Effect of Sulfur on the Reduction of Ilmenite by Syngas in Chemical Looping Combustion

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ABSTRACT: The reactivity of ilmenite as an oxygen carrier (OC) in the presence of H2S was studied. A simulated syngas (66% CO, 34% H2) was used as the fuel. H2S concentrations were set to 4700 and 6580 ppm. The effect of the presence of CO2 was also investigated. The experiments were carried out using a thermogravimetric analyzer (TGA) at atmospheric pressure, with temperatures varying from 1073 to 1223 K. The results showed that the presence of H2S had no effect on the reduction kinetics of ilmenite. With the presence of only CO2 in the syngas, deposition on ilmenite samples was not observed. In the presence of H2S, deposition was observed regardless of the presence of CO2. Higher H2S concentration led to more pronounced deposition. It was shown that deposition only occurred after the ilmenite sample was previously reduced in the presence of H2S. For ilmenite oxidation, the mass change curves display a distinct peak followed by a valley when the sample was previously reduced in the presence of H2S, indicating reactions between the sulfur deposit and air. The amount of the sulfur deposit could be calculated using the oxidation curves. Scanning electron microscope-energy dispersive X-ray (SEM-EDX) and X-ray diffraction (XRD) analyses were conducted to examine the surface of the reduced samples and the results from these analyses confirmed the presence of the sulfur deposit on the surface of the samples that were reduced in H2S-containing atmospheres.

INTRODUCTION

Chemical looping combustion (CLC) has been recognized as a promising technology to reduce greenhouse gas emissions from fossil fuel combustion.1 In CLC, an oxygen carrier (OC), typically represented as MeOx, where Me is any transition metal, is used to transport oxygen between (a) a fuel reactor where OC is reduced by its reactions with the fuel to MeOx−1 and (b) an air reactor where OC is oxidized by air to MeOx. Because nitrogen is absent from this scheme, the flue gas from the fuel reactor is concentrated CO2 that is ready to be captured. Compared to other CO2 capture technologies, CLC does not require a power-consuming air separation unit or complicated post-combustion CO2 capture units.

One of the main challenges for CLC is the search for the appropriate OC with acceptable reaction kinetics and low cost. At CanmetENERGY, we have identified ilmenite as a promising OC. It is abundant in Canada, cheap, nontoxic, and has acceptable reaction kinetics. It has some other advantages such as stable reactivity over many cycles224 and reactivity not affected by agglomeration. We have studied that the kinetics of ilmenite for fuels, such as CO, CH4, simulated natural gas under widely ranging conditions such as temperature, pressure and the presence of contaminants such as H2S.2,58 Our test results on the influence of H2S on the reactivity of the ilmenite oxygen carrier for methane under high pressure (0.4 MPa) showed that the presence of H2S improved reactivity of the ilmenite oxygen carrier for both the reduction and the oxidation steps. In this work, we expand our test fuels to include a simulated syngas with H2S as a contaminant.

Because H2S is a common contaminant in syngas, the effects of H2S on various OCs have also been studied before by other researchers, including some iron-based OCs similar to ilmenite. Some of these studies showed that the presence of H2S had significant effects on the OC performance. Jerndal et al. conducted a thermal analysis of chemical looping combustion with various OCs, including Ni, Fe, Cd, Zn, Ce, W, Mo, BaS, and SrS.9 The study was done at 1073 and 1273 K, using CH4, CO, and H2 as fuels. Solid-phase reactions involving sulfur were studied. Their study showed that, for the Fe2O3-Fe system, there was no risk of sulfate formation at any investigated concentration of sulfur-containing gases and that H2S was completely converted to SO2. Wang et al. conducted a thermodynamic calculation study on sulfur evolution and carbon deposition in chemical looping combustion with a simulated syngas containing H2, CO, CO2, H2O, H2S, and N2, with Fe2O3 as one of the five OCs in this study.10 The effects of pressure (0.1–1 MPa) and temperature...
(1173–1323 K) were investigated. The study found that the formation of solid sulfur compounds increased with increasing pressure and decreased with increasing temperature. They also found that an increase in the CO₂ concentration could inhibit carbon formation, and an increase in H₂S concentration led to more carbon deposition. The study showed that the most possible solid sulfur compounds for Fe₂O₃-based OC were Fe₈O₈S.

