# Reaction Process between Iron(II) Chloride and Oxygen

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The product formed by heating $FeCl_2$ in an oxygen stream has been examined in detail. The reaction processes of gaseous $FeCl_3$ and FeOCl, formed during the reaction between $FeCl_2$ and oxygen, with oxygen were also examined. The reaction process between $FeCl_2$ and oxygen can be represented as follows: $FeCl_2$ reacts with oxygen above about 250 °C to form FeOCl and gaseous $FeCl_3$, $2FeCl_2(s)+1/2O_2(g) \rightarrow FeOCl(s)+1/2Fe_2Cl_6(g)$. Subsequently, the resulting FeOCl reacts with oxygen to form $\alpha$-$Fe_2O_3$ and chlorine, $2FeOCl(s)+1/2O_2(g) \rightarrow Fe_2O_3(s)+Cl_2(g)$. Above about 320 °C, the decomposition of the FeOCl to $\alpha$-$Fe_2O_3$ and gaseous $FeCl_3$, $3FeOCl(s) \rightarrow Fe_2O_3(s)+1/2Fe_2Cl_6(g)$, also occurs. Above about 370 °C, the reaction between gaseous $FeCl_3$ formed and oxygen to form $\eta$-$Fe_2O_3$ and chlorine, $Fe_2Cl_6(g)+3/2O_2(g) \rightarrow Fe_2O_3(s)+3Cl_2(g)$, occurs in addition to the above reactions.

During the chlorination of ilmenite and many ores, iron(II) chloride($FeCl_2$) is usually formed in addition to the main products. This work was undertaken to obtain fundamental information on the chemical process for dechlorinating the $FeCl_2$ with oxygen(air) to produce a non-polluting iron oxide product and chlorine for recycle.

It has been reported in the early literature[1] that on heating $FeCl_2$ in a stream of air or oxygen, the reaction, $6FeCl_2+3/2O_2 \rightarrow 2Fe_2Cl_6+Fe_2O_3$, occurs. Teterevkov *et al.*[2] have examined the relationship between the amount of chlorine evolved upon heating $FeCl_2$ in an oxygen stream and the heating time in the temperature range of 300—500 °C, and have conducted the experiment on the recovery of chlorine from $FeCl_2$. However, the reaction process between $FeCl_2$ and oxygen was not clarified.

In this paper, the product formed by heating $FeCl_2$ in an oxygen stream has been examined in detail. The reaction processes of gaseous iron(III) chloride($FeCl_3$) and iron chloride oxide(FeOCl), which were formed during the reaction between $FeCl_2$ and oxygen, with oxygen were also examined. From these experimental results, the reaction process between $FeCl_2$ and oxygen was revealed.

## Experimental

The $FeCl_2$ used was prepared by the reaction between pure iron (Fe 99.98%) and HCl at 850 °C, and confirmed as $FeCl_2$ by X-ray analysis.[3] The chemical analysis gave Fe, 44.0; Cl, 55.9% (calcd for $FeCl_2$: Fe, 44.06; Cl, 55.94%). $FeCl_3$ was prepared by the reaction between pure iron and chlorine at 500 °C, and confirmed as $FeCl_3$ by X-ray analysis.[4] The chemical analysis gave Fe, 34.3; Cl, 65.5% (calcd for $FeCl_3$: Fe, 34.43; Cl, 65.57%). FeOCl was prepared from guaranteed reagent $FeCl_3 \cdot 6H_2O$ and $FeCl_3$ by the method based on the report of Schäfer,[5] and confirmed as FeOCl by X-ray analysis.[6] The chemical analysis gave Fe, 52.0; Cl, 32.9% (calcd for FeOCl: Fe, 52.05; Cl, 33.04%). Oxygen was dried by passing it through conc. sulfuric acid and over phosphorus(V) oxide.

The Fe content of the sample was determined by chelatometric titration[7] after dissolving the sample in dilute hydrochloric acid followed by oxidation of $Fe^{2+}$ ion to $Fe^{3+}$ ion with aqueous $H_2O_2$ solution. The Cl content of the sample was gravimetrically determined as AgCl after dissolving the sample in dilute nitric acid. The chlorine evolved during the reaction was passed through KI solution and determined by iodometry.

X-ray analysis of the sample was performed with an X-ray powder diffractometer, equipped with a proportional counter, using Mn filtered Fe radiation. The sample chamber of the diffractometer was maintained under dry nitrogen atmosphere to prevent the contamination of the sample with moisture in the air during the irradiation.

Thermogravimetry (TG) was performed in an oxygen stream at 50 ml/min. The sensitivity of the quartz helix used was approximately 0.14 mg/0.01 mm. The heating rate was 2.5 °C/min.

