} \text{ m}^{-2}_{\text{cat}} \text{ min}^{-1}$) was more than twice that with CeO₂ ($7.9 \times 10^{-4} \text{ g}_{\text{carbon}} \text{ m}^{-2}_{\text{cat}} \text{ min}^{-1}$). To validate this conclusion, we can examine the rate of CO oxidation over the exact same catalysts, as summarized in Table 9. Again the CO oxidation rate over Ce_{0.8}Zr_{0.2}O₂ ($68 \times 10^{-7} \text{ mol}_{\text{CO}} \text{ m}^{-2}_{\text{cat}} \text{ min}^{-1}$) was more than twice that over CeO₂ ($29 \times 10^{-7} \text{ mol}_{\text{CO}} \text{ m}^{-2}_{\text{cat}} \text{ min}^{-1}$). In fact, the results in Figure 17 reveal that coke oxidation rates are completely correlated to the CO oxidation rates over the entire series of catalysts.

Figure 2.17 Correlation of coke oxidation rates at 673 K and CO oxidation rates at 573 K over Ce-based materials.

We searched for a correlation between coke oxidation (or CO oxidation) rate and either oxygen storage capacity or reducibility of the catalyst, but found none. The highest coke oxidation rate was observed with $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ whereas the highest OSC and the lowest reduction temperatures were observed with $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$.

The correlation between coke oxidation and CO oxidation over the catalyst is likely the result of proper normalization of the rates and similar mechanisms of reaction. Indeed, the first order dependence on reactant (coke or CO), the low order dependence on O_2 , and the similar apparent activation energy are consistent with similar mechanism.

It is generally accepted that the mechanism of CO oxidation over ceria-based oxides involves a redox Mars-van Krevelen path,^{8, 36, 37, 40} as illustrated in Figure 2.18. During the reaction, surface lattice oxygen reacts with the adsorbed CO to form CO_2 , followed by the

desorption of CO₂ and the reoxidation of the surface by gas-phase O₂. If a simple rate expression (Equation 1) associated with the Mars-van Krevelen mechanism is considered,⁵² it can be further simplified to the expression in equation 2 when the surface reoxidation step is much faster than the surface reduction step. In this way, first order behavior in CO and zero order behavior in O₂ can be easily explained and are consistent with our experimental results.

$$\frac{1}{r} = \frac{1}{k_1 P_{CO}^n} + \frac{2}{k_2 P_{O_2}^m} \quad \text{Equation 1}$$

$$r = k_1 P_{CO} \quad \text{Equation 2}$$

Figure 2.18 Scheme of the CO oxidation mechanism over Ce-based catalysts.

For coke oxidation in the presence of ceria-based oxides, two reaction mechanisms have been proposed previously, a redox Mars-van Krevelen path and a spill-over of active oxygen path,⁵³ as illustrated in Figure 2.19. The redox path involves the reaction of surface lattice oxygen with solid coke at their interface, followed by the reoxidation of the catalyst surface. This path has been demonstrated by studies with environmental transmission electron microscopy⁵⁴ and ¹⁸O isotopic labelling experiments.^{53,55} The second reaction path involves the formation of active oxygen species, such as superoxide and peroxide ions, followed by the spill-over of these species to the coke surface and their subsequent reaction with coke.^{12,53} Such active oxygen

species have been detected in ESR measurements⁵³ and FT-IR experiments,⁵⁶ however, these experiments were not performed at reaction conditions and the distance of active oxygen spill-over is unknown but is believed to be only several nanometers.⁵⁴ Therefore, in both paths, the active catalytic sites are at or very close to the interface between the catalyst and the coke. In our study, the ratio of maximum active catalyst surface area to the initial surface area of coke was close to unity for all of the four catalysts (Table 2.5), and combined with the fact that both the catalyst and the coke were nonporous, suggest coke oxidation mainly occurs at or near the interface of the catalyst and the coke. We therefore imaged a catalyst/coke mixture by SEM after partial conversion of coke (Figure 2.20). Most of the pits on the coke surface from oxidation are in the vicinity of catalyst particles.

Figure 2.19 Scheme of the mechanism of coke oxidation over Ce-based materials: 1. redox path, 2. spill-over of active oxygen path. Colors associated with various components can be found in the on-line version of the article.

Figure 2.20 SEM image of coke- $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ mixture at 50% coke conversion.

The correlation between coke and CO oxidation rates over the Ce-based materials confirms that the methodology to quantify coke oxidation rates is reasonable. Both of the reactions involve the participation of surface lattice oxygen of the catalyst without significant involvement of oxygen from the bulk of the catalyst. Therefore, it is reasonable that the oxidation rates are not correlated with bulk OSC or reducibility of the oxides. During the OSC and H_2 -TPR experiments, a large amount of bulk oxygen is involved, as evidenced by the large number of layers reduced for the Zr-rich mixed oxides (Table 2.3). The correlation between coke and CO oxidation rates also suggests that CO oxidation might be used as a rapid probe to screen new catalysts for coke oxidation.

