Studies on fluorination of Fe₃O₄ (magnetite) by NH₄HF₂

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Synopsis

Fluorination of magnetite (Fe₃O₄) by NH₄HF₂ was investigated using simultaneous thermogravimetry and differential thermal analysis (TG-DTA), and observing the morphology and phase changes using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and X-ray diffractometry (XRD). The results indicate that fluorination with the involvement of oxygen begins at room temperature, peaks at 178.4°C, and is completed at 200°C with the formation of only (NH₄)₃FeF₆.

On heating, (NH₄)₃FeF₆ gradually releases NH₄F by the formation of NH₄FeF₄ at 259°C, then (NH₄)₀.₁₈FeF₃ at 327°C, and finally FeF₃ with minor FeF₂ at 400°C due to the partial reduction of Fe (III) to Fe (II). At 550°C, FeF₃ is oxidized to FeOF/Fe₂O₃.

Keywords

Ammonium bifluoride; fluorination; thermal decomposition; FeF₃; XRD.

Introduction

Transitional metal fluorides such as FeF₃ have gained growing attentions due to their potential for use as electrode materials in lithium ion batteries owing to their low cost and high specific capacities (Ignatiev et al., 2020; Shimoda et al., 2020; Zhou et al., 2017; Zhou et al., 2018). Fe is the fourth most abundant element in the Earth’s crust and the cheapest metal in the market. In particular, the theoretical capacity of FeF₃ is up to 712 mA h g⁻¹ because of its unique reaction mechanism during the charge and discharge processes. However, FeF₃ prepared by hydrometallurgical processes always contains crystal water such as FeF₃·₃H₂O. During the dehydration process, iron oxides form (Sophronov et al., 2016) because Fe fluorides are unstable in the presence of water vapour. The formation of iron oxides significantly decreased the capacity. FeF₃ can also be prepared via thermal process using anhydrous HF or F₂ gas at high temperature in special corrosion-resistant equipment (Johnson., 1981). NH₄F and NH₄HF₂ are recognized as cheaper and versatile fluorinating agent used at low temperatures (<240°C) (Andreev, 2008; Claux et al., 2016; Gordienko et al., 2017; Juneja et al., 1995; Laptash and Maslennikova, 2012; Laptash and Polyshchuk, 1995; Mukherjee et al., 2011; Pourroy and Poix, 1989; Sophronov et al., 2016). However, excess NH₄F should be added in order to produce oxygen-free fluorides due to the highly hygroscopic nature of NH₄F (Mukherjee et al., 2011; Pourroy and Poix, 1989; Sophronov et al., 2016). Fluorination of different oxides by NH₄HF₂ therefore appears to be the most convenient method for obtaining oxygen-free fluorides.

The melting and boiling point of NH₄HF₂ are 126.8°C and 238.8°C, respectively. It is known that NH₄HF₂ can react with Fe₂O₃ or FeTiO₃ (Andreev, 2008; Gordienko et al., 2017; Juneja et al., 1995; Laptash and Maslennikova, 2012; Laptash and Polyshchuk, 1995; Mukherjee et al., 2011; Pourroy and Poix, 1989; Sophronov et al., 2016). However, excess NH₄F should be added in order to produce oxygen-free fluorides due to the highly hygroscopic nature of NH₄F (Mukherjee et al., 2011; Pourroy and Poix, 1989; Sophronov et al., 2016). Fluorination of different oxides by NH₄HF₂ therefore appears to be the most convenient method for obtaining oxygen-free fluorides.

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FeO₃+6NH₄HF₂= 2(NH₄)₃FeF₆+3H₂O↑  \[1\]

2FeO₃+3NH₄HF₂= 2NH₄FeF₃+NH₄⁺+2H₂O↑  \[2\]

Thus, for Fe₂O₃, the reactions can be written as:

2Fe₂O₃+15NH₄HF₂= 4(NH₄)₃FeF₆+2NH₄FeF₃+NH₄⁺+8H₂O↑  \[3\]

On heating, (NH₄)₃FeF₆ decomposes to form FeF₃ in ammonium media at 350°C (Andreev., 2008); while (NH₄)₀.₁₈FeF₃ gradually releases NH₄F to form FeF₃ via two or three steps (Alexeiko et al., 2008; Juneja et
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al., 1995; Kraidenko, 2008; Laptash and Polyshchuk, 1995; Pourroy and Poix, 1989; Shinn et al., 1966; Sophronov et al., 2016), as listed in Table I. According to Alexeiko et al. (2008), Juneja et al. (1995), Pourroy and Poix (1989), Shinn, Crocket, and Haendler (1966); and Sophronov et al. (2016) the reaction proceeds in two stages:

\[(\text{NH₄})₃\text{FeF₆} \rightarrow \text{NH₄FeF₄} \rightarrow \text{FeF₃}\]

