Rare Earth/Transition Metal Oxides For Syngas Cleanup

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RARE EARTH/TRANSITION METAL OXIDES FOR SYNGAS CLEANUP

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor in Philosophy

in

The Department of Chemical Engineering

by
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ABSTRACT

Syngas from gasification of biomass or biomass and coal is a potential source of renewable energy. However, byproducts such as H$_2$S and tars must be removed before further utilization or processing of syngas. Rare earth oxides (REOs, e.g., Ce/LaO$_x$ (1.7 < x < 2)) mixed with transition metals (e.g., Mn, Fe) were synthesized by various methods, and in some cases supported on a thermally stable alumina. Both desulfurization and tar reforming experiments were conducted at high temperatures under similar conditions with synthetic effluents in order to achieve better heat integration and higher yield to desired products CO and H$_2$. The sulfur capacities at temperatures from 900-1025 K with air regeneration were measured for repeat cycles until a stable, reversible capacity was obtained. The oxidized and sulfided (reduced) sorbents were characterized by XRD, XANES, XAFS, TPR and BET. Density functional theory calculations were used to aid in interpreting characterization data and in explaining the enhanced S adsorption capacities. The results showed that mixed REOs, such as Ce/Tb, and Ce/La synthesized by a templated sol-gel approach do not have high sulfur capacities. The presence of either CO$_2$ or H$_2$O inhibits the adsorption of H$_2$S. However, addition of Mn to REOs effectively increased the sulfur capacity, and Mn-REO sorbents are regenerable even in the presence of air, although there is some sulfate formation. The formation of elemental sulfur during regeneration could be related to the oxygen vacancies promoted by doping Mn into the ceria lattice. DFT calculations suggested doping Mn into CeO$_2$ decreased the vacancy formation energies and lowered the H$_2$S adsorption energy. In contrast, for MnO-doped REOs supported on γ-Al$_2$O$_3$, although their surface areas remained high after multi-cycle usage, the probable formation of MnAl$_2$O$_4$ as observed by XANES reduces the sulfur capacities.

Reforming experiments were carried out using synthetic syngas mixtures with C$_{10}$H$_8$ as a tar model compound, both with and without H$_2$S. The results showed that CO$_2$ and H$_2$O inhibit
the reforming activities to some extent. Fe- or Mn-doped supported REOs are promising tar cleanup catalysts. They exhibited higher sulfur tolerance, less coking, and less methanation than typical Ni-based high temperature reforming catalysts. This behavior is in part attributed to enhanced generation of oxygen vacancies in the doped REOs.
CHAPTER 1: INTRODUCTION

1.1 ENERGY OUTLOOK

In the Annual Energy Outlook 2014 prepared by U.S. Energy Information Administration, total energy consumption will increase by ~60% by the end of 2040 (98 to 162 quadrillion Btu). Liquid, primarily fossil, fuels remain the world’s largest source of energy (>30%, Figure 1.1). However, due to limited fossil resources but increasing fuel demand, oil prices will continue go up, and renewable energy must eventually be exploited to replace traditional fossil fuels.

![Figure 1.1 World market energy consumption from different fuel sources.](image)

1.2 LIQUID FUEL PRODUCTION

There are several ways to produce liquid fuels from non-liquid sources, such as coal to liquid (CTL) and gas to liquid (GTL). An example CTL process is direct coal liquefaction, a hydrogenation process proceeding under medium-high temperature and high pressure (20 – 70
MPa). GTL refers to syngas from CH$_4$ or coal and/or biomass gasification converted to liquid fuels by means of (e.g.) the Fischer Tropsch process. The projections for CTL and GTL production are sensitive to world oil prices, as shown in Figure 1.2.

Figure 1.2 (a) Brent crude oil spot prices for three cases, 1990-2040 (2011 $/bbl); (b) World production of liquids from biomass, coal, and natural gas for the three cases, 2011 and 2040 (MMbbl/d)$^1$ (reprint permitted)
1.2.1 Direct Coal Liquefaction

Direct coal liquefaction (DCL) technology is a process for converting coal to liquid fuels by dissolving coal in an organic hydrogen donor solvent in the presence of hydrogen and a catalyst under high temperature and pressure. One drawback of this process is the formation of 7 – 20% low value heavy residue, whose likely disposal would adversely impact the environment.\(^2\)\(^3\)

1.2.2 Fast Pyrolysis

Pyrolysis is the thermal destruction of biomass in the absence of air/oxygen. A higher yield of desirable liquid product can be obtained by fast pyrolysis at ~300 K/min temperature ramp to 723 - 873 K. However, the predominantly liquid product bio-oil has high viscosity, oxygen content, and corrosiveness, along with poor thermal stability. Considerable research has been carried out to upgrade pyrolysis products, but large-scale commercial technology is still under investigation.\(^4\)

1.2.3 Biomass GTL

Unlike coal, biomass is not limited by geological region and its utilization has drawn great research interest. There are many ways other than fast pyrolysis to convert biomass to liquid fuels. Plant oils can be physically extracted and purified to generate biodiesel, or biomass aqueous slurries can be biochemically fermented to ethanol. Gasification is another way to utilize biomass, by converting it to syngas at high temperature with a gasifying agent (air, steam, CO\(_2\) or a mixture). The product syngas can be further converted by the methanol, dimethyl ether or Fischer-Tropsch (to ethanol or liquid hydrocarbons) processes. A schematic diagram of an updraft fixed bed oxi-gasifier is presented in Figure 13. Biomass enters from the top while the gasifying agent enters from the bottom. The sensible heat of the product raw gas (typical
temperature \(>923 \text{ K}\) is used to dry the fuel and to initiate pyrolysis and gasification. In this manner, the raw gas is cooled to temperatures in the ranges necessary for further catalytic syntheses. However, syngas from gasification usually contains a considerable amount of tars (heavy hydrocarbons), nitrogen and sulfur compounds and other contaminants which must be dealt with prior to the synthetic processes.

![Schematic diagram of an updraft gasifier](image)

Figure 1.3 Schematic diagram of an updraft gasifier.

### 1.3 MAIN RESEARCH QUESTION

The syngas contaminants such as tars and sulfur compounds can pose severe problems for downstream processes. The most important sulfur contaminant \(\text{H}_2\text{S}\) can deactivate downstream catalysts (both water-gas shift and Fischer-Tropsch), while the tars can do the same and also block downstream pipelines and deposit on downstream equipment. Therefore, it is necessary to reduce these contaminants considerably. As further discussed in Chapter 2, cost-
effective cleanup operations are still not available. A need exists for the development of more efficient adsorbents for cyclic desulfurization and regeneration over many cycles and at higher temperatures. A further need exists for tar reforming catalysts with better sulfur resistance at reasonable temperatures (i.e., nearer to those of the gasifier) than Ni-based catalysts, and better coking resistance in lower steam-to-carbon ratio feeds.
CHAPTER 2: LITERATURE REVIEW

2.1 COAL/BIO MASS GASIFICATION: EF FLUENT CHARACTERISTICS AND BYPRODUCTS

Gasification is a process to convert carbonaceous fuel, such as coal, biomass, petroleum, etc., to gaseous products with a gasifying agent. It includes the technologies of partial oxidation, steam reforming, pyrolysis, and oxypyrolysis. The gaseous products depend on the carbonaceous fuel composition, gasification agent and reaction conditions, but consist primarily of a mixture of hydrogen, carbon monoxide, carbon dioxide, water, nitrogen, and other byproducts such as H$_2$S, tar, halides and NH$_3$.

Gasification of coal has a long history dating back to the industrial revolution but still draws a lot of interests due to coal’s abundance. Typical gas compositions of an O$_2$-blown gasifier are (vol %) 28-32% H$_2$, 33-39% CO, 13-28% CO$_2$, 18-24% H$_2$O, 0.2-1% H$_2$S, and 0-3.2% N$_2$.\textsuperscript{5,6} Typical gas compositions of an air-blown gasifier are (vol %) 12-14% H$_2$, 10-23% CO, 6-15% CO$_2$, 7-10% H$_2$O, 0.08-0.5% H$_2$S, and 50-60% N$_2$.\textsuperscript{6,7}

As a renewable resource, biomass now contributes about 14% of the world’s total energy supply with 25% of the total biomass energy usage in developed countries and 75% in developing countries.\textsuperscript{8,9} The elemental composition of typical biomass feedstocks is 35-53% C, 5-6% H, 32-43% O, 0.1-1.4% N, 0.02-0.5% S and 0.01-0.08% Cl.\textsuperscript{10} The four major chemical components of biomass are cellulose, hemicellulose, lignin and extractives; of these the first three are polymers and account for most of the total mass.\textsuperscript{11} The composition of the biogas from a gasifier depends upon fuel composition, gasifying agent, temperature, pressure and space velocity.\textsuperscript{12} The gasifying agents include air, pure O$_2$, steam, CO$_2$ and mixtures. Air, since it contains N$_2$, lowers the heating value of the syngas produced, while utilization of pure O$_2$ increases the operating costs. If steam is used as the gasifying agent, the H$_2$ content of the syngas
can be increased, which increases the heating value. The use of CO₂ as the gasifying agent with a catalyst can transform products such as CH₄, char and tar into H₂ and CO.¹³⁻¹⁵ Since gasification with CO₂ or H₂O needs an external heat source while gasification with O₂ is exothermic, a mixture of CO₂ and O₂ or H₂O and O₂ can also be used; this is called “autothermal” or oxidative steam reforming.¹⁶ Typical effluent gas compositions of an oxygen-blown biomass gasifier are (vol%) 15-21% H₂, 7-15% CO, 17-24% CO₂, 31-50% H₂O, 0.0002-0.02% H₂S, 0-0.3% NH₃ and 0-0.4% N₂.¹⁰,¹⁷,¹⁸ Typical gas compositions of a steam-blown biomass gasifier are (vol%) 11-23% H₂, 15-19% CO, 11-13% CO₂, 7-46% H₂O, 0.0002-0.02% H₂S, 0-0.3% NH₃ and 0-0.4% N₂.¹⁰,¹⁹ Typical gas compositions of an air-blown biomass gasifier are (vol%) 12-17% H₂, 10-17% CO, 11-19% CO₂, 7-19% H₂O, 0.0002-0.02% H₂S, and 37-53% N₂.¹⁰,²⁰

2.1.1 Allowable Sulfur Levels for Various Syngas Applications

Sulfur in the biomass feedstock is primarily converted to hydrogen sulfide (H₂S), along with some carbon disulfide (CS₂), mercaptans (CH₃SH and CH₃CH₂SH), thiophene (C₄H₄S), carbonyl sulfide (COS) and elemental sulfur (Sₓ) during gasification.²¹

H₂S is detrimental to turbines, downstream catalysts, and fuel cell anodes. Besides, there is environmental regulation for sulfur discharge, requiring less than 50 ppmv released to the atmosphere.²² Table 2-1 lists the allowable levels for various syngas applications.

2.1.2 Allowable Tar Levels from Biomass/coal Gasification

Other byproducts of biomass or coal gasification include tars, which are defined differently by various research groups. In the EU/IEA/US-DOE meeting on tar measurement protocol (Brussels, 1998), it was agreed to define tars as all organic contaminants with a molecular weight larger than benzene.²³ Another commonly accepted definition is the
condensable fraction of organic gasification products, largely consisting of aromatic compounds, such as benzene, toluene, and naphthalene.\textsuperscript{24,25}

Table 2-1 Sulfur levels for various syngas applications

<table>
<thead>
<tr>
<th>application</th>
<th>allowable sulfur</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia synthesis</td>
<td>&lt;0.1 ppmv</td>
<td>26</td>
</tr>
<tr>
<td>methanol synthesis</td>
<td>&lt;0.1 ppmv</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>&lt;0.5 ppmv</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>&lt;1 ppmv</td>
<td>21</td>
</tr>
<tr>
<td>solid oxide fuel cell</td>
<td>&lt;1 ppmv</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>&lt;9 ppmv</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>&lt;60 ppb</td>
<td>30</td>
</tr>
<tr>
<td>phosphoric fuel cell</td>
<td>&lt;50 ppmv</td>
<td>28</td>
</tr>
<tr>
<td>molten carbonate fuel cell</td>
<td>&lt;0.5 ppmv</td>
<td>31</td>
</tr>
<tr>
<td>Fischer-Tropsch</td>
<td>&lt;1 ppmv</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>&lt;60 ppb</td>
<td>33</td>
</tr>
<tr>
<td>gas turbines</td>
<td>&lt;100 ppmv</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>&lt;750 ppmv</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>&lt;20 ppmv</td>
<td>30</td>
</tr>
</tbody>
</table>

Depending on the type of reactor and gasification conditions, the tar content from biomass gasifiers usually varies from 1200-75000 mg/Nm\textsuperscript{3} (gas volume, 1000 mg/Nm\textsuperscript{3} = 175 ppmv for naphthalene) and a typical tar consists of (wt%) 9-39% benzene, 7-24% naphthalene, 12-48% toluene, 6-10% heterocyclics, 4-7% phenolics, 0.8-1% four-ring PAHs, 3-6% three-ring PAHs, and 5-13% other two-ring PAHs.\textsuperscript{35-45} Tars from coal gasification contain (wt%), 40-44% toluene, 0-14% one-ring aromatics (xylenes, styrene, ethylbenzene), 8%-13% naphthalene, 10-12% two-ring PAHs (indene, dibenzofurans, methylnaphthalene), 0-7% three ring PAHs, and 0-8% 4-6 ring PAHs.\textsuperscript{36,46} Tars can cause several problems, such as cracking the pores of filters and blocking downstream pipelines. High concentrations of tars can damage engines and turbines. Tars also have detrimental effects on the life cycle and operational characteristics of a fuel cell by depositing carbon on the anode.\textsuperscript{47} Tar tolerance limits for various end uses are 50-500
mg/Nm$^3$, 50-100 and 5 mg/Nm$^3$ for compressors, internal combustion systems, and direct-fired industrial gas turbines, respectively.$^{48}$ The tar tolerance level for a solid oxide fuel cell is $\sim$5000 mg/Nm$^3$, and tars can be partially converted to light hydrocarbons without condensation on the nickel anode.$^{47}$ The impact of tars on the Fischer-Tropsch catalysts is not well studied, but it is claimed that tars cannot poison the catalyst as long as they are not condensing.$^{49}$

### 2.1.3 The Role of Syngas Cleanup in Biomass or Biomass/coal Gasification

Tars can be removed from gasifier effluents by physical methods, thermal cracking or catalytic conversion. Physical methods such as filtration and liquid scrubbing require significant heating and cooling steps, imposing higher treatment costs. Thermal cracking requires temperatures ($>1373$ K) higher than biomass gasification temperatures.$^{50}$ Compared to physical separation methods which only remove the tars from the gas phase, catalytic conversion of tar at $873-1173$ K increases the yield of useful products and net carbon conversion efficiency. Catalytic conversion can also avoid using more expensive materials for high temperature reactors and additional heat exchangers, since biomass gasification processes would operate at a temperature range similar to that of the catalysts. Removal of H$_2$S at high temperatures from both biomass and coal gasification is also a critical step toward better process economics and heat integration.$^{51}$

The expense of syngas cleanup and conditioning represents roughly 70% of the conversion and processing costs of (e.g.) ethanol.$^{52}$ Figure 2.1 shows the importance of gas cleanup and conditioning to a gasification process. If the cleanup operates at high temperature ($>873$ K), there is a $\sim$3% gain in overall thermal efficiency, where thermal efficiency is defined as the ratio of net work done to the heat content of the fuel that is consumed.$^{53,54}$
2.2 DESULFURIZATION

High temperature (> 873 K) desulfurization techniques have received a great deal of attention since they are capable of reducing H₂S down to sufficiently low levels while at the same time saving a lot of energy.⁵⁵-⁵⁷ General requirements for metal oxide sorbents are summarized as follows:⁵³ (1) large equilibrium constant and fast kinetics for the sulfidation reaction; (2) high selectivity towards sulfur capture to minimize side reactions; (3) resistance to reduction by H₂ in order to preserve the fuel or chemical value of the biogas; (4) high mechanical stability to minimize mass losses by attrition; (5) good regeneration capability.

Figure 2.1 Economics for biomass gasification / cleanup / Fischer-Tropsch processes to produce ethanol (U.S. DOE, 2009).
Zeolites are good sorbents only at low temperatures.\textsuperscript{58} At 873 K with a gas mixture containing 1.06\% H$_2$S in helium, the sorption capacity of sulfur was about one third of a Cu-based sorbent.\textsuperscript{58}

Eleven candidate oxides based upon the metals Fe, Zn, Mo, Mn, V, Ca, Sr, Ba, Co, Cu, and W show thermodynamic feasibility for high temperature desulfurization.\textsuperscript{59} ZnO exhibits favorable sulfidation thermodynamics and kinetics at temperatures from 673 to 973 K.\textsuperscript{21} At >773K with reducing gases, ZnO is reduced to metallic Zn which is partly lost by evaporation.\textsuperscript{60,61} Zinc ferrite was also developed but was limited to a maximum temperature of 823 K for desulfurization due to the chemical transformation to ZnO followed by evaporation of metallic zinc.\textsuperscript{61,62} The addition of Ti to zinc ferrite prevented its decomposition and stabilized the structure at up to 873 K.\textsuperscript{63} Compared with ZnO, zinc titanates are even more resistant to reduction, with a higher possible operating temperature (~973 K), but the sulfur capacity is about half of the ZnO.\textsuperscript{64}

CaO is thermodynamically favorable at temperatures around 1273 K.\textsuperscript{59} But at temperatures below 1073 K, CaCO$_3$ was formed in the presence of CO$_2$, decreasing the sulfur capacity. COS, H$_2$ and CO also hindered the reaction between CaO and H$_2$S.\textsuperscript{65} Furthermore, regeneration of CaS needs to be done at temperatures higher than 1373 K to avoid the formation of CaSO$_4$, which is the main product at lower temperature.\textsuperscript{66}

2.2.1 Mn-based Sorbents

Of the oxides studied by Westmoreland and Harrison (1976), the Mn-based sorbent exhibited the highest initial reaction rate with H$_2$S in the temperature range 573-1073 K. For a simulated syngas mixture (30\% CO, 20\% H$_2$, 49\% N$_2$ and 1\% H$_2$S), Mn-based sorbents exhibited 100\% oxide utilization and the highest sulfur capacity.\textsuperscript{67} In a gasifier atmosphere,
Mn₃O₄ is readily reduced to MnO, but MnO cannot be further reduced at temperatures below 1923 K.⁶⁸ Manganese sulfate, formed during air regeneration, is stable below 1073 K.⁶⁹

With an Al₂O₃ support under reducing conditions, MnAl₂O₄ can be formed. TGA studies found that MnAl₂O₄ could not be fully sulfided except at temperatures above 1073 K.⁵³ Also, the unsupported MnOₓ adsorbs more H₂S, even in the presence of water.⁵³ Still, Turkdogan et al. (1979) examined MnOₓ supported on alumina (3:1 by weight) and found that it could readily capture sulfur and be regenerated with air at 1073 K (0.2 mmol-S/g-sorbent).

Wakker et al. (1993) studied MnOₓ/γ-Al₂O₃ at 873 K with a syngas mixture (17% H₂, 35% CO, 0.64% H₂S and 2.1% H₂O) for more than 300 cycles and found that most of the deactivation occurred in the first ten cycles, from 0.46 to 0.15 mmol/g-sorbent. Sulfur capacity increased with temperature from 0.19 to 2.0 mmol/g-sorbent (two-cycle average) from 703 K to 1073 K with a simulated gas mixture containing 17% H₂, 35% CO, 0.64% H₂S, 2.1% H₂O in argon.⁵³ A high Mn loading (36 wt%) is the reason for high sulfur retention.

To avoid the formation of manganese sulfate during regeneration, several alternative regeneration strategies have been proposed.⁷⁰ Regeneration with SO₂ is feasible at 873 K, forming an elemental sulfur product.⁵³ Steam regeneration can also prevent the formation of MnSO₄, and reduce hot spots, which can cause sintering. However, steam regeneration cannot replace completely the oxidative regeneration process, and it is slow, about two times slower than even SO₂ regeneration.⁷¹ Regeneration with diluted air at temperatures higher than 1073 K can decompose sulfate, however, the capacity decays progressively due to sintering.⁷² Regeneration with H₂ was also studied for sulfided MnO and MnO/SiO₂ sorbents. Pure MnSO₄ could only be decomposed at 1093 K in 10% H₂, while silica-supported, sulfated MnO was
regenerated at 933 K. Different regeneration strategies have also been tested using CO₂, diluted air, and diluted air in combination with water; regeneration with CO₂ was ineffective.

Among other common supports, TiO₂ is the worst due to conversion of TiO₂ from anatase to rutile, while γ-Al₂O₃ is the best. MnO eventually reacts with SiO₂, to become inactive for sulfur adsorption.

Manganese-copper mixed sorbents were investigated at 873 K with simulated syngas containing 10% H₂, 15% H₂O, 5% CO₂, 15% CO, balance N₂. Cu could not be completely stabilized by Mn and was partially reduced. Both MnS and Cu₂S were observed by XRD studies. Regeneration with diluted air at temperatures of 1073 K or more avoided the formation of sulfates. As the copper content increased, the porosity decreased due to sintering. Similar results that the presence of Cu in Mn-based sorbents lowered the H₂S concentration in the outlet gas were also obtained with Mn-Cu mixed oxides for a gas mixture containing 1% H₂S and 10% H₂ in helium at 900 K. But the sulfur retention capacity (4.6 mmol S/g-sorbent) decreased by 90% after six cycles due to both sintering and sulfate formation. Purging with pure nitrogen led to partial decomposition of sulfates at 973 K. Caglayan et al. (2006) found that a Mn-Fe-Cu sorbent could be sulfided (2.1 mmol S/g-sorbent) at 873 K with a gas mixture containing 1% H₂S, 10% H₂ in He and regenerated at 973 K with diluted air. Some elemental sulfur was formed during regeneration.

Mn-Ce mixed oxides (Ce/Mn=1:3) were used for desulfurization at 873 K with a gas stream containing 2.5% H₂S, 10% H₂ and 87.5% He. The sorbent had a much higher sulfur capacity (3.5 mmol S/g-sorbent) than pure CeO₂ and maintained its high capacity even after ten cycles. Sulfur retention was apparently due to the Mn in the mixed sorbent; there was no Ce₂O₃S found. CeO₂ was believed to inhibit the formation of MnSO₄ and improve the regenerability of
Mn; 90% of the sulfur adsorbed during sulfidation was converted to elemental sulfur during regeneration with diluted air at 973 K.

In addition, the fact that MnO\textsubscript{x} does not form carbonates in a CO\textsubscript{2} atmosphere at temperatures higher than 873 K suggests that MnO\textsubscript{x} - oxide mixtures are promising for desulfurization of syngas containing some CO\textsubscript{2}.\textsuperscript{78}

### 2.2.2 Cu-based Sorbents

Copper oxide-based sorbents could decrease H\textsubscript{2}S concentration to sub-ppm levels according to equilibrium calculations.\textsuperscript{79} But the sulfidation reactivity of pure CuO is lower than that of supported CuO, and this is attributed its low surface area and the formation of a dense sulfide layer.\textsuperscript{80} Another problem with CuO is the formation of metallic copper under a reducing environment; the sulfidation equilibrium constant of CuO is higher than that of metallic copper.\textsuperscript{81} Therefore, CuO can be the active sorbent material, but with additives to retard the reaction of CuO to Cu in a reducing atmosphere.

CuO\textsubscript{x} with MnO reduced sulfur levels below 30 ppmv at 923 K with a syngas mixture containing 47.07% N\textsubscript{2}, 27.3% H\textsubscript{2}, 14.3% CO\textsubscript{2}, 10.4% CO, and 0.93% H\textsubscript{2}S.\textsuperscript{82} CuO-Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}, CuO-Fe\textsubscript{2}O\textsubscript{3}, and CuO-Al\textsubscript{2}O\textsubscript{3} have been investigated as sorbents for desulfurization at 811-923K with a gas mixture containing 20% H\textsubscript{2}, 25% H\textsubscript{2}O, 1% H\textsubscript{2}S and balance N\textsubscript{2}.\textsuperscript{83} CuO-Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} (3.8 mmol S/g-sorbent) was found to be superior to the other two, yielding low H\textsubscript{2}S levels (~40 ppmv at breakthrough). But CuO/Al\textsubscript{2}O\textsubscript{3} has a problem with sulfate formation during oxidative regeneration, and the results also suggest stepwise reduction of copper from 2+ to 1+ to the 0 (inactive) oxidation state.

Cr\textsubscript{2}O\textsubscript{3} has been reported to retard the reduction CuO to metallic Cu, and CuO-3Cr\textsubscript{2}O\textsubscript{3} (1.3 mmol S/g-sorbent), exhibiting better stability and sulfur capacity at temperatures below 923 K
with a gas mixture containing 0.5% H₂S, 10% H₂, 10% H₂O, and balance N₂.⁷⁹ Though the stability of CuO-3CeOₓ (0.68 mmol S/g-sorbent) is relatively low, this mixture also improves the sulfidation efficiency (fraction of active metal converted to the sulfide) and the sulfur capacity is higher than either single oxide, at both low and high temperatures.⁷⁹ XRD confirmed the formation of both Ce₂S₃ and CuSₓ in a used CuO-CeOₓ sorbent. It was found that a greater surface reduction of cerium oxide at a given temperature (20% more at 923 K) and better Cu dispersion contributed to the higher sulfur capacity.⁸⁴

### 2.2.3 Fe-based Sorbents

Iron sorbents are low cost materials and they have also received considerable attention. In gases mainly consisting of CO and H₂, almost all Fe₂O₃ is reduced to metallic iron before it reacts with H₂S.⁸³ For 45 wt.% Fe₂O₃ and 55 wt.% SiO₂, the iron oxide was rapidly reduced to metallic iron, which then reacted with H₂S. A form of pyrrhotite (Fe₁₋ₓS) was formed.⁸³ For sulfur removal at 973 K (1% H₂S, 30% CO, 20% H₂ and 49% N₂) with Mn, Fe, Cu, Co and Zn oxides supported on γ-Al₂O₃, the sulfur capacity of iron was second to that of manganese.⁶⁷ However, the experiment was flawed due to the lack of CO₂ in the syngas, since FeCO₃ can form at up to 1273 K under certain CO₂ partial pressures.⁷⁸ Also, calcination and repeated regeneration of Fe/Al sorbents leads to partial formation of FeAl₂O₄, which does not react with H₂S.⁸⁵

While Fe-Zn mixed oxides form ZnFe₂O₄ at temperatures below 773 K, it decomposes to constituent oxides above 773 K, leading to zinc vaporization.⁶¹,⁶² Fe-Mo mixed oxides supported on fly ash showed high sulfur capacity (4.3 mmol/g-sorbent) at 773 K with a gas mixture containing 40% H₂, 32% CO, 19% CO₂, 0.51% H₂S in N₂.⁸⁶ Addition of Mo slightly improved the sulfur capacity of the iron sorbent but lowered the pre-breakthrough value a lot. Regeneration of the Fe-Mo sorbents was not studied, however.
Both O\(_2\) and SO\(_2\) have been studied for regeneration of iron sorbents in the temperature range 873-1173 K\(^{87,88}\). Oxygen oxidizes FeS\(_x\) to Fe\(_2\)O\(_3\) primarily, with release of SO\(_2\), while SO\(_2\) reacts with FeS\(_x\) to form Fe\(_3\)O\(_4\) primarily, with release of elemental sulfur. White et al. further studied the regeneration of FeS\(_x\) using a steam-O\(_2\) mixture. With H\(_2\)O only, all sulfur was converted to H\(_2\)S; with O\(_2\) and H\(_2\)O, H\(_2\)S, SO\(_2\) and elemental S were observed. Temperatures, flow rates and steam to oxygen ratio affected the yield of elemental sulfur, the maximum being ~75% of the theoretical.\(^{87}\) Other experimental observations reported considerable elemental sulfur yields, larger than the maxima predicted from equilibrium thermodynamics.\(^{89}\)

### 2.2.4 V-based Sorbents

Sulfidation of V\(_2\)O\(_3\) is thermodynamically favorable at high temperatures, but is kinetically slow.\(^{90}\) At 923-973 K, H\(_2\)S was strongly but reversibly adsorbed on a nonstoichiometric reduced form of vanadium oxide. As much as 0.42 mol H\(_2\)S was absorbed per mol catalyst, and the amount of sulfur adsorbed could be reduced up to one fourth of the capacity with nitrogen purge.\(^{90}\) A lower sulfur capacity was observed upon addition of 7 mol% H\(_2\)O in the feed gases, because H\(_2\)O competed with the adsorption of H\(_2\)S on the surface.\(^{90}\)

The sulfur capacity was smaller with Cu-V mixed sorbent than with CuO alone with a gas mixture (10% H\(_2\), 1% H\(_2\)S, balance He).\(^{81}\)

### 2.2.5 Rare Earth Oxide (REO)-based Sorbents

Cerium oxide in its higher oxidation state (4+) does not react with H\(_2\)S.\(^{91}\) However, given its redox properties and the high mobility of its capping surface oxygens, it can still adsorb sulfur. Its thermal stability is good up to 1273 K when doped with other REOs, and all adsorbed sulfur can be rapidly recovered in the elemental form through regeneration with SO\(_2\).\(^{92}\)
desulfurization reactions under a reducing environment and during regeneration with O₂ and SO₂ are listed below, according to phase diagrams.\(^{93}\)

\[
\begin{align*}
2\text{CeO}_2 (s) + \text{H}_2\text{S} (g) + \text{H}_2 (g) & \rightarrow \text{Ce}_2\text{O}_5\text{S} (s) + 2\text{H}_2\text{O} (g) \quad (2-1) \\
2\text{Ce}_2\text{O}_5\text{S} (s) + 2\text{O}_2 (g) & \rightarrow 4\text{CeO}_2 (g) + \text{S}_2 (s) \quad (2-2) \\
\text{Ce}_2\text{O}_5\text{S} (s) + \text{SO}_2 (g) & \rightarrow 2\text{CeO}_2 (s) + \text{S}_2 (s) \quad (2-3)
\end{align*}
\]

The capability of storing oxygen under oxidizing conditions and releasing oxygen under reducing conditions (at similar temperature) is termed oxygen storage capacity (OSC). A good way to increase the OSC of pure CeO₂ by a factor of 3 to 4 is to dope it with other REOs. The introduction of dopants disrupts the fluorite lattice and induces the formation of structural defects associated with oxygen vacancies, which increase the mobility of oxygen both at the surface and in the bulk.\(^{94-98}\)

CeO₂ sorbents with different surface areas (42 and 3 m²/g) were studied at a temperature range from 773-1073 K with a gas mixture containing 1000 ppmv H₂S, balance N₂.\(^{99}\) The one with high surface area performed better for sulfur removal (0.3 mmol S/g-sorbent). A rapid sulfidation occurred at temperatures from 773 to 873 K with low pre-breakthrough (~20) ppmv H₂S levels, while sulfidation at temperatures from 973 to 1073 K showed poor kinetics. Addition of ZrO₂ to ceria forms a solid solution, increases the oxygen mobility within the CeO₂ crystal lattice and the reducibility of ceria, and suppresses sintering.\(^{100}\) Ce\(_x\)Zr\(_{1-x}\)O₂ had a higher sulfur capacity (0.008 mmol S/g-sorbent) than CeO₂ at 973 K with a gas mixture containing 10% H₂, 88.75% N₂, 0.25% H₂S and 1% CO₂.\(^{101}\) Ce\(_x\)Zr\(_{1-x}\)O₂ has also been applied to the Claus process and found to increase the conversion of H₂S and SO₂ to elemental sulfur, compared with just CeO₂.\(^{89}\)
La$_2$O$_3$ also has a high affinity for H$_2$S over a wide temperature range, and the sulfur capacity of pure La$_2$O$_3$ was 0.025 mmol S/g-sorbent for a reacting gas of 0.1% H$_2$S, 20% H$_2$, 20% CO, 1% CO$_2$, 10% H$_2$O and balance He at 1073 K with a space velocity of 40000 h$^{-1}$. Regeneration was carried out at the same conditions with the same gas mixture, excluding H$_2$S. Desorption of H$_2$S was rapid from 923 to 1073K. As the concentration of La$_2$O$_3$ in CeO$_2$/La$_2$O$_3$ increased, the surface area decreased, but between 30 and 70 at% La$_2$O$_3$ sorbents, the 70 at% sorbent had the higher initial capacity (0.0375 mmol S/g-sorbent), also higher than either pure ceria or lanthana. Only 4% surface area was lost after 15 cycles. Further studies on the effects of the gas mixture found that substituting H$_2$ and H$_2$O, respectively, for CO and CO$_2$ had no effect on the sulfur capacity. Dooley et al. found that the sulfur capacity of mixed Ce/La oxides can be increased by addition of dopants such as Tb or Gd or addition of similar amounts of Mn or Fe. La$_2$O$_3$ was also used to reduce the spalling of zinc titanate, but was then found to be a major reactant in the desulfurization itself. However, La$_2$(SO$_4$)$_3$ was observed by XPS in the regenerated sorbents.

