ABSTRACT: The removal of tars from syngas generated in biomass or coal/biomass gasifiers plays an important role in syngas cleanup. Rare earth oxides (REOs, e.g., Ce/LaOx) mixed with transition metals (e.g., Mn, Fe) were synthesized by various methods and in some cases supported on a thermally stable alumina. These catalysts were applied to tar removal in the temperature range <1100 K using synthetic syngas mixtures with C₁₀H₈ as a tar model compound, both with and without H₂S. Some commercial Ni reforming catalyst formulations were examined comparatively. Fresh and used catalysts were characterized by XANES, XAFS, XRD, TPO, and BET. We found that the C₁₀H₈ is reformed to at least methane, although further reforming to CO and H₂ is not always achieved. While CO₂, H₂S, and coke formation all inhibited or deactivated the catalysts at certain temperatures and to different extents, it was determined that 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.

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 cell by depositing carbon on the anode. Tar cleanup is complicated by the presence of residual sulfur. A typical effluent from an O₂-blown coal gasifier includes 0.2–1% H₂S, and from an air-blown coal gasifier 0.08–0.5% H₂S. For biomass gasifiers (air- or steam-blown) this range is 0.0002–0.02% H₂S. 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 to 75000 mg/Nm³ (gas volume, 1000 mg/Nm³ = 175 ppmv for naphthalene). 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 to 75000 mg/Nm³ (gas volume, 1000 mg/Nm³ = 175 ppmv for naphthalene).

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) and Ni/alkali and/or alkaline earth 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. Non-Ni-based (or bimetallic with Ni as one component) systems are also under examination, due to rapid deactivation of monometallic Ni-based catalysts caused by both carbon deposition and sulfur poisoning at the lower temperatures.

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, CO₂ reforming methane reforming and CO hydrogenation to methane, as does residual O₂ from the gasifier. This suggests that a more stringent test of a catalyst’s activity for tar reforming may be in the absence of feed CO₂ and O₂, 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, and also by reforming studies with simple feeds (tar + steam) under similar temperature conditions.

The addition of REOs improves both Ni- and non-Ni-based reforming catalysts’ resistance to carbon deposition and possibly to sulfur poisoning. For carbon deposition, this is the case in both steam reforming and dry reforming of CO₂. Both DFT and experimental studies show that for Ni the crystal steps should be better for adsorption of CH₄ than terraces and that additive species such as sulfur preferentially locate at step sites. However, the overall coking rates can be faster on terrace sites (larger nanoparticles). Therefore, it may be possible to mitigate both sulfur poisoning (by spillover to the
REOs 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 \(^{16-18}\) 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 reheat 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.\(^{8,11,29,39,64,75}\)

### 2. EXPERIMENTAL SECTION

#### 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\(_2\)O\(_3\) (BASF Ga-200-L, which contains 3% La). The precursors were (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) (Aldrich 99.9%), La\(_2\)(NO\(_3\))\(_3\)-6H\(_2\)O (Alfa Aesar 99.9%), Mn(NO\(_3\))\(_2\) (JT Baker 99.9%), Ca(NO\(_3\))\(_2\) (Aldrich 99%), and Mg(NO\(_3\))\(_2\) (Alfa Aesar 99%). In a typical synthesis, (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) was 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(NO\(_3\))\(_2\)-6H\(_2\)O and calcined in air as before.

#### 2.2. Reforming Activity Testing

A schematic of the reactor system is shown as Figure 1. The simulated gasifier effluent for the adsorption/reaction step typically contained, 4.1% CH\(_4\), 0.33% C\(_\text{en}\)H\(_8\), 30.8% H\(_2\), 54.3% CO, 9.1% H\(_2\)O, 40 ppmv H\(_2\)S, balance N\(_2\). This gas approximates a bio- or coal gasifier effluent but without NH\(_3\) and with a water amount typical of an air-blown oxysteam gasifier. Reforming tests were performed at 923–1073 K with GHSVs 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-Al\(_2\)O\(_3\). 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.