The best catalyst composition of the Ce-Zr mixed oxides for coke oxidation was $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$. Coke oxidation with other similar mixed oxides was also studied by Aneggi et al.⁵⁷ The values in Table 2.11 are reaction rates derived from the results of Aneggi et al. The reaction rates are an order of magnitude higher than those in our study, which may be caused by a higher reaction temperature (723 K) and a different type of coke (Printex-U) used in their study. Aneggi

et al. report that $\text{Ce}_{0.44}\text{Zr}_{0.56}\text{O}_2$ was the most active catalyst composition, which is slightly different from the result in the current study. As pointed out earlier, the area of catalyst cannot exceed the area of coke in the mixture, or rates cannot be properly normalized. The high ratio of catalyst area to coke area for CeO_2 and $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (Table 2.11) indicates there might be a significant over supply of catalyst in those cases, which will affect the ranking of catalyst activities.

Table 2.11 Coke oxidation rates and its reaction conditions for cerium zirconium mixed oxides in literature.⁵⁷

	CeO_2	$\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$	$\text{Ce}_{0.44}\text{Zr}_{0.56}\text{O}_2$	$\text{Ce}_{0.28}\text{Zr}_{0.72}\text{O}_2$
Catalyst surface area ($\text{m}^2 \text{g}^{-1}$)	54	27	11	10
Initial ratio of total surface area of catalyst over coke ($\text{m}^2_{\text{cat}} \text{m}^{-2}_{\text{carbon}}$)	11	5.5	2.2	2.0
Coke oxidation rate ($10^{-4} \text{g}_{\text{carbon}} \text{m}^{-2}_{\text{cat}} \text{min}^{-1}$)	29	44	49	36

2.5 Conclusions

Coke oxidation over ceria-based oxides was studied under isothermal tight contact conditions to obtain normalized reaction rates on a catalyst surface area basis. A methodology involving the evaluation of maximum active catalyst surface area has been developed. The weight loss of coke in catalyzed coke oxidation was first order in coke, which enabled the straightforward calculation of a first order rate constant. When reaction rates were determined in a regime that was strictly proportional to catalyst loading, then $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ was found to be the most active oxidation catalyst. Coke oxidation rates were very well correlated with CO oxidation rates, but not with oxygen storage capacity or reducibility of the catalyst, indicating that CO oxidation might be a useful probe for the discovery of new coke oxidation catalysts. Detailed

kinetic studies of coke and CO oxidation revealed similar reaction orders and apparent activation energy, and suggested the participation of surface lattice oxygen of the catalyst in the two reactions. For coke oxidation, the ratio of catalyst area to coke area in the mixture should be close to unity to maximize rate and catalyst utilization.

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Chapter 3. Catalytic Gasification of Coke with Dioxygen and Steam over Alkaline-earth-metal-doped Cerium-Zirconium Mixed Oxides

Abstract:

A series of cerium zirconium mixed oxides doped with alkaline earth metals was prepared by calcining a mixture of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and the nitrate salt of alkaline earth metals at 1173 K. The results of X-ray diffraction, Raman spectroscopy and analytical electron microscopy indicated the alkaline earth compounds were dispersed on the surface of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$. The doped mixed oxides were evaluated in the catalytic gasification of solid coke under tight contact conditions with 10 vol% O_2 in He at 693 K and with 100 vol.% H_2O at 993 K using thermogravimetric analysis. For coke gasification with O_2 , the weight loss was first order in coke and the measured first order rate constant was proportional to the total surface area of catalyst at low catalyst loadings. For coke gasification with H_2O , the weight loss was nearly zero order in coke and the measured reaction rate was independent of the total surface area of catalyst at low catalyst loadings. The addition of alkaline earth metals inhibited coke gasification with dioxygen but promoted coke gasification with steam.

3.1 Introduction

Ethylene is one of the most important building blocks for the chemical industry. Steam cracking has been widely used for the industrial production of olefins, which involves heating hydrocarbons to high temperatures (1023 K - 1123 K) in the presence of diluting steam.¹⁻³ The reactions of hydrocarbons in the steam crackers are free radical in nature because of the high temperature and the primary desired reaction for steam cracking of ethane involves its dehydrogenation to ethylene:

The product stream which contains a complex mixture of hydrocarbons is immediately cooled in a transfer line heat exchanger (TLE) to avoid the undesired side reactions and is separated by distillation and absorption processes to obtain the valuable olefinic products.⁴ One of the major by-products of the steam cracking process is the formation of carbonaceous deposits (coke) on the walls of the reactor. There are three coke formation mechanisms during steam cracking: catalytic coke formation, radical coke formation, and droplet condensation.^{2,5} Coke formation in steam crackers can cause a number of problems such as increase of pressure drop in the reactor, decrease of heat transfer at the reactor walls, increase of tube metal temperature and carburization of tube materials,^{2,6,7} which eventually leads to the shutdown of the furnace for coke removal every 1-3 months depending on the type of feed and reactor tubes.⁷ Coke formed in the reactor is combusted by passing a mixture of steam and air at high temperatures through the reactor. After multiple coking-decoking cycles, the cracker tubes also need to be replaced. These undesirable shutdowns motivate efforts directed towards increasing the continuous run of steam crackers.