Pr-doped La$_2$O$_3$ (~1.56 mmol/g-sorbent) was tested at 1073 K with a gas mixture containing 70% H$_2$, 250 ppm H$_2$S, 5% H$_2$O, balance He. The pre-breakthrough of H$_2$S was ~1 ppmv, and the corresponding oxycarbonates were rapidly sulfided at such high temperature. Further studies were carried with 13 ppmv COS addition to the same stream at the same temperature. COS did not inhibit the adsorption of H$_2$S, and both were adsorbed simultaneously. Rare earth oxides were also found to be very effective for hydrolysis of COS at temperatures from 473-573 K. Fe-Mn-Ce is structurally stable and has a higher COS capacity than does Fe-Mn sorbent at temperatures around 573 K.
Bulk sulfidation of pure REOs is not recommended due to large structure changes during regeneration which decreases the cyclic performance.\textsuperscript{102}

**2.2.6 The Effects of Impurities on Sulfur Sorbents**

The effects of chlorine have been studied for different sorbents. The presence of 0.5-1\% HCl in the feed gas reduced the H\textsubscript{2}S breakthrough capacity of Mn supported on a γ-Al\textsubscript{2}O\textsubscript{3} sorbent by 30-40\%.\textsuperscript{108} The deactivation by HCl was found to be reversible during regeneration. In the presence of 0.2\% HCl, the sorption capacities of Co- and Ni-doped zinc titanate at 923 K were not affected.\textsuperscript{109} But for desulfurization at 923 K with a ZnO/TiO\textsubscript{2} sorbent, it was claimed that the sulfur capacity increased significantly with increasing HCl concentrations.\textsuperscript{110}

Depending on the type of biomass used, as well as the gasifier parameters and operating conditions, the content of NH\textsubscript{3} is about 1000-5000 ppmv.\textsuperscript{111} The effect of NH\textsubscript{3} has not been investigated enough, and may vary with sorbents. But existing evidence is that NH\textsubscript{3} is less of a problem. For example, adding 0.5\% ammonia in the regeneration gas stream actually prevents sulfate formation in manganese ore.\textsuperscript{70} Fe catalysts were reported to be effective for NH\textsubscript{3} decomposition at high temperatures in a reducing environment, but without H\textsubscript{2}S.\textsuperscript{112}

**2.3 FORMATION AND REMOVAL OF TARS**

Numerous investigations have been made to uncover the mechanisms of biomass/coal gasification over the last 40 years.\textsuperscript{113} However, the Boudouard reaction, steam reforming, dry reforming and oxidation are not simple reactions; the products can react with each other, with the gasifying agent and with deposited carbon and tars.\textsuperscript{113}
2.3.1 Reactions in Tar Gasification

Many reactions are involved in gasification of tars, including steam reforming to CO and H₂, hydro/thermal craking to light hydrocarbons, and the water gas shift (WGS) reaction. Wu et al. studied tar pyrolysis in the presence of CO₂, H₂O or O₂ and found out that the primary products are H₂ and CO, and tar conversion increased with CO₂ or H₂O feed rates. Both CO₂ and H₂O served as oxidants.

\[
\text{Tar} + \text{H}_2\text{O (CO}_2) \rightarrow \text{CO} + \text{H}_2
\]

Simell et al. studied gasifying agent effects on toluene decomposition in empty tubes and with Ni/Al₂O₃ and found that toluene decomposed at roughly the same rate in two H₂ containing (H₂, or H₂ and H₂O) atmospheres, but at a much lower rate in others (H₂O, CO₂, CO₂ and H₂O). The picture was more complex with Ni/Al₂O₃, with H₂, CO or N₂ best in decomposing toluene. Both results show that hydrocracking is a primary reaction, but oxidation reactions are competitive with hydrocracking in the catalytic process (in the case of CO producing carbon). The benzene yield with a H₂ and H₂O containing feed was lower than with a pure H₂ feed, indicating steam reforming can take place after hydrocracking. Hydrocracking is the way CH₄ and other light hydrocarbons are produced hydrocracking.  

\[
\text{Tar} + \text{H}_2 \rightarrow \text{C}_n\text{H}_m
\]

The reversible WGS is another major reaction, especially in downstream operations, such as H₂ production or H₂/CO ratio regulation.  

\[
\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_{298\text{ K}} = -41.5 \text{ kJ/mol}
\]

Coke deposition takes place on many catalysts due to the Boudouard and related reactions. The different tar compounds have different effects on coking. The minimum S/C
ratio needed to avoid coking increases as follows: toluene < naphthalene < pyrene, using the same catalyst under the same reaction condition.43

2.3.2 Catalyst Deactivation

Catalysts could be deactivated due to both carbon deposition and sulfur poisoning. Aznar et al.40 studied tar conversion using Ni/MgAl₂O₄. The catalyst started to deactivate after 1 h and tar conversion decreased from 100% to 30% after 3 h, with CH₄ in the outlet also increasing significantly. Sulfur also negatively impacts tar removal. With H₂S addition to the feed, the activity for toluene conversion decreased (Table 2-2, line 7), and the selectivity to benzene increased to 40% after 1 h.121 Sulfur poisoning at the lower temperatures is irreversible but less so at high temperature.122-126

Monometallic Ni-based catalysts usually experience rapid deactivation caused by carbon deposition10,114,124,127 The coke formation was less severe at high temperature (> 1073 K).40 However, a high temperature for Ni is not desirable due to permanent catalyst deactivation by sintering and phase transformation. An alternative way to inhibit coking is to add promoters to a Ni-based catalyst. For example, Bampenrat et al.128 found the addition of Mn to Ni/CeO₂ could reduce the coking rate by an order of magnitude. Almost no carbon was deposited on the surface with CeO₂- or Ca₁₂Al₁₄O₃₃-supported Ni catalysts.121,129 High steam to carbon ratios (SCR) can also alleviate coke formation on a Ni-based catalyst. However, from the industrial point of view, it is often preferred to operate at low SCR, because the H₂/CO ratio in the product is higher (close to 3/1), while the formation of CO₂ by WGS is kept at a low level. Also, the energy consumption to vaporize excess water and heat it to reaction temperature is reduced.120,130
2.3.2.1 Model compounds for tar removal

Heptanes, benzene, toluene, naphthalene, and 1-methylnaphthalene have all been used as model compounds for catalytic tar removal in beds downstream from the gasifier (the “secondary” method). In the presence of Ni-based catalysts, the activity for steam reforming of naphthalene at ~1073 K is less than benzene, toluene, anthracene and pyrene. Therefore naphthalene was claimed to be the most suitable tar model compound.

Table 2-2 Details of catalytic conditioning studies for tar removal

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Feed</th>
<th>T (K)</th>
<th>GHSV</th>
<th>tar</th>
<th>Tar (ppmv)</th>
<th>Conversion</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Mo/Al₂O₃</td>
<td>N₂/H₂</td>
<td>823</td>
<td>3000</td>
<td>l-mn</td>
<td>473</td>
<td>100%</td>
<td>115</td>
</tr>
<tr>
<td>Ni/Mo/Al₂O₃</td>
<td>N₂/H₂</td>
<td>823</td>
<td>10000</td>
<td>l-mn</td>
<td>473</td>
<td>70%</td>
<td>137</td>
</tr>
<tr>
<td>Cu/Mn</td>
<td>N₂/H₂</td>
<td>823</td>
<td>3000</td>
<td>l-mn</td>
<td>473</td>
<td>Low</td>
<td>137</td>
</tr>
<tr>
<td>Ni/Mg</td>
<td>H₂/CO/N₂/CO₂</td>
<td>1023</td>
<td>15000</td>
<td>b, n</td>
<td>9560</td>
<td>~100%</td>
<td>137</td>
</tr>
<tr>
<td>Ni/MgO</td>
<td>H₂/CO/N₂/CO₂</td>
<td>1023</td>
<td>15000</td>
<td>b, n</td>
<td>9560</td>
<td>Low</td>
<td>115</td>
</tr>
<tr>
<td>Ni/Ca₁₂Al₁₄O₃₃</td>
<td>H₂O/Ar</td>
<td>923</td>
<td>6000</td>
<td>t</td>
<td>4000</td>
<td>100%</td>
<td>121</td>
</tr>
<tr>
<td>Ni/Ca₁₂Al₁₄O₃₃</td>
<td>H₂O/Ar/H₂S</td>
<td>923</td>
<td>6000</td>
<td>t</td>
<td>4000</td>
<td>70%</td>
<td>121</td>
</tr>
<tr>
<td>Ni/CeZrO₂/Al₂O₃</td>
<td>H₂/N₂/H₂O</td>
<td>1073</td>
<td>6000</td>
<td>t, n</td>
<td>20000</td>
<td>100%</td>
<td>115</td>
</tr>
<tr>
<td>Ni/CeZrO₂/Al₂O₃</td>
<td>H₂/N₂/H₂O/H₂S</td>
<td>1073</td>
<td>6000</td>
<td>t, n</td>
<td>20000</td>
<td>90%</td>
<td>115</td>
</tr>
<tr>
<td>Ni/Ce-ZrO₂</td>
<td>H₂O/Ar</td>
<td>973</td>
<td>10000</td>
<td>t</td>
<td>2000</td>
<td>100%</td>
<td>119</td>
</tr>
<tr>
<td>Co/Ce-ZrO₂</td>
<td>H₂O/Ar</td>
<td>973</td>
<td>10000</td>
<td>t</td>
<td>2000</td>
<td>100%</td>
<td>119</td>
</tr>
<tr>
<td>Ni/Ce-ZrO₂</td>
<td>H₂O/Ar</td>
<td>773</td>
<td>10000</td>
<td>t</td>
<td>2000</td>
<td>65%</td>
<td>119</td>
</tr>
<tr>
<td>Ni/ZY-30</td>
<td>H₂/CO/N₂/CO₂</td>
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<td>12800</td>
<td>n</td>
<td>2100</td>
<td>99%</td>
<td>139</td>
</tr>
<tr>
<td>Fe/Cu/Al₂O₃</td>
<td>H₂/N₂/H₂O</td>
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<td>6000</td>
<td>n</td>
<td>2600</td>
<td>~75%</td>
<td>135</td>
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<tr>
<td>Fe/MgCeO</td>
<td>H₂O/He</td>
<td>973</td>
<td>80000</td>
<td>p</td>
<td>2500</td>
<td>63%</td>
<td>140</td>
</tr>
<tr>
<td>Ni/Al₂O₃</td>
<td>H₂O/He</td>
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<td>80000</td>
<td>p</td>
<td>2500</td>
<td>84%</td>
<td>140</td>
</tr>
<tr>
<td>Co/MgO</td>
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<td>3000</td>
<td>n</td>
<td>35000</td>
<td>23%</td>
<td>134</td>
</tr>
<tr>
<td>Ni/MgO</td>
<td>H₂/N₂/H₂O</td>
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<td>3000</td>
<td>n</td>
<td>35000</td>
<td>7%</td>
<td>134</td>
</tr>
</tbody>
</table>
2.3.2.2 Catalysts/Sorbents for Tar Removal

There has been extensive research on catalysts to remove tars from gasification effluents using downstream beds. A variety of metal catalysts, including Ni, Fe, Rh, Co, Zn, Pt, and Pd, have been evaluated.\textsuperscript{137,141-143} Table 2-2 below summarizes the results of some of these studies.

Calcined dolomites consisting of MgO and CaO have also been applied as secondary catalysts for tar removal and have shown almost complete tar decomposition at above 1173 K.\textsuperscript{132} The operating temperature of the dolomite catalysts has to be above 1073 K to avoid the formation of carbonates.\textsuperscript{144,145} Steam gasification of pine sawdust with dolomites improved tar conversion by 21% over noncatalytic results and removed 66% of the tar at 1023 K.

Nickel catalysts have been found to be very active for tar removal initially, but lose their activity gradually due to carbon deposition and/or sulfur poisoning. Different supports were tested in both the partial oxidation and steam reforming of tar derived from the pyrolysis of cedar wood at 873 K.\textsuperscript{129} The order of activity is found to be:
Ni/Al\textsubscript{2}O\textsubscript{3}>Ni/ZrO\textsubscript{2}>Ni/TiO\textsubscript{2}>Ni/CeO\textsubscript{2}>Ni/MgO, but Ni/CeO\textsubscript{2} showed the lowest amount of carbon deposition. Ni/Ca\textsubscript{12}Al\textsubscript{14}O\textsubscript{33} was found to be much more active for toluene reforming compared with Ni/Al\textsubscript{2}O\textsubscript{3} and Ni/MgO/CaO at 1073 K and it maintained activity for more than 60 h.\textsuperscript{121} Almost no carbon was deposited on the surface; this was attributed to more mobile lattice oxygens. But with 500 ppmv H\textsubscript{2}S addition to the stream, the activity for toluene conversion decreased (Table 2-2, line 7) and the selectivity to benzene increased to 40% after 1 h. Air regeneration could not recover the lost activity.\textsuperscript{121} Ni/Ce-ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} was also studied for steam reforming of both toluene and naphthalene.\textsuperscript{115} Both were completely converted and no carbon deposition was found on the surface (Table 2-2, line 8). In the presence of 250 ppmv H\textsubscript{2}S, the activity was still high after 7 h (Table 2-2, line 9). Ni supported on Ce-ZrO\textsubscript{2} was studied with
toluene as a tar model compound.\textsuperscript{119} The catalyst showed great resistance to coking (Table 2-2, line 12). NiMo/Al\textsubscript{2}O\textsubscript{3} was found to be superior to several other catalysts for 1-methylnaphthalene removal.\textsuperscript{137} However, the experiments were limited in that H\textsubscript{2}O, CO\textsubscript{2} and H\textsubscript{2}S were not in the feed stream (Table 2-2, lines 1 and 2). NiW/MgOCaO was found to be sulfur resistant at high temperatures (>1123 K) for woodchip gasification in the presence of 500 ppmv H\textsubscript{2}S.\textsuperscript{126} The WO\textsubscript{3} inhibits the catalyst from adsorbing sulfur.

As seen, the addition of many different metals or metal oxides can improve Ni-based catalysts’ resistance to carbon deposition and sulfur deactivation. DFT studies showed that crystal steps are better nucleation sites for carbon than crystal terraces, and that species such as, potassium, sulfur, etc, are preferentially located at step sites.\textsuperscript{146,147} Therefore, it is possible to inhibit both sulfur adsorption and carbon formation by doping with a metal or metal oxide that is located at these reactive step sites.

The catalytic activity of iron species is related to their oxidation state, with metallic iron thought to be the active species.\textsuperscript{141} At 973-1173 K, only reduced iron showed significant activity for tar decomposition.\textsuperscript{141} Olivine, which contains (FeMg)\textsubscript{2}SiO\textsubscript{4}, has a higher attrition resistance than dolomite but is only active at above 1173 K (H\textsubscript{2}, CO, H\textsubscript{2}O, CH\textsubscript{4}, balance H\textsubscript{2}, GHSV = 1166); with 400 ppmv C\textsubscript{10}H\textsubscript{8} the benzene yield is up to 50\%.\textsuperscript{50} Noiichi et al. (2010) compared Fe/Al\textsubscript{2}O\textsubscript{3} and Fe/ZrO\textsubscript{2} at 1123 K for the steam reforming of naphthalene and found that the catalytic activity increased with iron content. The addition of CuO enhanced the activity of iron by facilitating the reduction of iron oxides to the metallic state.\textsuperscript{135} Steam reforming of phenol with Fe/MgO/CeO\textsubscript{x} at 973 K gives a higher H\textsubscript{2} product yield than does a Ni/Al\textsubscript{2}O\textsubscript{3} commercial catalyst (SudChemie C11-PR).\textsuperscript{140} The catalytic activity of the iron catalyst increased significantly with temperature from 923-1073 K, probably due to reduction to metallic iron at
The catalytic activity for steam reforming of naphthalene was also higher with Co/MgO than with Ni/MgO at 873 K, but it decreased gradually due to carbon deposition (Table 2-2, lines 17 and 18).

CeO₂ prepared by a homogeneous precipitation method with urea is an effective material for naphthalene oxidation under relatively high oxygen partial pressures at ~473 K. It showed high selectivity to CO₂. CeO₂-ZrO₂ mixed oxide catalysts also showed good activity for the oxidation of naphthalene. The catalytic activity increased with the reducibility of the mixed oxide. However, these catalysts have not been investigated for naphthalene removal under reducing conditions.

Among the precious metal catalysts (supported Rh, Ru, Pd, and Pt) tested for tar removal or biomass gasification, a CeO₂/SiO₂ supported Rh catalyst performed best. The order of the activity for gasification of wood was: Rh>Pt>Pd>Ni~Ru. Rh/CeO₂/SiO₂, Rh/LaCoO₃/Al₂O₃ and Rh/CeZrO₂ all exhibited higher activity for steam reforming of biomass and tars, better coking resistance, sulfur tolerance and thermal stability than Ni-based catalysts. However, it is probably not feasible to use Rh considering its high price.

Although, it is well known that sulfur has a detrimental effect on tar reforming catalysts, especially on nickel-based ones, the potential effects of tars on high temperature sulfur sorbents is still not clear. Carbon deposition on Ni/YSZ with and without H₂S has been investigated. At 1023-1173 K, carbon deposition is negligible with H₂S in the feed.
CHAPTER 3: EXPERIMENTAL METHODS

3.1 CATALYST SYNTHESSES BY SURFACTANT-TEMPLATED METHODS

The CeO$_2$/La$_2$O$_3$ and CeO$_2$/Tb$_2$O$_3$ mixed oxides were synthesized as high surface area mesoporous materials at >2.0 nm average pore diameter by adapting a surfactant-templated method.$^{155,156}$ Measured amounts of ceric (IV) ammonium nitrate (NH$_4$)$_2$Ce(NO$_3$)$_6$ (Aldrich 99.9%) and either lanthanum precursor La(NO$_3$)$_3$•$6$ H$_2$O (Alfa Aesar, 99.9%) or terbium precursor (TbCl$_3$•$6$ H$_2$O, Aldrich, 99.9%) were added to measured amounts of water and $1\%$ tetramethylammonium hydroxide (Acros, 25% in methanol) surfactant with stirring. The salts dissolved immediately to a clear solution, to which was slowly added aqueous NH$_3$ (Alfa Aesar, 28-30%), until precipitation occurred (pH ~10.3-10.5). The temperature was raised to 363 K and the gel stirred for 4 days, adjusting the pH as necessary. The centrifuged precipitate was washed with acetone and deionized water, dried at 373 K, then calcined in flowing air at 773 K with a ramp of $2\,\text{K/min}$ and a final hold of $6\,\text{h}$.

The pure CeO$_2$ was synthesized by dissolving Ce(OAc) hydrate with water and tetrapropylammonium hydroxide. The salts dissolved immediately to a clear solution, to which was slowly added aqueous NH$_3$ (Alfa Aesar, 28-30%), until precipitation occurred (pH ~10.8). The temperature was raised to 363 K and the gel stirred for 4 days, adjusting the pH as necessary. They were calcined as given above. For Mn/Ce and Mn/Ce/La materials, a similar method was used except the pH was 9.8-10 and the reaction time was only two days.

Alternative preparation methods also used for Mn-containing sorbents were hydrothermal synthesis (cetyl trimethyl ammonium bromide template) and evaporation induced self-assembly (EISA). For the hydrothermal synthesis, we used (molar) ratios of $1$ total salts/ $2$
NaOH / 0.333 CTAB/230 water. This mixture was reacted in a teflon-lined autoclave at 373 K for two days, then filtered, dried and calcined as discussed previously.

The EISA synthesis method was adapted from the literature.\textsuperscript{157,158} The starting (molar) ratios were 1 total precursor salts/10 water/20 ethanol in the first solution. The second solution contained the same amount of ethanol as the first, and 0.025 g Pluronic 123 (BASF) template/g ethanol. The precursor salts were Ce(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}•1.5H\textsubscript{2}O (Alfa, 99.9%) and Mn(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}•4H\textsubscript{2}O (Alfa, 22 wt% Mn). After mixing the two solutions and stirring at room temperature for 30 min, 0.1 M NH\textsubscript{3} was added slowly until 1 mL per 20 mL solution. The solution was spread out, added to a dessicator and gelled over calcium sulfate for 4 days, then dried in static air at 100°C for 2 days, and finally calcined as discussed previously.

Manganese was also supported on some dried CeO\textsubscript{2}/La\textsubscript{2}O\textsubscript{3} mixed oxides, or on Al\textsubscript{2}O\textsubscript{3}, by incipient wetness impregnation from Mn(NO\textsubscript{3})\textsubscript{2} followed by drying and calcining as before. The supported mixed oxides were prepared by incipient wetness impregnation from concentrated solutions of the nitrate salts on a thermally stable Al\textsubscript{2}O\textsubscript{3} (BASF Ga-200-L, which contains 3% La). All of these samples were dried and calcined as discussed previously.

### 3.2 POROSIMETRY

The BET surface areas of the oxides were measured by N\textsubscript{2} adsorption - desorption using a Quantachrome AS-1 BET apparatus. The BET theory assumes multi-layer physical adsorption of gas molecules on the catalyst surface. A sample was placed into a glass cell and degassed at 573 K under vacuum for at least 30 min to remove volatile compounds adsorbed on the surface. The amount of adsorbed N\textsubscript{2} was recorded in the relative pressure range (P\textsubscript{0} = atmospheric pressure) 0.05 < P/P\textsubscript{0} < 0.3. The surface area is then calculated with the BET equation based on the cross-sectional area of N\textsubscript{2} molecules (0.162 nm\textsuperscript{2}).
### 3.3 X-RAY DIFFRACTION

X-ray diffraction (XRD) spectra of ground, powdered samples were obtained using either a Rigaku Miniflex 2005C103 XRD at the LSU Materials Characterization Center, or using the powder XRD beamline at the LSU Center for Advanced Microstructures and Devices, both using Cu Kα radiation. The sample was ground into very fine powder in order to randomize crystal orientation. It was placed into either a sample holder or mounted with double-sided tape depending upon the amount of sample available. Typically these samples were scanned with a step size of 0.04°, 2-6 s integration time. XRD was used to determine the crystallographic structure (phases) of sorbents or catalysts after sulfidation, regeneration or tar reforming. Phases were identified by comparing to the ICDD database.\(^{159}\)

### 3.4 X-RAY ABSORPTION SPECTROSCOPY

#### 3.4.1 The Physical Basis of XAS

X-ray absorption spectroscopy includes two parts: X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (XAFS). XANES provides information on coordination geometry and oxidation state, and XAFS provides information about local environment such as neighboring elements and coordination number. By exciting an atom using an X-ray source, the electron configuration of the atom is changed; one (usually a core-shell) or more electrons populate unoccupied bound or continuum states. This results in the steplike shaped absorption edge. The photoelectron” wave scatters from the atoms around the X-ray absorbing atom, creating interferences between the outgoing and scattered parts of the photoelectron wave function. The observed oscillations and can then be described by the XAFS equation as shown below:\(^{160,161}\)
\[ \chi(k) = \sum_{i}^{n} \left( \frac{N_i S_0^2 F_i(k) e^{\frac{2R_i}{\chi(k)}e^{-2k^2\sigma_i^2}}}{kR_i^2} \sin(2kR_i + \delta_i(k)) \right) \]  

where \( \chi \) is the fractional change in absorption coefficient. The coordination number \( N \), radical distance \( R \), amplitude reduction factor \( S_0 \), and thermal and structural mean square variation \( \sigma^2 \) are of interest and can be determined. \( (F_i \) is the backscattering amplitude of element \( i. \) \( \delta \) is the phase shift from the central atom absorber. \( \lambda \) is the mean free path length. \( k \) is the wave number of the photo electron.)

### 3.4.2 Experimental XAS

XAS is typically measured in either transmission or fluorescence mode. Transmission mode simply involves measuring the X-ray flux before and after the beam is passed through a uniform sample. In fluorescence mode one measures the incident flux \( I_0 \) and the fluorescence X-rays \( I_f \) that are emitted following the absorption event. Usually the fluorescence detector is placed at 90° to the incident beam in the horizontal plane, with the sample at an angle of 45° to the beam. For good data the signal to noise ratio (S/N) should be greater than \( 10^3 \) for XANES region and \( 10^5 \) for the EXAFS region. The duration of a run primarily depends on the specific energy range, step length and integration time. For example, \( \sim 1 \) h for S K-edge XANES; \( \sim 0.5 \) h for Ce L_{III}-edge XAFS; \( \sim 2 \) h for Fe K-edge XAFS.

X-ray absorption near-edge spectroscopy (XANES) and XAFS were performed at the LSU synchrotron using the Ge (2 2 0) double crystal monochromator (DCM) beamline. The Ce L_{III} edge spectra were measured at room temperature in either transmission or fluorescence mode. The energy range was 5623 to 5923 eV for XANES and 5923 to 6139 eV for XAFS. Cerium
acetate and CeO$_2$ were used as references for the Ce$^{3+}$ and Ce$^{4+}$ states, respectively. The sulfur K-edge data were acquired at room temperature in fluorescence mode, due to the low sulfur content in the sample. An InSb (1 1 1) double crystal monochromator was used, and the energy ranges scanned were 2320-2450, 2450-2510, 2510-2570, 2570-2670, 2670-2886, 2886-3122, and 3122-3417 eV, with interval step sizes of 5, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 eV, respectively. Sublimed S, ZnS and ZnSO$_4$ were used as S$^0$, S$^{2-}$ and S$^{6+}$ oxidation state references respectively. The Mn K-edge data were also acquired at room temperature in fluorescence mode over a scan range of 6439-6739 eV. Manganese (II) acetate and Mn(OH)$_3$ were used as Mn$^{2+}$ and Mn$^{3+}$ standards, respectively. MnS, MnO, and Mn$_3$O$_4$, were also used as reference standards. The data were processed (background subtraction, deglitching, linear combination fitting) using Athena 0.8.061. Fe K-edge spectra were measured at room temperature in either transmission or fluorescence mode. The energy range was 6992 to 8059 eV. FeO, Fe$_3$O$_4$, FeS and FeOOH were used as references. For further details of how the XANES and XAFS data were processed and fit to structural models, see Appendix C.

### 3.5 TEMPERATURE-PROGRAMMED OXIDATION (TPO)

TPO was used to estimate the amount of coke (carbon deposits) present in used reforming catalysts and was carried out in a thermogravimetric analyzer (Perkin-Elmer TGA 7). The used sample (~20 mg) was heated first to 523 K in air and held for 1 h to remove physically adsorbed hydrocarbons and water. Then, the temperature was further increased to 923 K for 1 h to remove carbon and sulfur. A residual gas analyzer (SRI RGA 300) was used to monitor the effluent gas compositions at m/e =32, 44, 64.
3.6 TEMPERATURE-PROGRAMMED REDUCTION (TPR)

Temperature-programmed reduction (TPR) in the TGA was carried out on 20 mg samples in H\(_2\). The samples were heated first to 773 K in air for 2 h to remove adsorbed carbonates and water. Then, the temperature was lowered to 373 K in He, the gas switched to H\(_2\), and the TGA temperature programmed with 3 K/min ramps as follows: to 903 K, 2 h hold; to 993 K, 1 h hold, to 1043 K, 1 h hold. The H\(_2\) consumption was determined from the weight loss of water from the sample.

3.7 INDUCTIVELY COUPLED PLASMA (ICP)

In ICP-MS, a plasma consisting of ions, electrons and neutral particles, is formed from argon gas, which is then utilized to atomize and ionize the elements in the sample matrix. The resulting ions are then passed through a series of apertures (cones) into a high vacuum mass analyzer where the elements are identified by their mass-to-charge ratio. Samples were completely dissolved into a solution by a strong acid (HNO\(_3\)/HCl = ~ 1/3) under continuous stirring and heating at temperature ~353 K. Standards of Ce, La, and Gd(1, 30, 100 mg/L) were prepared to accurately determine the elemental compositions. As seen in Table 3-1, the agreement between the nominal and experimental ratios is very good.

Table 3-1 Composition of REO-based sorbents

<table>
<thead>
<tr>
<th>Nominal Molar Ratios</th>
<th>Molar Ratios by ICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd0.0036/Ce3/La</td>
<td>Gd0.004/Ce3.1/La</td>
</tr>
<tr>
<td>Mn0.4/Ce3/La/Al</td>
<td>Ce3.1/La</td>
</tr>
<tr>
<td>Gd0.083/Ce3/La/Al</td>
<td>Gd0.08/Ce3.0/La</td>
</tr>
<tr>
<td>Mn0.8/Ce3/La/Al</td>
<td>Ce3.0/La</td>
</tr>
</tbody>
</table>
3.8 DESULFURIZATION TESTS

To explore these materials’ utility in gasifier effluent purification, we adsorbed H₂S and other components from a simulated gasifier effluent, followed by regeneration, usually in air. The simulated gasifier effluent for the adsorption/reaction step typically contained 0.1% H₂S, 23.4% H₂, 32% of either CO or CO₂, 5.0% H₂O, balance N₂ (caution: toxic mixture). This gas approximates a bio- or coal gasifier effluent, but without NH₃ and with slightly less water. The sulfur content is higher than is characteristic of effluents from biogasifiers, but lower than from coal gasifiers.¹⁰,⁷²,¹⁶³-¹⁶⁵ A schematic of the reactor system is shown as Figure 3.1. The H₂S was fed as a 4 mol% mixture in N₂. Sulfidation (adsorption) tests were performed at 900-1023 K with a Gas Hourly Space Velocity (GHSV) of 15500 h⁻¹. A syringe pump was used to inject the water into the system. The gas mixture passed through a 1/4” Silcosteel 2000 U-tube containing about ~1.0 g of oxide with quartz wool on both ends, seated in a temperature-controlled sand bath. After saturation plus 5 min, the gas was switched to helium to purge the system and then to the regeneration gas at 873 K for at least 30 min. Multiple adsorption/regeneration cycles were performed, and results are generally quoted for data where capacities were changing by less than 10% cycle-to-cycle.

