Removal of Hydrogen Sulfide and Ammonia by Goethite-Rich Limonite in the Coexistence of Coke Oven Gas Components

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Hydrogen sulfide (H$_2$S) removal and catalytic ammonia (NH$_3$) decomposition performance of limonite in the presence of coke oven gas (COG) components has been studied in a cylindrical quartz reactor at 300–850°C under a high space velocity of 51 000 h$^{-1}$ to develop a novel hot gas cleanup method. The H$_2$S removal behavior in 50% H$_2$/He depends on the temperature, with high performance observed at lower temperature. An investigation of the removal behavior of H$_2$S in the presence of COG components (CH$_4$, CO, CO$_2$ and H$_2$O) at 400°C reveals that CH$_4$ does not affect the removal performance. On the other hand, the coexistence of CO drastically decreases the H$_2$S removal performance. However, the addition of 5% H$_2$O to 50% H$_2$/30% CH$_4$/5% CO/He dramatically improves the H$_2$S removal performance, whereas the performance is low at 5% CO with 50% H$_2$/30% CH$_4$/5% CO/He. In addition, the H$_2$S breakthrough curve strongly depends on the space velocity.

The limonite catalyst achieves almost complete decomposition of NH$_3$ in He at 850°C until 240 min. When the decomposition run is performed in the presence of COG components, the coexistence of 30% CH$_4$ deactivates limonite with significant formation of deposited carbon. On the other hand, the addition of 5% CO$_2$, 5% H$_2$O or 5% CO$_2$/5% H$_2$O to 50% H$_2$/30% CH$_4$/5% CO improves the catalytic activity without carbon deposition, and >99% conversion of NH$_3$ to N$_2$ is maintained until 240 min.

KEY WORDS: hydrogen sulfide; ammonia; removal; decomposition; catalyst; limonite; coke oven gas.

1. Introduction

Coke oven gas (COG) produced during coal carbonization is generally used as a fuel source for coke ovens and other combustion units in iron steel making process. COG has recently attracted much attention as a low-cost source of hydrogen and value-added products for the chemical industry. However, COG contains a variety of impurities, such as hydrogen sulfide (H$_2$S) and ammonia (NH$_3$), which are detrimental in some industrial applications. In conventional processes, the hot raw COG (>800°C) must be quenched to near room temperature using aqueous ammonia solution to remove tarry materials contained in the COG. On the other hand, the catalytic or noncatalytic reforming of COG is a promising technology that effectively utilizes the energy of the hot COG. Upon coal carbonization, some of the nitrogen and sulfur present in coal are retained in the solid phase, and the rest is released as volatile-N (N$_2$, NH$_3$, HCN and tar-N) and -S (H$_2$S, COS, CS$_2$, and tar-S) species. It is well known that NH$_3$, HCN, tar-N, H$_2$S, organic-S and tar-S not only serve as sources of NO and SO, but also are catalyst poison materials used for COG reforming and/or gas tube corrosion.

Our research group has been working on vapor deposition of gaseous-tar, which is contained in COG, into the pores of limonite or cold-bonded pellets to develop carbon-containing iron materials (composite) with enhanced strength and reducibility for blast furnaces. A vapor deposition temperature of 350°C is optimum for obtaining completely filled mesopores in limonite or cold-bonded pellets using carbonaceous materials derived from tar via vapor infiltration. However, during vapor deposition treatment, N and S in the feed gases are likely to transfer from the gas-phase to the composite, which may cause high N and S contents in the resulting composite. When such a composite is used for blast furnaces, the N and S species in the composite may have adverse effects on the reduction rate, strength or exhaust gas purification equipment. N and S in COG mainly exist as NH$_3$ and H$_2$S, with contents of approximately 1 vol% and 3 000 ppmv, respectively. Therefore, it is very important to develop a removal method for gaseous-N and -S species in COG.