However, Laptash and Polyshchuk (1995) and Kraidenko (2008) indicated that there exists an intermediate phase between \((\text{NH₄})₂\text{FeF₅}\) and \(\text{NH₄FeF₄}\), comprising \((\text{NH₄})₃\text{FeF₆}\) at 235°C and \((\text{NH₄})₃\text{FeF₅}\) at 255°C. Wang et al. (2021) indicated that \((\text{NH₄})₃\text{FeF₆}\) forms at 320°C between \(\text{NH}_4\text{FeF}⁴\) and \(\text{FeF}⁵\). With further temperature increase up to 400°C, \(\text{FeF}_₂\) with minor \(\text{FeF}_₃\) forms due to the reduction of Fe (III) (Alexeiko et al., 2008; Laptash and Polyshchuk, 1995; Pourroy and Poix, 1989). Furthermore, \(\text{FeF}_₂\) is oxidized due to the destruction of \(\text{NH}_4\text{FeF}_₄\) (Alexeiko et al., 2008; Juneja et al., 1995; Sophronov et al., 2016). Therefore, the reaction pathways between \(\text{NH}_4\text{HF}_₂\) and \(\text{Fe}_3\text{O}_₄\) are complicated. However, to authors' knowledge, there are no reports about the fluorination of \(\text{Fe}_3\text{O}_₄\) by \(\text{NH}_4\text{HF}_₂\). In the present work, the possible reaction pathways involved during the fluorination of \(\text{Fe}_3\text{O}_₄\) by \(\text{NH}_4\text{HF}_₂\) were simultaneously determined by TG-DTA. The fluorides in each stage were prepared by direct thermal treatment and analysed using SEM-EDS and XRD. The results of this work may be useful for studies of the fluorination of Fe-containing minerals and the production of oxygen-free fluorides.

Experimental

Commercial analytical grade magnetite (\(\text{Fe}_3\text{O}_₄\) 99.8 wt.%) and ammonium bifluoride (99.5 wt.%) were supplied by Sinopharm Group (China). To ensure complete fluorination, the theoretical mass ratio of \(\text{NH}_4\text{HF}_₂\): \(\text{Fe}_3\text{O}_₄\) is 1.8450 according to Equation [3]. In order to investigate the reaction progress, two mass ratios of \(\text{NH}_4\text{HF}_₂\): \(\text{Fe}_3\text{O}_₄\) were chosen for investigation. TG-DTA runs with pure \(\text{NH}_4\text{HF}_₂\) and \(\text{Fe}_2\text{O}_₃/\text{NH}_4\text{HF}_₂\) mixtures were carried out in a Shimadzu DTG-60 unit at a rate of 5°C/min from 25°C to 600°C under 20 mL/min \(\text{N}_2\) gas. Derivative thermogravimetry (DTG) curves were obtained as the first derivative of the TG curves. Based on TG-DTG-DTA results, the critical reaction temperatures of DTA curves were determined. In order to analyse the composition and determine the morphologies and phases of products before and after each reaction stage, \(\text{Fe}_3\text{O}_₄\) was first mixed with \(\text{NH}_4\text{HF}_₂\) at different mass ratios (\(\text{NH}_4\text{HF}_₂/\text{Fe}_3\text{O}_₄ = 2.5\) or \(3.5\)), put into a pure nickel crucible, then placed in a furnace for the assays. Heating was carried out at a rate of 5°C/min. Once the selected temperature was reached, the samples remained isothermal for 1 hour, and then allowed to cool to room temperature for further characterization. In order to increase repeatability, each test was repeated three times using 100 g \(\text{Fe}_3\text{O}_₄\).

The phases, morphologies, and composition of \(\text{Fe}_3\text{O}_₄\) powder, \(\text{NH}_4\text{HF}_₂\) agent, and fluorides produced were determined by XRD (D/Max-2500 pc type X-ray diffractometer) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) (Oxford Instruments, INCA).