Samples taken after the adsorbent bed were injected directly into a Varian CP-3800 GC pulsed flame photometric detector (PFPD) which is specific for sulfur compounds down to ~1 ppmv sulfur. Other samples were also analyzed for CO, CH₄ and CO₂ using the Varian CP-3800 thermal conductivity detector with an Alltech CTR-1 dual packed column (1/4” outer column, activated molecular sieve, and 1/8” inner column, porous polymer) used for separation. Retention times were determined by injecting standard gas mixtures of fewer components. The sample split ratio between the columns was determined by injecting various air/CO₂ standards and taking the area ratio of air (inner) to the sum of air (inner), O₂ (outer), and N₂ (outer). The
column was programmed with initial temperature 300 K for 4 min, 20 K/min to 403 K, and a 4 min final hold. Further details on the GC analyses and flow control are given in Appendix A.

\[
S_{\text{capacity}} = \sum_t \frac{\text{Area} \cdot \text{Response Factor} \cdot \text{Flow rate} \cdot \Delta t \cdot T_{\text{loop}}}{\text{loop volume} \cdot \text{catalyst load} \cdot T_{\text{room}}} \quad (3-2)
\]

After the last adsorption test, the sample was cooled down in the flowing syngas and then purged for 15 min in N\textsubscript{2} prior to any post-test characterization.

Figure 3.1 Schematic of reactor system for sulfur adsorption from syngas. V1 and V2 are automated switching valves.
3.9 C_{10}H_{8} REFORMING TESTS

The simulated gasifier effluent for the adsorption/reaction step typically contained, 4.1% CH₄, 0.33% C_{10}H₈, 30.8% H₂, 54.3% CO, 9.1% H₂O, 40 ppmv H₂S, balance N₂. This gas approximates a bio- or coal gasifier effluent, but without NH₃ and with slightly less water. Reforming tests were performed at 923-1073 K with a GHSV of 33000 h⁻¹. A schematic of the reactor system is shown as Figure 3.2. The naphthalene was injected by sublimation at controlled temperature from a separate bed, and a syringe pump injected the water just prior to the reactor. The gas mixture passed through a 1/2” stainless steel tube containing 0.2 g of catalyst diluted with mullite and with α-Al₂O₃ as bed support. The tube was heated by a clamshell furnace [Model F-5-1000-V-1-3/4V-SSK, 320 watt] which was controlled by a Eurotherm 3504 PID controller. Further details on startup and shutdown are given in Appendix B.

Figure 3.2 Schematic of reactor system for C_{10}H_{8} reforming.
Samples taken after the reactor (Valco A90 valve, loop size = 2 mL) were injected directly into a HP-5890 GC with flame ionization detector; an Alltech Econo-Cap SE-54 capillary column was used to separate C₆ and higher hydrocarbons. Samples were also analyzed for CO, CO₂ and C₁-C₆, using an Agilent 490 Micro GC with thermal conductivity detectors, using one molecular sieve column and one CP-PoraPLOT U column. The HP-5890 was programmed with initial temperature 313 K for 1 min, 8 K/min to 453 K, and a 35 min final hold. The Micro GC was operated isothermally at 353 K. The sampling time was 40 ms. The GC column was frequently backflushed at high temperature (423 K) to remove sulfur and C₁₀H₈. Further details on the Micro GC operational method is given in Appendix B.

\[
C_{10}H_8_{\text{conversion}} = \frac{\text{Area} \cdot \text{Response Factor} \cdot R \cdot T}{P \cdot V_{\text{loop}} \cdot C_{10}H_8 \text{ mol} \%} \tag{3-3}
\]

The yields of the products on a carbon basis and the weight-based rate for C₁₀H₈ removal were calculated using Eqs. (3-2) to (3-4):

\[
Y(\text{CO}_2) = \frac{[\text{CO}_2]_{\text{prod}}}{[\text{CO}]_{\text{in}} + 10[C_{10}H_8]_{\text{in}} + [\text{CH}_4]_{\text{in}}} \tag{3-4}
\]

\[
Y(\text{CH}_4) = \frac{[\text{CH}_4]_{\text{prod}}}{10[C_{10}H_8]_{\text{in}} + [\text{CH}_4]_{\text{in}}} \tag{3-5}
\]

\[
R(C_{10}H_8) = \frac{[C_{10}H_8]_{\text{in}} - [C_{10}H_8]_{\text{out}}}{[C_{10}H_8]_{\text{in}}} \times \text{GHSV} \tag{3-6}
\]

The theoretical values were calculated by HYSYS assuming the three reactions (3-7) to (3-7) come to equilibrium (Gibbs Free Energy Minimization). The C₁₀H₈ reforming/cracking was not included due to the small amount of reactant and an unclear reaction mechanism.
\[ \text{CH}_4 + H_2O \rightarrow CO + 3H_2 \] (3-7)

\[ 2CO \rightarrow C + CO_2 \] (3-8)

\[ CO + H_2O \rightarrow CO_2 + H_2 \] (3-9)

The calculation is as follows:

Let \( F_x \) to be the inlet mol flow rate of \( x \), \( y_x \) to be the outlet mol fraction of \( x \), \( F_T \) is the total outlet flow rate, and \( \xi_x \) the extent of reaction \( x \) of (3-7) to (3-9)

\[ y_{CO} \cdot F_T = F_{CO} + \xi_7 - 2\xi_8 \] (3-10)

\[ y_{CO2} \cdot F_T = F_{CO2} + \xi_8 + \xi_9 \] (3-11)

\[ y_{CH4} \cdot F_T = F_{CH4} - \xi_7 \] (3-12)

\[ y_{N2} \cdot F_T = F_{N2} \] (3-13)

The mol fractions were determined from the micro GC analysis. The gas response factors were calculated by injecting a standard mixture of known composition with response peak areas. The unknowns \( F_T \), \( \xi_4 \), \( \xi_5 \) and \( \xi_6 \) were computed in Excel 2007 by solving (3-10) to (3-13) simultaneously.

Turnover number calculation (\( \text{C}_{10}\text{H}_8 \) only):

\[ \text{Turnovers} = \frac{GHSV \cdot \%\text{Conv} \cdot \text{Concentration} \cdot t}{1000\text{mL/L} \cdot \frac{22.4L}{\text{mol}} \cdot \text{mol metal/g}} \] (3-14)

Further details on the GC analyses and flow control are given in Appendix B.
CHAPTER 4: ENERGETICS AND MECHANISM FOR H₂S ADSORPTION BY CERIA-LANTHANIDE MIXED OXIDES: IMPLICATIONS FOR THE DESULFURIZATION OF BIOMASS GASIFIER EFFLUENTS

4.1 INTRODUCTION

Gasification of biomass to syngas facilitates energy production from a renewable feedstock when coupled with downstream catalytic processing to liquid fuels or direct utilization in a fuel cell. Syngas produced from biomass contains up to as much as 1% H₂S, which must be removed prior to further processing or utilization steps to avoid poisoning of downstream catalysts and SOₓ production. It is advantageous to perform syngas desulfurization at the high temperatures of gasification (>850 K) to permit efficient integration of desulfurization in between gasification and further processes. Ceria is stable at gasification temperatures, and the sulfur adsorption capacity of ceria may be altered by mixing ceria with other rare earth oxides such as lanthana. Mixing ceria with lanthana may alter the kinetics or thermodynamics of H₂S adsorption and dissociation, however the mechanism and energetics on ceria-based rare earth oxides are not well characterized. The optimization of ceria-based high temperature desulfurization sorbents is thus dependent on characterizing the H₂S sorption process at the atomic scale and identifying kinetic or thermodynamic limits for H₂S removal.

Numerous properties are necessary for efficient and long-term high temperature desulfurization operation, including rapid initial H₂S adsorption kinetics, favorable sulfidation thermodynamics, and high temperature stability including both bulk phase stability and surface area stability. Biomass gasification temperatures range from approximately 673K-1473K.

---

motivating the use of materials with high temperature stability such as ceria. Mixed rare earth oxides of ceria maintain the lattice structure of cubic CeO$_2$ upon mixing with lanthana or terbia, up to $x = 0.6$ for Ce$_{1-x}$La$_x$O$_y$\cite{169} and $x = 0.5$ for Ce$_{1-x}$Tb$_x$O$_y$.\cite{170} Flytzani-Stephanopoulos et al. showed that ceria-lanthana (Ce$_{0.7}$La$_{0.3}$O$_y$) has a higher sulfur adsorption capacity (mg S/g$_{sorbent}$), at 1073K and a H$_2$S pressure of 0.001 atm than either pure CeO$_2$ or pure La$_2$O$_3$.\cite{102} The increased capacity of ceria-lanthana with respect to pure ceria evidences the potential for the design and optimization of mixed oxide ceria-based sulfur sorbents. It is unclear, however, which properties of the mixed metal oxide lead to the increased sulfur capacity realized experimentally.

The increased sulfur adsorption capacity of ceria-based mixed oxides with respect to pure ceria may arise from increased surface area stability, increased reducibility of the oxide mixture, stronger adsorption and faster kinetics on the mixed oxide surface, or a thermodynamically favorable bulk transition from the oxide to an oxysulfide (M$_x$O$_y$S$_z$) with a higher sulfur stoichiometry. The addition of low valency metals such as La(3+)\cite{171} and Tb(3+)\cite{170} to CeO$_2$ results in the presence of stoichiometric oxygen vacancies and also lowers the energy to form additional oxygen vacancies (reduction of Ce$^{4+}$ to Ce$^{3+}$). Oxygen vacancies may serve as active sites for surface adsorption and dissociation of H$_2$S, and may also increase bulk diffusion rates of sulfur atoms within the ceria lattice to facilitate bulk sulfidation. Kay et al. proposed that the increased sulfur adsorption capacity of ceria-lanthana is due to more exergonic free energies of formation of lanthanum oxysulfides and sulfides than those of cerium,\cite{172} where the word exergonic refers to a favorable (negative) free energy change. Breakthrough curves for H$_2$S adsorption over ceria and ceria-lanthana display gradual increases in outlet H$_2$S concentration, however, which the authors attribute to kinetic limitations.\cite{172} The H$_2$S adsorption capacity of pure ceria is proportional to surface area,\cite{173} evidencing that surface kinetics of H$_2$S adsorption
and dissociation influence adsorption capacity. The sulfur capacity per surface area of ceria-lanthana also exceeds that of pure ceria, suggesting that the surface chemistry influences sulfur capacity.\textsuperscript{102} The relevance of surface functionality and kinetics are thus established experimentally, however the reaction mechanism and energetics of H\textsubscript{2}S adsorption and dissociation have not been determined.

Experimental characterization of ceria-based sulfur sorbents in situ is complicated by structural and chemical transformations which occur during the desulfurization process, and previous computational studies of H\textsubscript{2}S chemistry on the ceria surface have been limited to consideration of pure ceria as well as energetics only over the intact (fully oxidized) surface. Lin et al. report density functional theory (DFT+U) calculated reaction energies and activation barriers for H\textsubscript{2}S dissociation on CeO\textsubscript{2}(111), however their study does not consider adsorption and dissociation energetics over oxygen vacancies on the reduced surface.\textsuperscript{174} The partial pressure of oxygen may be very low (< 10\textsuperscript{-20} atm, see Section 2.4 for calculation of equilibrium oxygen pressure) in gasifier streams. At these low oxygen pressures and temperatures exceeding 850K, oxygen vacancies, which may adsorb and dissociate H\textsubscript{2}S, will be present on the ceria surface. Lin et al.’s study also only included DFT-calculated internal energy differences, which are not accurate estimates of free energy differences for H\textsubscript{2}S adsorption at high temperatures and low H\textsubscript{2}S pressures (< 10\textsuperscript{-2} atm\textsuperscript{166}). To the best of our knowledge, no previous computational study considered the free energies of H\textsubscript{2}S adsorption and dissociation over reduced ceria or ceria-based rare-earth oxide mixtures.

The work utilizes density functional theory and \textit{ab initio} thermodynamics to calculate the free energies of H\textsubscript{2}S adsorption and dissociation on CeO\textsubscript{2}(111) as well as La-doped and Tb-doped CeO\textsubscript{2}(111).\textsuperscript{175} The free energies of H\textsubscript{2}S adsorption, dissociation, and oxygen vacancy
formation are evaluated at 1100K and the low partial pressures of H\textsubscript{2}S(g) and O\textsubscript{2}(g) corresponding to operating conditions for the high temperature desulfurization of biomass gasifier effluents. Surface adsorption and subsurface incorporation of sulfur are considered, and the equilibrium sulfur content of the surface is calculated over a range of possible pressures of H\textsubscript{2}S(g) and O\textsubscript{2}(g). Experimental studies of H\textsubscript{2}S adsorption on ceria, ceria-lanthana, and ceria-terbia are reported for comparison of observed trends in sulfur adsorption capacity with computational results. Previous studies have evaluated the relative trends in sulfur adsorption capacity between pure ceria and ceria-lanthana, however sulfur adsorption capacities for ceria-terbia mixtures have not been reported. These results provide insight into limiting factors in the desulfurization reaction over ceria, ceria-lanthana, and ceria-terbia. We identify kinetic and thermodynamic limitations to H\textsubscript{2}S adsorption and dissociation from the gas phase, and discuss each in the context of the optimization of ceria-based high temperature desulfurization sorbents.

4.2 METHODS

4.2.1 Experimental Methods

Mesoporous CeO\textsubscript{2}/La\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2}/Tb\textsubscript{2}O\textsubscript{3} mixed oxides and pure CeO\textsubscript{2} were synthesized at >2.0 nm average pore diameter by adapting a surfactant-templated method\textsuperscript{155,176}. Measured amounts of ceric (IV) ammonium nitrate (NH\textsubscript{4})\textsubscript{2}Ce(NO\textsubscript{3})\textsubscript{6} (Aldrich 99.9%) and either lanthanum precursor La(NO\textsubscript{3})\textsubscript{3}•6 H\textsubscript{2}O (Alfa Aesar, 99.9%) or terbium precursor (TbCl\textsubscript{3}•6 H\textsubscript{2}O, Aldrich, 99.9%) were added to measured amounts of water and 1% tetramethylammonium hydroxide (Acros, 25% in methanol) surfactant with stirring. The salts dissolved immediately to a clear solution, to which aqueous NH\textsubscript{3} (Alfa Aesar, 28-30%) was slowly added until precipitation occurred (pH ~10.3-10.5). The temperature was raised to 363 K and the gel stirred for 4 days, adjusting the pH as necessary. The centrifuged precipitate was washed with acetone.
and deionized water, dried at 373 K, then calcined in flowing air at 773 K with a ramp of 2 K/min and a final hold of 6 h.

For the as-calcined and used materials, surface areas were determined by the BET method (Quantachrome AS-1). X-ray diffraction (XRD) spectra of as-calcined powdered samples were obtained using a Rigaku Miniflex 2005C103 diffractometer with Cu-Kα radiation. Samples were scanned from 5-60º 2θ at 1º/min with a 0.05º step.

To probe the desulfurization performance of these ceria-based materials, we conducted continuous flow adsorption tests at 900 K until saturation by H₂S, and then regenerated the adsorbent materials with air at 873 K in air for 30 min. The simulated gasifier effluent contained 0.1% H₂S, 24% H₂, 32% CO₂, 3.3% H₂O, and balance N₂. This approximates a bio- or coal gasifier effluent, but without CO and with slightly less water. The sulfur content is higher than is characteristic of effluents from biogasifiers, but lower than from coal gasifiers. These are short-bed, non-equilibrium tests with a 1 g bed at GHSV = 15500, and a pre-breakthrough concentration of roughly 10 ppmv. The average of three cycles of adsorption and regeneration, after the first cycle, is reported. The first cycle is not used in the results because there is often considerable decrease in sulfur capacity and surface area during the first cycle that is not observed in subsequent cycles.

4.2.2 Electronic Structure Method

Calculations were performed using the Vienna ab initio simulation program (VASP), an ab initio total-energy and molecular dynamics program developed at the Institute for Material Physics at the University of Vienna. The projector augmented wave method was used to represent the core region, with valence electron wavefunctions expanded in a tractable plane wave basis set. The energy cutoff of the plane wave basis set used herein was 450 eV (chosen to
ensure convergence of total energy with respect to energy cutoff). Valence configurations were $5s^25p^66s^24f^15d^1$ for cerium, $2s^22p^4$ for oxygen, $5s^25p^65d^16s^2$ for La, $4f^9$ for Tb, $3s^23p^4$ for S, and $1s^1$ for H. Structural optimizations were performed by minimizing the forces on all atoms to below 0.05 eV Å$^{-1}$, and all calculations were spin-polarized. The Perdew-Wang (PW91) version of the generalized gradient approximation (GGA) was used to incorporate exchange and correlation energies.\textsuperscript{183} Due to well-established difficulties within DFT to accurately represent the nature of $4f$ states in ceria,\textsuperscript{184-186} we implemented the DFT+$U$ approach. The DFT+$U$ method introduces the Hubbard $U$ term as an on-site Coulombic interaction in the $f$ states of ceria, which localizes $4f$ electrons on Ce$^{3+}$ in reduced ceria. We used a value of $U = 5$ eV, which is consistent with recommended values within the DFT+$U$ method used in previous studies of ceria\textsuperscript{187-192} and ensures proper localization of $4f$ electrons. Absolute reduction energies are a function of the $U$ value, though relative trends in reduction energetics are preserved with varying $U$.\textsuperscript{193} The absolute free energies presented herein thus may not directly compare to experimental values and as such we focus on relative trends in energetics between ceria, ceria-lanthana, and ceria-terbia. The methods used herein reproduce the bulk lattice constant of ceria within 1\% of the experimental value.\textsuperscript{8}

### 4.2.3 Surface Models

Figure 4.1 displays the slab models used for the ceria, ceria-lanthana and ceria-terbia surfaces. Each surface model consists of a mirrored slab on which adsorption and oxygen vacancy formation are considered on both sides of the slab. The mirrored slab model of the ceria surface was used specifically to minimize slab to slab interactions which may result from a large net surface dipole moment upon the interaction of the surface with adsorbates and the reduction of surface metal ions. The ceria surface is modeled as a 12-layer (Ce$_{16}$O$_{32}$) mirrored slab of the
(111) termination of cubic fluorite CeO$_2$ separated by 15 Å of vacuum in the direction perpendicular to the surface. All atom positions are relaxed during structural optimization. The surface energy of CeO$_2$(111) is lowest among single crystal terminations of ceria,\textsuperscript{187,188,193} indicating that this surface termination will represent a large portion of a polycrystalline CeO$_2$ surface. The Brillouin zone was sampled using a (2×2×1) Monkhorst-Pack grid for the (111) surface, with the third vector perpendicular to the surface.\textsuperscript{194} We use a $p(2\times2)$ expansion of the surface unit cell, which results in a termination of four surface oxygen atoms on each side of the slab and four Ce atoms in the atomic layer below. Two lanthanum or terbium atoms are substituted for Ce atoms into each side of the slab, with a single oxygen atom removed to maintain the 3+ oxidation state of La and Tb. The La and Tb pairs are substituted into the ceria slab with one atom in the surface metal layer and one atom in the subsurface metal layer. We limit our study to this single configuration of La or Tb atoms in the ceria surface to identify trends in H$_2$S adsorption and dissociation energetics over ceria and rare earth doped ceria, however, ceria-lanthana and ceria-terbia surfaces may contain a heterogeneous distribution of metal atoms, oxygen atoms and oxygen vacancies. The formation energy for the stoichiometric oxygen vacancy in our ceria-terbia surface model is lowest (most exothermic) at a surface oxygen coordinated to Tb. For ceria-lanthana, the oxygen vacancy formation energy is lowest at the next nearest neighbor position to La.

4.2.4 Free Energies of H$_2$S Adsorption and Dissociation

Reaction intermediates for H$_2$S dissociation over each surface were optimized by placing H$_2$S, SH, S, and H adsorbates in each surface unit cell. Each adsorbate was placed at all high symmetry adsorption sites and configurations on each surface, and the lowest energy adsorption
Figure 4.1 Top (a), (c), (e), and side (b), (d), (f) views of surface unit cell for (a), (b), CeO$_2$(111), (c), (d) La$_2$O$_3$/CeO$_2$(111), and (e), (f) Tb$_2$O$_3$/CeO$_2$(111). Ce atoms are colored tan (light), O atoms red (dark), La atoms blue (gray), and Tb atoms teal (dark gray).
configuration for each adsorbate-surface pair was used to calculate the relative energies of elementary reaction steps. Harmonic vibrational modes were calculated to determine zero-point vibrational energy (ZPVE) corrections to the total energy of isolated molecules and adsorbed species. Optimizations of isolated gas-phase molecules were performed with one free molecule within a $(15 \, \text{Å})^3$ unit cell. The free energies of gas-phase molecules and surface adsorbates were calculated as the sum of the electronic energy ($E_{\text{DFT}}$), ZPVE correction, entropy ($S_T$), and a pressure volume term (PV) as follows:

$$G_{\text{gas}} = E_{\text{DFT}} + \text{ZPVE} - (S_{\text{vib}} + S_{\text{trans}} + S_{\text{rot}}) T + PV \quad (4-1)$$

For surface adsorbates, translational and rotational entropy terms are zero. Constrained vibrational calculations were done for adsorbed species. For these calculations, the Hessian matrix is populated solely with the second derivatives of energy with respect to position of the adsorbate atoms. This approach approximates that the vibrational degrees of freedom of the adsorbates are local, decoupled from vibrational motion of the other surface atoms. Free energy differences for elementary reaction steps were calculated by subtracting the sum of free energies of the initial state from the sum of free energies of the product state, as follows for the example of $\text{H}_2\text{S}$ dissociation to adsorbed SH and H ($\text{H}_2\text{S}^* \rightarrow \text{SH}^* + \text{H}^*$):

$$\Delta G_{\text{rxn}, \text{H}_2\text{S}^* \rightarrow \text{SH}^* + \text{H}^*} = \frac{[G_{\text{SH}^*} + G_{\text{H}^*}] - [G_{\text{H}_2\text{S}^*} + G_{\text{bare}}]}{2} \quad (4-2)$$

where $G_{\text{SH}^*}$, $G_{\text{H}^*}$, and $G_{\text{H}_2\text{S}^*}$ represent the free energies of adsorbed SH, H, and $\text{H}_2\text{S}$ species, respectively, and $G_{\text{bare}}$ is the DFT energy of the bare surface. The denominator of two is included in equation 2 to account for the fact that mirrored slab models are used with one adsorbate on each side of the mirrored slab.
Adsorption and dissociation of H$_2$S was considered over the intact (fully oxidized) and oxygen partially reduced ceria, ceria-lanthana, and ceria-terbia surfaces. Oxygen vacancy formation free energies were incorporated into the free energy diagrams for H$_2$S adsorption and dissociation, calculated as follows:

$$
\Delta G_{\text{vac}} = \frac{G_{\text{reduced}} + G_{\text{O}_2} - G_{\text{intact}}}{2}
$$

(4-3)

where $G_{\text{reduced}}$ and $G_{\text{intact}}$ are the free energies of the surface containing an oxygen vacancy and the intact surface, respectively, and $G_{\text{O}_2}$ the free energy of O$_2$(g). Free energies of gas phase species are calculated at 1100K, and $P_{\text{H}_2} = 0.35$ atm, $P_{\text{H}_2\text{S}} = 10^{-2}$ atm, and $P_{\text{H}_2\text{O}} = 0.03$ atm to approximate high temperature desulfurization conditions. Due to DFT errors associated with the overestimation of the O$_2$ binding energy, we estimate the free energy of O$_2$ by assuming equilibrium between H$_2$O(g), H$_2$(g), and O$_2$(g):

$$
G_{\text{O}_2} = (G_{\text{H}_2\text{O}} - G_{\text{H}_2}) \cdot 2
$$

(4-4)

where $G_{\text{O}_2}$ is the free energy of O$_2$(g), $G_{\text{H}_2\text{O}}$ is the free energy of H$_2$O(g), and $G_{\text{H}_2}$ is the free energy of H$_2$(g).

4.3 RESULTS AND DISCUSSION

4.3.1 Experimental Results

The adsorbents used and their surface areas are given in Table 4-1. The modified surfactant-templated method reliably produced high initial surface areas for the as-calcined oxide mixtures regardless of precursor salts, ≥200 m$^2$/g except for the sample with the largest La concentration. We observed a smaller crystallization exotherm (by calorimetry) and less crystallinity (by XRD peak intensities) upon calcination for materials with intermediate Ce/M (La, Tb) ratios, and no XRD evidence of a second phase (La or Tb oxide or hydroxide) in the as-
calcined materials. The XRD estimates of the particle size of some as-calcined materials are also in Table 4-1. These were obtained using the Scherrer equation for the fluorite structure peak near $2\theta = 28^\circ$, with the constant $k = 0.9$. The XRD spectra of used materials were more difficult to interpret, because these materials were characterized by low intensity in XRD, suggesting irregular structures.

The pure CeO$_2$ synthesized by our method is characterized by relatively large crystalline nanoparticles (from XRD), which is inconsistent with its high initial surface area; the high initial surface area may be due to very small pores within the crystalline nanoparticles or else other more disordered small particles are present.

Table 4-1 Composition and Properties of Adsorbents

<table>
<thead>
<tr>
<th>Designation</th>
<th>Molar Ratio</th>
<th>Calcined Surface Area (m$^2$/g)</th>
<th>Used, $\geq$ 3 cycles (m$^2$/g)</th>
<th>XRD Particle Size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce0.9/La</td>
<td>Ce/La = 0.9</td>
<td>110</td>
<td>21</td>
<td>43</td>
</tr>
<tr>
<td>Ce3/La</td>
<td>Ce/La = 3</td>
<td>240</td>
<td>94</td>
<td>20</td>
</tr>
<tr>
<td>Ce6/La</td>
<td>Ce/La = 6</td>
<td>200</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>Ce3/Tb</td>
<td>Ce/Tb = 3</td>
<td>210</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Ce6/Tb</td>
<td>Ce/Tb = 6</td>
<td>200</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>Ce1</td>
<td>CeO$_2$</td>
<td>220</td>
<td>180</td>
<td>95</td>
</tr>
</tbody>
</table>

The averaged sulfur adsorption data are shown in Figure 4.2. What is evident from the Figure is that the ratio of Ce/M has at least as great an effect on the sulfur capacity as the identity of the second rare earth. However, comparing results at a Ce/M ratio of 3, the order in capacity for dopants is La > Tb > pure ceria. At a Ce/M ratio of 6, pure CeO$_2$ is actually better than Ce/Tb, but both have much lower sulfur capacity than Ce/La. The high error bar on the pure CeO$_2$ (Ce1) results from further decrease in sulfur capacity upon use in repeated cycles.
4.3.2 H$_2$S Adsorption and Dissociation

Figure 4.3 displays the lowest energy adsorption configurations for H$_2$S, SH, and S on an oxygen vacancy on the CeO$_2$(111) surface. Adsorption of H$_2$S, SH, and S was also considered over the intact CeO$_2$(111) surface, however adsorption is more exergonic over a surface oxygen vacancy. The adsorption configurations and orientation of adsorbates with respect to surface atoms are similar for H$_2$S, SH, and S adsorption on ceria, ceria-lanthana, and ceria-terbia, with small differences in surface atom-adsorbate distances. Adsorption configurations and inter-atom distances are included in detail in the Supplementary Information.
Figure 4.3 Top (a), (c), (e), and side (b), (d), (f) views of surface unit cell for H$_2$S* (a), (b), SH* (c), (d), and S* (e), (f) on CeO$_2$(111). Ce atoms are colored tan (light), O atoms red (dark), S atoms green (gray), and H atoms white. Surface metal atoms are denoted Ce$_1$, Ce$_2$, and M as referenced in Table 4-1 for bond lengths between surface atoms and adsorbed sulfur species.

Figures 4.4(a), 4.5(a), and 4.6(a) display the free energy diagrams for H$_2$S adsorption and dissociation over the ceria, ceria-lanthana, and ceria-terbia surfaces, respectively, at 1100K, and $P_{H_2} = 0.35$ atm, $P_{H_2S} = 10^{-2}$ atm, and $P_{H_2O} = 0.03$ atm. Free energies for H$_2$S adsorption and dissociation are plotted over each fully oxidized surface as well as over reduced surfaces. The free energy of forming a substoichiometric oxygen vacancy is exergonic on all three surfaces.
Vacancy formation energies for each reduced surface are included on the free energy diagrams prior to adsorption and dissociation steps, and the most favorable product state is labeled in bold.

Figure 4.4 (a) Free energy diagram for H$_2$S adsorption dissociation over CeO$_2$(111) at 1100K, and $P_{H_2} = 0.35$ atm, $P_{H_2S} = 10^{-2}$ atm, and $P_{H_2O} = 0.03$ atm and (b) phase diagram for CeO$_2$(111) surface at 1100K as a function of H$_2$S(g) and O$_2$(g) pressure. Oxygen vacancies are denoted $V_O^-$. 

50
Figure 4.5. (a) Free energy diagram for H$_2$S adsorption dissociation over La$_2$O$_3$/CeO$_2$(111) at 1100K, and $P_{H_2} = 0.35$ atm, $P_{H_2S} = 10^{-2}$ atm, and $P_{H_2O} = 0.03$ atm and (b) phase diagram for La$_2$O$_3$/CeO$_2$(111) surface at 1100K as a function of H$_2$S(g) and O$_2$(g) pressure. Oxygen vacancies are denoted $V_{O^*}$.
Figure 4.6 (a) Free energy diagram for H$_2$S adsorption dissociation over Tb$_2$O$_3$/CeO$_2$(111) at 1100K, and $P_{H_2} = 0.35$ atm, $P_{H_2S} = 10^{-2}$ atm, and $P_{H_2O} = 0.03$ atm and (b) phase diagram for Tb$_2$O$_3$/CeO$_2$(111) surface at 1100K as a function of H$_2$S(g) and O$_2$(g) pressure. Oxygen vacancies are denoted V$_O$. 
4.3.3 H$_2$S Adsorption and Dissociation on CeO$_2$(111)

Molecular adsorption of H$_2$S on the intact CeO$_2$(111) surface is highly endergonic (a positive Gibbs free energy change of +4.00 eV) at 1100K and P$_{H_2S}$ = 10$^{-2}$ atm due to large translational entropy contributions to the free energy of H$_2$S(g) at this high temperature and low partial pressure, and weak interaction between the H$_2$S molecule and the ceria surface. The DFT energy ($\Delta E_{ads}$) of molecular H$_2$S adsorption is -0.22 eV (in contrast to the free energy of +4.00 eV), illustrating the magnitude of entropic contributions to adsorption energies. Analysis based purely on 0 K energetics, for which H$_2$S adsorption is exothermic and vacancy formation is endothermic, can be significantly misleading. Dissociation of H$_2$S to SH* is also endergonic (+0.34 eV), with dissociation of SH* to S* and subsequent desorption of 2H* to H$_2$(g) exergonic.