Our research group has been investigating the catalytic decomposition of NH$_3$ or model tar-N compounds (pyridine or pyrrole) using inexpensive iron catalysts. We have found that fine particles of metallic iron (α-Fe) formed from low-value iron ore (limonite) give high activity in the decomposition of NH$_3$ and model tar-N compounds. Limonite can achieve almost complete decomposition of 2 000 ppmv NH$_3$ in inert or simulated fuel gas from coal gasification at 500–850°C. In addition, we have recently...
shown that the limonite-derived α-Fe can provide stable activity for the decomposition of 100 ppmv C₄H₇N to N₂ in He, with fuel gas or COG components at 500–850°C. On the other hand, iron oxide is known to be effective for the removal of H₂S in fuel gas at 300–700°C. Thus, it is possible that limonite-derived α-Fe will be a good adsorbent for H₂S in COG. However, only a few studies have reported H₂S removal in COG by iron-based absorbents, such as iron oxide and/or iron-bearing sorbents combined with other metals. It is well-known that a typical COG is composed of 54–59% H₂, 24–28% CH₄, 4–7% CO, 3–5% CO₂, 1–3% CO and 1–3% H₂O with impurities, but the influence of the individual COG components on H₂S removal has not been investigated in previous reports.

In this paper, therefore, we focus on investigating H₂S removal and catalytic NH₃ decomposition performance using an Australian limonite in the presence of COG components to develop a novel gas cleaning method for removing H₂S and NH₃.

2. Experimental

2.1. Sample

An Australian natural limonite ore composed of about 70% goethite (α-FeOOH) was employed in the present study. The metal composition of the limonite was Fe, 44; Si, 9.4; Al, 7.2; Mg, 0.15; and Ca, 0.07 mass%-dry. The as-received limonite was sieved to select the 250–500 μm size fractions, and the Brunauer-Emmett-Teller (BET) specific surface area was measured as 40 m²/g.

2.2. Hydrogen Sulfide Removal and Ammonia Decomposition

The experiments to evaluate H₂S removal and catalytic NH₃ decomposition performance were carried out in a cylindrical fixed-bed quartz reactor (8 mm i.d.) under ambient pressure. The details of the experimental apparatus have been described elsewhere. The temperature was controlled with a K-type thermocouple attached to the exterior surface of the reactor. Approximately 0.25 g of limonite was first charged into the reactor with quartz wool, and a flow of high-purity H₂ (>99.99995%) was then passed through the charged into the reactor with quartz wool, and a flow of high-purity H₂ (>99.9995%) was then passed through the reactor until the concentration of N₂ in the experimental reactor was maintained at 51 000 h⁻¹. The space velocity (SV) was maintained at 51 000 h⁻¹ throughout each run, unless otherwise noted.

2.3. Gas Analysis

In the H₂S removal experiments, the H₂S concentration in the exit gas was measured using a standard detector tube (Gastec) at arbitrary times to obtain the breakthrough curves. The breakthrough and saturation points were defined as C/C₀ = 0.1 and 0.9, respectively. Here, C₀ and C are the initial concentration and the H₂S concentration in the exit gas at arbitrary time, respectively. The extent of sulfidation was calculated based on the iron content in limonite and the results of the breakthrough curves.

In the NH₃ decomposition runs, the amount of N₂ produced during the decomposition of NH₃ was measured at 3 min intervals with a high-speed micro gas chromatograph (GC; Agilent) equipped with a thermal conductivity detector. The conversion of NH₃ to N₂ was calculated based on the amount of NH₃ inlet and the N₂ concentration at the reactor exit.

2.4. Characterization

Powder X-ray diffraction (XRD; Shimadzu) measurements of the samples (as-received, after H₂ reduction and after H₂S removal or NH₃ decomposition) were performed with Mn-filtered Fe-Kα radiation. To avoid rapid oxidation of the α-Fe particles upon exposure to laboratory air, the limonite after H₂ reduction, H₂S removal or NH₃ decomposition was passivated using 1% O₂/He at room temperature and then recovered from the reactor.

Temperature-programmed oxidation (TPO) was carried to quantitate the formation amounts of Fe₃C and C deposition during H₂S removal or NH₃ decomposition runs. In a TPO run, the limonite in the reactor after H₂S removal or NH₃ decomposition was first quenched to room temperature in a stream of high purity He and then heated at 10°C/min to 950°C in 10% O₂/He. The concentrations of CO and CO₂ evolved in this process were monitored using the micro GC. Some samples after TPO were also subjected to XRD measurements.