Tian et al. studied bentonite-supported Fe₂O₃ oxygen carriers for syngas combustion. The study was carried out in a thermogravimetric analyzer (TGA) at 1073 and 1173 K with 4042 ppm H₂S. They found that H₂S addition decreased the reaction rates of both reduction and oxidation by ~1.5 times compared to syngas without H₂S. Their test results indicated that the initial reaction between OC and CO and H₂ was fast. This reaction was then followed by sulfidation reaction between OC and H₂S. While they did not indicate whether they observed metal sulfide formation from the mass change curves, it was clear from their sample analyses that metal sulfide did form during the OC reduction because the bentonite-supported Fe₂O₃ oxygen carrier contained ~6% of sulfur after being reduced at 1073 K.

Gu et al. studied the effect of sulfur on the iron ore oxygen carrier in chemical looping combustion with a TGA and using CO as fuel. The reduction of the OC was conducted with 3000–6000 ppm H₂S at 1193 K and pressure at 0.1 and 0.6 MPa in both N₂ and CO₂ atmospheres. Their results showed that the initial iron ore reduction was not affected by the presence of H₂S although a difference in mass change appeared after ~2000 s. The mass loss rate during the later portions of the reduction cycle was somewhat lower when H₂S was present. A mass gain was observed in the cases of 4000 and 3000 ppm H₂S when the reaction time was long enough. The mass gain was faster and more pronounced in the CO₂–H₂S–N₂ atmosphere than in the CO–H₂S–N₂ atmosphere.

Overall, there are some limited experimental data on the effect of sulfur on the iron-based OC for chemical looping combustion. These experimental data indicated that sulfide formation occurred during the reduction of the OC, contrary to Jerndal et al.’s thermodynamic analyses. While some data indicated that the presence of H₂S could decrease reaction kinetics, others indicated that the reaction kinetics were not significantly affected, at least not initially. These works used various forms of Fe₂O₃ as OCs. The objective of this work is to investigate the effect of sulfur on the reduction and oxidation kinetics of a natural iron ore, ilmenite, as an OC using a simulated syngas as fuel. This is because ilmenite is a cheap and abundant material and, as a result, a very appealing candidate as an OC.

### RESULTS AND DISCUSSION

The test conditions are presented in Table 1. The syngas flow rate was set at 0.15 NL/min balanced in N₂ and CO₂ (0.1 NL/min when used) for a total gas flow rate of 0.5 NL/min. Our previous results showed that ilmenite reactivity and oxygen-transport capacity stayed stable after the first four cycles.

**Test Data Analyses.** In simple terms, upon oxidation above 1173 K, ilmenite Fe₂TiO₅ is oxidized to pseudobrookite Fe₇TiO₄, which is reduced by syngas according to the following reaction scheme

Fe₇TiO₄ + TiO₂ + CO = 2Fe₇TiO₃ + CO₂

(R1)

Fe₇TiO₃ + TiO₂ + H₂ = 2Fe₇TiO₃ + H₂O

(Pseudobrookite is often considered as Fe₂O₃ + TiO₂ and ilmenite as FeO + TiO₂. TiO₂ can be considered as inert. In this case, the reduction of ilmenite by syngas, in the presence of CO₂, can be simplified by the following reaction scheme)

3Fe₂O₃ + CO = 2Fe₃O₄ + CO₂

(R3)

3FeO₂ + O₂ = 2Fe₂O₃

(R9)

4FeO + O₂ = 2Fe₂O₃

(R10)

4Fe + 3O₂ = 2Fe₂O₃

(R11)

Data analyses were done according to the following formulae. The OC conversion ratio, Xₐ, is calculated using the equation

Xₐ = \frac{m_0 - m_t}{m_0 - m_r}

(1)

where m₀ is the mass of the ilmenite ore sample after oxidation; m₉ is the mass at time t and m_r is the sample mass at the end of the reduction phase.