Researchers have studied different methods to reduce the coke formation in steam crackers, with a focus on the development of coatings on the internal walls of the cracker tubes. One type of coating contains materials that are inert to coke formation at steam cracking conditions, such as aluminum,^{8,9} TiC and SiC.³ This type of coating act as a barrier between the gas phase and the active metallic sites on the reactor wall, thus preventing catalytic coke formation. Another type of coating contains materials that not only inhibit metal-catalyzed coke formation, but additionally catalyze coke gasification. A novel furnace coil coating technology called catalyzed assisted manufacture of olefins (CAMOL) was developed by BASF.^{10,11} The CAMOL coating is inert to filamentous coke formation and facilitates gasification of amorphous coke.

Ceria-based materials have received a lot of interest because of their demonstrated catalytic activity in several reactions, such as CO oxidation and soot oxidation, which can be attributed to the redox property of cerium.^{12–15} Ceria-based materials have been widely used in the Three Way Catalysts (TWC) for the emission control of gasoline cars since the mid-1980s.^{16–18} In addition, the presence of cerium in the catalysts inhibit coke formation during the steam reforming of hydrocarbons.^{19–22} Zhuang et al. investigated the effect of cerium oxide in MgAlO₃ supported Ni catalyst for methane steam reforming.¹⁹ Cerium oxide not only decreased the rate of coke deposition, but also increased the catalytic activity of steam reforming. Natesakhawat et al. reported the beneficial effects of cerium promoter in a Ni/Al₂O₃ catalyst for propane steam reforming by both inhibiting coke formation and improving catalytic activity.²⁰ Wang et al. compared the steam reforming rates of methane, ethane, n-butane, n-hexane on a Pd/ceria catalyst and a Pd/alumina catalyst.²² The Pd/ceria catalyst had much higher reaction rates than the Pd/alumina catalyst, as well as higher resistance to coke formation. Therefore, ceria-based

oxides are promising coating materials for steam crackers. Since cerium oxide itself is not stable at high temperature and sinters severely at typical steam cracking conditions, the addition of zirconium is required to increase its thermal stability and improve its redox property.^{23–29} To further increase the activity of ceria-based materials for coke gasification, the doping of alkali and alkaline earth metals to cerium zirconium mixed oxides is desired since they have been shown previously to have high activity for steam gasification of carbon.³⁰ However, alkali metals suffer from a relatively high volatility at elevated temperatures in steam whereas the volatility of alkaline earth metals is relatively low at the same conditions.³¹ In this study, alkaline earth metals were added to $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ since $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ is the most active in coke oxidation of the Ce-Zr mixed oxides.^{23,32,33} As the decoking step during the shutdown of a steam cracker involves both steam and dioxygen, the catalysts in this study were tested in coke gasification with both steam and dioxygen.

3.2 Experimental methods

3.2.1 Catalyst preparation

Cerium-zirconium mixed oxide ($\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, which is referred as CZ82) was prepared using a controlled precipitation method. First, an aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Sigma Aldrich) and $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (99.99%, Sigma Aldrich) was prepared with a total metal ion concentration of 0.2 M. The metal precursor solution was added dropwise to 100 cm³ of distilled deionized water (DDI) at 298 K while a solution of 15 wt.% aqueous ammonia was added continuously during precipitation to maintain a pH of 10. The resulting suspension was stirred for 20 h at 298 K. The precipitate was recovered by vacuum filtration, washed 3 times with DDI water, dried in air at 400 K overnight. The samples were then heated to 1173 K in air at a rate of

5 K min⁻¹ and held at 1173 K for 6 h. The obtained CZ82 was mixed with the nitrate salt of alkaline earth metals and ground for 10 min, followed by calcination of the mixture in air at 1173 K for 2 h. The resulting materials are designated as xM/CZ82, where M represents the alkaline earth metals and x represents the atomic ratio of M/Ce.

3.2.2 Characterization of catalyst

Powder X-ray diffraction (XRD) patterns of the catalysts and coke were obtained on a PANalytical X'Pert Pro MPD Diffractometer with Cu K α radiation. Each sample was scanned at a rate of 0.2° s⁻¹, over a range of 2 θ from 10° to 90°.

Specific surface area of the catalysts and coke was obtained by N₂ adsorption measured at 77 K using the BET method on a Micromeritics ASAP 2020 automated analyzer.

Raman spectra of the oxide catalysts and coke were recorded with a Renishaw InVia Raman Microscope with an Ar laser (514 nm) and a 3000 g mm⁻¹ grating. The Raman scope was calibrated using a silicon wafer.

Scanning transmission electron microscopy (STEM) was performed with a JEOL 2010 F instrument operating at 200 kV that was equipped with an Oxford Aztec energy dispersive spectrometer (EDS) system. To prepare a sample, ~1 mg of catalyst was suspended in 10 cm³ of ethanol by agitating the mixture for 30 min in a sonication bath. A copper grid was dipped into the solution to capture the particles, and the ethanol was thoroughly evaporated before microscopy.