3. Results and Discussion

3.1. Effect of COG Components on H₂S Removal

This section focuses on the effect of coexisting of H₂, CH₄, CO, CO₂ and H₂O on H₂S removal by reduced-limonite. The changes in the breakthrough curves of reduced-limonite with temperature in 50% H₂/He were first examined, and the results are summarized in Table 1. In addition, the relationship between the extent of sulfidation and H₂S concentration in the exit gas based on the breakthrough curves are presented in Fig. 1. In the H₂S breakthrough curve at 300°C, a removal extent of 100% was measured until about 30 min, and the H₂S concentration in the exit gas increased after the breakthrough point at 40 min with increasing time on stream. The saturation point was observed at 65 min. Although similar tendencies were measured at 400, 500 and 600°C, the breakthrough points decreased with increasing temperature and were observed at 35, 30 and 24 min, respectively. On the other hand, at 700°C, the removal extent of H₂S decreased to 85% at 1 min after the experimental run start, and this value was maintained until 15 min. Subsequently, the H₂S removal extent decreased slightly to 75% until to 40 min, and then decreased with increasing time on stream, reaching saturation at 80 min. Although a similar tendency was observed at 800°C, the removal extent...
of H2S at 2 min after the experimental run start was 67%, which was smaller than that of 700°C. The above-mentioned breakthrough points corresponded to sulfidation extents of 0.75, 0.65, 0.55 and 0.45 at 300, 400, 500 and 600°C, respectively, as seen in Fig. 1, and these values decreased with increasing temperature. At 700 and 800°C (Fig. 1(b)), the reduced-limonite attained breakthrough points immediately after the runs started. These results suggest that H2S removal by reduced-limonite in a reduction atmosphere (50% H2/He) depends on the temperature and has higher efficiency at lower temperatures.

XRD measurements of limonite after the H2S removal runs were carried out to clarify the temperature dependencies of H2S removal in 50% H2/He. Table 1 also summarizes the results of the XRD measurements. The main peak attributed to Fe1−xS at approximately 55.8° was observed for the samples obtained after runs in 50% H2/He at 300–400°C. On the other hand, the intensity of this peak gradually decreased with temperature (300–600°C), whereas the main peak at 600–800°C was observed at approximately 55.15°. This peak is attributed to FeS, and this observation indicates that the form of adsorbed H2S on α-Fe changes with temperature. The H2S/Fe ratios at after reaction in 50% H2/He ranged from 0.9 to 1.05 (Table 1), and these values trended to decrease with increasing temperature. This result shows that almost all Fe in limonite was sulfidized by H2S, and the difference in removal performance with increasing temperature is due to different adsorption forms (Fe1−xS and FeS).

The sulfidation extent of more than 1.0 at 300°C in Fig. 1 and Table 1 is due to analytical error. As mentioned in the Introduction, the optimum vapor deposition conditions for preparing the composites, in which the carbonaceous material fills the mesopores in de-hydrated limonite via vapor deposition of gaseous-tar, is 350°C. Therefore, 400°C was used for H2S removal by reduced-limonite in subsequently investigations.

**Fig. 2** shows the influence of coexisting gases on the relationships between the extent of sulfidation and H2S concentration in the exit gas calculated from the H2S breakthrough curves measured at 400°C in different feed gas compositions. The breakthrough and saturation points of the H2S breakthrough curves and the extent of sulfidation at these points are summarized in **Table 2**. The breakthrough and saturation points in 50% H2/He were observed at sul-

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**Table 1.** Summaries of breakthrough and saturation point at breakthrough curves, the extent of sulfidation and crystalline forms of Fe before and after H2S removal in 50%H2/He.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Breakthrough point (min)</th>
<th>Saturation point (min)</th>
<th>Extent of Sulfidation (H2S/Fe)*</th>
<th>Iron species after H2S removal b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced limonite</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>α-Fe</td>
</tr>
<tr>
<td>300</td>
<td>40</td>
<td>65</td>
<td>1.04</td>
<td>Fe1−xS(m)</td>
</tr>
<tr>
<td>400</td>
<td>35</td>
<td>60</td>
<td>0.95</td>
<td>Fe1−xS(m)</td>
</tr>
<tr>
<td>500</td>
<td>30</td>
<td>60</td>
<td>0.94</td>
<td>Fe1−xS(m), FeS(w)</td>
</tr>
<tr>
<td>600</td>
<td>24</td>
<td>58</td>
<td>0.92</td>
<td>Fe1−xS(m), FeS(m)</td>
</tr>
<tr>
<td>700</td>
<td>&lt;1</td>
<td>80</td>
<td>0.93</td>
<td>Fe1−xS(w), FeS(s)</td>
</tr>
<tr>
<td>800</td>
<td>&lt;1</td>
<td>90</td>
<td>0.90</td>
<td>FeS(s)</td>
</tr>
</tbody>
</table>