Adsorption of H$_2$S, SH, and S on the intact CeO$_2$(111) surface occurs atop a surface Ce atom, atop a surface oxygen atom, and bridged between a surface Ce and surface O, respectively, in equivalent configurations to those presented by Lin et al.$^{174}$ Hydrogen atoms adsorb atop surface oxygen atoms, equivalent to surface hydroxyls (-OH). The overall process of S* formation on the stoichiometric CeO$_2$(111) surface is highly endergonic (+2.12 eV) indicating that this adsorption, also studied by Lin et al.,$^{174}$ will not occur to a significant extent ($K_{ads} = 1.9 \times 10^{-10}$ at 1100 K). This result highlights the need to consider $\Delta G(T)$ versus 0K $\Delta E$ values when evaluating H$_2$S adsorption processes.

We have not included energy barriers for H$_2$S dissociation. Our attempts to apply climbing image nudged elastic band (CI-NEB) searches indicated a monotonic increase in energy along an H- abstraction pathway (H$_2$S(g) $\rightarrow$ SH(g) + H* $\rightarrow$ SH* + H*), suggesting the barrier is not substantially greater than the reaction energy. Lin et al. report activation barriers of 0.08 eV for H$_2$S* $\rightarrow$ SH* + H* and 0.36 eV for SH* + H* $\rightarrow$ S* + 2H* over CeO$_2$(111).$^{174}$ The barrier
of 0.36 eV for $\text{SH}^* + \text{H}^* \rightarrow \text{S}^* + 2\text{H}^*$ suggests, based on our free energy diagram, that the transition state for this reaction step will be the highest energy state and dictates the apparent activation free energy (+4.70 eV, the free energy difference between the $\text{SH}^*$ dissociation transition state and the initial bare surface and $\text{H}_2\text{S}$ gas) over $\text{CeO}_2(111)$, however the highly endergonic thermodynamics of $\text{H}_2\text{S}$ adsorption contributes the majority of this energy barrier.

Formation of two oxygen vacancies in our unit cell (50% of surface oxygen) is exergonic on $\text{CeO}_2(111)$ at 1100K, $P_{\text{H}_2} = 0.35$ atm, and $P_{\text{H}_2\text{O}} = 0.03$ atm. Free energies for $\text{H}_2\text{S}$ adsorption and dissociation over the $\text{CeO}_2(111)$ with one (25% vacant) and two (50% vacant) vacancies per surface unit cell are displayed in Figure 4.4(a). Molecular adsorption of $\text{H}_2\text{S}$ is still highly endergonic over the reduced $\text{CeO}_2(111)$ surface, at +3.77 eV (-0.45 eV at 0 K) with one vacancy and +2.91 eV (-1.31 eV at 0 K) with two vacancies, however it is less endergonic than over intact $\text{CeO}_2(111)$. Molecular adsorption of $\text{H}_2\text{S}$ occurs via interaction between the sulfur atom of $\text{H}_2\text{S}$ and Ce atoms nearest neighbor to an oxygen vacancy ($V_\text{O}$) on reduced $\text{CeO}_2(111)$. Dissociation of $\text{H}_2\text{S}$ to $\text{SH}^*$ and $\text{S}^*$ is exergonic over each reduced ceria surface, and $\text{SH}^*$ and $\text{S}^*$ adsorb on the oxygen vacancy site. With $\text{S}^*$ replacing a surface oxygen, it is exergonic to form an additional $V_\text{O}$, leaving a surface with $2V_\text{O}$ and $\text{S}^*$ adsorbed to a third oxygen vacancy. The lowest energy path for $\text{H}_2\text{S}$ adsorption and dissociation (labeled in red on Figure 4.4(a)) results in a final product with stoichiometry in the surface layer (top Ce layer, top 2 oxygen layers) of $\text{CeO}_{1.25}\text{S}_{0.25}$. The reaction free energy diagram for $\text{H}_2\text{S}$ adsorption and dissociation over $\text{CeO}_2(111)$ at 1100K, and $P_{\text{H}_2} = 0.35$ atm, $P_{\text{H}_2\text{S}} = 10^{-2}$ atm, and $P_{\text{H}_2\text{O}} = 0.03$ atm thus illustrates that it is thermodynamically favorable for sulfur atoms from $\text{H}_2\text{S}(g)$ to substitute into the ceria surface for oxygen atoms. The overall process of adding an $\text{S}^*$ from $\text{H}_2\text{S}$ to the doubly vacant surface is exergonic by 0.57 eV. Further sulfidation involving addition of $\text{S}^*$ to oxygen vacancy
sites or further replacement of surface oxygen atoms with sulfur atoms is not favorable, as will be discussed in Section 3.3.

The S* incorporation reaction can be taken as a two-step process of H₂S adsorption (equilibrium constant K_{ads}) followed by H-S bond dissociation (rate constant k). As K_{ads} is extremely small under desulfurization conditions, the apparent activation free energy will be given by the exponential term in the product of k and K_{ads}. As mentioned above, the activation barrier incorporated in k is small, and therefore the adsorption free energy can be taken as an approximation of the S incorporation free energy barrier. This value will serve as a minimum, as it can be further increased by the undetermined (small) H-S dissociation barrier. For the pure CeO₂(111) surface with two oxygen vacancies, this value is +2.91 eV.

In summary, the sulfur adsorption process occurs via H₂S adsorption and dissociation over oxygen vacancies, and is rate limited by a strongly endergonic molecular adsorption of H₂S.

### 4.3.4 H₂S Adsorption and Dissociation on La₂O₃/CeO₂(111)

Molecular adsorption of H₂S is also highly endergonic (+3.88 eV at 1100 K, -0.34 eV at 0 K, Figure 4.7(a)) on the La₂O₃/CeO₂(111) surface, adsorbing atop the stoichiometric oxygen vacancy. Subsequent dissociation steps to SH* and S* are endergonic, as is the overall sulfidation reaction to form S* and desorb H₂(g). It is not favorable for sulfur atoms from H₂S(g) to incorporate into the stoichiometric oxygen vacancy on La₂O₃/CeO₂(111) because La and Ce atoms in the surface are in their highest stable oxidation states (La³⁺ and Ce⁴⁺). In the presence of a second, substoichiometric oxygen vacancy (-0.74 eV V'O formation free energy), which results in the reduction of 2Ce⁴⁺ to 2Ce³⁺, molecular H₂S adsorption is less endergonic (+2.22 eV at 1100 K, -2.00 eV at 0 K) and H₂S dissociation more exergonic than on the intact La₂O₃/CeO₂(111) surface. Adsorption and dissociation of H₂S over the reduced La₂O₃/CeO₂(111)
surface occurs via adsorption of $\text{H}_2\text{S}^*$, $\text{SH}^*$ and $\text{S}^*$ species at an oxygen vacancy site nearest neighbor to the 3 surface Ce atoms in the unit cell. Formation of an additional oxygen vacancy is exergonic with $\text{S}^*$ present, and the surface stoichiometry of the final product state over $\text{La}_2\text{O}_3/\text{CeO}_2(111)$ is $\text{La}_{0.25}\text{Ce}_{0.75}\text{O}_{1.25}\text{S}_{0.25}$, equivalent to the oxygen and sulfur stoichiometry of the final product over $\text{CeO}_2(111)$. The overall free energy of formation of this final product from the doubly vacant surface is -0.25 eV, in comparison to -0.57 eV over pure ceria, which illustrates that the thermodynamics of sulfur incorporation over the pure ceria surface are more favorable than over the ceria-lanthana surface. The apparent energy barrier for $\text{H}_2\text{S}$ adsorption and dissociation over $\text{La}_2\text{O}_3/\text{CeO}_2(111)$ is at a minimum +2.23 eV (the molecular adsorption energy of $\text{H}_2\text{S}$, assuming no S-H breaking activation barrier), much lower than over $\text{CeO}_2(111)$ (at a minimum +2.91 eV). Thus the kinetics of $\text{H}_2\text{S}$ adsorption and dissociation over $\text{La}_2\text{O}_3/\text{CeO}_2(111)$ are much faster than over $\text{CeO}_2(111)$, which would dictate a higher sulfur adsorption capacity under kinetically limited operating regimes.

### 4.3.5 $\text{H}_2\text{S}$ Adsorption and Dissociation on $\text{Tb}_2\text{O}_3/\text{CeO}_2(111)$

Molecular adsorption of $\text{H}_2\text{S}$ on $\text{Tb}_2\text{O}_3/\text{CeO}_2(111)$ is slightly stronger (+3.86 eV at 1100 K, -0.36 eV at 0 K) than on $\text{CeO}_2(111)$ or $\text{La}_2\text{O}_3/\text{CeO}_2(111)$, however adsorption is still highly unfavorable over the stoichiometric oxygen vacancy. Adsorption and dissociation are more exergonic over the reduced $\text{Tb}_2\text{O}_3/\text{CeO}_2(111)$ surface, which occurs by adsorption of $\text{H}_2\text{S}^*$, $\text{SH}^*$ and $\text{H}^*$ over an oxygen vacancy nearest neighbor to two surface Ce atoms and one surface Tb atom. Adsorption of $\text{H}_2\text{S}$ is slightly more endergonic (+2.30 eV) over the reduced $\text{Tb}_2\text{O}_3/\text{CeO}_2(111)$ surface than over the reduced $\text{La}_2\text{O}_3/\text{CeO}_2(111)$ surface (+2.22 eV). Dissociation steps subsequent to $\text{H}_2\text{S}$ adsorption are exergonic, and the final product of the
lowest energy path is \( \text{Tb}_{0.25}\text{Ce}_{0.75}\text{O}_{1.25}\text{S}_{0.25} \), equivalent to that formed on CeO\(_2\)(111) and La\(_2\)O\(_3\)/CeO\(_2\)(111).

### 4.3.6 Thermodynamic Limit for Sulfidation of Oxide Surfaces

The free energy diagrams presented in section 3.2 are evaluated at specific conditions (1100K, and \( P_{\text{H}_2} = 0.35 \text{ atm}, P_{\text{H}_2\text{S}} = 10^{-2} \text{ atm}, \) and \( P_{\text{H}_2\text{O}} = 0.03 \text{ atm} \)). We also calculated the equilibrium composition of the ceria, ceria-lanthana, and ceria-terbia surfaces over a range of possible \( \text{H}_2\text{S}(g) \) and \( \text{O}_2(g) \) pressures. Pressure ranges for \( \text{H}_2\text{S}(g) \) are estimated from compositional analysis of syngas produced from the gasification of ten different biomass sources.\(^{166}\) Effective \( \text{O}_2(g) \) pressure ranges are estimated by assuming equilibrium between \( \text{H}_2(g) \) and \( \text{H}_2\text{O}(g) \), or \( \text{CO}(g) \) and \( \text{CO}_2(g) \) in the syngas streams, and setting range limits as the largest and smallest values for \( \text{O}_2(g) \) pressure calculated from either \( \text{H}_2(g) \) and \( \text{H}_2\text{O}(g) \) equilibrium or \( \text{CO}(g) \) and \( \text{CO}_2(g) \) equilibrium in the ten compositions studied by Vermeulen et al.\(^{166}\) We estimate the pressure ranges in syngas produced from biomass gasification as \( 10^{-6}-10^{-2} \text{ atm} \) \( \text{H}_2\text{S}(g) \) and \( 10^{-26}-10^{-20} \text{ atm} \) \( \text{O}_2(g) \).

Phase diagrams for the sulfur content of the ceria, ceria-lanthana, or ceria-terbia surfaces are constructed by calculating the free energy of the following reaction as a function of \( \text{H}_2\text{S} \) and \( \text{O}_2 \) pressure:

\[
 z \text{H}_2\text{S} + \text{MO}_{x-y}\text{S}_y \rightarrow \text{MO}_{x-z}\text{S}_{y+z} + z \text{H}_2 + \frac{z}{2} \text{O}_2 \quad (4-5)
\]

where sulfur atoms from \( \text{H}_2\text{S} \) substitute into the ceria lattice for oxygen atoms. Formation of either \( \text{O}_2(g) \) and \( \text{H}_2(g) \) or \( \text{H}_2\text{O}(g) \) as reaction products is equivalent by assuming equilibrium between \( \text{H}_2\text{O}(g), \text{H}_2(g), \) and \( \text{O}_2(g) \) as stated in equation (4). Substitution of oxygen atoms for sulfur atoms is considered for the surface and subsurface layers of oxygen atoms in the
ceria, ceria-lanthana, and ceria-terbia surfaces. Stoichiometries considered for the surface metal layer include configurations of sulfur and oxygen from fully oxidized (MO\textsubscript{2}) to reduced (M\textsubscript{2}O\textsubscript{3}):\

\[ 1.5 < \frac{n_{\text{oxygen}} + n_{\text{sulfur}}}{n_{\text{metal}}} < 2 \]  

(4-6)

where \( n_{\text{oxygen}} \), \( n_{\text{sulfur}} \), and \( n_{\text{metal}} \) are the number of oxygen atoms, sulfur atoms, and metal atoms, respectively in the surface CeO\textsubscript{2} layer (surface metal layer and surface and subsurface oxygen atom layers). In equation (6), \( n_{\text{metal}} = 4 \) for all stoichiometries as the p(2x2) surface unit cell contains 4 metal atoms in the surface metal layer, and \( n_{\text{oxygen}} + n_{\text{sulfur}} = 6, 7, \) or \( 8 \) corresponding to the total number of oxygen and sulfur atoms in the surface and subsurface layers. To locate the lowest energy structure for each stoichiometry, structural optimizations were performed with oxygen and sulfur atoms in all possible configurations with respect to surface metal atoms and oxygen vacancies. The optimized structures reported for each stoichiometry of oxygen and sulfur are constrained by the size of the surface unit cell, which only permits surface reordering on the length scales of the p(2x2) expansion. The phase diagrams we report are useful, however, in identifying trends between ceria, ceria-lanthana, and ceria-terbia for the thermodynamic limit of surface sulfur incorporation while the underlying cubic fluorite bulk lattice is maintained.

4.3.7 Phase Diagram for Sulfdation of CeO\textsubscript{2}(111)

Figure 4.4(b) displays the phase diagram for the sulfidation of the CeO\textsubscript{2} (111) surface as a function of H\textsubscript{2}S(g) and O\textsubscript{2}(g) pressure at 1100K. At low H\textsubscript{2}S and the highest relevant O\textsubscript{2} pressure, the reduced ceria surface (surface stoichiometry of CeO\textsubscript{1.75}) is stable with respect to other surface compositions. At lower O\textsubscript{2} pressure and increasing H\textsubscript{2}S pressures, the CeO\textsubscript{1.25}S\textsubscript{0.25} surface stoichiometry is favorable, and at the edge of the range of biomass gasifier partial pressures (high H\textsubscript{2}S and low O\textsubscript{2} pressure), CeO\textsubscript{1.00}S\textsubscript{0.5} is favorable. The CeO\textsubscript{1.25}S\textsubscript{0.25} surface is
stable over a wide range of H₂S and O₂ pressures, including the conditions used to evaluate H₂S adsorption free energies in Section 3.2. The wide range over which the CeO₁.₂₅S₀.₂₅ surface is thermodynamically favorable indicates that further sulfidation relative to this stoichiometry is not favorable, though we again note that this is under the constraint of maintaining the fluorite lattice dimensions. The surface stoichiometry of CeO₁.₀₀S₀.₅ is comprised of 2 surface sulfur atoms, 1 surface oxygen and 3 subsurface oxygen (1 oxygen vacancy formed subsurface). Kay et al. report that over the same H₂S (10⁻⁶-10⁻² atm) and O₂ (10⁻₂⁶-10⁻₂⁰ atm) pressure ranges considered here, Ce₂O₂S, CeOₓ (1.73 < x < 1.83), and Ce₂O₃ are thermodynamically favorable bulk phases.¹⁷² Over the majority of these H₂S and O₂ pressures, the authors report that Ce₂O₂S is thermodynamically favorable,¹⁷² which is equivalent to a surface stoichiometry of CeO₁.₀₀S₀.₅ in the p(2x2) unit cell.

Both the H₂S adsorption free energy diagram and the phase diagram for the CeO₂(111) surface show that substitution of sulfur atoms into oxygen lattice positions is only favorable when multiple adjacent oxygen vacancies are present. Sulfur-metal distances are longer than oxygen-metal distances in the ceria surface, and the ionic radius of sulfur is approximately 1 Å compared to approximately 0.6 Å for oxygen.¹⁹⁶ Sulfur incorporation into the ceria surface is thus only favorable if multiple adjacent oxygen vacancies are present to provide the structural flexibility necessary to accommodate the larger coordination shell of sulfur atoms than oxygen atoms in the ceria lattice.

4.3.8 Phase Diagram for Sulfidation of La₂O₃/CeO₂(111)

Figure 4.5(b) displays the phase diagram for the sulfidation of the La₂O₃/CeO₂(111) surface as a function of H₂S (g) and O₂ (g) pressure at 1100K. The phase diagram for La₂O₃/CeO₂(111) is comprised of regions of identical surface sulfur and oxygen stoichiometry to
those of CeO$_2$(111), however the transition from La$_{0.25}$Ce$_{0.75}$O$_{1.75}$ to La$_{0.25}$Ce$_{0.75}$O$_{1.25}$S$_{0.25}$ occurs at lower O$_2$ and higher H$_2$S pressure than the transition from CeO$_{1.75}$ to CeO$_{1.25}$S$_{0.25}$. Sulfur incorporation is also only favorable with the formation of multiple oxygen vacancies within the surface unit cell over the La$_2$O$_3$/CeO$_2$(111) surface. The phase diagram over La$_2$O$_3$/CeO$_2$ is consistent with the free energies of H$_2$S adsorption over La$_2$O$_3$/CeO$_2$ and pure ceria. The thermodynamics of H$_2$S dissociation are more exergonic over pure ceria, and thus transition to a sulfided surface stoichiometry occurs at lower H$_2$S(g) and higher O$_2$(g) pressures on ceria than on ceria-lanthana. The positions of lanthanum dopants in the ceria surface are arbitrary and fixed, however these results illustrate that the ceria-lanthana mixtures may not stabilize higher surface sulfur concentrations with respect to pure ceria under equilibrium conditions.

4.3.9 Phase Diagram for Sulfidation of Tb$_2$O$_3$/CeO$_2$(111)

Figure 4.6(b) displays the phase diagram for the sulfidation of the Tb$_2$O$_3$/CeO$_2$(111) surface as a function of H$_2$S(g) and O$_2$(g) pressure at 1100K. The transition from Tb$_{0.25}$Ce$_{0.75}$O$_{1.75}$ to Tb$_{0.25}$Ce$_{0.75}$O$_{1.25}$S$_{0.25}$ occurs at a slightly lower O$_2$ and slightly higher H$_2$S pressure than the transition from CeO$_{1.75}$ to CeO$_{1.25}$S$_{0.25}$. The phase diagram over ceria-terbia, however, does show that formation of a more highly sulfided surface than on ceria or ceria-lanthana (Tb$_{0.25}$Ce$_{0.75}$O$_{0.75}$S$_{0.75}$) is thermodynamically favorable at high H$_2$S and low O$_2$ pressure. The Tb$_{0.25}$Ce$_{0.75}$O$_{0.75}$S$_{0.75}$ surface is terminated by 3 surface sulfur atoms with 3 oxygen atoms in the subsurface layer. This transition to a greater sulfur content at the ceria-terbia surface suggests that the equilibrium sulfur capacity of such surfaces could be larger than that of ceria or ceria-lanthana for certain syngas compositions (high P$_{H_2S}$, low P$_{O_2}$).

The phase diagrams for sulfidation of the ceria, ceria-lanthana, and ceria-terbia surfaces illustrate the importance of oxygen vacancies as active sites for high temperature H$_2$S adsorption
and dissociation. The thermodynamic driving force for the H$_2$S adsorption process is dictated by the relative energy of substituting sulfur atoms from H$_2$S for oxygen atoms in the metal oxide lattice. The equilibrium sulfur capacity of the metal oxide surface is thus a function of the partial pressure of H$_2$S and the effective O$_2$ partial pressure (dictated by the partial pressures of H$_2$, H$_2$O, CO, and CO$_2$) in the gas phase. The free energy to form a surface stoichiometry of MO$_{1.25}$S$_{0.25}$ is most exergonic on the pure ceria surface, and the ceria-terbia surface may have the largest equilibrium sulfur capacity under high P$_{H_2S}$ and low P$_{O_2}$. Considering the H$_2$S pressures at which formation of the MO$_{1.25}$S$_{0.25}$ stoichiometry forms, our calculations indicate that from a thermodynamic standpoint the adsorption of H$_2$S is most favorable on pure ceria, with adsorption on ceria-terbia more favorable than on lanthana-ceria. Because this is largely contrary to the experimental results, we can conclude that other considerations dictate adsorption from constant composition feeds in packed adsorbent beds. We consider two other possibilities: (1) the adsorption is kinetically limited by the initial adsorption of H$_2$S at an oxygen vacancy; (2) the presence of the dopants (La, Tb) results in the formation of more oxygen vacancies by greater distortion of the CeO$_2$ crystalline lattice.

4.3.10 Thermodynamic Cycle for H$_2$S adsorption by Ceria-Based Mixed Oxides

Figure 4.7 displays the thermodynamic cycle considered for H$_2$S adsorption and dissociation over the reduced ceria surface. The surface in Figure 4.7 is denoted MO$_{1.75}$, to signify a surface stoichiometry of either CeO$_{1.75}$, La$_{0.25}$Ce$_{0.75}$O$_{1.75}$, or Tb$_{0.25}$Ce$_{0.75}$O$_{1.75}$. The free energies for each step (vacancy formation, H$_2$S adsorption, and H$_2$S dissociation) over CeO$_{1.75}$, La$_{0.25}$Ce$_{0.75}$O$_{1.75}$, and Tb$_{0.25}$Ce$_{0.75}$O$_{1.75}$ at 1100K, and $P_{H_2} = 0.35$ atm, $P_{H_2S} = 10^{-2}$ atm, and $P_{H_2O} = 0.03$ atm are listed in Table 4-2. The overall free energy to form MO$_{1.25}$S$_{0.25}$ is most exergonic over CeO$_2$. The ceria-terbia surface is more reducible than the ceria or ceria-lanthana surfaces,
with an oxygen vacancy formation free energy of -1.05 eV. Molecular H₂S adsorption is strongest over ceria-lanthana at +2.23 eV, compared to +2.30 eV over ceria-terbia and +2.91 eV over ceria. The thermodynamics of the overall H₂S adsorption process do not correlate with oxygen vacancy formation energy, implying that the optimization of ceria-based sulfur sorbents cannot be achieved by tailoring composition to maximize the exergonicity of vacancy formation.

The rate limiting step for H₂S adsorption and dissociation involves reaching the transition state for dissociation of the first S-H bond to form SH*+H* (>2.23 eV over each surface), and the rate is highest over ceria-lanthana (rate over ceria-lanthana > ceria-terbia > ceria). This is the same order as the experimental sulfur capacities, if these capacities are compared at the similar Ce3M molar basis. Agreement with the experimental capacities suggests that the actual sulfur capacities of ceria-based mixed oxides are largely determined by the kinetics of the H₂S dissociation.

Table 4-2 Energies for thermodynamic cycle (Figure 4.7) over CeO₂, LaCeOₓ, and TbCeOₓ.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>CeO₂</th>
<th>La₂O₃/CeO₂</th>
<th>Tb₂O₃/CeO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall</td>
<td>-1.35</td>
<td>-0.98</td>
<td>-1.3</td>
</tr>
<tr>
<td>1</td>
<td>-0.78</td>
<td>-0.74</td>
<td>-1.05</td>
</tr>
<tr>
<td>2</td>
<td>2.91</td>
<td>2.23</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>-3.48</td>
<td>-2.47</td>
<td>-2.55</td>
</tr>
</tbody>
</table>

4.3.11 Differences in Oxygen Vacancy Formation in Ceria-Based Mixed Oxides

Because converting CeO₂ to the oxysulfide follows the formation of oxygen vacancies (reduction to Ce³⁺), it is likely that increasing the concentration of oxygen vacancies will also increase the sulfur capacity. It has been established experimentally that disordered, small particle CeO₂ exhibits larger concentrations of Ce³⁺ than larger particles of crystalline CeO₂.197-
The smaller XRD particles sizes of Ce/La oxide vs. CeO$_2$ (Table 4-1) therefore are expected to display greater sulfur capacities, as observed, but the sizes determined from XRD do not correlate with the S capacities. Mixing 10-30 at% La with CeO$_2$ enhances the experimental (TPR) rates of reduction of Ce$^{4+}$ over a wide range of temperatures.$^{197,201,202}$ However, adding even more La$_2$O$_3$ results in a poorer adsorbent (lower sulfur capacity for Ce0.9/La in Fig. 4.2), probably due to both lower surface area/larger particle size (see Table 4-1), and also stronger adsorption of CO$_2$, neither of which could be captured in the present DFT calculations. Lanthanum carbonates do not decompose in flowing dry air until ~720-800 K, and the decomposition is not complete until ~1200 K at 1 atm,$^{203-205}$ ~300 K higher than for Ce(CO$_3$)$_2$.$^{206}$

![Thermodynamic cycle for H$_2$S adsorption and dissociation on ceria-based mixed metal oxide.](image)

**Figure 4.7** Thermodynamic cycle for H$_2$S adsorption and dissociation on ceria-based mixed metal oxide.

### 4.4 CONCLUSIONS

The DFT+$U$ method and *ab initio* thermodynamics were used to evaluate the free energies of H$_2$S adsorption and dissociation over ceria, ceria-lanthana, and ceria-terbia. Surface models consisted of the (111) single crystal termination of CeO$_2$, as well as the CeO$_2$(111) surface with lanthanum and terbium atoms substituted for Ce atoms. We evaluated the free energies of H$_2$S adsorption and dissociation in contrast to purely DFT energies, which illustrated
the importance of entropic contributions to quantify the driving force for adsorption of gas phase species at high temperature and low partial pressure. Molecular adsorption of H$_2$S is endergonic over the fully oxidized and intact ceria, ceria-lanthana, and ceria-terbia surfaces at high temperature desulfurization conditions. Adsorption of H$_2$S involves $V_0^-$ formation, filling of $V_0^-$ with S*, and subsequent $V_0^-$ formation; H$_2$S adsorption requires multiple adjacent oxygen vacancies to provide structural flexibility to accommodate large S$^{2-}$ ions. The apparent activation free energy of H$_2$S adsorption and dissociation over ceria are much larger than those over ceria-lanthana and ceria-terbia, suggesting that the larger sulfur adsorption capacity observed experimentally for ceria-lanthana is due to faster surface kinetics over the mixed oxide surfaces. Trends in experimentally measured sulfur capacities of ceria-lanthanide mixtures suggest that particle size also influences sulfur capacity, though not by merely modulating surface area. The thermodynamic reducibility of the oxide mixture as given by DFT calculations does not correlate with sulfur adsorption and dissociation energetics, and the optimization of ceria-based mixed oxide sulfur sorbents may therefore lie in the design of mixed oxides with faster H$_2$S dissociation kinetics and smaller nanoparticle sizes which can remain stable under sulfiding conditions.
CHAPTER 5: CE-MN OXIDES FOR HIGH-TEMPERATURE GASIFIER EFFLUENT DESULFURIZATION

5.1 INTRODUCTION

Mixed rare-earth oxides (REOs) such as CeO$_2$/La$_2$O$_3$ can adsorb H$_2$S at high temperatures from gases produced in fuel (biomass or coal) gasification processes.$^{84,92,101,103,207}$ For CeO$_2$, the sulfidation process is dependent upon the formation of vacancies and reduction to the Ce$^{3+}$ state.$^{175}$ Whereas unpromoted CeO$_2$ is sulfided (reduced) relatively slowly by H$_2$S/H$_2$ mixtures, the rate can be enhanced by as much as an order of magnitude if it is intimately mixed with certain other oxides such as La$_2$O$_3$. Other oxide dopants (e.g., ZrO$_2$, Tb$_2$O$_3$, Gd$_2$O$_3$, Al$_2$O$_3$) can be added to further stabilize the sorbent in repetitive redox reactions, preventing REO crystal growth, possibly by limiting cation diffusion.$^{100,208-217}$ Though these mixed ceria-based oxides can offer rapid adsorption and increased capacities relative to the single metal oxide systems, capacities still fall short of desired values.

Of all single oxides studied, MnO exhibits the highest initial reaction rate with H$_2$S in the temperature range 600-1100 K.$^{59}$ Under a simulated syngas mixture (30% CO, 20% H$_2$, 49% N$_2$ and 1% H$_2$S), MnO$_x$/Al$_2$O$_3$ exhibited initial 100% oxide utilization and a high sulfur capacity at 770-970 K.$^{67}$ In a gasifier atmosphere, Mn$_3$O$_4$ is readily reduced to MnO, but MnO cannot be further reduced at temperatures below 1920 K.$^{68}$ Manganese sulfate (MnSO$_4$), formed during air regeneration, is stable below 1070 K,$^{69}$ and this stability constitutes a serious problem in utilizing MnOx-based sorbents for long term use.

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Supporting MnO\textsubscript{x} on Al\textsubscript{2}O\textsubscript{3} can partially alleviate regeneration difficulties, though MnAl\textsubscript{2}O\textsubscript{4} gradual formation can also limit long term stability. With an alumina support under reducing conditions, MnAl\textsubscript{2}O\textsubscript{4} is formed gradually, and it cannot be fully sulfided except above 1070 K.\textsuperscript{53} The unsupported (on Al\textsubscript{2}O\textsubscript{3}) MnO\textsubscript{x} adsorbs more H\textsubscript{2}S, even in the presence of water.\textsuperscript{53} But the 3:1 (by weight) MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} system can rapidly react with sulfur gases, and it also can be regenerated with air at 1073 K.\textsuperscript{218} A study of MnO\textsubscript{x}/\gamma-Al\textsubscript{2}O\textsubscript{3} at 873 K with a syngas mixture (17% H\textsubscript{2}, 35% CO, 0.64% H\textsubscript{2}S and 2.1% H\textsubscript{2}O) for greater than 300 cycles found that most of the deactivation occurred in the first ten cycles, from 0.46 to 0.15 mmol S/g-sorbent.\textsuperscript{108}

To avoid the formation of MnSO\textsubscript{4} during regeneration, several alternative regeneration strategies have been proposed.\textsuperscript{70} Regeneration with SO\textsubscript{2} is slow but feasible at 873 K, forming elemental sulfur.\textsuperscript{53} Steam regeneration also precludes the formation of MnSO\textsubscript{4}, and reduces hot spots during regeneration that can cause sintering. However, steam regeneration is not completely effective and it is slow.\textsuperscript{71} Regeneration with diluted air at temperatures higher than 1070 K can decompose sulfate, however, the sorbent capacity decays progressively due to sintering.\textsuperscript{72} Regeneration with H\textsubscript{2} was also studied for sulfided MnO and MnO/SiO\textsubscript{2} sorbents. Pure MnSO\textsubscript{4} could only be decomposed at ~1100 K in 10% H\textsubscript{2}, while silica-supported, sulfated MnO was readily regenerated at 933 K.\textsuperscript{73} Different regeneration strategies have also been tested using CO\textsubscript{2}, diluted air, and diluted air in combination with water; only the first was ineffective.\textsuperscript{74} Each of these has drawbacks in terms of regeneration rate, extent, or in requiring high temperatures. It would be preferable to develop a MnO\textsubscript{x}-containing sorbent that could be regenerated rapidly with air at near-adsorption temperatures while avoiding significant irreversible sulfate formation.
An extension of this past work is an attempt to combine the thermal stability and low H$_2$S equilibrium concentration of the mixed REOs with the high sulfur capacity and rapid sulfidation kinetics of MnO$_x$. Recent work has shown that such REO/MnO$_x$ mixtures can significantly outperform the REOs in terms of sulfur capacity when adsorbing from model syngas mixtures.$^{77,103}$ Our goal in this study is to extend this work over a wide range of MnO$_x$ compositions, using streams more closely simulating real syngas (in particular, containing competitive sorbents CO$_2$ and H$_2$O, as well as CO, H$_2$ and H$_2$S), and to explore both thermal stability and the capability for simple regeneration with undiluted air. A series of characterization techniques (XRD, XANES, EXAFS, TPR) and density functional theory methods are employed to provide greater insight into the sorbent features that dictate capacities and stabilities.