Throughout this work, the chlorides and chloride oxide of iron were handled in an argon atmosphere to prevent any contamination with moisture in the air.

## Results and Discussion

*Reaction Products between $FeCl_2$ and Oxygen.* The TG curves of $FeCl_2$ in an oxygen and an argon stream are shown in Fig. 1.

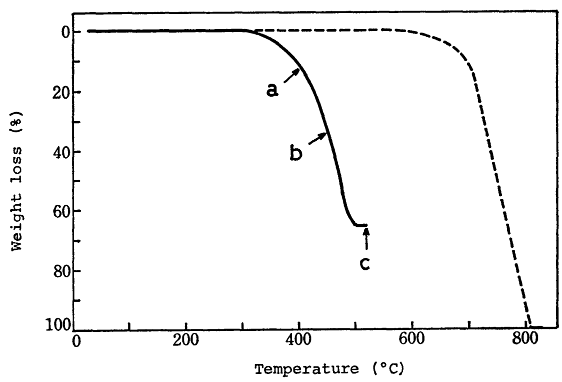


Fig. 1. TG curves of $FeCl_2$ in oxygen and argon streams. —— in $O_2$, ---- in Ar.

The results showed that $FeCl_2$ reacted with oxygen before vaporizing. The samples heated up to Points a(400 °C), b(450 °C), and c(520 °C) in Fig. 1 were found by X-ray analysis to be a mixture of $FeCl_2$ and FeOCl, a mixture of $FeCl_2$ and $\alpha$-$Fe_2O_3$,[8] and $\alpha$-$Fe_2O_3$, respectively. It was also observed that the weight loss was accompanied by the evolution of chlorine and gaseous $FeCl_3$.

To obtain more detailed information on the reaction between $FeCl_2$ and oxygen, $FeCl_2$ (4.0 g) in a quartz

Table 1. Reaction products between $FeCl_2$ and oxygen at various temperatures

| Temp (°C) | Product | | | Unreacted $FeCl_2$ (%) |
|---|---|---|---|---|
| | In the boat (%) | Outside the heating zone (%) | Amount of $Cl_2$ formed (mg) | |
| 250 | FeOCl (<0.1) | $FeCl_3$ (0.1) | 0.1 | 99.8 |
| 280 | FeOCl (0.8) | $FeCl_3$ (1.3) | 0.9 | 97.8 |
| 300 | FeOCl $\gg\alpha$-$Fe_2O_3$ (2.1) | $FeCl_3$ (3.0) | 3.1 | 95.1 |
| 320 | FeOCl $\gg\alpha$-$Fe_2O_3$ (4.1) | $FeCl_3$ (6.2) | 6.6 | 90.1 |
| 350 | FeOCl $\gg\alpha$-$Fe_2O_3$ (9.9) | $FeCl_3$ (15.8) | 18 | 75.4 |
| 370 | FeOCl $>\alpha$-$Fe_2O_3$ (18.1) | $FeCl_3$ (30.2), $\eta$-$Fe_2O_3$ (<0.1) | 29 | 53.9 |
| 400 | FeOCl $>\alpha$-$Fe_2O_3$ (27.8) | $FeCl_3$ (60.6), $\eta$-$Fe_2O_3$ (0.2) | 80 | 15.5 |
| 420 | $\alpha$-$Fe_2O_3$ >FeOCl (21.5) | $FeCl_3$ (70.8), $\eta$-$Fe_2O_3$ $\gg$FeOCl (1.0) | 127 | 8.9 |
| 450 | $\alpha$-$Fe_2O_3$ (23.5) | $FeCl_3$ (77.6), $\eta$-$Fe_2O_3$ $\fallingdotseq$ FeOCl (1.2) | 190 | 0 |

boat (70 mm length, 15 mm width, 7 mm depth) was placed in a straight reaction tube (28 mm i.d., 1000 mm length). Oxygen was introduced into the reaction tube at a flow-rate of 100 ml/min. The sample part was then placed in the centre of an electric furnace (300 mm heating length) maintained at a specified temperature for 2 h. The temperature of the sample part was controlled to within ±2 °C. The temperature of the reaction tube outside the heating zone was below 50 °C.

At 230 °C, no reaction product was observed. The reaction products obtained at various temperatures above 250 °C are summarized in Table 1. The value in parentheses is the weight percentage of the product to the initial $FeCl_2$. The product obtained in the boat was identified by X-ray analysis after dissolving the unreacted $FeCl_2$ in ethyl alcohol. Small amounts of $\eta$-$Fe_2O_3$ and FeOCl formed outside the heating zone above 370 °C in addition to $FeCl_3$ were identified by X-ray analysis[9] after dissolving the $FeCl_3$ in ethyl alcohol.