The OC reactivity can also be assessed using the conversion rate Xₐ as calculated using the equation

\frac{dX_a}{dt}

(2)

where t is time in seconds.

The oxygen-transport capacity Rₒ (in %) can be calculated using the equation

Rₒ = \frac{m_0 - m_r}{m_0} \times 100%

(3)

Table 1. Test Parameters

| test ID     | test gas      | H₂S concentration (ppm) | temperature, K |
|-------------|---------------|-------------------------|----------------|
| 20180927a   | syngas-CO₂  | 0                        | 1173           |
| 20180926a   | syngas-H₂S–CO₂→N₂ | 4700                  | 1173           |
| 20180926b   | syngas-H₂S–N₂  | 6580                    | 1173           |
| 20181024a   | syngas-H₂S–CO₂→N₂ | 4700                  | 1073           |
| 20181024b   | syngas-H₂S–N₂  | 6580                    | 1073           |
| 20181115a   | syngas-H₂S–CO₂→N₂ | 4700                  | 1123           |
| 20181115b   | syngas-H₂S–N₂  | 6580                    | 1123           |
| 20181120a   | syngas-H₂S–CO₂→N₂ | 4700                  | 1123           |
| 20181120b   | syngas-H₂S–N₂  | 6850                    | 1223           |

Fe₂TiO₃ + TiO₂ + H₂ = 2Fe₇TiO₃ + H₂O
OC performance can be evaluated using both the oxygen-carrying capacity $R_o$ and the conversion rate $X_r$. An ideal OC should have a high $X_r$ and a high $R_o$.

In this work, ilmenite reactivity is presented in the form of mass change (in %) vs time curves. The mass change $C$, in percentage, is calculated using the equation:

$$ C = \frac{m_f - m_i}{m_i} \times 100\% $$

(4)

According to eq 4, $C$ is negative during the reduction stage and positive during the oxidation stage.

**Ilmenite Reduction.** Figure 1 shows the ilmenite reaction kinetics from 1073 to 1223 K with and without the presence of H$_2$S, while CO$_2$ was present (20 vol %) in the feed gas in all cases. For tests with H$_2$S, its concentration was set at 4700 ppm.

Excluding the first ~100 s that are marked by a period of gas diffusion when the purge gas (N$_2$) was being replaced by the reaction gas, Figure 1 shows that temperature had minor effects on the ilmenite reduction kinetics in the absence of H$_2$S. For example, for the oxidized ilmenite sample to reach a 3% mass reduction, it took 191 s at 1073 K and 195 s at 1173 K. Considering the uncertainties associated with the gas diffusion, this difference of 4 s is negligible. Similar observations could be made when H$_2$S was present. In this case, it took 208 s at 1073 K and 198 s at 1173 K for the ilmenite sample to reach a 3% mass reduction.

From these figures, we can see that the mass loss curves remained constant after the reduction was completed in the absence of H$_2$S from the fuel gas, indicating the absence of carbon deposition. The final mass losses of the ilmenite samples that, according to eq 3, correspond to its oxygen-carrying capacity, were about 6%. On the other hand, when H$_2$S was present, the mass curves displayed a clear upward trend after ilmenite reduction was completed, indicating formation of deposits on the sample surface. The maximum mass losses in the presence of H$_2$S, between 5 and 6%, were slightly lower than those in the absence of H$_2$S. Figure 1 also showed that surface deposition occurred under all temperatures from 1073 to 1223 K, when H$_2$S was present.

This result was also corroborated by our thermodynamic calculations, as shown in Figure 2. The thermodynamic calculations were done with the HSC Chemistry 6.1 software (Outotec Research Oy). These calculations showed that the Fe$_{O.87}$S compound was formed in the whole temperature range studied (1073–1273 K) at substoichiometric conditions ($\phi < 1$). The stoichiometry ratio, $\phi$, is defined as

$$ \phi = \frac{F_{MeO}}{b \times F_{fuel}} $$

(5)

where $F_{MeO}$ is the molar flow rate of the ilmenite and $F_{fuel}$ is the inlet molar flow rate of the fuels present in the gaseous mixture in the fuel reactor (CH$_4$ and H$_2$S); parameter $b$ is the stoichiometric coefficient of the fuel gas.