The measurement of oxygen storage capacity (OSC) and H₂-temperature programmed reduction (H₂-TPR) were performed on a Micromeritics Autochem II 2920 equipped with a thermal conductivity detector (TCD) using 0.20 g of sample. For OSC measurement, the catalyst

was heated to 673 K in a 10 vol.% O₂/He mixture at a rate of 5 K min⁻¹ and held at 673 K for 30 min, followed by a He purge at 673 K for 30 min. The gas was then switched to 5 vol.% H₂/Ar and reduced for 6 h at 673 K, followed by a He purge at 673 K for 30 min. The catalyst was then pulsed with 10 vol.% O₂/He at 673 K until saturation was reached. For H₂-TPR, the catalyst was heated to 673 K in a 10 vol.% O₂/He at a rate of 5 K min⁻¹ and held at 673 K for 30 min, followed by a He purge at 673 K for 30 min prior to cooling to room temperature in He. The catalyst was then heated to 1273 K in 5 vol% H₂/Ar using a rate of 5 K min⁻¹.

3.2.3 Coke gasification by O₂ and H₂O

The samples for coke gasification were prepared in tight contact conditions by grinding the catalyst with the coke using a mortar and pestle for an extensive time (about 70 min). The preparation and characterization of the coke used in this study can be found in our previous work.³³ The coke was obtained by thermal reaction of ethylene at 1150 K and was a mixture of both graphitic and amorphous carbon. The coke gasification with dioxygen and steam was performed in both temperature-programmed oxidation (TPO) experiments and isothermal reactions. The coke gasification with dioxygen was carried out in a thermogravimetric analyzer (SDT Q600, TA instruments). Approximately 5 mg of sample (coke mixed with catalyst) was placed in a small, flat Al₂O₃ sample cup. For TPO experiments, the sample was heated at a ramp rate of 5 K min⁻¹ up to 1273 K. For isothermal reactions, samples were heated to the target isothermal temperature at a rate of 20 K min⁻¹, then held at the temperature for a specified time. The coke gasification with steam was carried out in a customized thermogravimetric analyzer (STA449F3 Jupiter, NETSCH). Approximately 2 mg of sample (coke mixed with catalyst) was placed in a small, flat Al₂O₃ sample cup. For TPO experiments, the sample was heated at a ramp rate of 5 K min⁻¹ up to 1273 K in 100 vol.% H₂O. For isothermal reactions, samples were heated

to the target isothermal temperature at a rate of 20 K min⁻¹ in protective N₂. Once the desired temperature was reached, pure steam was injected into the TGA and the temperature was held for 3 h. Before each measurement, the TGA was evacuated and subsequently purged with N₂ to remove oxygen in the system.

3.3 Results and Discussions

3.3.1 Characterization of undoped and alkaline-earth-metal-doped Ce_{0.8}Zr_{0.2}O₂

Table 3.1 Physical properties of undoped and alkaline-earth-metal-doped Ce-Zr mixed oxides

Composition of oxides	BET surface area (m ² g ⁻¹)	Internal surface area (m ² g ⁻¹) ^a	External surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹) ^b	Average pore diameter (Å) ^c
CZ82	15	3.2	12	0.10	239
0.1Mg/CZ82	12	2.6	9.4	0.08	264
0.05Ca/CZ82	8.8	1.3	7.5	0.07	274
0.1Ca/CZ82	12	1.4	11	0.08	259
0.2Ca/CZ82	7.9	1.0	6.9	0.06	289
0.1Sr/CZ82	12	2.8	9.2	0.07	258
0.1Ba/CZ82	11	2.6	8.4	0.07	240

^a Calculated from t-plot

^b BJH cumulative pore volume

^c Calculated by BJH adsorption method

The results from N₂ physisorption are summarized in Table 3.1. The internal surface area, calculated from the t-plot method, provides an estimate of the surface area inside of micropores, which is very small compared with the BET surface area. The pore volume of the oxides was calculated by the BJH adsorption method and revealed very low values ($< 0.1 \text{ cm}^3 \text{ g}^{-1}$), indicating the oxides are essentially non-porous. The pores characterized by diameter between 200-300 Å are likely the voids between primary particles present in aggregates.³³

Figure 3.1 X-ray diffraction patterns of undoped and alkaline-earth-metal-doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$.

Figure 3.1 shows the X-ray diffraction patterns of alkaline earth metal doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ compared to undoped oxide. The Ce-Zr mixed oxide remained the patterns of cubic structure after the addition of Mg, Ca and Sr. The mixed oxide doped with Ba exhibited an additional small reflection near the main peak of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ at 28.8° (Figure 1b), which may be the

reflection of BaCeO_3 or BaZrO_3 .³⁴ Since there was no shift of the peaks of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, the formation of BaCeO_3 or BaZrO_3 is must be limited to the surface or subsurface layers instead of the bulk of the mixed oxides.

Figure 3.2 Raman spectra of undoped and alkaline-earth-metal-doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$.