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 × 30 m) was used to separate C\(_6\) and higher hydrocarbons. Samples were also analyzed for CO, CO\(_2\), and C\(_1\)−C\(_5\) 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 H\(_2\)S.

The yields of the products on a carbon basis and the weight-based rate for C\(_{10}\)H\(_8\) removal were calculated using eqs 1–3:

\[
Y(\text{CO}_2) = \frac{[\text{CO}_2]}{[\text{CO}]+10[\text{C}_{10}\text{H}_8]+[\text{CH}_4]} 
\]
$Y(CH_4) = \frac{[CH_4]}{[CO]_in + 10[CO_2]_in + [CH_4]_in}$ \hspace{1cm} (2)

$R(C_{10}H_8) = \frac{[C_{10}H_8]_in - [C_{10}H_8]_{lost} \times GHSV}{[C_{10}H_8]_in}$ \hspace{1cm} (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 4−6, but neglecting the C_{10}H_8 reactions, given its lesser amount.

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ \hspace{1cm} (4)

$2CO \leftrightarrow C + CO_2$ \hspace{1cm} (5)

$CO + H_2O \leftrightarrow CO_2 + H_2$ \hspace{1cm} (6)

### 2.3. Characterization.

The BET surface areas of the oxides were measured by N₂ adsorption - desorption using a Quantachrome AS-1 porosimeter. X-ray diffraction (XRD) spectra of ground, powdered samples were obtained with either a Rigaku Miniflex 2005C XRD or at the powder XRD beamline at the LSU Center for Advanced Microstructures and Devices, both using Cu Kα 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, Fe₃O₄, FeS, and FeOOH were used as reference spectra. The Mn K-edge data were also acquired at 6439 eV for XANES and 6923 to 7139 eV for XAFS. The spectra for MnS, MnO, Mn₃O₄, and Mn₄O₇ were obtained as reference standards. The Ce LIII edge spectra of ground, powdered samples were obtained with either fluorescence mode over a scan range of 5923−6139 eV.

### 3. RESULTS AND DISCUSSION

#### 3.1. Materials.

The designations for the catalysts, their elemental (molar ratios) metallic compositions (except for Al), and the surface areas are given in Table 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.

#### 3.2. C_{10}H_8 Reforming Activity.

#### 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 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-

<table>
<thead>
<tr>
<th>Catalyst designation</th>
<th>BET S.A. (m²/g)</th>
<th>fresh</th>
<th>used</th>
<th>yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn1/Ce3/Zr/Al (22)</td>
<td></td>
<td>170</td>
<td>150</td>
<td>97</td>
</tr>
<tr>
<td>Mn0.4/Ce/Zr/Al (20)</td>
<td></td>
<td>260</td>
<td>170</td>
<td>87</td>
</tr>
<tr>
<td>Mn0.4/Ce3/Zr/Al (19)</td>
<td></td>
<td>180</td>
<td>180</td>
<td>87</td>
</tr>
<tr>
<td>Mn0.2/Ce/Zr/Al (18)</td>
<td></td>
<td>180</td>
<td>170</td>
<td>91</td>
</tr>
<tr>
<td>Ni0.008/Mn0.003/Al (3)</td>
<td></td>
<td>130</td>
<td>-</td>
<td>97</td>
</tr>
<tr>
<td>Ni5/K/Mg4/Al (20)</td>
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<td>92</td>
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<td>Ni2/Ca/Mg2/Al (40)</td>
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<td>47</td>
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<td>99</td>
</tr>
<tr>
<td>Fe/Ce3/La/Al (19)</td>
<td></td>
<td>220</td>
<td>180</td>
<td></td>
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<tr>
<td>Ce3/La/Al (20)</td>
<td></td>
<td>170</td>
<td>150</td>
<td>94</td>
</tr>
<tr>
<td>Mn0.4/Ce3/La/Al (19)</td>
<td></td>
<td>180</td>
<td>180</td>
<td>87</td>
</tr>
<tr>
<td>Mn0.8/Ce3/La/Al (11)</td>
<td></td>
<td>210</td>
<td>170</td>
<td>84</td>
</tr>
<tr>
<td>La0.01/Al (3)</td>
<td></td>
<td>200</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>Mn0.8/Al (25)</td>
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<td>150</td>
<td>120</td>
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<td></td>
<td>290</td>
<td>26</td>
<td>100</td>
</tr>
<tr>
<td>Mn1/Ce4</td>
<td></td>
<td>155</td>
<td>70</td>
<td>98</td>
</tr>
</tbody>
</table>