*aAfter reaction. bXRD intensities designated by w (weak), m (medium), and s (strong).
Table 2. Summaries of breakthrough and saturation point at breakthrough curves and sulfidation curves with H2S/Fe ratio at 400°C.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Breakthrough curve</th>
<th>Extent of sulfidation (H2S/Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Breakthrough point (min)</td>
<td>Saturation point (min)</td>
</tr>
<tr>
<td>50%H2/He</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>50%H2/30%CH4/He</td>
<td>32</td>
<td>65</td>
</tr>
<tr>
<td>50%H2/30%CH4/5%CO/He</td>
<td>10</td>
<td>38</td>
</tr>
<tr>
<td>50%H2/30%CH4/5%CO/5%CO2/He</td>
<td>10</td>
<td>42</td>
</tr>
<tr>
<td>50%H2/30%CH4/5%CO/5%H2O/He</td>
<td>32</td>
<td>67</td>
</tr>
<tr>
<td>50%H2/30%CH4/5%CO/5%CO2/5%H2O/He</td>
<td>28</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 3. Crystalline form of Fe after H2S removal in different atmosphere and the amount of CO and CO2 evolved during temperature programmed oxidation of samples after sulfidation.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Iron species after H2S removal*</th>
<th>Evolution amount (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe1−xS(m)</td>
<td>CO</td>
</tr>
<tr>
<td>50%H2/30%CH4/He</td>
<td>Fe1−xS(m)</td>
<td>0</td>
</tr>
<tr>
<td>50%H2/30%CH4/5%CO/He</td>
<td>Fe1−xS(m)</td>
<td>290</td>
</tr>
<tr>
<td>50%H2/30%CH4/5%CO/5%CO2/He</td>
<td>Fe1−xS(m)</td>
<td>210</td>
</tr>
<tr>
<td>50%H2/30%CH4/5%CO/5%H2O/He</td>
<td>Fe1−xS(m)</td>
<td>40</td>
</tr>
<tr>
<td>50%H2/30%CH4/5%CO/5%CO2/5%H2O/He</td>
<td>Fe1−xS(m)</td>
<td>30</td>
</tr>
</tbody>
</table>

*XRD intensities designated by m (medium)

3.2. Possible Mechanisms of Influence of COG Components on H2S Removal Performance

XRD measurements of the samples recovered after reaction were carried out to investigate the difference in H2S breakthrough curves with coexisting gases at 400°C. The results are summarized in Table 3. In these samples, iron always takes the form of Fe1−xS, regardless of the gas composition used, and thus, it was difficult to clarify the influence of coexisting gases on the H2S removal performance from the XRD results alone. Therefore, TPO of the samples were investigated in 10% O2/He up to 950°C, as shown in Fig. 3. No CO and CO2 evolution was measured during TPO of the sample recovered after the 50% H2/30% CH4/He run. However, during TPO of the sample after the 50% H2/30% CH4/5% CO/He run, CO and CO2 were evolved above approximately 300°C (Fig. 3(a)), with main and shoulder peaks for the CO and CO2 formation rates at approximately 350 and 450°C, respectively. As similar profile was observed for sample recovered after the 50% H2/30% CH4/5% CO/5% CO2/He run (Fig. 3(b)). On the other hand, the peaks of the CO and CO2 formation rates from the samples recovered after the 50% H2/30% CH4/5% CO/5% H2O/He and 50% H2/30% CH4/5% CO/5% CO2/5% H2O/He runs were considerably smaller than those for coexisting CH4/CO and CH4/CO/CO2 (Fig. 3(c)). Table 3 summaries of the amounts of CO and CO2 evolved during the TPO runs. The Fe1−xS observed in all samples after H2S treatment was completely transformed into Fe2O3 after TPO. The order of the amounts of CO and CO2 evolved during TPO is 50% H2/30% CH4/He < 50% H2/30% CH4/5% CO/5% CO2/He < 50% H2/30% CH4/5% CO/5% H2O/He < 50% H2/30% CH4/5% CO/5% CO2/5% H2O/He. This order was almost the inverse of that for the amount of H2S removal.