Results

Properties of \(\text{Fe}_3\text{O}_₄\) powder and \(\text{NH}_4\text{HF}_₂\) agent

Figure 1 shows a SEM image and the corresponding EDS trace of \(\text{Fe}_3\text{O}_₄\) particles. \(\text{Fe}_3\text{O}_₄\) particles exhibit a spherical morphology with particle size less than 500 nm. EDS results in Figure 1b indicate that only Fe and O were detected. The atomic ratio of Fe to O is close to 3:4, which coincides well with the chemical formula of \(\text{Fe}_3\text{O}_₄\). The XRD results indicate that this phase is \(\text{Fe}_3\text{O}_₄\) (11110629) (magnetite). Figure 2 shows the XRD spectrum of \(\text{NH}_4\text{HF}_₂\) agent (51210302). Clearly, \(\text{NH}_4\text{HF}_₂\) agent has a crystalline nature.

Thermal analysis of \(\text{NH}_4\text{HF}_₂\)

Figure 3 shows the TG-DTG-DTA curve of \(\text{NH}_4\text{HF}_₂\) between 25 and 600°C. A weak endothermic peak is observed at 126.8°C due to the melting of \(\text{NH}_4\text{HF}_₂\). The second well-defined endothermic peak overlaps the previous endotherm to Fe O is close to 3:4, which coincides well with the chemical formula of \(\text{Fe}_3\text{O}_₄\). The XRD results indicate that this phase is \(\text{Fe}_3\text{O}_₄\) (11110629) (magnetite). Figure 2 shows the XRD spectrum of \(\text{NH}_4\text{HF}_₂\) agent (51210302). Clearly, \(\text{NH}_4\text{HF}_₂\) agent has a crystalline nature.

Table I

Decomposition of \((\text{NH}_4)_₃\text{FeF}_₆\)

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Reference</th>
<th>Reaction progress</th>
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<tbody>
<tr>
<td>Two-step</td>
<td>Sophronov et al., 2016</td>
<td>((\text{NH}_4)_3\text{FeF}_6) \rightarrow \text{NH}_4\text{FeF}_4\rightarrow \text{FeF}_3\rightarrow \text{FeF}_2\rightarrow \text{FeF}_₅\rightarrow \text{FeF}_₆\</td>
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<td></td>
<td>Alexeiko et al., 2008</td>
<td>((\text{NH}_4)_3\text{FeF}_6) \rightarrow \text{NH}_4\text{FeF}_4\rightarrow \text{FeF}_₃\rightarrow \text{FeF}_₅\rightarrow \text{FeF}_₆\</td>
</tr>
<tr>
<td></td>
<td>Shinn et al., 1966</td>
<td>((\text{NH}_4)_3\text{FeF}_6) \rightarrow \text{NH}_4\text{FeF}_4\rightarrow \text{FeF}_₃\rightarrow \text{FeF}_₅\rightarrow \text{FeF}_₆\</td>
</tr>
<tr>
<td></td>
<td>Juneja et al., 1995</td>
<td>((\text{NH}_4)_3\text{FeF}_6) \rightarrow \text{NH}_4\text{FeF}_4\rightarrow \text{FeF}_₃\rightarrow \text{FeF}_₅\rightarrow \text{FeF}_₆\</td>
</tr>
<tr>
<td></td>
<td>Pourroy and Poix, 1989</td>
<td>((\text{NH}_4)_3\text{FeF}_6) \rightarrow \text{NH}_4\text{FeF}_4\rightarrow \text{FeF}_₃\rightarrow \text{FeF}_₅\rightarrow \text{FeF}_₆\</td>
</tr>
<tr>
<td>Three-step</td>
<td>Laptash and Polyshchuk, 1995</td>
<td>((\text{NH}_4)_3\text{FeF}_6) \rightarrow \text{NH}_4\text{FeF}_4\rightarrow \text{FeF}_₃\rightarrow \text{FeF}_₅\rightarrow \text{FeF}_₆\</td>
</tr>
<tr>
<td></td>
<td>Kraidenkos, 2008</td>
<td>((\text{NH}_4)_3\text{FeF}_6) \rightarrow \text{NH}_4\text{FeF}_4\rightarrow \text{FeF}_₃\rightarrow \text{FeF}_₅\rightarrow \text{FeF}_₆\</td>
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Furthermore, the mass loss of NH₄HF₂ reagent begins from room temperature, as found in previous investigations (Carling and Westrum, 1976; House and Rippon, 1981; Resentera et al., 2020; White and Pistorius, 1972).