For example, this catalyst contained three times as much Ce as Mn or Zr on a molar basis. The wt % of the Al₂O₃ is 78% (22% non-Al₂O₃). The surface area of the original Al₂O₃ is 200 m²/g.

![Figure 2. Tar reforming at 873 K, GHSV = 6600, naphthalene molar conversion. The feed mole %'s are CO or CO₂, 56 (black/dark with CO₂); yellow/light with CO; H₂, 32.4; CH₄, 8.2; water, 3.1; naphthalene, 0.3. Catalysts: 1 = La0.01/Al; 2 = Ce3/La/Al; 3 = Mn0.4/Ce3/La/Al; 4 = Mn0.8/Ce3/La/Al; 5 = Mn0.2/Ce/Zr/Al; 6 = Mn0.4/Ce3/Zr/Al; 7 = Fe/Ce3/La/Al; 8 = Mn0.8/Al; 9 = Fe/Al.](image-url)
containing products. The initial feed contained methane and trace C_{2}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 and 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.\(^{16,29,60}\) The role of CO\_2 as a pure inhibitor is shown also in Figure 3 for a related series of catalysts. Each data point represents an average or 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. These findings were confirmed for the Mn-containing catalysts also, specifically Mn0.2/Fe/Ce/Zr/Al. Furthermore, from Figure 3 it appears that the supported Fe on Al\_2O\_3 (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.

From Figure 2 we concluded that since some CO\_2 is always present in gasifier effluents, the best TMO/REO combinations would be Fe with the Ce/Zr mixed REO and Mn (in low loads) with the Ce/La mixed REO. Our previous work showed that the addition of H\_2S affected the pure REOs more than the Mn/REOs.\(^{81}\) 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 of H\_2S added.

The reforming behavior of a typical REO under such conditions is shown in Figure 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 Figure 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 ~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 (Figure S1, Supporting Information), Fe/Ce3, and Mn0.2/Ce/Zr/Al (Figure S, upper curve); the catalysts remained active through several turnovers, as summarized in Table 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\_2O\_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.

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 (Figures S2–S4, Supporting Information)\(^{32,83}\) and also to the complementary material lacking a TMO (Ce3/La/Al), when the syngas included sulfur (Figure 4). The Ni catalysts did show high initial reforming activity but poor sulfur resistance (Figures S2–S4) and, except for Ni2/Ca/Mg2/Al, severe coking (Table 2). Even for this catalyst some reactor blockage actually took place at ~30 h, prior to maximum accumulation of sulfur. This was true also of the other Ni-based catalysts and Ce3/La/Al.

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 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 Figure 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 Figure 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 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 3. The CO2 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 CH4 yields are lower for the supported REO/TMOs, as might be expected given their generally higher activity in tar reforming.

Table 2. Summary of Tar Reforming Results - Catalyst Stability in the Presence of Sulfur

<table>
<thead>
<tr>
<th>catalyst</th>
<th>coke (g/gcat)</th>
<th>turnovers(^a) 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>0.20</td>
<td>13000/8900</td>
</tr>
<tr>
<td>Mn1/Ce4</td>
<td>1.0</td>
<td>4</td>
<td>-</td>
<td>8500/n.a.</td>
</tr>
</tbody>
</table>

\(^a\)Turnovers based on total metal (not including Al) atoms and \(C_{10}H_8\) conversion only.