The reaction between metallic Fe and H2S is well known to occur according to Eqs. (1) and (2) to form pyrrhotite (Fe1−xS) and iron sulfide (FeS), and these reactions are supported by thermodynamic calculations because the corresponding standard Gibbs free energies (ΔG) at 400°C are −13 and −14 kcal/mol.
The \( \Delta G_{400}^0 \) values for Eqs. (3) and (4) are 3.6 and 6.0 kcal/mol, respectively, and thus, C deposition or \( \text{Fe}_2\text{C} \) formation via these is not thermodynamically favorable under these conditions. Therefore, the H\(_2\)S breakthrough curve is similar to that in 50% H\(_2\)/He. In other words, CH\(_4\) does not affect H\(_2\)S removal by reduced-limonite active sites, and C deposited from Eqs. (5)–(7) and (9) will be a main factor for the decreased H\(_2\)S removal performance. The H\(_2\)S breakthrough curve in 50% H\(_2\)/30% CH\(_4\)/5% CO/5% CO\(_2\)/He was similar to that in 50% H\(_2\)/30% CH\(_4\)/5% CO/5% CO\(_2\)/He. The Boudouard reaction (\( \Delta G_{400}^0 = 13 \) kcal/mol), expressed as Eq. (10), is not thermodynamically favorable. In addition, if \( \text{Fe}_2\text{C} \) forms under the present conditions, Eq. (11) also does not occur (\( \Delta G_{400}^0 = 10 \) kcal/mol). Therefore, coexisting CO may not affect the removal performance of H\(_2\)S. This speculation supported by the similar amounts of CO and CO\(_2\) evolved during TPO of the samples recovered from the 50% H\(_2\)/30% CH\(_4\)/5% CO/He and 50% H\(_2\)/30% CH\(_4\)/5% CO/5% CO\(_2\)/He runs (Table 3).

\[
\text{C} + \text{CO}_2 \rightarrow 2\text{CO} \tag{10}
\]

\[
\text{Fe}_2\text{C} + \text{CO}_2 \rightarrow 3\text{Fe} + 2\text{CO} \tag{11}
\]

In contrast, in the cases of H\(_2\)O coexisting in the feed gases (50% H\(_2\)/30% CH\(_4\)/5% CO/5% H\(_2\)O/He or 50% H\(_2\)/30% CH\(_4\)/5% CO/5% CO\(_2\)/5% H\(_2\)O/He), the H\(_2\)S breakthrough curves showed the similar tendencies to that of 50% H\(_2\)/30% CH\(_4\)/He, and the performance of the sample with 5% CO was improved by H\(_2\)O addition. In addition, the amounts of CO and CO\(_2\) evolved during TPO were significantly smaller than those with coexisting CO, as seen in Table 3. These results shows that C deposition is inhibited by H\(_2\)O. Although the \( \Delta G_{400}^0 \) values of two water-gas reactions (6.0–9.4 kcal/mol) expressed as Eqs. (12) and (13) are not thermodynamically favorable, the water-gas shift reaction of Eq. (14) (\( \Delta G_{400}^0 = -3.3 \) kcal/mol) may occur. Although \( \text{Fe}_2\text{C} \) was not observed by XRD, the H\(_2\)S removal performance may be proceeded by the reaction shown in Eq. (9), which has a \( \Delta G_{400}^0 \) value (−45 kcal/mol) that is smaller than those of Eqs. (15) and (16) (3.6–7.0 kcal/mol), even if \( \text{Fe}_2\text{C} \) is formed under these present conditions. Thus it may be possible that H\(_2\)O addition prevents C deposition according to Eqs. (5)–(7) due to the water-gas shift reaction (Eq. (14)), and as a result, the H\(_2\)S removal performance is improved.