Figure 3 shows the results obtained for a test done at 1123 K under three different atmospheres. Once again, the first ~100 s were dominated by gas diffusion.

This figure shows that, with syngas-CO$_2$ (cycle #11), the mass loss stabilized at the end of ilmenite reduction with no signs of any deposition; with syngas-H$_2$S (cycle #10) or with syngas-H$_2$S-CO$_2$ (cycle #12), the ilmenite test sample showed clear mass gains at the end of the reduction with cycle #10 showing the most mass gain due to deposition. However, the rate of ilmenite reduction was not affected by the changing atmospheres as all mass loss curves displayed a similar rate of change during the first 200 s of the tests. This observation is in disagreement with Tian et al.’s results that showed that the reaction rate decreased even in the presence of small concentration of H$_2$S decreased reaction rates with their bentonite-supported iron oxide OC and syngas. On the other hand, our observations are in agreement with Gu et al.’s findings that showed that the presence of H$_2$S, up to 6000 ppm, had no meaningful effect on reaction kinetics until later in the reduction stage. This may be due to the difference in the OCs used. Tian et al. used bentonite-supported Fe$_2$O$_3$, while we used a natural ilmenite ore and Gu et al. used a natural iron ore (Fe$_3$O$_4$). It is possible that the interactions between bentonite and H$_2$S interfered with reactions between H$_2$S and Fe$_3$O$_4$ in Tian et al.’s study. It is worth pointing out that modified bentonite can be used as adsorbents of H$_2$S gas, as proposed by Stepova et al. Their study showed that depositing iron oxide on bentonite significantly increased its BET surface area and enhanced the adsorption of H$_2$S.

With H$_2$S and the syngas (cycle #10), the amount of mass loss of the ilmenite test sample (4.5%) was clearly less than the other two cases (5–5.3%), where the difference in the mass losses was negligible. This was likely due to the more pronounced surface deposition caused by higher H$_2$S concentration (6580 ppm). With this high H$_2$S concentration, deposition may have started before the OC sample was completely reduced so that less Fe is available for reactions with syngas. If sulfur deposition does occur earlier during the reduction stage, which means that pseudobrookite is not...
completely reduced, and then the following reactions could take place:

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} & \rightarrow \text{Fe}_2\text{S}_3 + 3\text{H}_2\text{O} \quad \text{(R12)} \\
\text{FeTiO}_3 + \text{H}_2\text{S} & \rightarrow \text{TiO}_2 + \text{FeS} + \text{H}_2\text{O} \quad \text{(R13)}
\end{align*}
\]

Therefore, some water could be formed, and if the initial \( \text{H}_2\text{S} \) concentration is high enough, the amount of water formed could prevent further reduction of the ilmenite through Reactions R2 and RRR4.

While some of our observations are in agreement with Gu et al.’s findings,12 there is a major difference between our results and theirs. In Gu et al.’s study, mass loss in the \( \text{N}_2 \) atmosphere was much higher than in the \( \text{CO}_2 \) atmosphere. They observed OC mass loss of 15–20% in the \( \text{CO}_2\text{–H}_2\text{S}–\text{N}_2 \) atmosphere and of less than 4% for the \( \text{CO}–\text{H}_2\text{S}–\text{CO}_2 \) atmosphere. In our work, the OC mass loss was consistent between 4.5 and 6% for syngas-\( \text{H}_2\text{S}–\text{CO}_2 \), syngas-\( \text{H}_2\text{S}–\text{N}_2 \), and syngas-\( \text{CO}_2–\text{N}_2 \) atmospheres.

Another difference between our work and Gu et al.’s work12 is that, in their work, when in the \( \text{N}_2 \) atmosphere, the maximum mass loss occurred at \(~3000\) s, while in the \( \text{CO}_2 \) atmosphere, it occurred at \(~200\) s. In our work, the maximum mass loss occurred at about the same time irrespective of the reaction atmospheres. This can be clearly seen in Figure 3. The ilmenite samples in all three cases reached full conversion in approximately the same amount of time, i.e., about 300 s.