For the optimal Fe-containing catalysts (Fe/Ce3/La/Al or the unsupported Fe/Ce3) extensive data (summarized in Table 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 3. The CO2 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 CH4 yields are lower for the supported REO/TMOs, as might be expected given their generally higher activity in tar reforming.

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 (Figures 4-5). 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 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.

The weight accumulations in Table 2 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).

![Figure 6. Temperature-programmed oxidation of used reforming catalyst Fe/Ce3/La/Al.](image)

There is a possibility that some sulfur from the catalyst could desorb as elemental S\(_2\), which would not be distinguishable from background O\(_2\), but as the signal at \( > 650 \) K, which corresponds to the value in the table, was primarily associated with CO\(_2\) and not SO\(_2\) (Figure 6).

![Figure 7. XRDs of used supported REO/TMOs. Peaks labeled “1” are characteristic of graphite, “2” of \( \gamma \)-Al\(_2\)O\(_3\), “3” of CeO\(_{1.7}\), and “4” of Ce\(_2\)O\(_3\).](image)

3.3. Used Catalyst Characterization. 3.3.1. XRD. The diffraction patterns shown in Figure 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\(_2\), MnO\(_2\) and FeO\(_2\) 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 8). Either the TMOs are present as dispersed crystallites on CeO\(_2\) that are too small to observe by XRD, 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 ∼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. The particle sizes (by the Scherrer equation) of the dominant fluorite phases in Figure 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 Al\(_2\)O\(_3\) (i.e., the REO phase dominates), the surface area will therefore be greatly reduced upon use, as was observed (Table 1).

The peaks of Mn0.2/Ce/Zr are broadened and characteristic of the Ce/ZrO\(_3\) solid solution, especially that of the tetragonal phase (ICDD 01-074-8060). However, there are also indications of small amounts of monoclinic ZrO\(_2\) and reduced fluorite CeO\(_2\). There was an apparently small amount of Fe\(_3\)C present in used Fe/Ce3. Nevertheless, the overall picture is still of a dominant REO phase.
In order to better determine whether a separate MnO\textsubscript{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\textsubscript{1}/Ce\textsubscript{4} (same diffractogram as in Figure 8). The comparison is shown in Figure 9. Even though the Mn\textsubscript{1}/Ce\textsubscript{4} is far richer in Mn, it still shows no distinguishable MnO\textsubscript{x} phase (the small new reflection at 26.2° is carbon), as evident from the absence of the characteristic α-MnO\textsubscript{2} reflections at 21.8, 55.3, 63.1, and 41.2°. The MnO\textsubscript{2} phase is clearly visible in the oxidized Mn\textsubscript{0.8}/Ce\textsubscript{3}/La/Al, less so in Mn\textsubscript{0.4}/Ce\textsubscript{3}/Zr/Al and almost not at all in Mn\textsubscript{0.2}/Ce\textsubscript{3}/Zr/Al (not shown). Of the commonly found oxides of Mn, MnO\textsubscript{2} is probably easiest to identify, with a large number of strong reflections. From these results we conclude that a separate MnO\textsubscript{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 2 and those for Mn\textsubscript{0.8}/Al showing strong deactivation, we conclude that the separate MnO\textsubscript{x} phase promotes coke formation.

3.3.2. Characterization by XAS. An advantage of using XAS over other characterization methods is its applicability to the catalysts supported on Al\textsubscript{2}O\textsubscript{3} 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., T\textsubscript{d}) environment has a more intense pre-edge feature than a centrosymmetric (e.g., O\textsubscript{h}) one, due to 4p mixing into 3d orbitals, which imparts some dipole-allowed 1s-4p character to the transition.\textsuperscript{89−92} The position of the pre-edge also shifts to higher energy with increasing oxidation state.\textsuperscript{89,93} 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, Fe\textsubscript{3}O\textsubscript{4}, 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 Fe\textsuperscript{2+} to Fe\textsuperscript{3+} ratio from known standards.\textsuperscript{90,93−95} The pre-edge features were isolated by subtracting an arctangent function which fit the tail of the main edge,\textsuperscript{96} with some results shown in Figure 10. As seen, FeO has low pre-edge absorption because all of the Fe is octahedrally coordinated, while the broad pre-edge of Fe\textsubscript{3}O\textsubscript{4} is a combination of three environments: 1/3 octahedral Fe(II), 1/3 octahedral Fe(III), and 1/3 tetrahedral Fe(III).