5.2 EXPERIMENTAL METHODS

Materials. Using templated sol-gel and impregnation techniques, we prepared several mixed REOs and pure CeO$_2$.\textsuperscript{103,155} The precursors were (NH$_4$)$_2$Ce(NO$_3$)$_6$ (Aldrich 99.9%), La(NO$_3$)$_3$•6 H$_2$O (Alfa Aesar 99.9%) with 1% tetramethylammonium hydroxide (Acros, 25% in methanol) surfactant in water. To this solution aqueous NH$_3$ (Alfa Aesar, 28-30%) was added, until precipitation occurred (pH ~10.3-10.5). The temperature was raised to 363 K and the gel stirred for 4 days, adjusting the pH as necessary. The centrifuged precipitate was washed with acetone and deionized water, dried at 373 K, then calcined in flowing air at 773 K with a ramp of 2 K/min and a final hold of 6 h. For Mn/Ce and Mn/Ce/La materials, a similar method was used except the pH was 9.8-10 and the reaction time was only two days.

Alternative preparation methods also used for Mn-containing sorbents were hydrothermal synthesis (cetyl trimethyl ammonium bromide template) and evaporation induced self-
assembly (EISA). For the hydrothermal synthesis, we used (molar) ratios of 1 total salts/2 NaOH / 0.333 CTAB/230 water. This mixture was reacted in a teflon-lined autoclave at 373 K for two days, then filtered, dried and calcined as discussed previously.

The EISA synthesis method was adapted from the literature. The starting (molar) ratios were 1 total precursor salts/10 water/20 ethanol in the first solution. The second solution contained the same amount of ethanol as the first, and 0.025 g Pluronic 123 (BASF) template/g ethanol. The precursor salts were Ce(O$_2$CCH$_3$)$_2$$\bullet$1.5H$_2$O (Alfa, 99.9%) and Mn(O$_2$CCH$_3$)$_2$$\bullet$4H$_2$O (Alfa, 22 wt% Mn). After mixing the two solutions and stirring at room temperature for 30 min, 0.1 M NH$_3$ was added slowly until 1 mL per 20 mL solution. The solution was spread out, added to a dessicator and gelled over calcium sulfate for 4 days, then dried in static air at 100°C for 2 days, and finally calcined as discussed previously.

Manganese was also supported on some dried CeO$_2$/La$_2$O$_3$ mixed oxides, or on Al$_2$O$_3$, by incipient wetness impregnation from Mn(NO$_3$)$_2$ followed by drying and calcining as before. The supported mixed oxides were prepared by incipient wetness impregnation from concentrated solutions of the nitrate salts on a thermally stable Al$_2$O$_3$ (BASF Ga-200-L, which contains 3% La). All of these samples were dried and calcined as discussed previously.

Desulfurization Tests. To explore these materials’ utility in gasifier effluent purification, we adsorbed H$_2$S and other components from a simulated gasifier effluent, followed by regeneration, usually in air. The simulated gasifier effluent for the adsorption/reaction step contained 0.1% H$_2$S, 23.4% H$_2$, 32% of either CO or CO$_2$, 5.0% H$_2$O, balance N$_2$ (caution: toxic mixture). This gas approximates a bio- or coal gasifier effluent, but without NH$_3$ and with slightly less water. The sulfur content is higher than is characteristic of effluents from biogasifiers, but lower than from coal gasifiers. A schematic of the reactor system is
shown as Figure 5.1. The H$_2$S was fed as a 4 mol% mixture in N$_2$. Sulfidation (adsorption) tests were performed at 900-1023 K with a GHSV of 15500 h$^{-1}$. A syringe pump was used to inject the water into the system. The gas mixture passed through a 1/4” Silcosteel 2000 U-tube containing about ~1.0 g of oxide with quartz wool on both ends, seated in a temperature-controlled sand bath. After saturation plus 5 min, the gas was switched to helium to purge the system and then to the regeneration gas at 873 K for at least 30 min. Multiple adsorption/regeneration cycles were performed, and results are generally quoted for data where capacities were changing by less than 10% cycle-to-cycle.

Figure 5.1 Schematic of reactor system for sulfur adsorption from syngas. V1 and V2 are automated switching valves.

Samples taken after the sorbent bed were injected directly into a Varian CP-3800 GC pulsed flame photometric detector (PFPD) which is specific for sulfur compounds down to ~1 ppmv sulfur. Other samples were also analyzed for CO, CH$_4$ and CO$_2$ using the Varian CP-3800 thermal conductivity detector with an Alltech CTR 1 dual packed column (1/4” outer column, activated molecular sieve, and 1/8” inner column, porous polymer) used for separation.
Retention times were determined by injecting standard gas mixtures. The sample split ratio between the columns was determined by injecting various air/CO\textsubscript{2} standards and taking the area ratio of air(inner) to the sum of air (inner), O\textsubscript{2}(outer), and N\textsubscript{2}(outer). The column was programmed with initial temperature 300 K for 4 min, 20 K/min to 403 K, and a 4 min final hold.

After the last adsorption test, the sample was cooled down in the flowing syngas and then purged for 15 min in N\textsubscript{2} prior to any post-test characterization.

Sorbent Characterization. The BET surface areas of the oxides were measured by N\textsubscript{2} adsorption - desorption using a Quantachrome AS-1 BET apparatus. The surface areas were computed from the adsorption branch of the isotherm by a 3-point BET algorithm. Inductively coupled plasma atomic emission spectroscopy (ICP) was used to determine the elemental compositions of the catalysts.

X-ray diffraction (XRD) spectra of ground, powdered samples were obtained using either a Rigaku Miniflex 2005C103 XRD at the LSU Materials Characterization Center, or using the powder XRD beamline at the LSU Center for Advanced Microstructures and Devices, both using Cu K\textalpha\ radiation. Typically these samples were scanned with a step size of 0.04\textdegree\ and a 2-6 s integration time. Phases were identified by comparing to the ICDD database.

X-ray absorption near-edge spectroscopy (XANES) and X-ray absorption fine-structure spectroscopy (XAFS) were performed at the LSU synchrotron using the Ge (2 2 0) double crystal monochromator (DCM) beamline. The Ce L\textsubscript{III} edge spectra were measured at room temperature in either transmission or fluorescence mode. The energy range was 5623 to 5923 eV for XANES and 5923 to 6139 eV for XAFS. Cerium acetate and CeO\textsubscript{2} were used as references for the Ce\textsuperscript{3+} and Ce\textsuperscript{4+} states, respectively. The sulfur K-edge data were acquired at room
temperature in fluorescence mode, due to the low sulfur content in the sample. An InSb (1 1 1) double crystal monochromator was used, and the energy ranges scanned were 2320-2450, 2450-2510, 2510-2570, 257-2670, 2670-2886, 2886-3122, and 3122-3417 eV, with interval step sizes of 5, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 eV, respectively. Sublimed S, ZnS and ZnSO$_4$ were used as S$^0$, S$^{2-}$ and S$^{6+}$ oxidation state references respectively. The Mn K-edge data were also acquired at room temperature in fluorescence mode over a scan range of 6439-6739 eV. Manganese (II) acetate and Mn(OH)$_3$ were used as Mn$^{2+}$ and Mn$^{3+}$ standards, respectively. The data were processed (background subtraction, deglitching, linear combination fitting) using Athena 0.8.061.$^{162}$

For XAFS analysis, the background subtraction, data merging, and smoothing were also performed using Athena. The spectra were Fourier-transformed over a k-range of 2 to 9 Å$^{-1}$.

Temperature-programmed reduction (TPR) was carried out on 20 mg samples in H$_2$. The samples were heated first to 773 K in air for 2 h to remove adsorbed carbonates and water. Then, the temperature was lowered to 373 K in He, the gas switched to H$_2$, and the temperature programmed with 3 K/min ramps as follows: to 903 K, 2 h hold; to 993 K, 1 h hold, to 1043 K, 1 h hold. The H$_2$ consumption was monitored by weight loss of water from the sample.

DFT Calculations. Calculations were carried out using the Vienna \textit{ab initio} simulation program (VASP), an \textit{ab initio} total energy and molecular dynamics program developed at the Institute for Material Physics at the University of Vienna.$^{180,181,219}$ The projector augmented wave (PAW) method was used to represent the core region.$^{220}$ The valence electrons were represented with a tractable plane-wave basis set with an energy cutoff of 450 eV. Valence configurations were 5s$^2$5p$^6$6s$^2$4f$^4$5d$^1$ for ceria, 2s$^2$2p$^4$ for oxygen, 1s$^1$ for hydrogen, 3s$^2$3p$^4$ for sulfur, and 3d$^6$4s$^1$ for Mn. Structural optimizations were performed minimizing the forces on all
atoms to below 0.05 eV Å\(^{-1}\); \(k\)-point sampling of \((2 \times 2 \times 1)\) was performed using the Monkhorst Pack scheme\(^{221}\) with the third vector perpendicular to the surface. All calculations were spin polarized. The Perdew-Wang (PW91) version of the generalized gradient approximation (GGA) was used to incorporate exchange and correlation energies\(^{183}\).

DFT has difficulties in representing the nature of the 4\(f\) orbitals of ceria\(^{184-186}\) hence we implemented the DFT+U approach\(^{222,223}\). The DFT+U approach introduces the Hubbard U term as an on-site Coulombic interaction in the \(f\) states of ceria, which localizes 4\(f\) electrons on Ce\(^{3+}\) in reduced ceria. A U value of 5 was utilized, which is consistent with values used in previous DFT studies of ceria\(^{224-234}\). Absolute reduction energies are a function of the U value, though relative trends in reduction energies are preserved with varying U\(^{231}\). DFT also has difficulties representing electrons in localized \(d\)-states of metal oxides\(^{195,235}\). The inclusion of a U term on the \(d\)-states of Mn becomes necessary to correctly represent the electronic structure of Mn doped in ceria\(^{236,237}\). A U value of 4 on the \(d\)-states of Mn is utilized as described by Wang, Maxish and Cedar\(^{195}\).

A Mn-doped fluorite CeO\(_2\)(111) surface model is used to examine the impact of Mn doping on surface reducibility and sulfur adsorption. The choice of a Mn-doped fluorite phase is motivated by characterization results presented below. The surface models used for ceria were mirrored 12-layer slabs doped with Mn. The (111) termination of ceria was used because it is the lowest energy surface of ceria\(^{231,237,238}\). All atom positions are relaxed during structural optimizations. Though the XANES/TPR measurements which are compared with DFT results potentially measure bulk reduction processes, a surface model is used because of our direct desire to capture surface behavior of H\(_2\)S adsorption. We previously demonstrated surface energetics of H\(_2\)S adsorption as empirically relevant to predicting dopant effects on H\(_2\)S.
adsorption capacity. All structural optimizations and relative energy definitions follow the same procedure as described previously.

5.3 RESULTS

Materials. The designations for the sorbent materials, their compositions on a molar basis, and their surface areas are given in Table 5-1. There were actually three different synthesis methods for Mn12/Ce3/La: templated sol-gel, hydrothermal, and EISA. All three methods produced a similar material with yields of 81, 92 and 90%, respectively, and as-calcined surface areas of 48, 46 and 60 m$^2$/g, respectively. The higher surface area material from the EISA synthesis was used in subsequent work.

Table 5-1 Sample Names and Basic Properties

<table>
<thead>
<tr>
<th>Designation and Molar Ratios (wt % Al$_2$O$_3$)</th>
<th>Surface area (m$^2$/g)</th>
<th>Pre-breakthrough H$_2$S (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>220</td>
<td>190</td>
</tr>
<tr>
<td>Ce6/Tb</td>
<td>200</td>
<td>76</td>
</tr>
<tr>
<td>Mn0.8/Al (75)$^2$</td>
<td>150</td>
<td>120</td>
</tr>
<tr>
<td>Mn1/Ce1</td>
<td>55</td>
<td>15</td>
</tr>
<tr>
<td>Mn1/Ce4</td>
<td>150</td>
<td>59</td>
</tr>
<tr>
<td>Mn4/Ce3/La</td>
<td>83</td>
<td>30</td>
</tr>
<tr>
<td>Mn12/Ce3/La</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>Mn1.1/Ce3/La/Gd0.05</td>
<td>130</td>
<td>50</td>
</tr>
<tr>
<td>Mn1.4/Ce6/La/Gd0.10</td>
<td>190</td>
<td>12</td>
</tr>
<tr>
<td>Mn0.8/Ce3/La/Al (89)</td>
<td>210</td>
<td>200</td>
</tr>
<tr>
<td>Mn0.4/Ce3/Zr/Al (81)</td>
<td>180</td>
<td>180</td>
</tr>
</tbody>
</table>

$^1$Used for at least three cycles of adsorption/regeneration.

$^2$Values in parentheses are wt% Al$_2$O$_3$ in supported materials.
The Ce/La molar ratios from ICP in all cases corresponded closely (within 10%) of the target ratios shown in Table 5-1. The Ce/Gd ratios from ICP indicated 10-30% less Gd incorporation in the final product.

Reaction with H₂S. Experiments where 1000 ppm H₂S were adsorbed from the CO₂-dominant syngas mixture are shown in Figure 5.2. At these conditions roughly half of the CO₂ would convert to CO at equilibrium, assuming that CO₂ and CO methanation and water-gas shift were the only three reactions taking place. GC measurements on selected runs showed CO₂/CO molar ratios between 1.2 and 3.3, with the lower ratios observed for those materials with more Mn. Therefore while this equilibrium state was not achieved, the experiments do approximate sulfur adsorption from a real syngas containing CO₂, but with a high CO₂/(CO + CH₄) ratio, and with sorbents containing more Mn showing a higher reverse water-gas shift activity.

The sulfur adsorption capacities indicate notable synergism upon combining CeO₂ and MnOₓ in the same material. By themselves, neither oxide has much sulfur capacity at these conditions, in long-term use. While Mn0.8/Al has more than double the sulfur capacity shown in Fig. 5.2 initially, its equilibrium pre-breakthrough H₂S concentration is high at this temperature, roughly 35-200 ppm. Clearly there is a transformation of the Mn0.8/Al material during the adsorption/regeneration cycles, one that is not associated with the loss of surface area (see Table 5-1), but which nevertheless results in a rapid loss of sulfur capacity. On the other hand, CeO₂ has a much lower equilibrium pre-breakthrough H₂S concentration (Table 5-1), but a low and stable total sulfur capacity, and this low sulfur capacity is also apparently not surface-area related (see Table 5-1). Combining the two oxides intimately in the same sorbent by the syntheses used here gives both the low pre-breakthrough concentration of CeO₂ and the higher
capacity of $\text{MnO}_x$, but with far higher capacities than might be expected based upon a simple linear combination of the capacities of the two individual oxides (which are shown in Fig. 5.2).

Figure 5.2 Sulfur adsorption capacity at 903 K, using synthetic gasifier effluent with 32% $\text{CO}_2$ for adsorption. All entries except for $\text{Mn12/ Ce3/ La}$ are the average of at least three cycles, not using the first cycle, with intermediate air regeneration at 873 K for 30 min. For $\text{Mn12/ Ce3/ La}$, data are for a single cycle, but after four cycles with 32% $\text{CO}$ in the feed over which the capacity stabilized. The numbers in parentheses are wt% $\text{Al}_2\text{O}_3$ for supported materials.

To further explore this behavior, we examined sorbents where other rare earths were admixed with the $\text{CeO}_2$. As discussed earlier, such additions would be expected to further stabilize the mixed oxides as high surface area, relatively amorphous materials. We have confirmed this in past work.\(^{103,234}\) From TPR, DSC and sulfur capacity measurements we concluded that an optimal Ce/La ratio for this purpose was roughly 3/1, and that small amounts of Gd or Tb were also of benefit when combined with Ce/La.\(^{103,240}\) But, as evident from Fig. 5.2, these effects are clearly secondary to the effects on sulfur adsorption resulting from combining a predominantly $\text{MnO}_x$ with a smaller amount of $\text{REO}$ in template-based mixed oxide syntheses. In fact, addition of Tb or Gd without La present was ineffective in increasing sulfur capacity.\(^{234}\)
For oxide sorbents containing Ce, La and Mn, there is only partial conversion to sulfided species. This is the case whether we calculate maximum conversion based on reaction to oxychalcogenides (e.g., Ce₄MnOS₆), perovskites (e.g., CeMnS₃), oxysulfides (e.g., CeO₂S₂), sulfides (e.g., MnS), or any combination of these. For example, the total sulfur capacity would be: 4.0 mmol/g for Mn1.1/Ce3/La/Gd0.05 assuming case (a), complete conversion of a separate Mn phase to MnS and all REOs to their respective oxysulfides, or 1.5 mmol/g assuming case (b) conversion of the REOs to (RE)₂O₁.₂₅S₀.₁₂₅, our previously computed DFT+U stoichiometry for the sulfided CeO₂ surface at equilibrium. The corresponding capacities would be (a) 9.1, (b) 5.0 mmol/g for Mn12/Ce3/La and (a) 6.2, (b) 2.2 mmol/g for Mn1/Ce1. But the observed sulfur capacities are far below these maximum values, and also far below the equilibrium calculations of others for sulfiding either rare earth or manganese oxides. We did observe modest increases in sulfur capacities with temperature – about 5-10% higher at 973 K vs. 903 K – consistent with our thermodynamic calculations showing that the sorbents are not at equilibrium with gas exiting the bed at 903 K.

One might then reasonably conclude that there are kinetics (not equilibrium) limitations on these sulfidation reactions arising from slow diffusion of sulfide ions from the surface to the interior, and that if the surface areas of the sorbents were increased further the fraction conversion to sulfide or oxysulfide phases might also increase. One way to further increase the surface areas of the active oxides would be to support MnOₓ/REOs on a thermally stable alumina by co-impregnation, which we did. While there was significant improvement in sulfur capacities for such materials when compared to the simpler single (Fig. 5.2) or binary oxides, these numbers still do not approach maximum conversion to sulfides on the supported materials. Note that the surface areas of these materials remained high throughout use (Table 5-1). Considering
Mn0.8/Ce3/La/Al, for example, the expected sulfur capacity would be ~0.41 mmol/g for case (a) and 0.27 for case (b), roughly 2-3 times the actual value.

In our past work we have noted that both CO$_2$ and H$_2$O can inhibit sulfur adsorption under these conditions, to different extents, with CO$_2$ possibly acting as more of an inhibitor while water can both inhibit sulfidation$^{74,242,243}$ and also accelerate loss of surface area.$^{240}$ Therefore we also measured sulfur capacities using a CO-dominant syngas feed. These results, shown in Figure 5.3, demonstrate that the sulfur capacities are indeed sensitive to the amount of CO$_2$ in the feed, which might explain some of the conflicting results in the literature. All classes of sorbent showed higher capacities with the CO-dominant feed; the only one where the increase was not very large was Mn12/Ce3/La. Again, while our thermodynamic calculations indicate that there would be roughly equimolar amounts of CO and CO$_2$ if the methanation and shift reactions come to equilibrium, our GC measurements showed this was not the case, as the actual CO$_2$/CO ratios varied between 0.17 and 0.28, with the higher numbers associated with temperatures <900 K.

![Figure 5.3 Sulfur adsorption capacity at 903 K, using synthetic gasifier effluent with 32% CO for adsorption. All entries are the average of at least three cycles, not including the first cycle, with intermediate air regeneration at 873 K for 30 min.](image)
A direct comparison of breakthrough curves with either dominant CO or CO$_2$ is shown in Figure 5.4 for Mn$_{12}$/Ce$_3$/La. Note that the curves closely correspond until breakthrough, which is at a shorter time for the dominant CO$_2$ feed. This suggests that the CO$_2$ occupies sites that otherwise would adsorb H$_2$S. It is also possible that when more CO$_2$ is present, there is less reduction of the REOs and fewer oxygen vacancies present; in this case the number of available surface sites would decrease, as observed.

![Figure 5.4 Adsorption of H$_2$S onto Mn$_{12}$/Ce$_3$/La at 903 K. Standard feeds with either 32% CO or 32% CO$_2$.](image)

Characterization by XRD. The diffraction patterns shown in Figure 5.5 are typical of those found for mixed MnO$_x$/REOs where there was a low ratio of Mn/(Ce + La). No peaks were observed for MnO, MnO$_2$, Mn$_2$O$_3$, LaMnO$_3$, or any La oxides, carbonates or hydroxides. The only crystalline phases observed were fluorite CeO$_2$ for both fresh and sulfided sorbents, and for the sulfided samples the reduced disordered fluorite phase of approximate stoichiometry CeO$_{1.7}^{244}$ and a small amount of MnS. The particle size of the fluorite phase increased from ~2
to ~5 nm upon repeat sulfidation/regeneration cycles, based on computation using the Scherrer equation.

Figure 5.5 XRDs of Mn1.1/Ce3/La/Gd0.05. “Sulfided” denotes taken after several adsorption and regeneration cycles. Peaks labeled “1” are characteristic of CeO$_2$, “2” of MnS, and “3” of the reduced fluorite phase commonly denoted CeO$_{1.7}$.$^{244}$

The diffraction patterns for materials with higher Mn/Ce ratios are more complex, especially after sulfidation, as in Figure 5.6. The as calcined materials were highly amorphous with only broad peaks similar to those shown in Fig. 5.5 for Mn1.1/Ce3/La/Gd0.05. The absence of crystalline MnO$_x$ for these high Mn/Ce oxides shows that claims$^{77,245}$ that they are not multiphasic materials may be correct, at least in the fully oxidized state. Either excess MnO$_x$ is present as dispersed crystallites on Mn/CeO$_x$ that are too small to observe by XRD,$^{246}$ or else it forms a solid solution with CeO$_2$/La$_2$O$_3$. There are indications of a Mn/REO solid solution in the observed shifts to higher 2θ values characteristic of a ~0.04-0.08 Å lattice contraction; this level of contraction has been observed by others for CeO$_2$ upon incorporation of Mn cations in the fluorite lattice.$^{247,248}$

For sulfided Mn12/Ce3/La, there is evidence that the rare earth oxysulfide is present, at least in small quantity, and that there is even phase separation of Mn/REO and Ce/La oxides,
which was not observed for the materials with lower Mn/Ce. There is slight evidence of a separate MnS phase, most likely in very small quantity. The fluorite phase peaks still show shifts to higher 2θ values, again suggestive of a Ce/Mn solid solution, but these shifts can also be partly explained by the presence of the new Ce₂O₂S and CeLaOₓ phases; for example, Ce₂O₂S has peaks at 2θ = 29.2 and 48.4°. The peak assignments for reduced CeLaOₓ are those of Weckhuysen.²⁴⁹

![XRD peaks labeled](image)

Figure 5.6 XRDs of MnOₓ/REOs, sulfided, after several adsorption-regeneration cycles. Peaks labeled “1” are characteristic of CeO₂, “2” MnS, “3” the reduced CeOₓ fluorite phase, “4” Ce₂O₃, “5” Ce₂O₂S, “6” LaCeOₓ.

Based on computation using the Scherrer equation, the particle sizes of the reduced fluorite phase were roughly 6.2 nm for Mn1/Ce4, 7.3 nm for Mn1.1/Ce3/La/Gd0.05, and 8.9 nm for Mn12/Ce3/La. So higher relative amounts of REO do result in materials which are more thermally stable, although this is not the determining factor in their sulfur adsorption capacities.

Characterization by XANES. Figure 5.7 shows XANES results at the sulfur K-edge for some of the sorbents in the sulfided, reduced state, along with standards for the 0, -2 and +6 oxidation states of sulfur. The edges of S⁰, S²⁻ and S⁶⁺ are located at 2470, 2471.7 eV and 2480 eV.
eV, respectively, which are consistent with previous data. There is clear evidence of sulfate buildup on both Ce6/Tb, less for Mn1/Ce4, and even less for Mn1.1/Ce3/La/Gd0.05. All three show evidence of both sulfide and sulfur(0). However, given the strong absorbance characteristic of sulfates, for none of the three sorbents was sulfate the dominant sulfur species.

Figure 5.7 Normalized sulfur K-edge XANES of sulfur standards and sulfided sorbents.

In order to estimate the amount of sulfate formed, the spectra of the $S^0$, $S^{2-}$ and $S^{6+}$ standards were used to generate linear combination fits for total sulfur composition; an example is shown in Figure 5.8 for Mn1/Ce4, and it is seen that the non-sulfate species dominate. The proximity of the edges for $S^0$ and $S^{2-}$ precludes precise quantification of the split between these states, but it is evident from the shift in the edge energies for the Mn-containing adsorbents that they contain more sulfide and less sulfur than the rare earth oxides/sulfides. This suggests more reaction of $H_2S$ to metal sulfides (or oxysulfides) and less oxidation of adsorbed $H_2S$, which possibly contributes to their much higher stable sulfur capacities. This finding is also in
agreement with the XRD results showing some crystalline sulfide for the Mn-containing sorbents.

![Graph showing normalized absorption vs. energy (eV) for Mn1/Ce4, 25% MnS, 47% sulfur, 27% MnSO4, and fit.]

Figure 5.8 Linear combination fit of the sulfur K-edge of Mn1/Ce4 to determine atomic sulfur distribution.

The Ce L\textsubscript{III} XANES spectra showed, as expected, very little Ce\textsuperscript{3+} in the as calcined or air regenerated states and far more Ce\textsuperscript{3+} in the sulfided, reduced state. But the more important result was that for the Mn-doped materials the amount of Ce\textsuperscript{3+} was much higher than for the simple mixed REOs in the same state (Figure 5.9). While linear combination fitting is especially difficult here due to the overlap of Ce\textsuperscript{3+} and Ce\textsuperscript{4+} edges, by our calculations there could be as much as three times more Ce\textsuperscript{3+} (atom\%) in the Mn-doped materials.

The Mn K-edge XANES results (Figure 5.10) also show evidence of CeO\textsubscript{x}-MnO\textsubscript{x} interactions where both are present. Comparing both standards in Fig. 5.10, there is an \textasciitilde1 eV pre-edge feature shift for Mn\textsuperscript{2+} (6539 eV) to Mn\textsuperscript{3+} (6540 eV). The pre-edge region for the Mn\textsuperscript{3+} standard shows a doublet with the two peaks centered at roughly 6541 and 6543 eV. While both peaks are believed to arise from the 1s to 3d transition, the presence of the second is associated with a strong Jahn-Teller distortion.\textsuperscript{29} For as calcined Mn0.8/Al (not shown) there is another Mn
pre-edge shift of +0.5 eV above that of the Mn$^{3+}$ standard, indicating the presence of some Mn$^{4+}$ in the as calcined material. But the pre-edge of the used, reduced Mn0.8/Al is centered at ~6540.5 eV, within the domain for Mn$^{2+}$ (6540.5-6540.7 eV). There is also a large jump for the pre-edge absorption (Fig. 5.10), suggesting tetrahedral coordination of Mn$^{2+}$, as in the spinel structure of MnAl$_2$O$_4$. This phase was evident in the XRD pattern.

![Normalized Ce L$_{III}$-edge XANES of sulfided sorbents.](image)

The spectrum for Mn0.8/Ce3/La/Al also shows evidence of reduction to Mn$^{2+}$ in the pre-edge intensity centered at ~6540.6 eV. The large jump at the pre-edge is similar to Mn0.8/Al, and the XRD also shows the major reflections of MnAl$_2$O$_4$, and therefore it is concluded that most of the Mn here is also tetrahedral, associated with the Al$_2$O$_3$. The pre-edge energies of both the as calcined Mn1/Ce4 and Mn4/Ce3/La (not shown) and the same but sulfided and reduced (Fig. 5.10) are centered at below 6541 eV, and so more consistent with Mn$^{2+}$ than Mn$^{3+}$. 

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However, the breadth of the pre-edge region and the shoulders on the edge suggest the presence of some Mn$^{3+}$. Therefore a mixture of both highly disordered MnO and Mn$_2$O$_3$ could be present, or this could be characteristic of the state of Mn in CeO$_x$. The latter is far more likely given the XRD results and is supported by the EPR results of Ramaswamy and co-workers.$^{252}$ The shape of the Mn pre-edge spectrum for Mn1/Ce4 is not characteristic of Mn in octahedral coordination (lacking a well-defined second pre-edge peak), and the shape of the K-edge itself differs greatly from that of Mn$_2$O$_3$ (lacking the three characteristic near edge peaks),$^{253,254}$ in both cases suggesting a coordination different from either the distorted octahedral of Mn in Mn$_2$O$_3$ or the tetrahedral in MnAl$_2$O$_4$.$^{255}$

![Normalized XANES spectra of Mn K pre-edge region. Other than the two standards, these were used (sulfided) and reduced for several cycles prior to analysis.](image)

In conclusion, XANES did provide some information on the local structure of the Mn and its oxidation state, but it cannot differentiate between two species with only slightly different
oxidation states and coordination environments. The dissolution of Mn$^{2+}$ into Al$_2$O$_3$ (which eventually leads to MnAl$_2$O$_4$) under reducing conditions, for those materials supported on alumina, is indicated by the XANES data. This in turn suggests that Mn-containing materials might work best when not supported on Al$_2$O$_3$, which is in agreement with the sulfur capacity data.

We also studied the effect of Mn doping on the local electronic structure properties of CeO$_2$ through XAFS at the Ce L$_{III}$-edge. The $k^2$-weighted EXAFS oscillation spectra of as calcined Ce1 and the sorbent Mn1/Ce4 in three different states are shown in Figure 5.11. For oxidized Mn1/Ce4 the spectrum was essentially that of CeO$_2$, with the same shell locations. Therefore mixing Mn with Ce did not much change the fluorite structure or the cerium environment of CeO$_2$ when oxidized.

![Figure 5.11](image_url)

**Figure 5.11** R-space Fourier transformed XAFS of the Mn1/Ce4 sorbent in various states, along with as calcined Ce1. The reduced sample was generated by reaction with the standard syngas mixture minus the H$_2$S at 900 K.
Theoretical XAFS were determined using FEFF 8.2. The coordination number N, radial distance R, amplitude reduction factor $S_0$, and thermal and structural mean square variation $\sigma^2$ were all obtained by regression employing Artemis version 0.8.014. Because these variables can correlate with each other, it is not possible to differentiate the effects of oxygen amplitude, sulfur amplitude, oxygen vacancies, and sulfur coordination numbers simultaneously. But as the total sulfur amounts are low relative to oxygen, at least away from the surface, sulfur was treated the same as oxygen in the model. This leads to a slightly larger computed N for the Ce-O(S) shell because the electron density of sulfur is higher. Only the most important single scattering paths were included in the calculations, since multiple scattering is negligible according to previous studies. The results of these somewhat simplified regressions for Mn1/Ce4 are given in Table 5-2.