A number of factors could lead to these differences, such as the characteristics of the OC (iron ore in Gu et al.’s work12 and natural ilmenite ore in ours) and the fuel used, which was pure CO in Gu et al.’s study and simulated syngas in ours.

Ilmenite can be reduced to different forms depending on the reaction gas composition, notably \( \text{CO}_2 \) in this case. Usually, when enough \( \text{CO}_2 \) is present, ilmenite reduction is limited to \( \text{Fe}_3\text{O}_4 \) (RRR3 and RRR4), and when \( \text{CO}_2 \) is absent, ilmenite can be further reduced to \( \text{FeO} \) (RRR5 and RRR6) or even \( \text{Fe} \) (RRR7 and RRR8). This can be clearly seen in Figure 4 for a reduction cycle done with syngas only (no \( \text{H}_2\text{S} \) and no \( \text{CO}_2 \)). \( T = 1173 \) K, cycle #6.
Ilmenite Oxidation. Figure 5 shows the ilmenite oxidation, both absolute and relative mass changes after the sample was first reduced under three different atmospheres at 1123 K. Similar to the reduction cycle, there was a period of about 80–90 s marked by gas diffusion when the purge gas (N₂) was being replaced by air.

Figure 5 shows the mass change during ilmenite oxidation after the sample was reduced in CO₂-syngas, in CO₂–H₂S-syngas, and in H₂S-syngas atmospheres. The mass curve for the CO₂-syngas-reduced sample showed a constant mass gain that topped at ~6%, in agreement with the mass change during the reduction period. Mass gain curves for the H₂S-syngas-reduced sample showed a sharp increase in the mass followed by a sharp decrease in mass before the mass change curve increased again. The CO₂–H₂S-syngas-reduced sample showed similar behavior with less pronounced mass increase and decrease. In both cases, the final mass gain observed was considerably less than the CO₂-syngas-reduced sample. However, these mass gains, around 2% for the H₂S-syngas-reduced sample and around 4% for the CO₂–H₂S-syngas-reduced sample, were not representative of the actual degree of oxidation because subsequent reduction cycles with these oxidized samples still showed mass losses of 5–6%.

One observation that can be made from Figure 5 is that the oxidation rates for all three samples are about the same. Unlike Tian et al.,¹¹ we did not see any decrease in the reaction kinetics during the oxidation stage due to sulfur deposition from the reduction stage.

The differences in the mass gain are a direct indication of the amount of sulfur deposited on the sample surface during the reduction cycle. By assuming that the observed mass differences were entirely due to sulfur deposition, the amount of sulfur deposited on the syngas-H₂S-reduced sample and the syngas-H₂S–CO₂-reduced sample was calculated to be 1.88 mg (3.69%) and 1.34 mg (2.66%), respectively. This assumption may not be 100% valid because some studies have shown that the presence of H₂S can lead to increased carbon deposition in addition to sulfur deposition, so it can be argued that some of the observed mass increase, especially for the syngas-H₂S atmosphere, could be due to carbon deposition. For the syngas-H₂S–CO₂ atmosphere, however, this assumption is likely acceptable because our previous studies,⁷,⁸ using methane and natural gas, showed that as long as enough CO₂ (CO₂:CH₄ ≥ 1) was present in the feed gas, carbon deposition did not happen.

Figure 6 shows the oxidation curves after the ilmenite sample was reduced under different atmospheres for a test done at 1223 K. Using the same assumption and performing the same calculations showed that the amount of sulfur deposited on the syngas-H₂S-reduced sample and the syngas-H₂S–CO₂-reduced sample was 0.33 mg (0.67%) and 0.23 mg (0.47%), respectively. These amounts are much lower than the amount of deposits observed for the 1123 K test. This observation is supported by the thermodynamic calculations, as shown in Figure 2, where it can be seen that Fe₀.₈₇₇S formed at a progressively lower stoichiometry ratio as temperature increased.