The Raman spectra of undoped and alkaline-earth-metal-doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ are shown in Figure 3.2. The $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ sample presented a band positioned at 469 cm^{-1} , which is the F_{2g} mode of the cubic fluorite structure.³⁵ After the addition of alkaline earth metals to $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, there were neither any new bands nor any change of the $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ band, indicating that the alkaline earth metals remained on the surface of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, which is consistent with the conclusion from the XRD results. The composition of 0.1Ca/CZ82 sample was examined by energy-dispersive X-ray spectroscopy (EDS) in the STEM mode (Figure 3.3) and the atomic

percentage of different elements are listed in Table 3.2. The average atomic percent of Ca was 4.6% for the regions at the edge of the particle, compared to only 0.8% for the regions in the middle of the particle. Thus, the results from XRD, Raman spectroscopy and STEM-EDS analysis all point to the conclusion that the alkaline earth metals remained highly dispersed on the surface of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ after calcination at elevated temperature. However, we cannot rule out the possibility that some of alkaline earth metals enter the subsurface lattice of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$.

Figure 3.3 Dark-field STEM image of 0.1Ca/Ce_{0.8}Zr_{0.2}O₂. The corresponding compositions of analysis region are shown in Table 3.2

Table 3.2 Elemental compositions from EDS of 0.1Ca/CZ82^a

Area	Ce (atom%)	Ca (atom%)	Zr (atom%)
1	97	3	0
2	94	0	5
3	88	0	12
4	86	0	14
5	92	3	5
6	92	8	0
7	92	3	5
8	84	6	10
9	85	3	11
10	92	1	7

a: The corresponding regions for EDS analysis are shown in Figure 3.3

Figure 3.4 Uptake of H₂ during temperature programmed reduction of undoped and alkaline-earth-metal-doped Ce_{0.8}Zr_{0.2}O₂.

The redox property of the samples was characterized by H₂-TPR and the results are shown in Figure 3.4. The undoped Ce_{0.8}Zr_{0.2}O₂ sample exhibited two reduction peaks at about 845 K and 1015 K. The low temperature peak is assigned to the reduction of surface cerium while the high temperature peak is attributed to the reduction of bulk cerium.³⁶ There was little change of the peak temperatures after the addition of Mg, Ca or Sr. After the doping of Ba, however, the surface reduction peak shifted to significantly lower temperature by 60 K, which may be the result of the reduction of BaCeO₃ formed on the surface.

Table 3.3 Oxygen storage capacity of undoped and alkaline-earth-metal-doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$.

Oxides	Surface area ($\text{m}^2 \text{g}^{-1}$)	Normalized surface area ^a	OSC ($\mu\text{mol O g}^{-1}$)	Normalized OSC ^b
CZ82	15	-	327	-
0.1Mg/CZ82	12	0.80	237	0.73
0.05Ca/CZ82	8.8	0.59	172	0.52
0.1Ca/CZ82	12	0.80	178	0.54
0.2Ca/CZ82	7.9	0.53	125	0.38
0.1Sr/CZ82	12	0.80	178	0.54
0.1Ba/CZ82	11	0.73	278	0.85

a: Ratio of surface area of alkaline-earth-metal-doped CZ82 to that of undoped CZ82

b: Ratio of OSC of alkaline-earth-metal-doped CZ82 to that of undoped CZ82

The oxygen storage capacity (OSC) of the oxides was measured by O_2 pulse chemisorption at 673 K after reduction in H_2 at 673 K for 6 h, and the results are listed in Table 3.3. The OSC decreased after the addition of alkaline earth metals, which is attributed to the decrease of surface area after doping, as indicated by the similar values of normalized surface area and normalized OSC relative to undoped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ in Table 3.3. Although bulk reduction of Ce contributes to the OSC, the OSC of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ involves primarily the reduction of Ce in the near surface region of the sample.³³ The OSC of the doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ samples is relatively unaffected by the presence of the alkaline earth metals beyond the reduction in surface area because the metals did not enter the bulk structure.

3.3.2 Coke gasification with O₂ and H₂O in the presence of undoped and alkaline-earth-metal-doped Ce_{0.8}Zr_{0.2}O₂

Temperature-programmed oxidation in the presence and absence of catalyst was performed to determine a reasonable isothermal reaction temperature that minimizes the contribution from non-catalytic gasification. The addition of Ce-based catalysts to coke decreased the peak oxidation temperature by 120-170 K, as shown in Figure 3.5. We chose to use 693 K as the isothermal reaction temperature to ensure the contribution from the uncatalyzed reaction was negligible. The weight loss profile of coke presented a first order decay and a first order equation matched well the weight loss profiles in the presence of undoped and alkaline-earth-metal-doped Ce_{0.8}Zr_{0.2}O₂ (Figure 3.6), which is similar to the results obtained from coke oxidation over a series of Ce-Zr mixed oxides.³³ To obtain reproducible reaction rates, tight contact coke-catalyst samples with different amounts of catalyst were prepared and evaluated in the gasification reaction. Figure 3.7 shows the relationship between rate constant and catalyst loading for those catalysts, which allows the calculation of reaction rates with the method described in our previous work.³³

Figure 3.5 Temperature-programmed oxidation of synthetic coke with and without catalyst.