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \tag{12}
\]

\[
\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}_2 \tag{13}
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \tag{14}
\]

\[
\text{Fe}_2\text{C} + 2\text{H}_2\text{O} \rightarrow 3\text{Fe} + \text{CO}_2 + 2\text{H}_2 \tag{15}
\]

\[
\text{Fe}_2\text{C} + \text{H}_2\text{O} \rightarrow 3\text{Fe} + \text{CO} + \text{H}_2 \tag{16}
\]
Figure 4 illustrated the effect of space velocity on the H$_2$S breakthrough curves in 50% H$_2$/30% CH$_4$/5% CO/5% CO$_2$/5% H$_2$O/He. Here, the space velocity was varied from 51,000 to 5,600 h$^{-1}$. When the SV decreased to 5,600 h$^{-1}$, H$_2$S was not detected in the exit gas until 120 min. The breakthrough increased more than 6-fold from 27 min at an SV of 51,000 h$^{-1}$ to 165 min at an SV of 5,600 h$^{-1}$. Therefore, the breakthrough curves strongly depend on SV.

3.3. Decomposition of Ammonia in the Presence of COG Components

This section focuses on the effect of CH$_4$, CO, CO$_2$ and H$_2$O on limonite-catalyzed NH$_3$ decomposition. These runs were carried out at 850°C to simulate the utilization of COG sensible heat for NH$_3$ decomposition. Limonite-catalyzed N-containing species decomposition at other temperatures has been already reported at our previous reports.10–18) Figure 5 presents the effect of the presence of CH$_4$, CO, CO$_2$ and H$_2$O on NH$_3$ decomposition. The decomposition of NH$_3$ was maintained until 240 min in He, whereas N$_2$ conversion in 50% H$_2$/30% CH$_4$/He and 50% H$_2$/30% CH$_4$/5% CO/5% CO$_2$/CO/He dramatically decreased after 90 min. A significant amount of C deposition was found on the catalyst surface in the presence of CH$_4$ and/or CO. As the formation of carbonaceous materials occurred under the present conditions, the catalyst deactivation observed in 50% H$_2$/30% CH$_4$ and 50% H$_2$/30% CH$_4$/5% CO (Fig. 5) may be ascribed to C deposition according to the Eqs. (3) and (4), with $\Delta G_{G850°C}$ values of $-7.8$ and $-8.0$ kcal/mol, respectively. These $\Delta G$ values are smaller than those of Eqs. (5), (6) and (7) ($\Delta G_{G850°C} = 6.3, 6.1$ and $6.0$ kcal/mol, respectively). On the other hand, the reaction show in Eq. (8) may also occur ($\Delta G_{G850°C} = -0.2$ kcal/mol).

Figure 5 also illustrates the effects of 5% CO$_2$, 5% H$_2$O or 5% H$_2$O/5% CO$_2$ coexisting to 50% H$_2$/30% CH$_4$/5% CO on NH$_3$ decomposition. In 50% H$_2$/30% CH$_4$/5% CO/5% CO$_2$/He, 50% H$_2$/30% CH$_4$/5% CO/5% H$_2$/H$_2$O/He and 50% H$_2$/30% CH$_4$/5% CO/5% CO$_2$/5% H$_2$/H$_2$O/He, the NH$_3$ decompositions performance was maintained until 240 min, and $>99$% conversion of NH$_3$ to N$_2$ was observed. Moreover, no significant C deposition was found on the catalysts recovered after the experimental runs. These results show that the coexistence of CO$_2$, H$_2$O or CO$_2$/H$_2$O with 50% H$_2$/30% CH$_4$/5% CO can improve NH$_3$ decomposition. As mentioned above, the deactivation of limonite for NH$_3$ decomposition mainly occurs due to deposition of C according to Eqs. (3) and (4). From the thermodynamic calculation results, preventing C deposition in the presence of CO$_2$ may occur by Eqs. (10) and (11) ($\Delta G_{G850°C} = -6.3$ and $-6.1$ kcal/mol, respectively). On the other hand, in the case of H$_2$O addition to 50% H$_2$/30% CH$_4$/5% CO, $\Delta G_{G850°C}$ values for Eqs. (12) and (13) are almost $-6.0$ and $-5.8$ kcal/mol, respectively, and these reactions are more favorable than Eq. (14), which has a $\Delta G_{G850°C}$ value of 0.2 kcal/mol. In addition, Eqs. (15) and (16) ($\Delta G_{G850°C} = -5.6$ and $-5.8$ kcal/mol, respectively) are also thermodynamically favorable. Therefore, preventing C deposition and retransformation of Fe$_3$C into metallic Fe, as shown in Eqs. (10), (12) and (13) and Eqs. (11), (15) and (16), respectively, may be the driving force for the high NH$_3$ decomposition performance with 5% CO$_2$, 5% H$_2$O or 5% CO$_2$/5% H$_2$O coexisted to 50% H$_2$/30% CH$_4$/5% CO. Similar results have been reported for NH$_3$ decomposition by limonite in a simulated air-blown coal gasification composition (10% CO$_2$ or 3% H$_2$O coexisted in 20% CO/10% H$_2$).12)