The mass change curves during the reduction stage clearly showed that, in CO₂–H₂S-syngas and H₂S-syngas atmospheres, deposition occurred on the test samples at the end of the reduction with the latter atmosphere producing more deposits. The mass change curves during the oxidation stage showed that the effects of the reducing atmosphere on sulfur deposition decreased at higher temperatures and the deposition was more pronounced at lower temperatures. This observation is in agreement with Wang et al.’s findings¹⁰ and our thermodynamic calculations that lower temperature favors sulfur and carbon deposition.

During the oxidation stage, the deposits were completely removed by reactions with oxygen. While the sulfide oxidation can be described by an overall reaction,

\[
4\text{FeS} + 7\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 4\text{SO}_2
\]

(R14)

it is actually a much more complex process because sulfide oxidation can go through various reactions according to the temperature.¹⁷–¹⁸ In our case, the initial mass increase could be attributed to the iron sulfate formation when the oxygen in air reacted with the iron sulfide formed on the reduced sample surface

\[
\text{FeS} + 2\text{O}_2 = \text{FeSO}_4
\]

(R15)

The iron sulfate could then react with O₂

\[
2\text{FeSO}_4 + 3\text{O}_2 = 2[\text{Fe}_2(\text{SO}_4)_3]_1\cdot\text{Fe}_2\text{O}_3
\]

(R16)

which is followed by

\[
[\text{Fe}_2(\text{SO}_4)_3]_1\cdot\text{Fe}_2\text{O}_3 = 3\text{Fe}_2\text{O}_4 + 6\text{SO}_3
\]

(R17)

Other reactions that could possibly take place are

\[
\text{FeS} + 1.5\text{O}_2 = \text{FeO} + \text{SO}_2
\]

(R18)

\[
\text{FeS} + 3\text{FeSO}_4 = 4\text{FeO} + 4\text{SO}_2
\]

(R19)
The exact oxidation mechanism of iron sulfide is beyond the scope of this work. As such, the observed initial mass increase followed by the mass loss before the sample mass increased again can be simplified to the following reaction18

\[ \text{FeS} + 0.75x\text{O}_2 = \text{Fe}_{1-x}\text{S} + x/2 \text{Fe}_2\text{O}_3 \]  

(R20)

The mass loss after the initial mass gain during the oxidation cycle can be attributed to the removal of sulfur deposits by air as gaseous \( \text{SO}_2 \). With the oxygen uptake, the sample mass increased initially. However, the subsequent mass loss due to the continued oxidation reaction of \( \text{Fe}_{1-x}\text{S} \) outpaced the mass increase due to the formation of \( \text{Fe}_2\text{O}_3 \). Once the sulfur was completely removed, the mass of the sample increased again in a way that was similar to the ilmenite sample reduced in the syngas-\( \text{CO}_2 \) atmosphere.

From the above discussion, an important conclusion can be drawn that the presence of sulfur does not have significant effects on the reduction kinetics of ilmenite. In these TGA tests, sulfur deposition occurred when particles were highly reduced. However, a continuous CLC unit that uses ilmenite as an oxygen carrier would operate with a high excess of oxygen, well above the stoichiometric conditions, at high solid circulation rates, which means that the oxygen carrier particles would be only partially reduced and sulfur deposition could be largely avoided. These conditions are obviously favorable from an environmental point of view because sulfur would be released in the fuel reactor in the form of \( \text{SO}_2 \) according to Reactions R21 and RRR22 instead of being released into the atmosphere through the air reactor as a consequence of the iron sulfide decomposition (RRR14)

\[ 3\text{Fe}_2\text{TiO}_3 + 3\text{TiO}_2 + \text{H}_2\text{S} = 6\text{FeTiO}_3 + \text{SO}_2 + \text{H}_2\text{O} \]  

(R21)

\[ 9\text{Fe}_2\text{O}_3 + \text{H}_2\text{S} = 6\text{Fe}_3\text{O}_4 + \text{SO}_2 + \text{H}_2\text{O} \]  

(R22)

**Surface Elemental Analyses.** The collected samples were submitted for surface elemental analyses. Sample analyses show clear signs of sulfur deposition on the sample surface. Figure 7 shows sulfur deposit, in yellow color, on the Test 20181024a sample, after reduction in the syngas-\( \text{CO}_2 \)–\( \text{H}_2\text{S} \) atmosphere at 1073 K with 4700 ppm \( \text{H}_2\text{S} \) for 20 min. We can see from this image that the reduced ilmenite sample was evenly covered by the syngas-\( \text{CO}_2 \) atmosphere.