Reaction conditions: 80 wt.% catalyst in the mixture, 5 K min⁻¹, 100 cm³ min⁻¹ 10 vol.% O₂/He, tight contact sample. The peak oxidation temperature are listed in the parentheses.

Figure 3.6 Weight loss profile of coke during coke oxidation catalyzed by $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ at 693 K.

Reaction conditions: 50 wt.% $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, $100 \text{ cm}^3 \text{ min}^{-1}$ 10 vol.% O_2/He , tight contact sample.

For coke gasification with steam, TPO experiments were also performed to determine the isothermal reaction temperature and the results are shown in Figure 3.8. Uncatalyzed steam gasification of coke had a peak temperature of 1182 K, which is much higher than the peak temperature of uncatalyzed coke oxidation at 929 K and illustrated the low rate of steam gasification. The peak steam gasification temperature in the presence of catalyst decreased by 30-60 K compared to that without catalyst. Isothermal coke gasification with steam over undoped and alkaline-earth-metal-doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ was then carried out at 993 K in 100 vol% steam. Unlike coke gasification with dioxygen, the coke weight loss profile presented a zero order decay with steam (Figure 3.9). A zero order rate equation was used to fit the weight loss profile over the range of conversion of coke from 0 to 20%.

Figure 3.7 Relationship between measured first order rate constant and normalized catalyst loading for (a) ■: CZ82, ●: 0.1Mg/CZ82, ▲: 0.1Ca/CZ82, ▼: 0.1Sr/CZ82, ◄: 0.1Ba/CZ82; and (b) Ce_{0.8}Zr_{0.2}O₂ doped with different amount of Ca.

Figure 3.8 Temperature-programmed oxidation of synthetic coke with and without catalyst.

Reaction conditions: 80 wt.% catalyst in the mixture, 5 K min^{-1} , $100 \text{ cm}^3 \text{ min}^{-1}$ 100 vol.% H_2O , tight contact sample. The peak gasification temperatures are listed in the parenthesis.

To investigate the effect of catalyst/coke mass ratio, samples with different amounts of catalyst were tested for the coke steam gasification. For all of the catalysts tested, the same trend was observed: at low catalyst loadings (total surface area of catalyst per gram of coke $< 20 \text{ m}^2 \text{ g}^{-1}$), the gasification rate was fairly independent of the total surface area of the catalyst (Figure 3.10) whereas at high catalyst loadings (total surface area of catalyst per gram of coke $> 20 \text{ m}^2 \text{ g}^{-1}$), the reaction rate was much lower (not shown in Figure 3.10). These results indicate there is an excess of catalyst present at high catalyst loadings and only a portion of the catalyst participates in the reaction, which is quite analogous to the case with coke gasification with dioxygen. To compare the activity of different catalysts, the average reaction rate at low catalyst loadings (total

surface area of catalyst per gram of coke $< 20 \text{ m}^2 \text{ g}^{-1}$) was calculated to represent the intrinsic rate.

Figure 3.9 Weight loss profile of coke during coke oxidation catalyzed by 0.1Ba/Ce_{0.8}Zr_{0.2}O₂ at 993 K. Reaction conditions: 80 wt.% 0.1Ba/Ce_{0.8}Zr_{0.2}O₂, 100 cm³ min⁻¹ 100 vol.% H₂O, tight contact samples

Figure 3.10 Relationship between measured reaction rate and normalized catalyst loading for Undoped and alkaline earth metal doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ (■: CZ82, ●: 0.05Ca/CZ82, ▲: 0.1Ca/CZ82, ▼: 0.2Ca/CZ82, ◄: 0.1Ba/CZ82). Reaction conditions: 993 K, $100 \text{ cm}^3 \text{ min}^{-1}$ 100 vol.% H_2O , tight contact samples.

Table 3.4 Coke gasification rate with dioxygen and steam over undoped and alkaline-earth-metal-doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$.

Composition of oxides	Rate of coke gasification	Rate of coke gasification with
	with dioxygen at 693 K	steam at 993 K
	($\times 10^{-3} \text{ g}_{\text{carbon}} \text{ m}^{-2} \text{ catalyst min}^{-1}$)	($\times 10^{-2} \text{ g}_{\text{carbon}} \text{ m}^{-2} \text{ catalyst min}^{-1}$)
CZ82	1.6	7.9
0.1Mg/CZ82	0.42	9.1
0.05Ca/CZ82	0.65	13