3.4. Possible Mechanisms of Influence of COG Components on NH$_3$ Decomposition

Figure 6 shows the XRD results for the catalysts after NH$_3$ decomposition in each gas composition, and these results are summarized in Table 4. When limonite was reduced in H$_2$, only $\alpha$-Fe was observed (Fig. 6(a)). This signal was also observed for the catalysts recovered after the He runs, and transformation of the iron form was not observed. According to previous our studies, the catalytic decomposition of NH$_3$ to N$_2$ with reduced-limonite occurs due to the cyclic reaction via iron nitride (Fe$_x$N) intermediates, according to Eqs. (17) and (18)8–14,16)

$$\text{Fe}_x\text{N} \rightarrow \text{Fe}_x\text{N} + 1.5\text{H}_2 \hspace{1cm} (17)$$
$$\text{Fe}_x\text{N} \rightarrow x\text{Fe} + 0.5\text{N}_2 \hspace{1cm} (18)$$

On the other hand, crystallized carbon (CC) was detected at around 32°C in the samples recovered after reaction in 50% H$_2$/30% CH$_4$/He, along with peaks corresponding to $\alpha$-Fe and Fe$_3$C. The peaks attributable to crystallized C and Fe$_3$C were also observed for the catalyst after the decomposition run in 50% H$_2$/30% CH$_4$/5% CO/He. The formation

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of crystallized C and Fe$_3$C may indicate that deactivation of the catalyst occurs by Eqs. (4) and (8) ($\Delta G^{\circ} = -8.0$ and $-0.2$ kcal/mol, respectively), in the presence of 30% CH$_4$. On the other hand, no measurable Fe$_3$C signals were observed in the sample obtained after reaction in 50% H$_2$/30% CH$_4$/5% CO/5% CO$_2$/He, and the diffraction peak of crystallized C was significantly smaller than those in 50% H$_2$/30% CH$_4$/He and 50% H$_2$/30% CH$_4$/5% CO/He. In addition, the intensity of the $\alpha$-Fe signal was almost that same as that of the catalyst before the reaction. Similar results were observed for the catalysts after NH$_3$ decomposition runs in 50% H$_2$/30% CH$_4$/5% CO/5% H$_2$O/He and 50% H$_2$/30% CH$_4$/5% CO/5% CO$_2$/5% H$_2$O/He.

Figure 7 presents the CO and CO$_2$ evolution profiles during TPO, and Table 4 summarizes the amounts of CO and CO$_2$ evolved during the TPO runs. CO and CO$_2$ formation started above 300$^\circ$C in the sample recovered after the 50% H$_2$/30% CH$_4$/He run, with main and shoulder peaks observed in the range from 400 to 650$^\circ$C (Fig. 7(a)). Similar profiles were observed for the sample obtained after the 5% CO coexisted to 50% H$_2$/30% CH$_4$/He run (Fig. 7(b)). The evolution rates of CO and CO$_2$ and these cumulative

![Figure 6](image)