Figure 8 shows the results of a quantitative analysis of the surface species. Calculations using the measured mass percentage numbers showed that the sulfur deposit was mainly in the form of FeS (Fe:S = 1.103 at the above sample surface site and Fe:S = 1.161 at the site of another sample from the same test).
The presence of iron sulfide was confirmed by wide-angle X-ray diffraction (XRD) analysis of a reduced sample from Test 20181120a, as can be seen in Figure 9. The appearance of the FeS phase further confirms the existence of sulfur in the sample, which is in accordance with the scanning electron microscope-energy dispersive X-ray (SEM-EDX) observation and thermodynamic calculations. In addition, the phase of iron sulfide identified by XRD analysis is FeS with Fe/S ratio 1, which is very close to the quantitative analysis obtained from the EDX. Figure 10 shows SEM-EDX images of a test done at 1173 K. In this case, sulfur deposition on the sample reduced in the syngas-H2S atmosphere (Test 20180926b) was much less pronounced, even though the H2S concentration was higher in this case (6580 ppm). This could have resulted from the effects of higher temperature or it could be due to the shorter reduction period, which was 10 min in this test instead of 20 min. Compared to the test at 1073 K, there was more observable Ti on the surface of the reduced sample (Figure 10, middle right) because of the lesser amount of sulfur deposited. It can be seen from Figure 10 that there were protrusions growing on the sample surface. These protrusions mainly consisted of iron and they likely formed during the redox cycles because of iron separation and migration from the sample core to the surface, which is a known behavior for ilmenite OC and has been demonstrated. As this migration continued, iron protruded from the sample surface, which is clearly shown in Figure 10.

Surface element analysis on this sample site (Figure 11) showed that, while Fe was the most abundant species, Ti was also present with a higher mass percentage than sulfur. Calculations show that there was almost three times more iron than sulfur on a molar basis (Fe/S = 2.909). It is possible that, with a longer duration reduction stage, sulfur deposition could have continued and covered more sample surface and the Fe/S ratio would decrease.

**CONCLUSIONS**

This work studied the effects of H2S on ilmenite as an oxygen carrier for chemical looping combustion of syngas using a TGA. The results showed that the presence of H2S did not have appreciable effects on the reduction kinetics of ilmenite. The presence of H2S slightly reduced the oxygen-carrying capacity of the ilmenite. In situations where CO2 was absent in the reaction gas, oxygen-carrying capacity was noticeably reduced due to the early onset of sulfur deposition. Sulfur deposition was observed whenever H2S was present, regardless of the test temperature (1073−1223 K). However, when CO2 was present, sulfur deposition was less severe. When only CO2 and the syngas were present, no deposition was observed. These observations are in agreement with our thermodynamic calculations, which showed that sulfur deposition on the ilmenite oxygen carrier can be avoided by maintaining a high oxygen carrier to fuel ratio in the fuel reactor.

The oxidation of ilmenite after it was reduced in sulfur-containing syngas showed an initial brief period of mass gain before a period of mass loss, which was followed by another period of mass gain typical of ilmenite oxidation. These initial mass gains and mass losses were attributed to the reactions between the sulfur deposit and air. It is obvious from the oxidation mass gain curves that sulfur deposition was more severe at lower temperatures as also shown by the thermodynamic calculations. Our results showed that the oxidation kinetics was not affected by sulfur deposition.