By using all standards in the calibration, the average oxidation state of used, sulfided Fe/Ce\textsubscript{3}/La/Al is found to be between Fe\textsuperscript{2+} and Fe\textsuperscript{3+}, with a ratio Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ~2.9. A linear combination fit making use of all the standards was constructed as shown in Figure 11. A good fit with an R-factor of 0.001 was obtained with only FeO (55%) and Fe\textsubscript{3}O\textsubscript{4} (45%) left after subtraction.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{XRDs of mixed REOs with transition metals. Peaks labeled “1” are characteristic of graphite, “2” of CeO\textsubscript{2}, “3” of Fe\textsubscript{3}C, “4” of tetragonal Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}, “5” of monoclinic ZrO\textsubscript{2}, and “6” of CeO\textsubscript{1.7}.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Comparison of XRDs of Mn/mixed REOs (oxidized at 873 K) to reduced Mn\textsubscript{1}/Ce\textsubscript{4}. Peaks labeled “1” are characteristic of CeO\textsubscript{2}, “2” of γ-Al\textsubscript{2}O\textsubscript{3}, “3” of MnO\textsubscript{2}, and “4” of CeO\textsubscript{1.7}.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{Normalized Fe K pre-edge XANES after baseline subtraction.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{Linear combination fit for the Fe K-edge of Fe/Ce\textsubscript{3}/La/Al.}
\end{figure}
iteration analysis, with no similarity of the sample to the standards Fe₃ and FeOOH. The large pre-edge peak also shows that the Fe is mostly located in a noncentrosymmetric environment. Since Fe₃O₄ can be completely reduced to metallic iron at >950 K,⁹⁷ for our conditions there should be no Fe³⁺ present in any monometallic phase, and little to no Fe²⁺ as in FeO.⁹⁸ However, both Fe³⁺ and Fe²⁺ can exist when Fe is doped into the fluorite phase.

Due to the low concentration of Fe and Ce in Fe/Ce₃/La/AI, 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 LIII XAFS (Figure 12). The peak locations of both samples suggest that the cubic fluorite structure of CeO₂ 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.⁹⁹,¹⁰⁰ 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 CeO₂, 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.

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/CeO₂. 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, Fe₂O₄, and Fe₂O₃ was used in a separate set of regressions, with the combination of elemental Fe(0) (35 mol %) and the Fe/CeO₂ solid solution providing the best fit, as shown in Figure 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 correct the regression of the Ce LIII-edge data in R-space. In both regressions (Fe K-edge XANES and Ce LIII-edge XAFS), the results were similar, giving some confirmation to the process. The first- (Ce–O) and second-shell (Ce–Ce) coordination numbers were 6.7 and 9.3, respectively, for radii of 2.3 and 3.8 Å, respectively. Further fit details can be found in Supporting Information, Tables S1 and S2.