**Table 4.** Summarize of TPO results and Fe forms after NH$_3$ decomposition run at different atmosphere.

<table>
<thead>
<tr>
<th>NH$_3$ decomposition atmosphere</th>
<th>Iron species after NH$_3$ decomposition$^a$</th>
<th>Evolution amount (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO</td>
</tr>
<tr>
<td>He</td>
<td>$\alpha$-Fe (s)</td>
<td>n.a.$^b$</td>
</tr>
<tr>
<td>50%H$_2$/30%CH$_4$/He</td>
<td>$\alpha$-Fe(m), Fe$_3$C(vw), Crystallized carbon(m)</td>
<td>10 700</td>
</tr>
<tr>
<td>50%H$_2$/30%CH$_4$/5%CO/He</td>
<td>$\alpha$-Fe(w), Fe$_3$C(w), Crystallized carbon(m)</td>
<td>15 300</td>
</tr>
<tr>
<td>50%H$_2$/30%CH$_4$/5%CO/5%CO$_2$/He</td>
<td>$\alpha$-Fe (s)</td>
<td>0</td>
</tr>
<tr>
<td>50%H$_2$/30%CH$_4$/5%CO/5%H$_2$O/He</td>
<td>$\alpha$-Fe (s)</td>
<td>0</td>
</tr>
<tr>
<td>50%H$_2$/30%CH$_4$/5%CO/5%CO$_2$/5%H$_2$O/He</td>
<td>$\alpha$-Fe (s)</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$XRD intensities designated by w (weak), m (medium), and s (strong), $^b$Not analyzed.

previous report about investigation of NH$_3$ decomposition by limonite and commercial Fe$_3$C in syngas, CO$_2$ or H$_2$O/syngas,$^{12}$ it has been suggested that the disproportionation of CO in syngas and the subsequent formation of Fe$_3$C are responsible for the catalyst deactivation. In addition, NH$_3$ decomposition performance of commercial Fe$_3$C is very small.$^{12}$ Therefore, the influence of Fe$_3$C formation on limonite-catalyzed NH$_3$ decomposition may be greater than that of crystallized C in this study.
amounts were quite different with those of H$_2$S. This distinction may cause by the difference of deposited-C forms in H$_2$S removal and NH$_3$ decomposition runs. These forms are distinguished to amorphous-C derived from disproportionation reaction of CO in H$_2$S removal run and crystallized-C derived from CH$_4$ decomposition in NH$_3$ decomposition run, respectively. On the other hand, the amount of CO and CO$_2$ evolved during TPO of the sample recovered after in the 5% H$_2$O and 5% CO$_2$ coexisted to 50% H$_2$/30% CH$_4$/5% CO/He run were considerably smaller than those for the run in the presence of 30% CH$_4$ and 5% CO. These results show that C deposition is not caused by deactivation of the catalyst for NH$_3$ decomposition in the presence of 5% CO$_2$ and 5% H$_2$O.

4. Conclusions

The removal of 3 000 ppmv H$_2$S and catalytic decomposition of 1 vol% NH$_3$ in the presence of COG components with limonite rich in α-FeOOH has been studied in a cylindrical quartz reactor under a pressure of 0.1 MPa, temperature of 300–850°C and an SV of 51 000 h$^{-1}$. The principal conclusions are summarized as follows:

(1) Although the reduced-limonite shows high H$_2$S removal performance in 50% H$_2$/He, the performance decreases with increasing temperature. The XRD analyses showed that α-FeOOH-derived active α-Fe is transformed into Fe$_3$C into Fe$_3$C in the presence of CH$_4$ and an SV of 51 000 h$^{-1}$.

(2) In the presence of 5% CO, the H$_2$S removal performance at 400°C decreases considerably due to carbon deposition. In addition, 5% CO$_2$ addition to 50% H$_2$/30% CH$_4$/5% CO/He did not affect the H$_2$S removal ability of reduced-limonite.

(3) The addition of 5% H$_2$O to 50% H$_2$/30% CH$_4$/5% CO/He suppresses carbon formation and consequently improves the H$_2$S removal performance of limonite significantly.

(4) Although the limonite catalyst achieves almost complete decomposition of NH$_3$ in inert He at 850°C, presence of 30% CH$_4$ or 30% CH$_4$/5% CO in 50%H$_2$/He deactivates limonite and causes appreciable formation of deposited carbon.

(5) When 5% CO$_2$, 5% H$_2$O or both is added to 50% H$_2$/30% CH$_4$/5% CO/He, the catalytic activity dramatically improves without carbon deposition. The NH$_3$ to N$_2$ conversion of > 99% is maintained until 240 min.

(6) The XRD analyses reveal the transformation of α-FeOOH-derived active α-Fe into Fe$_3$C in the presence of 30% CH$_4$ and 30% CH$_4$/5% CO. On the other hand, when 5% H$_2$O, 5% CO$_2$ or 5% CO/5% H$_2$O is added to 50% H$_2$/30% CH$_4$/5% CO/He, α-Fe is the only Fe form.

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REFERENCES