SEM-EDX analysis of the reduced ilmenite samples clearly confirmed the presence of the sulfur deposit when the sample was reduced in H2S-containing atmospheres. Quantitative analysis as well as XRD analysis showed that sulfur was mostly present in the form of FeS. SEM mapping and EDX indicated the increased formation of FeS at the particle surface with reduction in time. SEM analysis also showed indications of iron migration from the sample core to the surface.

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**Figure 8.** Quantitative analysis of surface species. Test 20181024a sample, after reduction in the syngas-CO2−H2S atmosphere at 1073 K with 4700 ppm H2S for 20 min.

**Figure 9.** XRD analysis of the reduced sample from Test 20181120a. The right image is the magnified pattern showing the details from 28 to 46°.
EXPERIMENTAL SECTION

Sample Preparation. The OC used in this work was an upgraded natural ilmenite ore provided by Rio Tinto Canada used in our previous work. The OC was crushed and sieved to 106−212 μm and was calcined in air at 1173 K for 2 h prior to be tested in the TGA. For each test, ~50 mg of the sample was used. Samples were placed in a ceramic pan and spread out to form a single thin layer.

Test Procedure. Experimental tests were conducted using a high-pressure, high-temperature thermogravimetric analyzer (TGA) manufactured by Linseis, which has been described in detail. For this work, the tests were conducted in the temperature range from 1073 to 1223 K and at atmospheric pressure. A simulated syngas, composed of 66% CO and 34% H₂, was used as fuel with the balance gas consisting of H₂S, N₂, and CO₂ (when used). The oxidation stage was carried out in air. The TGA was purged with nitrogen for 5 min between the reduction and oxidation stages. The total gas flow rate was 0.5...
NL/min. In a previous work, we varied the reaction gas flow rates up to 1 NL/min and did not observe any difference in the kinetic reactivity of the ilmenite between 0.5 and 1 NL/min. This showed that the mass diffusion effects due to the reaction gas flow rates were eliminated at 0.5 NL/min.

Each test started with four redox cycles in syngas/CO₂. These were performed to activate the ilmenite. Starting with the fifth cycle, reduction cycles were carried out in syngas/CO₂/H₂S, syngas/CO₂, and syngas/H₂S. In total, 10 to 12 redox cycles were completed. A full redox cycle is considered to consist of the OC being oxidized and then reduced. In this paper, the cycle number indicated with an integer (such as cycle #10) refers to a reducing step, while the oxidizing step is indicated with a floating number (such as cycle #8.5). The tests usually ended with a reduction sample, though a few tests ended with an oxidation cycle to verify that all sulfur deposits were removed with air.

For each test, the TGA was heated in nitrogen at a heating rate of 20 K/min to 15 K below the target test temperature. The heating rate was then decreased to 2 K/min until the desired sample temperature was reached. This was done to minimize overheating of the sample. After each test, the sample was cooled in nitrogen flow and then collected for analyses.

For personnel safety, a hand-held gas monitor with alarms was used. The gas monitor was bump-tested daily and calibrated monthly.

**Sample Characterization.** A Rigaku Ultima IV X-ray diffractometer (XRD) was used to analyze and identify the crystal phase of OCs. The measurements were performed at room temperature. The sample was ground and put on a silicon zero-background sample stage. The XRD instrument was set to operate at 40 kV and 40 mA over a scanning range (2θ) between 15 and 100° at a scanning rate of 0.02°/s. The XRD pattern displays multiple resolved diffraction peaks, which can be assigned to the reflections of the crystal phases of ilmenite (FeTiO₃, JCPDS Card Number 75-519), ulvöspinel (Fe₂TiO₄, JCPDS Card Number 73-1724), and iron sulfide (FeS, JCPDS Card Number 65-3356).

The element distributions on the particle surfaces were examined by using a scanning electron microscope (SEM, Hitachi S-3400 N) equipped with an energy-dispersive X-ray (EDX) analyzer (Oxford Instruments). Before the analyses, the samples were coated with a thin layer of carbon (~2 nm). The SEM and the EDX elemental mapping images were taken at a voltage between 15 and 20 kV at a working distance of ~10 mm.

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**Notes**

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