Table 5-2 Results of regression analysis of XAFS for Mn1/Ce4, Ce-anion and Ce-cation shells

<table>
<thead>
<tr>
<th></th>
<th>Ce-O (S)$^1$</th>
<th>Ce-Ce (Mn)</th>
<th>Ce-O (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>6.4</td>
<td>12</td>
<td>17.8</td>
</tr>
<tr>
<td>R (Å)</td>
<td>2.33±0.02</td>
<td>3.86±0.02</td>
<td>4.37±0.08</td>
</tr>
<tr>
<td>$\sigma^2$(Å)</td>
<td>0.010±0.002</td>
<td>0.006±0.002</td>
<td>0.016±0.031</td>
</tr>
<tr>
<td>reduced</td>
<td>Ce-O (S)</td>
<td>Ce-Ce (Mn)</td>
<td>Ce-O (S)</td>
</tr>
<tr>
<td>N</td>
<td>6</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>R (Å)</td>
<td>2.33±0.03</td>
<td>3.88±0.02</td>
<td>4.39±0.04</td>
</tr>
<tr>
<td>$\sigma^2$(Å)</td>
<td>0.015±0.004</td>
<td>0.004±0.003</td>
<td>0.003±0.021</td>
</tr>
<tr>
<td>as calcined</td>
<td>Ce-O (S)</td>
<td>Ce-Ce (Mn)</td>
<td>Ce-O (S)</td>
</tr>
<tr>
<td>N</td>
<td>6.8</td>
<td>12</td>
<td>18.2</td>
</tr>
<tr>
<td>R (Å)</td>
<td>2.33±0.02</td>
<td>3.86±0.02</td>
<td>4.38±0.09</td>
</tr>
<tr>
<td>$\sigma^2$(Å)</td>
<td>0.009±0.002</td>
<td>0.006±0.002</td>
<td>0.020±0.04</td>
</tr>
</tbody>
</table>

$^1$Sulfur was treated the same as oxygen in the model.
In general, shell amplitudes in R-space are related to the coordination numbers, neighboring elements, spatial structures and atomic distances.\textsuperscript{258} The spectrum of the oxidized Mn1/Ce4 shows the second highest amplitude (of the curves in Fig. 5.11) for the Ce-O(S) shell and the least number of oxygen vacancies, next to CeO\(_2\) itself (Table 5-2). The amplitude of the first oxygen shell for sulfided Mn1/Ce4 is less than when oxidized, due to the reduction that takes place along with the sulfidation, but the amplitude is higher than when Mn1/Ce4 is reduced without \(\text{H}_2\text{S}\) present. This can be ascribed to the adsorption of some sulfur into the oxygen vacancies, the sulfur atoms having higher atomic number and so larger backscattering amplitude. The amplitude of the first Ce shell for Mn1/Ce4 is significantly lower than that of pure CeO\(_2\), consistent with substitution of Ce by Mn; Mn has a smaller effective scattering amplitude, about 65\% of Ce, as estimated by FEFF 8.2 for the case of total first shell Ce replacement by Mn. All of the Mn1/Ce4 samples gave about the same amplitude for this shell, suggesting that the Mn/Ce ratio of Mn-doped ceria does not change significantly during multiple sulfidation and regeneration cycles. This is consistent with both the XRD data showing the relative absence of Mn oxides and sulfides and the desulfurization data showing no changes in sulfur capacity over several cycles.

Temperature-programmed reduction. TPR results for a typical low Mn-loading material, Mn1/Ce4, are shown in Figure 5.12. One notable feature of these results is that there is substantial further reduction in the temperature range where most of our adsorption data were taken (~900 K). If we compare these to results for pure CeO\(_2\) treated similarly,\textsuperscript{240} there is substantially more reduction associated with the Ce/Mn mixed oxides. Assuming some reduction of Mn in CeO\(_x\) can begin around 470 K,\textsuperscript{246,259} and that Mn is initially more in the 3+
state as calcined (in agreement with the XANES data and the DFT analysis below), and that Ce is present initially as Ce\(^{4+}\) (also in agreement with XANES data and the DFT analysis), the weight loss above 470 K is equivalent to \(-17\%\) reduction on an oxygen atom basis, compared to only \(-7\%\) reduction for pure CeO\(_2\). As MnO\(_x\) cannot be reduced further than MnO under these conditions,\(^{246,259}\) and as no MnO phase was observed in the XRDs, it appears that this excess reduction is mostly associated with a mixed Ce/Mn oxide, in agreement with past data on excess oxygen vacancies in Mn-doped CeO\(_x\).\(^{246,252}\)

![Figure 5.12 Weight loss in temperature-programmed reduction of Mn1/Ce4. The hold at 903 K was for 2 h, and at 1013 and 1043 K, 1 h.](image)

**5.4 DFT RESULTS AND DISCUSSION**

In previous DFT modeling, we have found that the conversion of a CeO\(_2\) (111) surface to an oxysulfide follows the formation of oxygen vacancies, with H\(_2\)S activated over an O vacancy and S eventually incorporated into a vacancy site. The addition of La\(^{3+}\) doped into CeO\(_2\)
promotes excess reduction to Ce$^{3+}$ over a wide range of temperatures.$^{197,201,202}$ Our DFT work shows that H$_2$S adsors and dissociates over sub-stoichiometric oxygen vacancies, and is rate-limited by a strongly endergonic molecular adsorption (low coverage) of H$_2$S.$^{233}$ DFT-computed free energy and phase diagrams showed that sulfur incorporation is only favorable if multiple adjacent oxygen vacancies are present to accommodate the larger coordination shell of sulfur atoms.

Therefore it is not surprising that mixing MnO$_x$ intimately with CeO$_2$ also greatly increased the sulfur capacity of a Mn-doped fluorite phase. Disordered, small particle CeO$_2$, promoted by either Mn, Zr or La dopants, exhibits far more oxygen vacancies than larger particles of crystalline CeO$_2$.$^{195,197-199,233,235,236,252,260-263}$ The results of Fig. 5.3 also suggest that Mn and La have synergistic (but not greatly so) effects on sulfur adsorption for CeO$_2$ sorbents with lower Mn loadings. The lesser sulfur capacities for these materials when compared to their maximum theoretical capacities can be attributed to the poor diffusion of sulfide ions into the bulk, coupled with the losses in surface area for those materials not supported on Al$_2$O$_3$ (see Table 5-1).

DFT calculations were used to examine the impact of Mn doping on CeO$_2$(111) reducibility and H$_2$S adsorption. Models with one and two Mn doped into the CeO$_2$(111) surface were considered. When one Mn atom is doped into the surface of CeO$_2$, the Mn atom replaces one cerium atom in the $2\times2$ surface, as illustrated in Figure 5.13b. We refer to this structure as containing an “isolated” Mn dopant, as there are no O atoms bridging two Mn atoms. Doping two Mn atoms into the slab creates a non-isolated model, with one surface Ce atom and one sub-surface Ce atom replaced, as seen in Figure 5.13a.
Figure 5.13 Side views of the surface unit cell for Mn-doped CeO$_2$ (111): (a) Intact 2 Mn-doped; (b) oxygen vacant 1 Mn-doped; (c) doubly oxygen vacant 2 Mn-doped; and (d) Sulfur adsorbed oxygen vacancy, 2 Mn-doped. Ce is displayed as tan (white), Mn as light blue (gray), O as red (dark), and S as yellow (light).

With two Mn atoms doped in the surface, the first surface oxygen vacancy is spontaneous, as evidenced by the exothermic vacancy formation energy given in Table 5-3. As vacancy formation, converting a surface oxygen atom to half an oxygen molecule, is driven entropically at non-zero temperatures, this spontaneous vacancy formation energy suggests that non-isolated Mn dopants will be accompanied by O vacancies following calcination. The two Mn atoms reduce to Mn$^{3+}$ with the formation of this first oxygen vacancy, with oxidation states determined by atomic charge analysis as described previously.$^{237}$ When one Mn atom is doped in the surface (isolated) the first oxygen vacancy formation energy is also slightly exothermic, and therefore likely present following calcination. This oxygen vacancy reduces the surface Mn
dopant to the Mn$^{2+}$ oxidation state. In the Mn K-edge XANES, the calcined sorbents Mn1/Ce4 and Mn4/Ce3/La contained Mn in both Mn$^{2+}$ and Mn$^{3+}$ states. This DFT analysis suggests Mn$^{3+}$ species may result from Mn atoms that are non-isolated and Mn$^{2+}$ may result from Mn atoms that are isolated. The spontaneity of “first vacancy” formation is consistent with the lack of Mn$^{4+}$ observed in the as-calcined samples. These “first vacancies” reduce only Mn atoms, and no Ce$^{4+}$ atoms are reduced to Ce$^{3+}$. The Ce L$_{III}$ XANES spectra showed very little Ce$^{3+}$ in the as-calcined samples, in agreement with the DFT calculations.

Forming a second surface oxygen vacancy with two doped Mn atoms reduces the Mn atoms from the Mn$^{3+}$ to Mn$^{2+}$ oxidation state. As given in Table 5-3, this second vacancy formation energy is endothermic. For an isolated Mn atom at the surface, the formation of a second surface oxygen vacancy does not reduce the Mn any further, instead reducing two Ce$^{4+}$ atoms to Ce$^{3+}$, characterized by a positive oxygen vacancy formation energy. Though these second vacancy formation energies are significantly positive (Table 5-3), they are still substantially less than the first vacancy formation energy in the undoped CeO$_2$(111) surface (+2.67 eV). In a reducing environment, the formation of both types of second oxygen vacancies will be entropically driven, further reducing non-isolated Mn atoms to the $2^+$ state and reducing some Ce$^{4+}$ to Ce$^{3+}$ states. The Mn XANES results did show reduction of Mn$^{3+}$ to Mn$^{2+}$ in the reduced/sulfided samples (Fig. 5.10), which might be interpreted as the further reduction of Mn atoms that are non-isolated. The Ce XANES results showed more Ce$^{3+}$ in the reduced sample, and TPR indicated a greater reducibility of the Mn-doped sample compared to a non-doped sample. These results are in agreement with the DFT results, suggesting that vacancy formation beyond the initial reduction of Mn$^{4+}$ accounts for the greater extent of reduction, affecting both Mn and Ce.
Table 5-3 Oxygen vacancy formation ($\Delta E_{\text{vac}}$) and H$_2$S adsorption ($\Delta E_{\text{ads}}$) energies for CeO$_2$ (111) with 1 Mn atom doped in the surface (isolated) and 2 Mn atoms doped in the surface (non-isolated), with one and two oxygen vacancies in the surface. The oxidation states of Mn are listed for each case, as well as the number of cerium atoms that reduce from Ce$^{4+}$ to Ce$^{3+}$.

<table>
<thead>
<tr>
<th>Number of Vacancies</th>
<th>$\Delta E_{\text{vac}}$ (eV)</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
<th>Oxidation State of Mn</th>
<th>Number of Ce atoms Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Mn Dopant</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>-0.38</td>
<td>4+</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>-0.14</td>
<td>-0.40</td>
<td>2+</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1.75</td>
<td>-1.40</td>
<td>2+</td>
<td>2</td>
</tr>
<tr>
<td>2 Mn Dopants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>-0.27</td>
<td>4+</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>-1.01</td>
<td>-0.49</td>
<td>3+</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1.69</td>
<td>-0.50</td>
<td>2+</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5-3 also lists the H$_2$S adsorption energies to the Mn-doped CeO$_2$(111) surfaces at various oxidation states. H$_2$S adsorption is considerably stronger to the vacant surfaces, further corroborating the role of O vacancies in desulfurization. We previously reported that stronger H$_2$S adsorption correlated with greater experimental sulfur capacities for undoped, Tb-doped, and La-doped CeO$_2$(111) surfaces, suggesting that the rate of uptake determined by the H$_2$S adsorption energy dictated ultimate sulfur capacity. However, all of the H$_2$S adsorption energies listed in Table 5-3 are weaker than those for La- and Tb-doped CeO$_2$(111), suggesting the further increases in Mn-doped ceria sulfur capacities cannot be attributed to a stronger H$_2$S adsorption.

The enhanced sulfur adsorption capacity of the Mn-doped system may instead arise from a greater number of “active” O-vacancy sites and a greater driving force to S$^*$ formation at O-vacancies. For La- and Tb-doped surfaces, each dopant pair forms a stoichiometric vacancy, allowing La and Tb to occupy 3+ oxidation states as opposed to the inaccessible 4+ state. The
formation of “second oxygen vacancies” in the Mn system may be compared with the formation of sub-stoichiometric vacancies in the La- and Tb-doped systems. For the Mn doped system, the second vacancy formation energies are more favorable than the substoichiometric vacancy formation energies in the La- and Tb-doped surfaces. Though additional vacancy formation in La- and Tb-doped surfaces was not examined, this result suggests the concentration of O vacancies will be greater in the Mn-doped system. Therefore, one explanation for the greater capacity of Mn-doped CeO₂ sorbents is their greater reducibility compared to the Tb- and La-doped systems.

A second factor that may explain the enhanced Mn-doped ceria sulfur capacities is that a larger fraction of the vacancies formed may be considered as “active sites” for H₂S conversion. In the La- and Tb-doped surfaces, the first stoichiometric vacancy is not active for H₂S conversion to S*, as such activation would require these dopants to occupy a 4+ oxidation state. However, the 4+ oxidation state is accessible for Mn-dopants, providing the possibility that this “first vacancy” can also be active for H₂S conversion. This possibility was evaluated computationally by considering the reaction energy of

$$\text{H}_2\text{S}_\text{gas} + \text{O-vacant surface} \rightarrow \text{S-incorporated} + \text{H}_2\text{gas}$$  

(1)

where “S-incorporated” represents a surface with a S atom filling the oxygen vacancy. The reaction energy for this reaction was calculated considering the “first vacancy” for the Mn-doped surface and the stoichiometric vacancy for the La- and Tb-doped surfaces. Table 5-4 reports these reaction energies. For the La- and Tb-doped systems, these reaction energies are highly endothermic, indicating that the stoichiometric vacancies cannot serve as active sites for H₂S conversion. For the isolated Mn-doped system, this reaction energy is exothermic, whereas it is mildly endothermic for the non-isolated doped system. For the Mn-doped system, these “first
vacancies” can serve as active sites, with H$_2$S adsorption and S incorporation reasonably favorable. Though these sites would be active for H$_2$S conversion, we would not expect to observe Mn$^{4+}$ in highly sulfided samples (and indeed did not), because S incorporation would engender further surface reduction, as vacancy formation from this S-incorporated surface would be highly favorable. Table 5-3 also indicates that “first vacancies” would also be active for the pure CeO$_2$(111) surface, however, the concentration of these vacancies would be considerably reduced compared to the doped surface, due to the substantially higher vacancy formation energy.

The overall picture provided by the DFT calculations suggests that 1:1 S:Mn ratios in Mn-doped CeO$_2$ are possible at the surface, as with MnO itself. The mismatch between the actual observed sulfur capacities and those consistent with 1:1 ratios, as detailed in the results, must therefore be attributed to slow diffusion/reaction of sulfide ions into the bulk of the doped fluorite structure, a problem exacerbated by the initial losses of surface areas in the Mn/REO sorbents.

Table 5-4 Reaction energies (Δ$E_{\text{reaction}}$, in eV) for conversion of H$_2$S$_{\text{gas}}$ and O-vacant surfaces to H$_2$,$\text{gas}$ and an S-incorporated surface (Reaction 1).

<table>
<thead>
<tr>
<th>Surface</th>
<th>Δ$E_{\text{reaction}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$(111)</td>
<td>-0.51</td>
</tr>
<tr>
<td>La$_2$-doped CeO$_2$(111)</td>
<td>2.21</td>
</tr>
<tr>
<td>Tb$_2$-doped CeO$_2$(111)</td>
<td>2.33</td>
</tr>
<tr>
<td>Mn$_1$-doped CeO$_2$(111)</td>
<td>-1.31</td>
</tr>
<tr>
<td>Mn$_2$-doped CeO$_2$(111)</td>
<td>0.67</td>
</tr>
</tbody>
</table>

The experimental results establish that while the presence of CO$_2$ and H$_2$O results in an almost 50% loss in sulfur capacity compared to some past work where both water and CO$_2$ were
not present in the feed, such Mn-REO sorbents are nevertheless stable even in a more realistic syngas, and are regenerable even in the presence of air rather than diluted air. Furthermore, the S K-edge XANES results (Fig. 5.7) suggest that the combination of Ce/La/MnO$_x$ or Ce/MnO$_x$ has only moderate tendency to form sulfates, which is probably the key to its regenerability with air. Although the sulfate inhibition mechanism is not known, it is reasonable to relate it to the formation of vacancies during the conversion of sulfide to elemental sulfur during regeneration. The more potential vacancies resulting from the presence of Mn doping the REOs, the easier this conversion. The fact that MnO$_x$ by itself does not typically form carbonates in a CO$_2$ atmosphere at $>873$ K may relate to the greater resistance of these high Mn-loading materials to CO$_2$ inhibition (compare Fig. 5.2 and Fig. 5.3).

Previous work has for the most part left unexplored the potential phase separation in high Mn-loaded REOs when used as high temperature sorbents. Some studies indicate that preparations up to 1:1 Mn/CeO$_x$ can constitute a single disordered fluorite phase under oxidative conditions, but other data suggest the binodal curve corresponds to a lesser Mn/Ce ratio. There is a lack of data at both reducing and reducing, sulfiding conditions, but no one has suggested that a material similar to Mn12/Ce3/La could be single phase under any such high-temperature conditions. Our XRD results for sulfide materials showing at least one distinct sulfide phase (Fig. 5.6) and a hexagonal LaCeO$_x$ phase suggest that some phase separation takes place. But the relative stability of the sorbent (the capacity in the first cycle was 2.2 mmol S/g vs. an average for the other cycles of 1.7 mmol S/g, even while the surface area changed dramatically), the low intensity of the crystalline MnS phase, and the absence of MnO$_x$ in the oxidized state all combine to suggest that most of the Mn remains intimately associated with the REOs, or as small crystalline domains interspersed with Mn-doped REO. The formation of
stable perovskites of type (RE)MnO$_3$ can be ruled out on the basis of the Mn K-edge XANES (mostly Mn$^{2+}$ as sulfided, Fig. 5.10) and XRD results (Fig. 5.6), in addition to the much lower sulfur capacities for such perovskites found in previous work.$^{264}$

The explanation for the relatively low capacities of MnO$_x$/Al$_2$O$_3$, especially in comparison to some previous work,$^{53,67,108}$ lies in the simultaneous presence of the competitive adsorbates CO$_2$ and H$_2$O as used here, and in the use of air for regeneration. The high O$_2$ content of air and faster reactivity with sulfides (leading to hot spots in a regenerating packed bed) apparently promotes formation of more inaccessible Mn in the Al$_2$O$_3$. This conclusion is suggested by the Mn K-edge XANES data (Fig. 5.10) showing transformation of Mn in Al$_2$O$_3$-supported materials to a lower coordination number. This transformation of Mn also probably explains why the sulfur capacities of the Mn/Ce/La/Al$_2$O$_3$ sorbents, while quite high if compared on a non-Al metal basis, nonetheless do not show high capacities on a weight basis. The relative inertness of MnAl$_2$O$_4$ to sulfidation has been confirmed.$^{53}$ The strong inhibition of sulfur adsorption by the combination of CO$_2$ and H$_2$O for Mn/Al$_2$O$_3$ sorbents has also been confirmed in recent work.$^{74}$

5.5 CONCLUSIONS

Mn-doped REOs, including Mn-doped CeO$_x$, are robust high temperature desulfurization sorbents that can be regenerated under a variety of conditions, including with plain air. The more complex oxide/sulfide materials are multiphasic, but there is no evidence of a separate bulk MnO$_x$ phase even at relatively high Mn/REO ratios, as determined by XRD, while XANES and XAFS provided abundant evidence of doping of Mn into the fluorite CeO$_2$ phase. Combining the two oxides intimately in the same sorbent gives both the low pre-breakthrough concentrations of REOs and the higher sulfur capacity of MnO$_x$, but with far higher capacities
than would be expected based upon a simple linear combination of the capacities of the two individual oxides. While the presence of both CO$_2$ and H$_2$O significantly reduce the ultimate sulfur capacities of such sorbents, no long term deactivation results from the presence of or both.

Many factors contribute to the desulfurization performance of these materials, but rather surprisingly thermal stability as reflected by retention of surface area is not one of them – the crystalline domains grow rapidly. Attempts to maintain high surface areas by spreading Mn/REOs on more stable alumina-based supports were successful but somewhat counterproductive, due to Mn dissolution into the alumina support under sulfiding conditions, as determined from XANES and XRD. Such dissolution reduced the sulfur capacity.

DFT calculations on model Mn/CeO$_2$ surfaces provided valuable clues to why Mn-doped CeO$_x$ is superior to CeO$_x$ doped with rare earths. Chief among causes are the ability of Mn to decrease vacancy formation energies in CeO$_2$ (compared to rare earth dopants), and the favorable H$_2$S adsorption energies for Mn doped in CeO$_2$, even without oxygen vacancies present. These characteristics manifest themselves in high-temperature Mn/CeO$_x$ desulfurization sorbents that can combine relatively high sulfur capacities at >900 K with low concentrations of effluent H$_2$S.

The DFT study suggests that a plausible structure for Mn-doped CeO$_x$ in both intact and oxygen-vacant states is 5-coordinate (pyramidal). In XANES this might be expected to produce a result somewhat between octahedral and tetrahedral Mn-O coordination in the Mn K pre-edge region, as observed. Therefore the DFT results are in qualitative agreement with the picture derived from the characterization results of an oxygen-defective, Mn-doped REO where Mn is formally 2$^+$. 

A more difficult question is: why the much higher sulfur capacities of the predominantly MnO$_x$ sorbents mixed with REOs (Figs. 5.2 and 5.3), especially given the very weak MnS
signature and the absence of MnO\textsubscript{x} phases in the XRD patterns (Fig. 5.6)? It should be noted that a similar Mn-Ce mixed oxide (Ce/Mn = 1:3) has been used for desulfurization at 873 K, with a gas composition of 2.5\% H\textsubscript{2}S, 10\% H\textsubscript{2} and 87.5\% He.\textsuperscript{77} This sorbent had a higher sulfur capacity (3.5 mmol S/g-sorbent) than reported here, and maintained this capacity even after ten cycles. It was assumed that sulfur retention was primarily due to MnO in the mixed sorbent, and no evidence of Ce\textsubscript{2}O\textsubscript{2}S was found. Roughly 90\% of the adsorbed sulfur was desorbed as S(0) during regeneration with N\textsubscript{2}-diluted air at 993 K. Whether these differences are solely attributable to the lack of CO\textsubscript{2} and H\textsubscript{2}O in this past work, and the milder regeneration technique employed, or whether there was also an especially active Ce-doped MnO\textsubscript{x} phase present (but not detected), is a question for future work.
6.1 INTRODUCTION

The economical cleanup/conditioning of biomass/coal effluents is an unsolved problem. Both sulfur and “tars” (any hydrocarbon of molecular weight benzene or higher) can poison downstream catalysts and block filters and pipelines. High concentrations of tars can damage engines and turbines. Tars also have detrimental effects on the life cycle and operational characteristics of a fuel cell by depositing carbon on the anode. Tar cleanup is complicated by the presence of residual sulfur. A typical effluent from an O$_2$-blown coal gasifier includes 0.2-1% $^5$,$^6$ and from an air-blown coal gasifier 0.08-0.5% H$_2$S. $^6$,$^7$ For biomass gasifiers (air- or steam-blown) this range is 0.0002-0.02% H$_2$S.$^{10,17,19}$ Even after sulfur adsorption at high temperature some residual sulfur would remain. Depending on the type of reactor and gasification conditions, the tar content from biomass gasifiers usually varies from 1200-75000 mg/Nm$^3$ (gas volume, 1000 mg/Nm$^3$ = 175 ppmv for naphthalene).$^{35-42}$

One goal of recent work has been to develop tar reforming catalysts that are active with typical syngas feeds even at $<1000$ K, that can tolerate as much as 30 ppm sulfur, and that minimize methanation and water-gas shift. A consensus from earlier work is that the simpler Ni-based systems are not optimal, although more complex Ni/REO (rare earth oxide) $^{115,119,128,267}$ and Ni/alkali and/or alkaline earth $^{10,18,40,45,121,124-126,267-275}$ systems show promise, especially near or above 1100 K. At such temperatures there is less poisoning of Ni by sulfur and irreversible transformations to Ni mixed oxides. $^{10,125,126,268,270,272-276}$ Non-Ni-based (or bimetallic with Ni as one component) systems are also under examination, $^{42,50,116,119,126,133-135,137,140,141,143,267,277-288}$

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$^3$ (This chapter previously appeared as Li, R.; Roy, A.; Bridges, J.; Dooley, K. M., Tar Reforming in Model Gasifier Effluents: Transition Metal/Rare Earth Oxide Catalysts. Industrial Engineering & Chemistry Research, 2014, 53, 7999, Copyright (2014) American Chemical Society.)
to the rapid deactivation of monometallic Ni-based catalysts caused by both carbon deposition\textsuperscript{10,114,124,127} and sulfur poisoning at the lower temperatures.\textsuperscript{122-125}

The complexity of biogasifier syngas dictates that many simultaneous reactions will take place during tar reforming. Detailed comparisons on inlet/outlet compositions suggest that these include, in addition to the major reforming and water-gas shift reactions, CO\textsubscript{2} reforming,\textsuperscript{18,118} methane reforming and CO hydrogenation to methane,\textsuperscript{39,40,42,114-117} and tar hydrocracking.\textsuperscript{10,115,117,118} While methane reforming often follows the same trends as tar reforming and has little apparent effect on it,\textsuperscript{40,114,115} in contrast the active oxygen generated by the reduction of CO\textsubscript{2} can enhance tar decomposition,\textsuperscript{45,118,119} as does residual O\textsubscript{2} from the gasifier.\textsuperscript{20,141} This suggests that a more stringent test of a catalyst’s activity for tar reforming may be in the absence of feed CO\textsubscript{2} and O\textsubscript{2}, as is the case here. In their (relative) absence, steam reforming is the primary mechanism for conversion of tar to syngas, as evidenced by catalytic activities that increase with respect to steam/carbon ratios up to high values,\textsuperscript{20} and also by reforming studies with simple feeds (tar + steam) under similar temperature conditions.\textsuperscript{10,119,128,140,289,290}

The addition of REOs improves both Ni- and non-Ni-based reforming catalysts’ resistance to carbon deposition,\textsuperscript{276,291-294} and possibly to sulfur poisoning.\textsuperscript{115} For carbon deposition, this is the case in both steam reforming and dry reforming of CO\textsubscript{2}. Both DFT and experimental studies show that for Ni the crystal steps should be better for adsorption of CH\textsubscript{x} than terraces, and that additive species such as sulfur preferentially locate at step sites.\textsuperscript{146,147,295} However, the overall coking rates can be faster on terrace sites (larger nanoparticles).\textsuperscript{296-298} Therefore, it may be possible to mitigate both sulfur poisoning (by spillover to the REO) and coke formation, by REOs stabilizing small metal domains. Whether this is the case in tar
reforming – whether the metal is doped into the REO, or whether it exists as small domains anchored by the REOs, with many metal atoms adjacent to the oxides, or whether the metal exists as completely separate larger domains, is key to understanding and improving these catalysts. Previous work on tar reforming with REO/TMO catalysts and syngas has focused on activity only,\textsuperscript{115,119,267} and found high tar conversions in the range of 60-100\% at 923-1073 K, although at relatively low GHSV (2000-13000).

So in this work we investigated the action of transition metal oxides (TMOs) other than Ni (e.g., Fe, Mn) mixed with REOs for tar reforming, at a medium temperature range (923-1073 K) and under conditions where direct reforming would dominate. We compared the longer-term stabilities of these materials to typical Ni-based high temperature reforming catalysts, with a syngas feed characteristic of oxysteam reforming effluent, including residual sulfur. The sulfur level is characteristic of effluent from a high temperature adsorbent bed preceding the tar reforming reactor, which in turn might precede a water-gas shift catalyst bed. Such a configuration makes sense from a heat integration standpoint; there would be no need to re-heat the syngas as is necessary after low temperature sulfur scrubbing. Because shift catalysis may not always be desirable, and methanation never is, we quantified the simultaneous tar reforming, shift, and methanation activity. Naphthalene was chosen as the model tar due to its refractory nature and because it is a key component in gasifier effluent tars of all types.\textsuperscript{25,35-38,43-45,117,277,290,299}

\section*{6.2 EXPERIMENTAL}
\subsection*{6.2.1 Catalyst Preparation.}

The supported mixed oxides were prepared by incipient wetness impregnation from concentrated solutions of the nitrate salts on a thermally stable Al\textsubscript{2}O\textsubscript{3} (BASF Ga-200-L, which
contains 3% La). The precursors were (NH₄)₂Ce(NO₃)₆ (Aldrich 99.9%), La(NO₃)₃•6 H₂O (Alfa Aesar 99.9%), Mn(NO₃)₂ (JT Baker 50.8%), and either Zr(IV) n-propoxide solution (Alfa Aesar 70%), or ZrOCl₂ (MCB). The samples are designated by their elemental ratios, e.g., Mn1/Ce4, except for Al when present as Al₂O₃ support.

After addition of metal precursor(s), the catalyst was dried at 363 K under vacuum, and for sequentially impregnated materials another metal precursor added. The catalyst was re-dried under vacuum at 363 K, and then calcined in flowing air at 773 K with a ramp of 2 K/min and a final hold of 2 h. For mixed REOs, we used templated sol-gel and impregnation techniques with the same precursors. For the sol-gel method, 1% tetrathylammonium hydroxide (Acros, 25% in methanol) was the surfactant in water/alcohol solution. To this solution aqueous NH₃ (Alfa Aesar, 28-30%) was added, until precipitation occurred (pH ~9.7-9.9 for Fe/Ce3). The temperature was raised to 363 K and the gel stirred for two days, adjusting the pH as necessary. The centrifuged precipitate was washed with acetone and deionized water and calcined as before. The synthesis of Mn1/Ce4 was discussed in previous work.

The Ni catalysts were also synthesized for comparative studies by incipient wetness, either co-impregnated (Ni0.008/Mn0.003/Al) or impregnated in two sequential steps (Ni2/Ca/Mg2/Al, Ni15/K/Mg4/Al). For example, for Ni2/Ca/Mg2/Al, Ca(NO₃)₂ (Aldrich 99%) and Mg(NO₃)₂•6H₂O (Baker 99%) were dissolved in deionized water, impregnated onto the support, dried overnight at 393 K, and calcined in air at 5 K/min to 1073 K with a 2 h final hold. This product was then impregnated with aqueous Ni(NO₃)₂•6H₂O, and calcined in air as before.