0.1Ca/CZ82	0.59	13
0.2Ca/CZ82	0.33	18
0.1Sr/CZ82	0.72	14
0.1Ba/CZ82	0.72	15

Table 3.4 summarizes the rate of coke gasification with dioxygen and steam over different undoped and doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$. After the addition of alkaline earth metals, the rate of coke gasification with dioxygen decreased whereas the rate with steam increased. Moreover, with increasing amount of calcium in the mixed oxide, the coke gasification rate with dioxygen decreased while the gasification rate with steam increased. The opposite effect of alkaline earth metals on the two reactions may result from oxidizing potential of O_2 versus H_2O . Coke gasification with dioxygen over Ce-based catalysts involves a redox mechanism.^{37,38} A redox mechanism over Ce-based catalysts is also reported to operate during steam gasification of ethanol³⁹ and methane.⁴⁰ It is likely that the reaction mechanism of coke steam gasification also includes a redox cycle, in which the lattice oxygen reacts with coke to form CO or CO_2 , followed by the replacement of the lattice oxygen vacancy by water. In the presence of alkaline earth metals, a reaction path for steam gasification with dioxygen and steam has been attributed to an oxygen transfer mechanism,^{41–43} with the general reaction sequence as follows:

where C_f is the free carbon site, OM and M are the non-stoichiometric alkaline earth oxygenated compound and the reduced form, respectively. Since the alkaline earth metals are highly dispersed on the surface of $Ce_{0.8}Zr_{0.2}O_2$, the normal redox pathway that is effective for oxidation of coke in the presence of ceria is inhibited by the alkaline earth metals at the surface. At the higher temperature of 993 K, the oxygen transfer mechanism becomes more important, especially in coke gasification with steam.

3.4 Conclusions

Calcination of a mixture consisting of $Ce_{0.8}Zr_{0.2}O_2$ and a nitrate salt of alkaline earth metals resulted in a high dispersion of alkaline earth metals on the surface of $Ce_{0.8}Zr_{0.2}O_2$. The presence of catalyst decreased the peak gasification temperature by 120-170 K with dioxygen and by 30-60 K with steam compared to those without catalyst. The normalized reaction rates on a catalysis surface area basis were obtained from the results of isothermal reaction of samples with different amounts of catalyst. The weight loss of coke in catalyzed coke gasification was first order in coke with dioxygen, but was zero order in coke with steam. The rates of alkaline-earth-metal doped $Ce_{0.8}Zr_{0.2}O_2$ were 20-45% of that with doped $Ce_{0.8}Zr_{0.2}O_2$ in coke gasification with dioxygen. However, the rates of alkaline-earth-metal doped $Ce_{0.8}Zr_{0.2}O_2$ were 115-230% of that with doped $Ce_{0.8}Zr_{0.2}O_2$ in coke gasification with steam. The best catalyst composition among those studied for steam gasification of coke was 0.2Ca/ $Ce_{0.8}Zr_{0.2}O_2$. The opposite effect of alkaline earth metal in the two reactions may be caused by different reaction mechanisms: redox mechanism for Ce-based materials and oxygen transfer mechanism for alkaline earth metals.

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Chapter 4. Conclusions and future work

4.1 Conclusions

The coke gasification with dioxygen and steam over ceria-based materials was investigated in this work, as an attempt to explore the possibility of utilizing ceria-based materials for anti-coking coating materials in steam crackers. In Chapter 2, a method was developed to obtain reproducible kinetics for reactions involving coke using coke gasification with dioxygen over cerium-zirconium mixed oxides as a model reaction. In Chapter 3, the method was applied to coke gasification with both dioxygen and steam to obtain the reactions rates over a series of alkaline-earth-metal-doped cerium-zirconium mixed oxides.

Solid coke was prepared by thermal reaction of ethylene at elevated temperature to mimic the coke formation during steam cracking. The results from XRD, Raman spectroscopy and TEM indicated the coke was mixture of both amorphous and graphitic coke. Cerium-zirconium mixed oxides were obtained by co-precipitation method, follows by the calcination at 1073 K. Solid solutions formed for the Ce-Zr mixed oxides with different compositions. The structure changed from cubic to tetragonal with increasing zirconium content in the mixed oxides. Two factors contribute to the OSC of Ce-Zr mixed oxides: the amount of cerium and the oxygen mobility in the oxides. The compromise of these two factors resulted in the highest OSC exhibited by $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$. Grinding had significant effect on the activity of coke gasification. With increasing grinding time, the rate constant increased first and then kept almost constant. Coke gasification with dioxygen over ceria-based oxides was studied under isothermal tight contact conditions to obtain normalized reaction rates on a catalyst surface area basis. A methodology involving the evaluation of maximum active catalyst surface area has been

developed. The weight loss of coke in catalyzed coke oxidation was first order in coke, which enabled the straightforward calculation of a first order rate constant. When reaction rates were determined in a regime that was strictly proportional to catalyst loading, then $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ was found to be the most active oxidation catalyst. The activation energy over Ce-Zr mixed oxides was about 120 kJ mol^{-1} compared to 150 kJ mol^{-1} of uncatalyzed reaction. The order of dioxygen in coke gasification was between 0.20-0.30. Oxidation of CO was carried out to confirm the method developed. The activation energy of CO oxidation over Ce-Zr mixed oxides was similar to that of coke gasification. The order of reaction in carbon monoxide was close to unity while the order in dioxygen was zero. The coke oxidation rates were very well correlated with CO oxidation rates, but not with oxygen storage capacity or reducibility of the catalyst, indicating that CO oxidation might be a useful probe for the discovery of new coke oxidation catalysts. For coke oxidation, the ratio of catalyst area to coke area in the mixture should be close to unity to maximize rate and catalyst utilization.