At 250—280 °C, FeOCl, $FeCl_3$, and a small amount of chlorine were formed as shown in Table 1. Calculations showed that FeOCl and $FeCl_3$ were the main products and that the molar ratio of FeOCl: $FeCl_3$ was approximately 1: 1. From this result, the formation of FeOCl and $FeCl_3$ was considered to be due to the reaction,

$$2FeCl_2(s) + 1/2O_2(g) \longrightarrow FeOCl(s) + 1/2Fe_2Cl_6(g). \quad (1)$$

It was assumed that the formation of chlorine was due to the reaction,

$$2FeOCl(s) + 1/2O_2(g) \longrightarrow Fe_2O_3(s) + Cl_2(g), \quad (2)$$

from the observation that the FeOCl obtained in the boat contained a small amount of insoluble product after dissolving the FeOCl in 1 M-$H_2SO_4$.[5,10]

The possible reactions which gave $\alpha$-$Fe_2O_3$ in the boat were considered to be Reaction 2 and the thermal decomposition of FeOCl in oxygen,

$$3FeOCl(s) \longrightarrow Fe_2O_3(s) + 1/2Fe_2Cl_6(g).^{10)} \quad (3)$$

Above 370 °C, a small amount of $\eta$-$Fe_2O_3$ was obtained outside the heating zone in addition to $FeCl_3$. It appeared that $\eta$-$Fe_2O_3$ was formed by the reaction,

$$Fe_2Cl_6(g) + 3/2O_2(g) \longrightarrow Fe_2O_3(s) + 3Cl_2(g).^{9)} \quad (4)$$

Above 420 °C, a small amount of FeOCl was obtained outside the heating zone in addition to $FeCl_3$ and $\eta$-$Fe_2O_3$. The amount of chlorine evolved, shown in Table 1, indicated that Reaction 1 proceeded markedly above about 420 °C to form a large amount of gaseous $FeCl_3$. Consequently, the reaction between gaseous $FeCl_3$ and oxygen has been thought to proceed under a low ratio of oxygen to gaseous $FeCl_3$ to form FeOCl in addition to $\eta$-$Fe_2O_3$.

To clarify the possible reactions occurring between $FeCl_2$ and oxygen, experiments on the reaction processes of gaseous $FeCl_3$ and FeOCl with oxygen were carried out.

*Reaction Process between Gaseous $FeCl_3$ and Oxygen.* A transparent quartz reaction tube with an inner concentric tube was used. Gaseous $FeCl_3$ was formed by heating $FeCl_3$ placed in the inner tube at 250 °C and carried by a stream of argon (30 ml/min) to the reaction zone of 28 mm i.d. and 250 mm length, held at a specified temperature. The mean flow-rate of gaseous $FeCl_3$ was about 1.5 ml $Fe_2Cl_6$/min. Oxygen was simultaneously introduced through a separate tube into the reaction zone at a flow-rate of 100 ml/min. The reaction was allowed to proceed for 2 h.

The products were only obtained outside the heating zone and the experimental results are summarized in Table 2.

The vaporization of $FeCl_3$ is accompanied by the decomposition of $FeCl_3$ to $FeCl_2$ and chlorine.[11]

Table 2. Reaction products between gaseous $FeCl_3$ and oxygen at various temperatures

| Temp (°C) | Product | | Unreacted $FeCl_3$ (%) |
|---|---|---|---|
| | Outside the heating zone (g) | Amount of $Cl_2$ formed(mg) | |
| 350 | Not detectable | 40 | 100 |
| 370 | $\eta$-$Fe_2O_3$ 0.02 | 63 | 99.8 |
| 400 | $\eta$-$Fe_2O_3$ 0.04 | 99 | 96.5 |
| 450 | $\eta$-$Fe_2O_3$ 0.12 | 213 | 89.7 |
| 500 | $\eta$-$Fe_2O_3$ 0.21 | 330 | 82.8 |
| 550 | $\eta$-$Fe_2O_3$ 0.43 | 621 | 65.7 |
| 600 | $\eta$-$Fe_2O_3$ 0.83 | 1156 | 34.3 |
| 650 | $\eta$-$Fe_2O_3$ 1.11 | 1521 | 11.0 |
| 700 | $\eta$-$Fe_2O_3$> $\alpha$-$Fe_2O_3$ 1.25 | 1710 | 0 |

Consequently, the amount of chlorine evolved by heating $FeCl_3$ in the inner tube at 250 °C was examined in the same manner as described above, except that argon was introduced into the reaction zone instead of oxygen at the same flow-rate as that of oxygen. The amount of chlorine evolved was always approximately 40 mg.

The molar ratio of the amount of $Fe_2O_3$ to the amount of chlorine obtained by subtracting the amount of chlorine evolved by heating $FeCl_3$ in the inner tube from the total amount of chlorine was calculated to be approximately 1: 3 above 370 °C.