6.2.2 Reforming Activity Testing

A schematic of the reactor system is shown as Figure 6.1. The simulated gasifier effluent for the adsorption/reaction step typically contained, 4.1% CH₄, 0.33% C₁₀H₈, 30.8% H₂, 54.3%
CO, 9.1% H₂O, 40 ppmv H₂S, balance N₂. This gas approximates a bio- or coal gasifier effluent, but without NH₃ and with a water amount typical of an air-blown oxysteam gasifier. Reforming tests were performed at 923-1073 K with GHSV s of 6600-33000 h⁻¹. The naphthalene was injected by sublimation at controlled temperature from a separate bed, and a syringe pump injected the water just prior to the reactor. The heated gas mixture passed through a 1/2” stainless steel tube containing 0.2-1 g of catalyst (40-60 mesh size) diluted with mullite and positioned between beds of α-Al₂O₃. The reactor tube was heated by a clamshell furnace, the bed temperature measured by a 1/16” sheathed K-thermocouple, and the temperature controlled by a Eurotherm 3504 PID controller.

![Schematic of reactor system for C₁₀H₈ reforming.](image)

Figure 6.1 Schematic of reactor system for C₁₀H₈ reforming.
Online samples (1 mL) taken after the reactor were injected directly into a HP-5890 GC with flame ionization detector; an Alltech SE-54 column (0.32 mm x 30 m) was used to separate C₆ and higher hydrocarbons. Samples were also analyzed for CO, CO₂ and C₁-C₆, using an Agilent 490 Micro GC with thermal conductivity detectors using one molecular sieve column and one CP-PoraPLOT U column. The HP-5890 was programmed with initial temperature 313 K for 1 min, 8 K/min to 453 K, and a 35 min final hold. The Micro GC was operated isothermally at 353 K and backflushed periodically to remove H₂S.

The yields of the products on a carbon basis and the weight-based rate for C₁₀H₈ removal were calculated using Eqs. (6-1) to (6-3):

\[
Y(CO_2) = \frac{[CO_2]}{[CO]_{in} + 10[C_{10}H_8]_{in} + [CH_4]_{in}} \quad (6-1)
\]

\[
Y(CH_4) = \frac{[CH_4]}{[CO]_{in} + 10[C_{10}H_8]_{in} + [CH_4]_{in}} \quad (6-2)
\]

\[
R(C_{10}H_8) = \frac{[C_{10}H_8]_{in} - [C_{10}H_8]_{out}}{[C_{10}H_8]_{in}} \times \text{GHSV} \quad (6-3)
\]

The theoretical values were calculated using the Aspen HYSYS® process simulator utilizing a Gibbs Free Energy Minimization algorithm that included the expected WGS, reforming and Boudouard reactions (6-4 – 6-6), but neglecting the C₁₀H₈ reactions, given its lesser amount.

\[
CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (6-4)
\]

\[
2CO \leftrightarrow C + CO_2 \quad (6-5)
\]

\[
CO + H_2O \leftrightarrow CO_2 + H_2 \quad (6-6)
\]
6.2.3 Characterization

The BET surface areas of the oxides were measured by N\textsubscript{2} adsorption - desorption using a Quantachrome AS-1 porosimeter. X-ray diffraction (XRD) spectra of ground, powdered samples were obtained with either a Rigaku Miniflex 2005C103 XRD or at the powder XRD beamline at the LSU Center for Advanced Microstructures and Devices, both using Cu K\textalpha radiation. Typically these samples were scanned with a step size of 0.05° and a 2-6 s integration time. Phases were identified by comparing to the ICDD database, Release 2010 RDB 2.1002.

X-ray absorption near-edge spectroscopy (XANES) and X-ray absorption fine-structure spectroscopy (XAFS) were performed at the LSU synchrotron using the Ge (2 2 0) double crystal monochromator (DCM) beamline. The Fe K-edge spectra were measured at room temperature in either transmission or fluorescence mode. The energy range was 6992 to 8059 eV, and FeO, Fe\textsubscript{3}O\textsubscript{4}, FeS and FeOOH were used as reference spectra. The Mn K-edge data were also acquired at room temperature in fluorescence mode over a scan range of 6439-6739 eV. The spectra for MnS, MnO, Mn\textsubscript{3}O\textsubscript{4}, and Mn(OH)\textsubscript{3} were obtained as reference standards. The Ce L\textsubscript{III} edge spectra were measured at room temperature in either transmission or fluorescence mode. The energy range was 5623 to 5923 eV for XANES and 5923 to 6139 eV for XAFS. The data were processed (background subtraction, deglitching, linear combination fitting) using Athena 0.8.061.\textsuperscript{162}

Temperature-programmed oxidation (TPO) was carried out on 20 mg samples in a thermogravimetric analyzer (Perkin-Elmer TGA 7). The samples were heated first (10 K/min) to 523 K in air, held for 1 h, then further increased to 923 K for 1 h. A residual gas analyzer (SRI RGA 300) monitored the effluent gas compositions. TPO was used to estimate the amount of coke (carbon deposits) present in used reforming catalysts.
6.3 RESULTS AND DISCUSSION

6.3.1 Materials

The designations for the catalysts, their elemental (molar ratios) metallic compositions (except Al) on a molar basis, and the surface areas are given in Table 6-1. The sum total wt% of all but the Al₂O₃ is also given, if Al₂O₃ is used. The two Mn-containing materials with the lower synthesis yields were checked by ICP-AES and the Ce/La ratios were within 4% of target. The REOs impregnated on Al₂O₃ have higher BET surface areas, in the range of 170 to 220 m²/g, and the surface area of the used catalysts only decreased somewhat. The fresh unsupported catalysts made by the templated sol-gel method gave high initial surface area, which decreased significantly upon reaction. The Ni-based catalysts, even when fresh, had lower surface area than the supported REOs.

6.3.2 C₁₀H₈ Reforming Activity

6.3.2.1 Effects of metal loading and feed composition

The primary products in all experiments were CO, CO₂ and H₂; light hydrocarbons were observed in some cases as noted below. Trace amounts of benzene and toluene were observed only occasionally, so reforming predominated over just hydrocracking.

Initial screening experiments were used to determine whether TMO/REO catalysts could actually outperform simpler supported REOs or TMOs. The results of some of these experiments at low temperature and space velocity are shown in Figure 6.2.

What these results show is that in the absence of sulfur even pure REOs can function effectively for tar reforming at short times onstream. After a brief initial period no more benzene was observed; CO, methane and C₂’s were the only carbon-containing products. The initial feed contained methane and trace C₂’s, but the amounts of these compounds in the products were less
than in the feed. We also measured the production of CO for several samples of a primarily CO$_2$-containing feed (one reason for using such a feed) and found that the total carbon conversion to CO (mols CO produced/sum of mols carbon in feed) varied between 11-31% with 20% a typical result in the 873-923 K range. From these observations we conclude that the primary reactions were (1) the reforming of the light hydrocarbons and the naphthalene to CO and H$_2$, and (2) CO$_2$ hydrogenation (reverse water gas shift), when CO$_2$ is present in high concentration. Clearly CO$_2$ is not reduced to provide active oxygen to the tars at these conditions, in contrast to others’ findings at higher temperatures. 45,118,119 The role of CO$_2$ as a pure inhibitor is shown also in Figure 6.3 for a related series of catalysts. Each data point represents an average for the type of feed used around this time period, with the feeds further explained in the caption. It is evident that no other common feed perturbation has the negative impact of CO$_2$ in the lower temperature range, and in particular CO is essentially uninvolved in the tar reforming at these conditions.

![Figure 6.2 Tar reforming at 873 K, GHSV = 6600. The feed mole %’s are: CO or CO$_2$, 56; H$_2$, 32.4; CH$_4$, 8.2; water, 3.1; naphthalene, 0.3. Catalysts: 1 = La0.01/Al; 2 = Ce$_3$/La/Al; 3 = Mn0.4/Ce$_3$/La/Al; 4 = Mn0.8/Ce$_3$/La/Al; 5 = Mn0.2/Ce/Zr/Al; 6 = Mn0.4/Ce$_3$/Zr/Al; 7 = Fe/Ce$_3$/La/Al; 8 = Mn0.8/Al; 9 = Fe/Al.](image-url)
These findings were confirmed for the Mn-containing catalysts also, specifically Mn0.2/Ce/Zr/Al. Furthermore, from Fig. 6.3 it appears that the supported Fe on Al₂O₃ (Fe/Al) is deactivating; for both Fe/Al and Mn0.8/Al such deactivation occurred, with the latter losing 2/3 of its initial activity in only 1 h.

Table 6-1 Synthesis yields and physical characteristics of catalysts

<table>
<thead>
<tr>
<th>Catalyst (wt% non-Al₂O₃)</th>
<th>BET S.A. (m²/g)</th>
<th>Yields %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Used</td>
</tr>
<tr>
<td>Mn1/Ce3/Zr/Al (22)</td>
<td>170</td>
<td>150</td>
</tr>
<tr>
<td>Mn0.4/Ce/Zr/Al (20)</td>
<td>260</td>
<td>170</td>
</tr>
<tr>
<td>Mn0.4/Ce3/Zr/Al (19)</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Mn0.2/Ce/Zr/Al (18)</td>
<td>180</td>
<td>170</td>
</tr>
<tr>
<td>Ni0.008/Mn0.003/Al (3)</td>
<td>130</td>
<td>-</td>
</tr>
<tr>
<td>Ni15/K/Mg4/Al (20)</td>
<td>94</td>
<td>90</td>
</tr>
<tr>
<td>Ni2/Ca/Mg2/Al (40)</td>
<td>47</td>
<td>-</td>
</tr>
<tr>
<td>Fe/Ce3/La/Al (19)</td>
<td>220</td>
<td>180</td>
</tr>
<tr>
<td>Ce3/La/Al (20)</td>
<td>170</td>
<td>150</td>
</tr>
<tr>
<td>Mn0.4/Ce3/La/Al (19)</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Mn0.8/Ce3/La/Al (11)</td>
<td>210</td>
<td>170</td>
</tr>
<tr>
<td>La0.01/Al (3)</td>
<td>200</td>
<td>-</td>
</tr>
<tr>
<td>Mn0.8/Al (25)</td>
<td>150</td>
<td>120</td>
</tr>
<tr>
<td>Fe/Al (25)</td>
<td>170</td>
<td>120</td>
</tr>
<tr>
<td>Fe/Ce3</td>
<td>290</td>
<td>26</td>
</tr>
<tr>
<td>Mn1/Ce4</td>
<td>155</td>
<td>70</td>
</tr>
</tbody>
</table>

From Fig. 6.2 we concluded that since some CO₂ is always present in gasifier effluents, the best TMO/REO combinations would be Fe with the Ce/Zr mixed REO and Mn (in low amounts) with the Ce/La mixed REO. Our previous work showed that the addition of H₂S
affected the pure REOs more than the Mn/REOs. Nevertheless we retained Ce3/La/Al, and added the three Ni-based catalysts that were based on commercial high temperature reforming catalysts, for comparison purposes. All of the chosen materials were tested in longer term experiments in the presence of a similar air-blown synthetic gasifier feed, but at higher GHSV (~33000), with 40 ppm H2S added.

Figure 6.3 Conversion of naphthalene using synthetic gasifier effluents at 923 K, GHSV = 6600. The feed mole %’s are: CO, N2 or CO2, 56; H2, 32.4; CH4, 8.2; water, 3.1 (5.5 for “hi-H2O”, other ratios held constant); naphthalene, 0.3.

The reforming behavior of a typical REO under such conditions is shown in Figure 6.4. We will denote the product of GHSV and fractional conversion the “productivity”, because it is directly proportional to the total amount of tars reacted. The first point corresponds to almost 100% conversion. In Fig. 6.4, partial deactivation did take place in the presence of sulfur in the feed. However, the activity apparently reached a stable state at any temperature up to 1073 K. The total number of turnovers were calculated on a total metal (Ce + La) basis with respect to naphthalene only, so there were many more turnovers associated with methane and CO.
conversions, which were significant even at 923 K. A potential downside to the catalyst is this conversion of CO to CO$_2$ by water-gas shift, but these CO$_2$ yields were well below the $\sim$30% yield expected at equilibrium for 923 K. The yield at 1073 K, though lower, is nearer the equilibrium value.

Similar activity stabilization took place with the catalysts Fe/Ce3/La/Al, Fe/Ce3, Mn0.2/Ce/Zr/Al, and Ce3/La/Al; the catalysts remained active through several turnovers, as summarized in Table 6-2. For the Mn/Ce/Zr series, the lowest metal loading was the only one showing complete stability with or without sulfur, while for the Fe/Ce/La series higher metal loadings could be tolerated. The TMO/REOs supported on Al$_2$O$_3$ showed higher reforming activities than the unsupported ones on a weight basis, but this is reversed if compared on a (final) surface area basis.

![Figure 6.4 Tar reforming at 923 – 1073 K with Ce3/La/Al. Feed: H$_2$O 9.1%, CO 54.5%, CH$_4$ 4.1%, H$_2$ 30.9%, N$_2$ 1.07%, C$_{10}$H$_8$ 0.33%, H$_2$S 40 ppm. Turnovers are calculated with respect to C$_{10}$H$_8$ only.](image-url)
In naphthalene reforming, the more active Mn- and Fe-supported REOs proved superior to several Ni-based high temperature reforming catalysts used in previous work,\textsuperscript{302,303} and also to the complementary material lacking a TMO (Ce3/La/Al), when the syngas included sulfur. The Ni catalysts did show high initial reforming activity, but poor sulfur resistance and, except for Ni2/Ca/Mg2/Al, severe coking (Table 6-2). Even for this catalyst some reactor blockage actually took place at \(~30\) h, prior to sufficient accumulation of sulfur. This was true also of the other Ni-based catalysts and Ce3/La/Al.

Table 6-2 Summary of tar reforming results - catalyst stability in presence of sulfur

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Coke (g/gcat)</th>
<th>Turnovers\textsuperscript{1} at deactivation/end</th>
<th>S/metal atom (total)</th>
<th>Productivity before/after S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn1/Ce3/Zr/Al</td>
<td>1.3</td>
<td>28</td>
<td>0.86</td>
<td>7200 / 3600</td>
</tr>
<tr>
<td>Mn0.4/Ce/Zr/Al</td>
<td>0.60</td>
<td>76</td>
<td>0.79</td>
<td>19400/ 10700</td>
</tr>
<tr>
<td>Mn0.2/Ce/Zr/Al</td>
<td>0.50</td>
<td>91</td>
<td>0.42</td>
<td>n.a. / 19600</td>
</tr>
<tr>
<td>Ni0.008/Mn0.003/Al</td>
<td>14</td>
<td>131</td>
<td>0.48</td>
<td>16000 / 0</td>
</tr>
<tr>
<td>Ni15/K/Mg4/Al</td>
<td>5.7</td>
<td>63</td>
<td>0.35</td>
<td>33000 / 0</td>
</tr>
<tr>
<td>Ni2/Ca/Mg2/Al</td>
<td>2.4</td>
<td>48</td>
<td>0.14</td>
<td>30200/ 15900</td>
</tr>
<tr>
<td>Fe/Ce3/La/Al</td>
<td>1.4</td>
<td>119</td>
<td>0.75</td>
<td>n.a. / 16700</td>
</tr>
<tr>
<td>Ce3/La/Al</td>
<td>6.7</td>
<td>59</td>
<td>0.27</td>
<td>n.a. /11500</td>
</tr>
<tr>
<td>Fe/Ce3</td>
<td>2.8</td>
<td>21</td>
<td>0.2</td>
<td>13000 /8900</td>
</tr>
<tr>
<td>Mn1/Ce4</td>
<td>1</td>
<td>4</td>
<td>-</td>
<td>8500 /n.a.</td>
</tr>
</tbody>
</table>

\textsuperscript{1}Turnovers based on total metal (not including Al) atoms and C\textsubscript{10}H\textsubscript{8} conversion only.

For the stable Mn0.2/Ce/Zr/Al we compared two runs with two different loads, one run entirely with sulfur and another mostly without it (Figure 6.5). In both cases the behavior at 923 K showed deactivation with the sulfur, but almost no deactivation at any temperature in its absence. After a prolonged period at a GHSV of 6600, and some deactivation in the presence of
40 ppm sulfur, the sulfur was removed and the GHSV increased to 33000. But the activity increased only slightly until the temperature was raised higher. This leads us to conclude that the sulfur is irreversibly bound at 923 K and eventual deactivation might take place. But comparing the lower and upper curves in Fig. 6.5, we also conclude that at temperatures >990 K this amount of sulfur could be tolerated. The run without sulfur was also extended to 191 turnovers at 1073 K (data not shown in Fig. 6.5), without loss of activity. For the optimal Fe-containing catalysts (Fe/Ce3/La/Al or the unsupported Fe/Ce3) extensive data (summarized in Table 6-2) suggested that even at 923 K the 40 ppm sulfur could be tolerated, although at a lower overall activity.

The yields for other major products are given in Table 6-3. The CO$_2$ yields are well below equilibrium at 923 K, essentially at equilibrium at high temperature, for all catalysts. Note that the methane yield, as defined in eq. (2), of the feed itself is 11%, so clearly methane accumulation from the naphthalene is taking place for some of the catalysts, and possibly some methanation. The CH$_4$ yields are lower for the supported REOs/TMOs, as might be expected given their generally higher activity in tar reforming.

6.3.2.2 Effects of temperature

All of the catalysts deactivated to some extent in the presence of sulfur at 923 K. However, as noted the optimal REO/TMOs appeared to stabilize and remained stable at higher temperatures (Figs. 6.5). For the Ni-based catalysts only Ni2/Ca/Mg2/Al did not deactivate completely during a run, but it was still losing activity and rapidly accumulating coke at 1073 K when the test was terminated at 30 h. Therefore for more optimal Ni-based materials it is possible to find compositions relatively stable to sulfur in this temperature range, yet these are still prone to severe coking at the low steam/carbon ratio used here. The overall coking rates can be inferred from the crude final coke values listed in Table 6-2, and specifically the rate of
coking at the highest temperature was evident from the pressure drop measurement on the reactor – for optimal Mn/Ce/Zr/Al and Fe/Ce/La/Al catalysts the coking rate was slower according to this metric.

Table 6-3 CO\textsubscript{2} and CH\textsubscript{4} yields after extended times online, and comparison with other studies

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO\textsubscript{2} % yield (LT)\textsuperscript{1}</th>
<th>CH\textsubscript{4} % yield (LT)</th>
<th>CO\textsubscript{2} % yield (HT)</th>
<th>CH\textsubscript{4} % yield (HT)</th>
<th>Ea\textsuperscript{2} (kJ/mol)</th>
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</thead>
<tbody>
<tr>
<td>Fe/Ce3/La/Al</td>
<td>14</td>
<td>7.8</td>
<td>7.8</td>
<td>7.2</td>
<td>71</td>
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<tr>
<td>Mn0.2/Ce/Zr/Al</td>
<td>14</td>
<td>8.6</td>
<td>6.1</td>
<td>8.5</td>
<td>62</td>
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<tr>
<td>Ce3/La/Al</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>8.7</td>
<td>76</td>
</tr>
<tr>
<td>Ni2/Ca/Mg2/Al</td>
<td>13</td>
<td>14</td>
<td>6</td>
<td>18</td>
<td>deactivate</td>
</tr>
<tr>
<td>Fe/Ce3</td>
<td>12</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn1/Ce4</td>
<td>12</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni/Ru/Ce/Al\textsuperscript{304}</td>
<td>59</td>
<td>5</td>
<td>49</td>
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</tr>
<tr>
<td>Ni/Ce/Zr\textsuperscript{128}</td>
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<tr>
<td>Ni/Mn/Ce/Zr\textsuperscript{128}</td>
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<td>Ni/Mg\textsuperscript{134}</td>
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</tr>
<tr>
<td>Co/MgO\textsuperscript{134}</td>
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<tr>
<td>FeOx\textsuperscript{305}</td>
<td>48</td>
<td>7.6</td>
<td>7.6</td>
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<td></td>
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<tr>
<td>Ni/K/Mg/Al\textsuperscript{39}</td>
<td></td>
<td>36</td>
<td>10</td>
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<tr>
<td>Ni/Mg/Al\textsuperscript{114}</td>
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<td>38</td>
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<tr>
<td>Ni/Co/Mo\textsuperscript{42}</td>
<td></td>
<td>15</td>
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</tr>
<tr>
<td>Ni/Al\textsuperscript{117}</td>
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<td>11</td>
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<tr>
<td>Ni/Al + CaO\textsuperscript{306}</td>
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<td>0.4</td>
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<td></td>
</tr>
<tr>
<td>Fe/Ti\textsuperscript{277}</td>
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<td></td>
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</tr>
<tr>
<td>THEORY (EQUIL.)</td>
<td>30</td>
<td>7.0</td>
<td>5.6</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{1}LT: 923-973 K; HT: 1073 K

\textsuperscript{2}The observed activation energy for tar disappearance
Figure 6.5 Tar reforming at 923 – 1073 K with Mn0.2/Ce/Zr/Al. Feed same as Fig. 6.4. The catalyst in the upper curve (“new”) was run for a total of 91 turnovers with 40 ppm H$_2$S, the one in the lower curve for 191 turnovers (C$_{10}$H$_8$ basis, all data not shown), with 40 ppm H$_2$S only as noted. The GHSV in the lower curve was changed from 6600 to 33000 as noted.

The weight accumulations in Table 6-3 are labeled “coke” because the TPO-MS results showed that the weight loss peak at ~ T > 650 K, which corresponds to the value in the table, was primarily associated with CO$_2$ and not SO$_2$ (Figure 6.6). There is a possibility that some sulfur from the catalyst could desorb as elemental S, which would not be distinguishable from background O$_2$, but as the signal at m/e 32 did not increase at any time this can be discounted. According to Table 6-2, the maximum S that could be adsorbed during the runs was relatively small anyway, for example the total amount of S passed over Mn0.2/Ce/Zr/Al comes to only 0.045 g/gcat.
Figure 6.6 Temperature programmed oxidation of used reforming catalyst Fe/Ce3/La/Al

Activation energies were obtained by assuming first-order reforming kinetics for naphthalene disappearance in a plug flow reactor.

\[
K = \frac{\ln(1 - X_{naph})}{\tau} \tag{6-7}
\]

The activation energy of Ni2/Ca/Mg2/Al (the most stable Ni-based catalyst) still could not be evaluated due to deactivation at high temperature. Nonetheless our values could be compared to activation energies of Ni-based catalysts evaluated under other more stable conditions (e.g., little or no sulfur), over a similar temperature range. For example, Aznar and co-workers\(^{40}\) studied a range of high temperature Ni-based naphtha reforming catalysts for tar reforming of steam gasifier effluents (from pine chips) and found activation energies from 58-62 kJ/mol. The only major difference from our conditions was a much higher water content. For the same biomass and one of the same catalysts, but water contents similar to those used here, Corella and co-workers obtained 72 kJ/mol.\(^{38}\) Both groups claimed that slight diffusional effects
reduced the apparent $\Delta E$’s somewhat, but nonetheless we obtained values in the same range using particle sizes smaller than theirs. Other groups using either mixed tars or model compounds with particulate catalysts observed activation energies from 30-55 kJ/mol.\textsuperscript{20,42,119,137,140,288} Aside from the different tar species reacting, the lower activation energies could also reflect the adverse effects of coke buildup, which would hinder pore transport. But the highest $\Delta E$ in this range,\textsuperscript{137} and the closest to ours, was for 1-methylnaphthalene.

### 6.3.3 Used Catalyst Characterization

#### 6.3.3.1 XRD

The diffraction patterns shown in Figure 6.7 are typical of used supported REOs. Carbon, $\gamma$-Al$_2$O$_3$ and reduced CeO$_2$ are the dominant phases. Other than carbon, these were also the dominant phases in the fresh catalysts, but there were small features attributable to MnO$_2$ in the Mn-containing catalysts. An important feature is the absence of ZrO$_2$, LaO$_x$, MnO$_x$ and FeO$_x$ phases, which suggests extensive doping into fluorite CeO$_2$ or small disordered domains. The size of the carbon peaks is consistent with the TPO results on the high levels of coke formation.

A separate TMO phase, if present, would be more apparent for the catalysts not supported on Al$_2$O$_3$. But for such used reforming catalysts, even without sulfur, still no separate TMO phase was observed (Figure 6.8). Either the TMOs are present as dispersed crystallites on CeO$_x$ that are too small to observe by XRD,\textsuperscript{246} or else they form a solid solution with CeO$_2$. For Mn1/Ce4 there are indications of a Mn/REO solid solution in the observed shifts to higher $2\theta$ values characteristic of a $\sim$0.04-0.08 Å lattice contraction; this level of contraction has been observed by others for CeO$_2$ upon incorporation of Mn cations in the fluorite lattice.\textsuperscript{247,248}
particle sizes (by the Scherrer equation) of the dominant fluorite phases in Fig. 6.8 were 4.8, 8.8 and 16.7 nm for Ce3/La, Mn1/Ce4 and Fe/Ce3, respectively. The large difference between the first used catalyst domain size and the other two also suggests that the latter two fluorite phases differed from a mixed REO. The comparable domain sizes for the fresh catalysts were all <2 nm. When the catalyst is not supported on Al2O3 (i.e., the REO phase dominates), the surface area will therefore be greatly reduced upon use, as was observed (Table 6-1).

![Figure 6.7 XRDs of used supported REO/TMOs. Peaks labeled “1” are characteristic of graphite, “2” of γ-Al2O3, “3” of CeO1.7 and “4” of Ce2O3](image)

The peaks of Mn0.2/Ce/Zr are broadened and characteristic of the Ce/ZrOx solid solution, especially that of the tetragonal phase (ICDD 01-074-8060). However, there are also indications of small amounts of monoclinic ZrO2 and reduced fluorite CeOx. There was an apparently small amount of Fe3C present in used Fe/Ce3. Nevertheless, the overall picture is still of a dominant REO phase.
Figure 6.8 XRDs of mixed REOs with transition metals. Peaks labeled “1” are characteristic of CeO$_2$, “2” of graphite, “3” of Fe$_3$C, “4” of tetragonal Ce$_{0.5}$Zr$_{0.5}$O$_2$, “5” of monoclinic ZrO$_2$ and “6” of CeO$_{1.7}$.

In order to better determine whether a separate MnO$_x$ phase could exist at any Mn/Ce ratios, we examined several used catalysts in an oxidized state by calcining them after use at 873 K, and comparing to the still reduced and sulfided Mn$_1$/Ce$_4$ (same diffractogram as in Fig. 6.8). The comparison is shown in Figure 6.9. Even though the Mn$_1$/Ce$_4$ is far richer in Mn, it still shows no distinguishable MnO$_x$ phase (the small new reflections at 26.2 and 31.3$^\circ$ are characteristic of carbon), as evident from the absence of the characteristic $\alpha$-MnO$_2$ reflections at 21.8, 55.3, 63.1 and 41.2$^\circ$ 2$\theta$. The MnO$_2$ phase is clearly visible in the oxidized Mn$_{0.8}$/Ce$_3$/La/Al, less so in Mn$_{0.4}$/Ce$_3$/Zr/Al and almost not at all in Mn$_{0.2}$/Ce/Zr/Al (not shown). Of the commonly found oxides of Mn, MnO$_2$ is probably easiest to identify, with a large number of strong reflections. From these results we conclude that a separate MnO$_x$ phase could
be present on the more highly loaded supported Mn/REOs, but that in the catalyst’s operating state these domains are X-ray invisible, disordered and/or nanocrystalline, if present. In combination with the reaction results in Table 6-2 and those for Mn0.8/Al showing strong deactivation, we conclude that the separate MnOx phase promotes coke formation.

6.3.3.2 Characterization by XAS

An advantage of using XAS over other characterization methods is its applicability to the catalysts supported on Al2O3, with relatively low Fe or Mn concentrations. We examined the optimal Fe/REO and Mn/REO catalysts in detail by both XANES and XAFS.

In XANES, the normalized Fe K-edge spectra display two sets of features: the pre-edge representing 1s-3d transitions and the main absorption edge representing the 1s-4p transition. A noncentrosymmetric (e.g., Td) environment has a more intense pre-edge feature than a centrosymmetric (e.g. Oh) one, due to 4p mixing into 3d orbitals, which imparts some dipole-allowed 1s-4p character to the transition.309-312 The position of the pre-edge also shifts to higher energy with increasing oxidation state.309,313 Therefore, the position and shape of the pre-edge feature can provide useful information on oxidation state, site distortion and coordination number. The spectra of FeO, Fe3O4, FeS and FeOOH standards were also obtained in order to investigate the speciation of iron in the complex catalyst.

Previous work demonstrated the feasibility of using the pre-edge for quantitative estimation of the Fe2+ to Fe3+ ratio from known standards.310,313-315 The pre-edge features were isolated by subtracting an arctangent function which fit the tail of the main edge,316 with some results shown in Figure 6.10. As seen, FeO has low pre-edge absorption because all of the Fe is octahedrally coordinated, while the broad pre-edge of Fe3O4 is a combination of three environments: 1/3 octahedral Fe(II), 1/3 octahedral Fe(III), and 1/3 tetrahedral Fe(III).
Figure 6.9 Comparison of XRDs of Mn/mixed REOs (oxidized at 873 K) to reduced Mn1/Ce4. Peaks labeled “1” are characteristic of CeO$_2$, “2” of $\gamma$-Al$_2$O$_3$, “3” of MnO$_2$, and “4” of CeO$_{1.7}$.

Figure 6.10 Normalized Fe K pre-edge XANES after baseline subtraction
By using all standards in the calibration, the average oxidation state of used, sulfided Fe/Ce3/La/Al is found to be between Fe$^{2+}$ and Fe$^{3+}$, with a ratio Fe$^{2+}$/Fe$^{3+}$ ~2.9. A linear combination fit making use of all the standards was constructed as shown in Figure 6.11. A good fit with an R-factor of 0.001 was obtained with only FeO (55%) and Fe$_3$O$_4$ (45%) left after iteration analysis, with no similarity of the sample to the standards FeS and FeOOH. The large pre-edge peak also shows that the Fe is mostly located in a non-centrosymmetric environment. Since Fe$_3$O$_4$ can be completely reduced to metallic iron at >950 K, for our conditions there should be no Fe$^{3+}$ present in any monometallic phase, and little to no Fe$^{2+}$ as in FeO. However, both Fe$^{3+}$ and Fe$^{2+}$ can exist when Fe is doped into the fluorite phase.

![Graph](image-url)

Figure 6.11 Linear combination fit for the Fe K-edge of Fe/Ce3/La/Al

Due to the low concentration of Fe and Ce in Fe/Ce3/La/Al, good XAFS cannot be obtained. However, the unsupported material, Fe/Ce3, while not as active, is similar in its lack of a XRD-visible iron oxide in either the as-calcined or used states. Therefore we also examined oxidized (as calcined) and reduced Fe/Ce3 samples by Ce L$_{III}$ XAFS (Figure 6.12). The peak
locations of both samples suggest that the cubic fluorite structure of CeO$_2$ is retained. The amplitude reductions for the first oxygen shell (the largest peak) in the calcined Fe/Ce3 sample can be attributed to the spontaneous generation of oxygen vacancies which occurs upon doping with Fe,\textsuperscript{319,320} this is also the reason for further amplitude reduction observed in the reduced sample. The amplitude of the first Ce shell for Fe/Ce3, significantly lower than pure CeO$_2$, is consistent with substitution of Ce by Fe; Fe has a smaller (by ~65\%) effective scattering amplitude than Ce for the first shell. The shifts of the first two shells (O and Ce) to slightly shorter distances suggest lattice contraction upon Fe doping, with more contraction occurring as the material is reduced and more oxygen vacancies generated.