The most active catalyst in coke gasification with dioxygen, $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, was doped with alkaline earth metals to improve the activity towards coke gasification with steam. The calcination of a mixture consisting of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and a nitrate salt of alkaline earth metals resulted in a high dispersion of alkaline earth metals on the surface of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$. The coke gasification with dioxygen and steam over alkaline-earth-metal-doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ was performed in both TPO and isothermal reactions. The presence of catalyst decreased the peak gasification temperature by 120-170 K with dioxygen and by 30-60 K with steam compared to those without catalyst. The method developed in Chapter 2 was applied to coke gasification with dioxygen to obtain the reaction rates. However, the order of coke was zero for coke gasification with steam. At low catalyst loadings, the rate of coke gasification with steam was relatively

constant, which could be used to represent the intrinsic rate. The rates of alkaline-earth-metal doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ were 20-45% of that with doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ in coke gasification with dioxygen. However, the rates of alkaline-earth-metal doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ were 115-230% of that with doped $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ in coke gasification with steam. The best catalyst composition among those studied for steam gasification of coke was $0.2\text{Ca}/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$.

In summary, a method to obtain reproducible kinetics was developed for reactions involving coke. The alkaline-earth-metal-doped cerium-zirconium mixed oxide exhibited high activity for coke gasification with steam, demonstrating its potential to be used as an anti-coking coating materials for steam crackers.

4.2 Future work

4.2.1 In-situ coke deposition and gasification over catalysts

As mentioned in Chapter 2, the contact conditions of coke and catalysts have a significant effect on reactivity of coke. During steam cracking, coke is formed on the surface of cracker tube. The contact conditions are different from either tight contact or loose contact conditions. It is desirable to deposit coke on catalyst surface and study its steam gasification activity.

Our collaborators at the Georgia Institute of Technology purchased a customized thermogravimetric analyzer (TGA, NETZSCH, STA449F3 Jupiter®), which enables the feed of hydrocarbon gases, allowing in-situ deposition of coke on catalyst and support samples with excellent coke-catalyst contact¹. The coke deposition on the catalysts and supports, which occurs via a gas phase radical mechanism, depends on the reaction time, temperature, hydrocarbon concentration and sample external surface area but not on the chemical composition of the support under the conditions used. The in-situ generated coke can be compared with ex-situ

formed coke by characterization of Raman spectra and temperature programmed oxidation (TPO) analyses. Thermal aging of coke is shown to be effective in increasing the hardness of the coke samples. Coke deposited in-situ is shown to oxidize similarly to catalyst-coke samples prepared by grinding (tight contact conditions), suggesting that in-situ coke deposition in the TGA can be used to generate samples with realistic coke–catalyst contacting, as might be found in an industrial reactor or catalyst bed.

In-situ coke deposition experiments can be carried out at Georgia Tech with our best catalysts. The kinetics of steam gasification can be studied and compared with tight contact samples prepared by grinding. The stability and sustained decoking performance of the lead catalyst formulations can be tested by consecutive decoking operations with steam in TGA over many cycles. In addition, our collaborators at Georgia Tech are exploring methods to prepare coating with ceria-based materials over metal coupons with similar compositions as the industrial cracker tubes. Once the method is developed, our best catalyst can be coated on the coupon, which will be tested for the inhibition of coke formation during steam cracking conditions.

4.2.2 Water gas shift reaction: A possible probe reaction for steam gasification of coke

In Chapter 2, it was shown that the coke gasification rates with dioxygen correlated well with the CO oxidation rates over cerium-zirconium mixed oxides. It is possible that there is a similar relationship between coke gasification with steam and the water gas shift reaction. If that is the case, the water gas shift reaction could be used as a probe for the screening of coke gasification catalysts.

The water gas shift reaction has been used widely in the manufacturing of ammonia, hydrocarbons, methanol and hydrogen ². There are four general types of water gas shift catalysts.

The first one is chromium-iron oxide catalyst used at temperature range of 623 K to 723 K, which was termed as the high temperature shift catalyst. The second one is low temperature shift catalyst used between 463 K and 523 K, which is a copper-zinc oxide catalyst. The third type of catalyst is a medium temperature shift catalyst used between 548 K and 623 K, which is a copper-zinc catalyst modified with iron oxide. The fourth type is precious metal-based catalyst used at temperatures lower than 523 K. There are few studies on the water gas shift reaction over ceria-based materials or alkaline earth metals, especially at elevated temperature. Boisen et al. studied the water gas shift reaction over 12 transition metals (Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Re, Ir, Pt and Au) supported on MgAl_2O_4 and $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ ³. They observed much higher activity over the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ supported catalysts except for Cu and Au. Alkaline earth metals are typically used as promoters for water gas shift catalysts. Whether or not the alkaline earth metals survive in steam at elevated temperature remains a question. The water gas shift reaction rates evaluated over alkaline-earth-metal-doped cerium-zirconium mixed oxides at elevated temperature can be compared with the rates of coke steam gasification and possibly address the question about the stability of the catalysts.

Reference for Chapter 4

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Appendix A. List of Publications at University of Virginia

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