From these results, the reaction between gaseous $FeCl_3$ and oxygen proceeds above about 370 °C according to Reaction 4. The $Fe_2O_3$ formed was $\eta$-$Fe_2O_3$ at 370—650 °C, and a mixture of $\eta$-$Fe_2O_3$ and $\alpha$-$Fe_2O_3$ at 700 °C.

The effect of the molar ratio of $FeCl_3$: $O_2$ on the reaction product between gaseous $FeCl_3$ and oxygen was examined at 450 °C. The molar ratio was changed by raising the heating temperature of $FeCl_3$. The results are shown in Table 3.

Table 3. Effect of $FeCl_3$: $O_2$ molar ratio on reaction product between gaseous $FeCl_3$ and oxygen

| $FeCl_3$: $O_2$ (molar ratio) | Product |
|---|---|
| 1:33 | $\eta$-$Fe_2O_3$ |
| 1:19 | $\eta$-$Fe_2O_3 \gg$ FeOCl |
| 1:11 | $\eta$-$Fe_2O_3 >$ FeOCl |
| 1:7 | FeOCl $> \eta$-$Fe_2O_3$ |

This confirms the estimation on the formation of FeOCl obtained outside the heating zone by heating $FeCl_2$ in an oxygen stream above 420 °C, described in the preceding paragraph.

*Reaction Process between FeOCl and Oxygen.* The products obtained by heating FeOCl (2.0 g) at various temperatures in an oxygen stream were examined in the same manner as described in the previous paragraph.

At 230 °C, no reaction product was observed. The products obtained at various temperatures above 250 °C are shown in Table 4. The product in the boat was identified by X-ray analysis after dissolving the unreacted FeOCl in 1 M-$H_2SO_4$. Identification of the product in the boat below 300 °C was carried out using 20 g of FeOCl, because of the small amount of the product formed.

The results indicated that the reaction between FeOCl and oxygen proceeded according to Reaction 2 at 250—300 °C. Above 320 °C, $FeCl_3$ was obtained in addition to $\alpha$-$Fe_2O_3$ and chlorine. The molar ratio of the amount of $FeCl_3$ to the amount of $\alpha$-$Fe_2O_3$ obtained by subtracting the amount of $\alpha$-$Fe_2O_3$ formed by Reaction 2 from the total amount of $\alpha$-$Fe_2O_3$ was calculated to be approximately 1: 1. This result indicated that Reaction 3 also occurred besides Reaction 2. It may be considered that the formation of a small amount of $\eta$-$Fe_2O_3$ obtained outside the heating zone in addition to $FeCl_3$ at 400 °C was due to the reaction between gaseous $FeCl_3$ formed by Reaction 3 and oxygen, Reaction 4, from the result described in the preceding paragraph.

From these results, FeOCl reacts with oxygen above about 250 °C according to Reaction 2. Above about 320 °C, Reaction 3 also occurs besides Reaction 2.

*Reaction Process between $FeCl_2$ and Oxygen.* From the experimental results, the reaction process between $FeCl_2$ and oxygen may be represented as follows: $FeCl_2$ reacts with oxygen above about 250 °C according to Reaction 1. Subsequently, the resulting FeOCl reacts with oxygen according to Reaction 2. Above about 320 °C, the decomposition of the FeOCl also occurs according to Reaction 3. Above about 370 °C, the reaction between gaseous $FeCl_3$, formed by Reactions 1 and 3, and oxygen occurs according to Reaction 4 (under a low ratio of $O_2$: $FeCl_3$, FeOCl is formed in addition to $Fe_2O_3$) in addition to the above reactions.

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Table 4. Reaction products between FeOCl and oxygen at various temperatures

| Temp (°C) | Product: In the boat (%) | Product: Outside the heating zone (%) | Product: Amount of $Cl_2$ formed (mg) | Unreacted FeOCl(%) |
|---|---|---|---|---|
| 250 | $\alpha$-$Fe_2O_3$ (<0.1) | Not detectable | 0.2 | 99.9 |
| 280 | $\alpha$-$Fe_2O_3$ ( 0.1) | Not detectable | 0.6 | 99.8 |
| 300 | $\alpha$-$Fe_2O_3$ ( 0.2) | Not detectable | 2.1 | 99.7 |
| 320 | $\alpha$-$Fe_2O_3$ ( 1.0) | $FeCl_3$ (0.3) | 6.5 | 98.5 |
| 350 | $\alpha$-$Fe_2O_3$ ( 12.4) | $FeCl_3$ (7.6) | 47 | 78.1 |
| 400 | $\alpha$-$Fe_2O_3$ ( 53.8) | $FeCl_3$ (41.7), $\eta$-$Fe_2O_3$ (0.1) | 112 | 0 |