Much of our XANES/XAFS data on Mn/REOs and Mn/REOs/Al₂O₃ appeared in previous work⁹⁹ and will only be summarized here. The XANES spectra for the more highly loaded catalysts (e.g., Mnₐ.⁸/Ceₐ.₃/La/Al and Mnₐ.₄/Ce₄) both showed primarily Mn³⁺, with Mn¹/Ce₄ showing also some Mn²⁺. The fresh samples were similar, just less reduced (more Mn³⁺). The presence of both oxidation states when doped in CeO₂ is supported by the EPR results of Ramaswamy and co-workers¹⁰¹ and our own DFT calculations.⁷⁹ However, XANES could not differentiate between Mn²⁺ doped in CeO₂ or in the Al₂O₃ itself (eventually leading to MnAl₂O₄) for the Al₂O₃-supported samples. The presence of MnAl₂O₄ was confirmed in Mnₐ.⁶/Al by both XRD and XANES but was not present in the XRDs of any of the Mn/REOs/Al₂O₃ 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.¹⁰² Nevertheless the energy of the largest crest has been used in many qualitative estimates of average oxidation state.¹⁰³ Our crest locations are 6555.8, 6557.8, 6558.6, and 6559.3 eV for MnO, Mnₐ.⁰/Ceₐ.₃/Zr/Al, Mnₐ.₄O₂, and Mn₂O₃, respectively, putting the crest for Mnₐ.⁰/Ceₐ.₃/Zr/Al close to MnO₂. This Mn oxide has a normal spinel structure of 16 octahedral Mn³⁺ and 8 tetrahedral Mn²⁺ per unit cell. The pre-edge analysis (Figure 14) confirms that the states for Mn correspond closely to those present in Mnₐ.⁰O₄. However, the K-edge spectrum itself shows great differences between Mnₐ.⁰/Ceₐ.₃/Zr/Al and Mnₐ.₄O₂ (Figure 15), and there is no Mnₐ.⁰O₂ evidence by XRD. Also, Mnₐ.⁰O₄ is completely reduced to MnO in H₂ at temperatures lower than used here and would be substantially reduced at 973 K even in CH₄.¹⁰⁴,¹⁰⁵ A fit of Ce LIII-edge XAFS for Mnₐ.⁰/Ce₄ (Table S3, Supporting Information) showed that

![Figure 12](image12.png)  
**Figure 12.** Experimental and theoretical XAFS for the Ce LIII-edge of reduced Fe/Ce₃, compared to as calcined Fe/Ce₃ and CeO₂ in R-space.

![Figure 13](image13.png)  
**Figure 13.** Experimental and theoretical XAFS for the Fe K-edge of reduced Fe/Ce₃.

![Figure 14](image14.png)  
**Figure 14.** Normalized Mn K pre-edge XANES after baseline subtraction.
there were excess oxygen vacancies due to Mn doping (a Ce−O first shell coordination number of only 6 upon reduction), as did H2 TPR of Mn1/Ce4 compared to pure CeO2 (Figure S5, Supporting Information). 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.

3.4. Discussion. The results in Figures 2-4 and Table 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 MnO2 on Al2O3 (Figure 2, catalyst 8) in the presence of CO2 and the lack of evidence for separate phase MnO2 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/Al2O3 oxides are stable for long periods, even in the presence of sulfur in the feed (Table 2 and Figure 5), but it is notable that Mn0.2/Ce/Zr/Al is measurably more active, with a lower activation energy (Table 3).