![Graph](image.png)

Figure 6.12 Experimental and theoretical XAFS for the Ce L$_{III}$-edge of reduced Fe/Ce3, compared to as calcined Fe/Ce3 and CeO$_2$ in R-space

Due to the correlation between the amount of Fe dopant and the Ce-Ce(Fe) coordination number, the coordination number of Fe in the fluorite phase cannot be determined until the dopant concentration is known. We first assumed a single phase solid solution of Fe/CeO$_2$.  

122
However, for all likely locations of Fe in that structure, bulk or surface, we could not fit the Fe K-edge EXAFS. Therefore we next attempted to fit the Fe K-edge by first assuming some amount of separate phase Fe(0) or Fe oxide. Each individual compound FeO, FeS, Fe, Fe$_3$O$_4$, Fe$_2$O$_3$ was used in a separate set of regressions, with the combination of elemental Fe(0) (35 mol%) and the Fe/CeO$_2$ solid solution providing the best fit, as shown in Figure 6.13. Therefore it is reasonable to assume that only ~65% of the Fe is actually doped into the fluorite phase, which number was also used to complete the regression of the Ce L$_{III}$-edge data in R-space. In both regressions (Fe K-edge XANES and Ce L$_{III}$-edge XAFS), the results were similar, giving some confirmation to the process. The first- (Ce-O) and second-shell (Ce-Ce) coordination numbers of 6.7 and 9.3, respectively, and radii of 2.3 and 3.8 Å, respectively. Further fit details can be found in Appendix. C, Tables C2 and C3.

![Figure 6.13 Experimental and theoretical XAFS for the Fe K-edge of reduced Fe/Ce3.](image)
Much of our XANES/XAFS data on Mn/REOs and Mn/REOs/Al$_2$O$_3$ appeared in previous work$^{300}$ and will only be summarized here. The XANES spectra for the more highly loaded catalysts (e.g., Mn$_{0.8}$/Ce3/La/Al and Mn$_1$/Ce4) both showed primarily Mn$^{2+}$, with Mn$_1$/Ce4 showing also some Mn$^{3+}$. The fresh samples were similar, just less reduced (more Mn$^{3+}$). The presence of both oxidation states when doped in CeO$_2$ is supported by the EPR results of Ramaswamy and co-workers,$^{252}$ and our own DFT calculations.$^{300}$ However, XANES could not differentiate between Mn$^{2+}$ doped in CeO$_2$ or in the Al$_2$O$_3$ itself (eventually leading to MnAl$_2$O$_4$) for the Al$_2$O$_3$-supported samples. The presence of MnAl$_2$O$_4$ was confirmed in Mn$_{0.8}$/Al by both XRD and XANES, but was not present in the XRDs of any of the Mn/REOs/Al$_2$O$_3$ samples, as calcined or used.

The Mn K pre-edge XANES was subjected to a more quantitative analysis in this work, similar to what was done for the Fe K pre-edge above. Analysis of the K-edge itself can lead to significant errors in estimating Mn oxidation states.$^{29}$ Nevertheless the energy of the largest crest has been used in many qualitative estimates of average oxidation state.$^{321}$ Our crest locations are 6555.8, 6557.8, 6558.6 and 6559.3 eV for MnO, Mn$_{0.2}$/Ce/Zr/Al, Mn$_3$O$_4$ and Mn$_2$O$_3$, respectively, putting the crest for Mn$_{0.2}$/Ce/Zr/Al close to Mn$_3$O$_4$. This Mn oxide has a normal spinel structure of 16 octahedral Mn$^{3+}$ and 8 tetrahedral Mn$^{2+}$ per unit cell. The pre-edge analysis (Figure 6.14) confirms that the states for Mn correspond closely to those present in Mn$_3$O$_4$. However, the K-edge spectrum itself shows great differences between Mn$_{0.2}$/Ce/Zr/Al and Mn$_3$O$_4$ (Figure 6.15), and there is no Mn$_3$O$_4$ evidence by XRD. Also, Mn$_3$O$_4$ is completely reduced to MnO in H$_2$ at temperatures lower than used here, and would be substantially reduced at 973 K even in CH$_4$.$^{322,323}$ We conclude that the Mn present in the lower loading, Mn-
containing catalysts is entirely doped, or present in disordered, nanocrystalline domains. The Mn
is present as both 2+/3+, with mixed coordination, in the used catalysts.

Figure 6.14 Normalized Mn K pre-edge XANES after baseline subtraction

Figure 6.15 Mn K-edge XANES of used catalyst compared to standards.
6.3.4 Discussion

The results in Figs. 6.2-6.4 and Table 6-2 comparing Ce3/La/Al to the other Al2O3-supported catalysts suggest that the primary role of the transition metals could simply be a modification of the REO surface to render it more reactive, e.g., by increasing the number of oxygen vacancies. In this role Fe and Mn function better than other additives used to date in the presence of large amounts of CO2, which inhibits hydrocarbon activation in this temperature range. In addition, CO would be expected to generate more oxygen vacancies by reduction of the surface. The relative inactivity of MnOx on Al2O3 (Fig. 6.2, catalyst 8) in the presence of CO2, and the lack of evidence for separate phase MnOx also suggest that the primary role of the Mn is the modification of the REO structure to generate additional oxygen vacancies. Clearly both Ce/La/Al and the low-loading Mn/Ce/Zr/Al oxides are stable for long periods, even in the presence of sulfur in the feed (Table 6-2 and Fig. 6.5), but it is notable that Mn0.2/Ce/Zr/Al is measurably more active, with a lower activation energy (Table 6-3).

DFT analysis suggests Mn3+ doped into fluorite CeO2 results from Mn atoms that are nonisolated, and Mn2+ from isolated Mn atoms.300 The DFT study also suggested that a plausible structure for Mn-doped CeOx in both intact and oxygen-vacant states is 5-coordinate (pyramidal) and, at the surface, distorted square planar. In XANES, this might be expected to produce a pre-edge spectrum somewhat between octahedral and tetrahedral Mn–O coordination in the Mn K pre-edge region, as observed. There could also be some Mn dissolved in Al2O3, where it would be expected to adopt tetrahedral positions, as in spinel MnAl2O4. Either or both ways, the picture is purely of “doped” REO and/or Al2O3. While the shape of the XANES spectrum (Fig. 6.15) is similar to Mn0.8/Al and MnAl2O4,324 the pre-edge and crest energies for Mn0.2/Ce/Zr/Al are shifted to higher energies for Mn0.2/Ce/Zr/Al (Fig. 6.15), suggesting a structure different than
for Mn/AlOₓ. Therefore the only things we can conclude from the XANES itself are that there are both Mn²⁺ and Mn³⁺ present, and there are both lower and higher coordination numbers associated with these oxidation states. The XANES, the DFT study, the fact that Mn0.8/Al is almost inactive for reforming after a short period online, and the strong evidence of Mn-doping of Ce/ZrOₓ from the XRDs (Figs. 6.8-6.9) all lead us to the conclusion that this is a highly Mn-doped REO system.

The evidence for Fe/Ce samples being REO-doped in the active state is even stronger, because in this case the combined characterizations of Fe K-edge XANES (Figs. 6.10-6.11), Ce L₃ XAFS (Fig. 6.12), Fe K-edge XAFS (Fig. 6.13) and XRD (Figs. 6.7-6.8) all point to doping of the Fe into CeOₓ, with some nanocrystalline metallic or metal carbidic domains. The emergence of such nanocrystalline domains in used samples is supported by our own XRDs (Fig. 6.8, Fe₃C) and by in-situ XRD evidence for H₂ reduction of doped Fe/CeOₓ to nanocrystalline Fe. The absence of a separate FeOₓ phase in Fe/CeO₂ mixed oxides is strong, even for Fe/Ce ratios to near 1, for lower temperature oxidizing conditions, and up to Fe/Ce = 0.8 for highly reducing conditions. At lower Fe/Ce ratios (e.g., <0.3) there is no XRD evidence for a separate FeOₓ phase under oxidizing conditions up to 1073 K, and there are spontaneous oxygen vacancies generated by the Fe doping. For H₂ reduction, the Fe in Fe/CeOₓ is almost totally reduced to Fe²⁺ at 673 K, along with a significant amount of Ce⁴⁺ reduction; there were more “active” oxygen vacancies (as measured by dynamic oxygen storage capacity) in Fe-doped CeO₂ or Ce/ZrOₓ than in comparable CeO₂ or Ce/ZrOₓ. While these findings are all consistent with our own, we point out that until now there has been a lack of characterization data for such systems under reduced, sulfiding conditions as used here. Also, there is known
phase separation at higher temperature (e.g., 973 K) oxidizing conditions with higher Fe loadings, so catalyst regeneration may be an issue. In order to reform tars completely to CO and H₂, both C-C and C-H bonds must be broken. While computational (DFT) work on C-C bond breaking is difficult and will take time to mature, results from analysis of C-H bond activation vs. reducibility of doped M-CeO₂ (111) are available; the C-H bond activation activity of doped ceria catalysts strongly correlates with reducibility. The free energy to refill O-vacancies from O₂(g) at 298 K and atmospheric O₂ pressure is greater than the methane activation barrier for the Group Ib and IIb dopants, and for Ni as well. This makes the refilling of vacancies with such dopants to the REOs unlikely, especially given that the process becomes even more difficult at higher temperature and lower O₂ pressure. For many other dopants such as Pt, Rh, Re, W, and Mo, the vacancy formation energy is strongly endergonic, correlating with weak methane adsorption. For doped CeO₂ therefore the dopants most likely to initiate C-H bond breaking should be those near where ΔEₜₐₓ for CH₄ ~ ΔEᵣᵉᶠᵢˡ, representing the peak of a “volcano” curve where the trade-off is being reducible enough to activate C-H bonds but not so reducible such that the active O vacancy sites cannot be refilled with O₂. This region includes Mn, Fe, La, Pd and some others, and as seen above the activities for the materials where the first three of these are doped into a CeO₂ lattice are comparable or better than Ni-based high temperature reforming catalysts, but with less susceptibility to sulfur poisoning.

The activation energies obtained for Fe/Ce3/La/Al, Mn0.2/Ce/Zr/Al and Ce3/La/Al were within a narrow band (Table 6-3), suggesting a common rate-controlling step in the initial tar reaction for all three types. This is also consistent with the picture that the active catalyst in all cases is the doped REO phase.
An interesting finding is that under these conditions the REOs/TMOs are better methane reforming catalysts than the Ni-based ones. While there are literature data suggesting high activity (low CH$_4$ yields) for Ni-based catalysts (Table 6-3), these data are misleading. For the italicized entries, the feeds were model compound studies with dilute H$_2$ and/or H$_2$O; these are not representative of syngas, and in particular a primary reaction in our mixture (water-gas shift) is not even present. For the other entries, note the high CO$_2$ yields (relative to ours) at both low and high temperatures. These yields arise from either high water partial pressures (syngas based on steam gasification) or excess O$_2$ leading to methane combustion. As no O$_2$ was present in our feed, combustion can be excluded, and as seen our CH$_4$ yields are relatively close to equilibrium for our calculated conditions, and lower relative to Ni-based catalysts in comparable situations. Of course, Ni$^0$ is a good methanation catalyst, and there is no significant deactivation of its methanation function even upon severe coking.$^{328}$ From the data in Table 6-3, some methanation is taking place (the yield is 11% if no new CH$_4$ is formed) for the Ni-based catalyst, but little to none for the others, especially taking into account that some of the tar reforming is stopping at methane.

The relatively high CH$_4$ yields under our conditions reflect the role of coking, which deactivates the more difficult methane (or other light alkane) reforming reaction preferentially, compared to tar hydrocracking reactions to light hydrocarbons. The relative ease of the hydrocracking vs. methane reforming reactions was noted previously for both Ni- and Fe-based catalysts.$^{18,38,39,117,287,329}$ These results and ours suggest that hydrocracking sites are poisoned to a lesser extent than reforming ones, or (more likely) the ensemble size for methane reforming is larger.
The Mn-containing REOs that showed a separate MnO\textsubscript{x} phase in the XRDs accumulated coke more rapidly than did Mn0.2/Ce/Zr/Al; the ultimate example of Mn1/Ce3/Zr/Al clearly deactivated more rapidly, showing quite low activity even at short times onstream (Table 6-2). While we did not investigate possible synergistic effects of coke and sulfur, clearly there are such effects given this behavior compared to that of Mn1/Ce4, which did not show any deactivation (absent sulfur) over its period of use. But as seen from Table 6-2 and the characterization results, the key finding on deactivation is that adding either Mn or Fe to REOs or supported (on Al\textsubscript{2}O\textsubscript{3}) REOs can reduce coke deposition at metal compositions consistent with metal dissolution in the REOs, but that at higher metal compositions where separate transition metal oxides form, the metals can actually accelerate deactivation.

The results from this work also demonstrate that the combination of XANES, XAFS, the use of many standards and theoretical fits (using FEFF) can lead to better understanding of even a fairly disordered tar reforming catalyst. However, great care is needed in interpreting these results. For example, while it is likely that the doped mixed REO phase in the Al\textsubscript{2}O\textsubscript{3}-supported catalysts is similar to what can be characterized more easily in a model system such as Fe/Ce3, there are differences in the characterizations which cannot be reconciled at present. However, these differences do not appear to be catalytically relevant to tar reforming.

6.4 CONCLUSIONS

We have shown that, for tar reforming of typical oxysteam gasifier (biomass or coal/biomass) effluents, rare earth oxides (REOs) and Fe- and Mn-doped REOs are in several ways superior to high temperature Ni-based catalysts, in the temperature range <1100 K. They are more tolerant of sulfur and accumulate less coke, both leading to a lower or negligible rate of deactivation. At these conditions CO\textsubscript{2} somewhat inhibits the reforming reactions, and there is
less methane reforming in general, leading to methane as a product from the tars. However, the optimal Mn/Ce/Zr and Fe/Ce/La catalysts produced less methane than either the simpler REOs or the Ni-based catalysts. All catalysts were similar in terms of shift activity.

In the used, sulfided, reduced state the active phases of Mn- and Fe-REOs are primarily doped oxides (metals in Ce, Ce/Zr or Ce/La oxides), but XANES provides some evidence of a nanocrystalline reduced metal phase as well. At higher Mn loadings, where a separate MnO$\_x$ phase appears, the reforming activity actually decreased. The higher activities of these doped systems is probably related to an increase in oxygen vacancies in the metal-doped REOs. The increase in oxygen vacancies was confirmed by XAFS.
REFERENCES


(48) Xu, C.; Donald, J.; Byambajav, E.; Ohtsuka, Y., Recent advances in catalysts for hot-gas removal of tar and NH3 from biomass gasification. **Fuel** **2010**, 89, 1784.


(97) Zhao, M. W.; Shen, M. Q.; Wang, J., Effect of surface area and bulk structure on oxygen storage capacity of Ce0.67Zr0.33O2. *J. Catal.* **2007**, *248*, 258.


(142) Perez, P.; Aznar, P. M.; Caballero, M. A.; Gil, J.; Martin, J. A.; Corella, J., Hot gas cleaning and upgrading with a calcined dolomite located downstream a biomass fluidized bed gasifier operating with steam-oxygen mixtures. Energy Fuels 1997, 11, 1194.


(247) Jia, L.; Shen, M.; Haoa, J.; Raoa, T.; Wang, J., Dynamic oxygen storage and release over Mn0.1Ce0.9Ox and Mn0.1Ce0.6Zr0.3Ox complex compounds and structural characterization. *J. Alloys Compd.* **2008**, *454*, 321.


(253) Datta, S.; Rule, A. M.; Mihalic, J. N.; Chillrud, S. N.; Bostick, B. C.; Ramos-Bonilla, J. P.; Han, I.; Polyak, L. M.; Geyh, A. S.; Breysse, P. N., Use of X-ray Absorption Spectroscopy To


(319) Singh, P.; Hegde, M. S., Sonochemical synthesis of Ce$_{1-x}$Fe$_x$O$_{2-d}$ (0 < x < 0.45) and Ce$_{0.65}$Fe$_{0.33}$Pd$_{0.02}$O$_{2-d}$ nanocrystallites: oxygen storage material, CO oxidation and water gas shift catalyst. *Dalton Trans.* 2010, 39, 10768.

(320) Li, K.; Haneda, M.; Ozawa, M., Oxygen release–absorption properties and structural stability of Ce$_{0.8}$Fe$_{0.2}$O$_{2-x}$. *J Mater. Sci.* 2013, 48, 5733.


APPENDIX. A. PROCEDURES FOR DESULFURIZATION EXPERIMENTS

A.1. H₂S LECTURE BOTTLE PREPARATION PROCEDURE

1. Exhaust gases are passed through dilute (~0.5 M) NaOH solution rather than to the hood directly.
2. Place H₂S alarm near the operator and the hood. Leak test with high pressure N₂ using LabView interface to monitor the pressure transducer (1-5 V = 0-500 psig)
3. Open the H₂S cylinder to fill the transfer line, and then close it.
4. Open the lecture bottle valve, releasing the gas in the transfer line to the lecture bottle.
5. Repeat step 4 until the desired pressure in the lecture bottle is reached.
6. Follow the same operations to fill N₂ into the lecture bottle.
7. When finished, purge all the lines with N₂ three times before disconnecting.

A.2. SULFUR ANALYSIS

For sulfur analysis, a Varian 3800 GC was used. It was equipped with a pulsed flame photometric detector (PFPD), which is specific for sulfur compounds down to ~1 ppmv.

Table A1 GC settings for product analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Oven temperature</td>
<td>403K</td>
</tr>
<tr>
<td>Sampling valve temperature</td>
<td>463K</td>
</tr>
<tr>
<td>PFPD detector temperature</td>
<td>493K</td>
</tr>
<tr>
<td>TCD detector temperature</td>
<td>473K</td>
</tr>
</tbody>
</table>
Table A2 Varian 3800 settings for sulphur compound analysis

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Column</strong></td>
<td>0.53 mm empty capillary</td>
</tr>
<tr>
<td><strong>Carrier gas</strong></td>
<td>He, 15mL/min</td>
</tr>
<tr>
<td><strong>Air 1</strong></td>
<td>34 mL/min</td>
</tr>
<tr>
<td><strong>Air 2</strong></td>
<td>10 mL/min</td>
</tr>
<tr>
<td><strong>Hydrogen</strong></td>
<td>20 mL/min</td>
</tr>
<tr>
<td><strong>PFPD Range</strong></td>
<td>9.0</td>
</tr>
<tr>
<td><strong>PFPD Photomultiplier voltage</strong></td>
<td>630 V</td>
</tr>
<tr>
<td><strong>PFPD Gate width</strong></td>
<td>20 ms</td>
</tr>
<tr>
<td><strong>PFPD Gate delay</strong></td>
<td>6.0 ms</td>
</tr>
<tr>
<td><strong>PFPD Trigger level</strong></td>
<td>220 mV</td>
</tr>
<tr>
<td><strong>Sample loop size</strong></td>
<td>1.5 mL</td>
</tr>
</tbody>
</table>

Sulfur calibration was done with a normal feed but the tube was loaded with inert material SiC. The number of mols of H$_2$S in the sample loop was calculated by ideal gas law: $n = 2.04288E^{-07}$ mol. The signal of H$_2$S shown in Figure A.1 was computed by peak area (average 666000, standard deviation 7.8% of mean). The calibration factor is $3.067E^{-13}$ mol H$_2$S/area.

CO, CH$_4$ and CO$_2$ were analyzed using the Varian CP-3800 thermal conductivity detector with an Alltech CTR 1 dual packed column (1/4" outer column, activated molecular sieve, and 1/8" inner column, porous polymer) used for separation. Splitless injection with carrier He 60 mL/min. Table A3 presented the retention times for major species.
Figure A.1 Chromatogram of a typical H$_2$S calibration

Table A3 Average retention times for major species (Alltech CTR 1 dual packed column)

<table>
<thead>
<tr>
<th>Species</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner (0.392) Air/CO</td>
<td>0.766</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.729</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>2.432</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>12.477</td>
</tr>
<tr>
<td>Outer (0.608)  O$_2$</td>
<td>3.143</td>
</tr>
<tr>
<td>N$_2$</td>
<td>5.34</td>
</tr>
</tbody>
</table>

Thermal conductivity response factors: $R_{CO_2} = 1.2$; $R_{N_2} = 1.05$; $R_{O_2} = 1$; $R_{H_2O} = 0.825$; $R_{H_2S} = 0.95$. Use area divided by inner/outer fraction and then response factor and finally normalized to get the mole fraction.
A.3. FLOW CONTROLLER CALIBRATION

H₂S : \( y = 20.051x - 1.1995, \ R^2 = 0.9991 \)

N₂ : \( y = 19.224x - 19.994, \ R^2 = 0.9934 \)

CO₂ : \( y = 30.817x - 2.7908, \ R^2 = 0.9994 \)

H₂ : \( y = 19.9x + 1.05, \ R^2 = 0.9956 \)

(y, mL/min; x, voltage)
APPENDIX. B. PROCEDURES FOR C_{10}H_{8} REMOVAL EXPERIMENTS

B.1. REACTOR OPERATING PROCEDURES - NAPHTHALENE REFORMING

1. Load catalyst from the bottom with quartz wool on both ends with a 1/16” sheathed K-thermocouple projecting from the top to the top of the catalyst bed.

2. Purge system with N_{2} flow.

3. Use temperature controller to slowly bring the reactor temperature up to starting value. Keep all process lines after the naphthalene saturator hot (> 400 K) to prevent water/C_{10}H_{8} condensation.

4. When at operating temperature, switch from inert to reacting gases. Gas flows are measured using mass flow controllers, recorded on a computer using LabView software.

5. Water is injected into the system by a syringe pump.

6. Automatic sampling is controlled by LabView software.

7. Shut down: purge the system with N_{2}, turn off the syringe pump and bring the temperature down.

B.2. HP5890 GC PARAMETERS

Program: Oven T from 313 K, hold for 1 min, ramp 8 K/min to 453 K and hold for ~7 (this number must be adjusted to be consistent with the LabView program) min. Range = 2, attenuation = 0, head pressure = 3.5 kPa (this controls the He flow rate to the column), splitless injection; injector T = 443 K; detector T = 473 K.

Flow controller calibration (y, mL/min; x, voltage):

- CH_{4} & H_{2} : y = 15.234x + 9.0342, R^2 = 0.9923
- N_{2}/CO : y = 105x - 5.6667, R^2 = 0.9815
- H_{2}S : y = 5.3019x + 1.4991, R^2 = 0.9989
Table B1 Average retention times for major species in tar removal (Alltech SE-54 column)

<table>
<thead>
<tr>
<th>Species</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₆</td>
<td>3.4</td>
</tr>
<tr>
<td>C₇H₈</td>
<td>5</td>
</tr>
<tr>
<td>C₁₀H₈</td>
<td>14</td>
</tr>
</tbody>
</table>

**B.3. C₁₀H₈ CALIBRATION**

Using the same gas composition as a normal run, the C₁₀H₈ is sublimed into the system at a saturator temperature of 373 K (vapor pressure = 339.9 Pa). The reactor temperature is set to 723 K to avoid reaction. The mol fraction of C₁₀H₈ is calculated from the saturation vapor pressure and total pressure, and multiple injections made.

For example, from a calibration done on 03/07/2012:

Peaks area of C₁₀H₈, 62250, 59918, 58880, 62896 obtained in four injections, with an average 61000 and standard deviation 3% of the average. This leads to a calibration factor of 2.34E-12 mol/area.

**B.4. AGILENT 490 MICRO GC PARAMETERS**

Table B2 Agilent 490 micro GC settings for light gas composition analysis

<table>
<thead>
<tr>
<th>Method use</th>
<th>MS 5A</th>
<th>PPU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Temp</td>
<td>353 K</td>
<td>353 K</td>
</tr>
<tr>
<td>Column Head Pressure</td>
<td>18 psi</td>
<td>15 psi</td>
</tr>
<tr>
<td>Injection Time</td>
<td>40ms</td>
<td>40ms</td>
</tr>
</tbody>
</table>

Gas response factors were calculated through correlating a gas standard composition with response peak areas. (R_{CO} = 0.946, R_{CH₄} = 0.839, R_{N₂} = 1.05, R_{CO₂} = 1.2, R_{H₂S} = 0.95). With knowing the response factors and peak area, yₓ can be obtained.
Table B3 Average retention times for major species in tar removal (Molecular sieve 5A and PoraPLOT U columns)

<table>
<thead>
<tr>
<th>Species</th>
<th>Retention time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS 5A</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>71</td>
</tr>
<tr>
<td>CO</td>
<td>92</td>
</tr>
<tr>
<td>PPU</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>13.5</td>
</tr>
</tbody>
</table>
APPENDIX. C. DETAILS OF DATA ANALYSIS, XANES XAFS AND XRD

C.1. RAW DATA PROCESSING

Pre-edge subtraction, data merging, and smoothing for the XANES data were performed using Athena version 0.8.061. The pre-edge range was chosen from -150 to -30 eV (relative to E0); the normalization range was above 150 eV. The built in AUTOBK routine could successfully subtract the background with this setting. For background subtraction of XAFS in R space, the default $R_{\text{bkg}}$ (radial distance below which $\chi$ (E) is reduced) =1 is used.

C.2. LINEAR COMBINATION FIT

Linear combination fit, which is a non-linear, least-squares minimization algorithm, was used to estimate the distribution of oxidation states of sulfur and iron species in the samples. The fitting range was chosen from -20 to 30 eV (relative to E0) using the normalized $\mu$(E) spectra. Each standard was weighted between 0 and 1, and the weight summation was forced to 1. A good fit usually requires a small R-factor (square summations of data-fit difference over square summations of data), smaller than 0.005 in our case.

C.3. XAFS FITTING

In Artemis, ATOMS was used to generate an input file for FEFF containing crystal structure data. A FEFF file contains information about the coordination number, effective path length and scattering amplitude of the atoms in one single shell. For example, Table C1 shows the major coordination information of CeO$_2$ with Ce as the center atom.

The experimental spectrum of CeO$_2$ was fitted with the above crystal structure information to obtain $S_0$ (amplitude reduction factor) for Ce with known N and $R_{\text{eff}}$ for the ideal ceria (fluorite) lattice. Only the most important single scattering paths were included in the calculations, since multiple scattering is negligible according to previous studies.$^{256,257}$ The
spectra were Fourier-transformed over a k-range of 2.9 to 9 Å⁻¹ for Fe/Ce3. For doping Fe or Mn into ceria, let $N_{AB}$ denote the coordination number of B to center A, and $x_A$ denote the mol fraction of A in the fully doped material. The following constraints were used:

$$\frac{N_{AB}}{N_{BA}} = \frac{x_B}{x_A}, \quad R_{AB} = R_{BA}, \quad \sigma_{BA}^2 = \sigma_{AB}^2$$

Table C1 Coordination environment of Ce in CeO₂, FEFF file

<table>
<thead>
<tr>
<th>Deg</th>
<th>R_eff</th>
<th>Amp</th>
<th>Scattering Path</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>2.343</td>
<td>100</td>
<td>O(1)</td>
</tr>
<tr>
<td>12</td>
<td>3.826</td>
<td>67</td>
<td>Ce(1)</td>
</tr>
<tr>
<td>24</td>
<td>4.487</td>
<td>51.2</td>
<td>O(2)</td>
</tr>
</tbody>
</table>

(Deg: coordination numbers; R_eff: effective radical distance; Amp: amplitude)

Artemis cannot simultaneously fit parameters for two separate edges, e.g. Fe K-Ce L₃-edge, no mention to a complex system. When the dopant concentrations went well beyond their known solubilities, the XAFS clearly showed two separate phases. A Fe/Ce3 sample was reduced in H₂ and CO for ~ 6 h, taken from the reactor, ground and sealed with Kapton tape in a glove box. In Fits K-edge XAFS (R-space) a peak at 3.6 Å indicated a second Fe-containing phase besides Fe-doped ceria. Therefore we attempted to fit the Fe K-edge data by first assuming some amount of a separate phase (FeO, FeS, Fe, Fe₂O₄, or Fe₂O₃, applying the constraints shown above. The combination of elemental Fe(0) (35 mol%) and the Fe/CeO₂ solid solution minimized the error. It was not possible to regress for additional parameters because of the limited number of independent data points: $N_{idp} = 2 \Delta k \Delta r/\pi$.³³³

The fitting parameters are given in Tables C2 and C3; the plots of the fits are given in Chapter 6. Compared to CeO₂, doping Fe into ceria generated more oxygen vacancies and cation defects, consistent with a smaller Ce-O distance indicating a lattice contraction. The high $\sigma^2$ of Fe-O indicates disorder of the Fe atoms in the lattice. A constraint to fix coordination number
variation in the metal-metal shell was set, because typically no more than 5% cation defects are usually reported.\(^\text{334}\)

The analysis of Mn1/Ce4 was based on the Ce L\(\text{III}\)-edge only, since Mn K-edge XAFS cannot be obtained due to overlap with the Ce L\(\text{II}\)-edge. From these data we could not conclude if there is separate MnO\(_x\) phase. If there were a separate phase, the major impact in XAFS would have been a decrease of Mn-Mn coordination numbers and structural disordering. The Ce L\(\text{III}\) fitting details/results were given in Chapter 5.

The uncertainty in the coordination numbers evaluated from the XAFS data can be up to 20\% even under a well-controlled environment, due to both random and systematic errors.\(^\text{335}\) Therefore, using XAFS as a tool to interpret multiphasic structure can provide some information but by itself is not sufficient for precise structural determinations.

Table C2 Results of fitting analysis of Fe K-edge XAFS for reduced Fe/Ce3

<table>
<thead>
<tr>
<th></th>
<th>Fe-O</th>
<th>Fe-Fe/Ce</th>
<th>Fe-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>6.4</td>
<td>2.6/9.3</td>
<td>8</td>
</tr>
<tr>
<td>R (Å)</td>
<td>2.27</td>
<td>3.7/3.74</td>
<td>2.47</td>
</tr>
<tr>
<td>(\sigma^2) (Å)</td>
<td>0.07</td>
<td>0.019/0.01</td>
<td>0.004</td>
</tr>
<tr>
<td>R-factor</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table C3 Results of regression analysis of Ce L\(\text{III}\)-edge EXAFS for reduced Fe/Ce3

<table>
<thead>
<tr>
<th></th>
<th>Ce-O</th>
<th>Ce-Ce/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>6.7</td>
<td>9.3/2.7</td>
</tr>
<tr>
<td>R (Å)</td>
<td>2.27</td>
<td>3.77/3.75</td>
</tr>
<tr>
<td>(\sigma^2) (Å)</td>
<td>0.014</td>
<td>0.009/0.009</td>
</tr>
<tr>
<td>R-factor</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

C.4. XRD RAW DATA PROCESSING

Raw XRD data were processed by the software package Jade 6. Data spikes were removed in the ‘filters’ menu and the background was removed in the ‘Analyze/Fit background’
menu with K-alpha2 stripping selected. I used ‘smooth whole pattern’ to smooth the spectrum.

Any data with signal to noise ratio less than \(~10\) were not considered as peaks.

A comparison of a raw data pattern versus a processed data pattern is given in Figure C.1

Figure C.1 Comparison of raw and processed XRD data for used Fe/Ce3. (presented in Figure 6.8)
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VITA

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