DFT analysis suggests Mn3+ doped into fluorite CeO2 results from Mn atoms that are nonisolated and Mn5+ from isolated Mn atoms.79 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 spectrum somewhat between octahedral and tetrahedral Mn−O coordination in the Mn K pre-edge region, as observed 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 (Figure 15) is similar to Mn0.8/Al and MnAl2O4, the pre-edge and core energies for Mn0.2/Al are shifted to higher energies for Mn0.2/Ce/Zr/Al (Figure 15), suggesting a structure different than for MnAl2O4. Therefore, the only things we can conclude from the XANES spectra are that there are both Mn2+ and Mn3+ present, and there are both lower and higher coordination numbers associated with these oxidation states. The fit of the Ce L3,5 XAFS data for Mn1/Ce4 (Table S3), the XANES and TPR (Figure S5) evidence, 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/ZrO2 from the XRDs (Figures 8-9) 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 the combined characterizations of Fe K-edge XANES (Figures 10-11), Ce L3,5 XAFS (Figure 12 and Table S1), Fe K-edge XAFS (Figure 13 and Table S2), and XRD (Figures 7-8) all point to doping of the Fe into CeOx with some nanocrystalline metallic or metal carbide domains. The emergence of such nanocrystalline domains in used samples is supported by our own XRDs (Figure 8, Fe/C), and by in situ XRD evidence for H2 reduction of doped Fe/CeO2 to nanocrystalline Fe.96 The absence of a separate FeO phase in Fe/CeO2 mixed oxides is strong, even for Fe/Ce ratios to near 1, for lower temperature oxidizing conditions,107,108 and up to Fe/Ce = 0.8 for highly reducing conditions.99 At lower Fe/Ce ratios (e.g., <0.3) there is no XRD evidence for a separate FeO phase under oxidizing conditions up to 1073 K,98,100,109 and there are spontaneous oxygen vacancies generated by the Fe doping. For H2 reduction, the Fe in Fe/CeO2 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 CeO299,100,109 or Ce/ZrO2109 than in comparable CeO2 or Ce/ZrO2. 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,110 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.110 The free energy to refil 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 ΔEact for CH4 ~ ΔE_refill, 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 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 CH₄ yields) for Ni-based catalysts (Table 3), these data are misleading. For the italicized entries, the feeds were model compound studies with dilute H₂ and/or H₂O 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 CO₂ yields (relative to data in Table 3, some methanation is taking place (the yield is gasi... of steam ours) at both low and high temperatures. These yields arise from either high water partial pressures (syngas based on steam reforming) or excess O₂ leading to methane combustion. As no O₂ was present in our feed, combustion can be excluded, and as seen our CH₄ yields are relatively close to equilibrium for our calculated conditions and lower relative to Ni-based catalysts in comparable situations. Of course, Ni is a good methanation catalyst, and there is no significant deactivation of its methanation function even upon severe coking. From the data in Table 3, some methanation is taking place (the yield is 11% if no new CH₄ 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 CH₄ 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 reaction was noted previously for both Ni- and Fe-based catalysts. 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 MnOₓ phase in the XRDs accumulated coke more rapidly than did Mn0.2/Ce/Zr/Al; the ultimate example of Mn1/Ce4/Zr/Al clearly deactivated more rapidly, showing quite low activity even at short times onstream (Table 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 2 and the characterization results, the key finding on deactivation is that adding either Mn or Fe to REOs or supported (on Al₂O₃) 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 Al₂O₃-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.

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 CO₂ 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 MnOₓ 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.

ASSOCIATED CONTENT

Supporting Information

Figures S1–S4 that provide tar reforming reaction data for four additional catalysts at 923–1073 K. Figure S5 shows sample temperature-programmed reduction data for catalyst Mn1/Ce4 compared to CeO2. Tables S1 and S2 provide detailed XAFS fits for the Fe/Ce3 catalyst, both at the Ce LIII-edge and the Fe K-edge. Table S3 gives detailed XAFS fits for the Mn1/Ce4 catalyst at the Ce LIII-edge. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES


(3) Stanczyk, K.; Howaniec, N.; Smolinski, A.; Swiadrowski, J.; Kapusta, K.; Wiatowski, M.; Grabowski, J.; Rogut, J. Gasification of lignite and hard coal with air and oxygen enriched air in a pilot scale ex...sorbet sorbent in moving bed and fluidized bed reactors. Environ. Prog. 1995, 14, 146.


(99) Singh, P.; Hegde, M. S. Sonochemical synthesis of CeO1-xFe2O3-δ (0 < x < 0.45) and Ce0.65Fe0.33Pd0.02O2 nanocrystallites: oxygen storage material, CO oxidation and water gas shift catalyst. Dalton Trans. 2010, 39, 10768.
(100) Li, K.; Haneda, M.; Ozawa, M. Oxygen release—absorption properties and structural stability of Ce0.8Fe0.2O2. J. Mater. Sci. 2013, 48, 5733.