Thermal analysis of the fluorination of Fe₃O₄ with NH₄HF₂

Figure 4 shows the TG-DTG-DTA curves of Fe₃O₄/NH₄HF₂ mixtures between 25 and 600°C at different mass ratios. Clearly, two endothermic peaks are observed for a mass ratio of 2.5: 144.9°C and 259.9°C as seen in Figure 4a. Moreover, a weak endothermic peak appears at 327°C. For a mass ratio of 3.5, two new endothermic peaks appear at 126.8°C and 178.4°C, as seen in Figure 4b. However, the peak at 144.9°C disappears or is overlapped by the peaks at 126.8°C and 178.4°C while the peak at 327°C increases significantly. From Figure 4a, it can also be seen that the mass loss of about 2-3% begins at room temperature for a mass ratio of 2.5, the same as for pure NH₄HF₂ (Figure 3); while a minor mass gain (less than 1%) is observed for a mass ratio of 3.5 before 100°C (Figure 4b). With increasing temperature, a mass loss of about 10% is observed between 100 and 150°C for a mass ratio of 2.5; after which a levelling off occurs between 150 and 200°C. However, significant mass loss (approx. 28.9%) is observed between 100 and 200°C for a mass ratio of 3.5 without the curve flattening. By comparison, there are at least three endothermic peaks, which coincide well with the peaks in the DTG curves with large mass loss at 178.4°C, 259.2°C, and 327−327.6°C. The masses of residues for different temperatures are listed in Table II. In this temperature range, Fe₃O₄ is stable even at ambient condition (Ouertani et al., 2020). These results indicate that the formation of the above three peaks may be due to chemical reactions.

Figure 1—(a) SEM image and (b) the corresponding EDS of Fe₃O₄ powder

Figure 2—SEM image, EDS trace, and XRD spectrum of NH₄HF₂ powder

Figure 3—TGA-DTG-DTA analysis of NH₄HF₂ at 5°C/min

Figure 4—TGA-DTG-DTA analysis of Fe₃O₄/NH₄HF₂ mixtures between 25 and 600°C at heating rates of 5°C/min with different mass ratios of NH₄HF₂ to Fe₃O₄: (a) 2.5:1 and (b) 3.5:1.
Characterization of the fluorination products of Fe₃O₄

In order to identify and analyse the products involved in TG-DTG-DTA curves of Figure 4, samples were prepared by direct thermal treatment at different temperatures for 1 hour and then analysed using XRD. The results are shown in Figure 5. Clearly, the products between 135 and 180°C at both mass ratios consist chiefly of (NH₄)₃FeF₆ (#22-1040) with minor NH₄HF₂ (#12-0302) and Fe₃O₄ (#19-0629); the peak intensity of NH₄HF₂ decreases with increasing temperature and disappears at 270°C; the peak of Fe₃O₄ appeared between 135 and 180°C disappears at 270°C; only NH₄FeF₄ (#20-0503) is detected at 270°C at both mass ratios. These results indicate that the mass ratio of NH₄HF₂ to Fe₃O₄ has no influence on the fluoride phases between 135 and 270°C. In this case, only the fluorides with the mass ratio of 2.5 after direct thermal treatment were chosen for analysis.

Macroscopic morphology investigation showed that the fluorides formed between 135 and 180°C exhibit a similar grey color with increasing temperature: light grey, grey, and dark grey. Figure 6 shows the SEM images and the corresponding EDS data for fluorides produced between 135 and 270°C. Clearly, the faceted particles formed between 135 and 180°C disappear while finer spherical particles with average size less than 100 nm appear. The EDS results in Figure 6b indicate that the fluorides consist of Fe, F, and N without O, and the atomic ratio of F:Fe further decreases to 4.0.

The fluorides become green at 330°C. The size of the spherical particles slightly increases to larger than 150 nm and significant agglomeration occurs, as seen in Figure 7a. The EDS results in Figure 7b indicate that the fluorides at 330°C also consist of Fe and F with minor N. However, the atomic ratio of F:Fe further decreases to 3.0, which is close to the formula of FeF₃. However, the XRD results in Figure 8a indicate that this is not FeF₃ but a new phase comprising (NH₄)₀.₁₈FeF₃ (#47-0646). The results suggest that an intermediate phase, (NH₄)₀.₁₈FeF₃ (#47-0646), forms between NH₄FeF₄ and FeF₃. In other words, a new chemical reaction occurs between 270 and 330°C.

The fluorides formed at 400°C (Figure 7c) are also green. Clearly, the particle size is the same as that formed at 330°C. However, the EDS results in Figure 7d indicate that the fluorides at 400°C consist of Fe and F without N. The atomic ratio of F:Fe is close to 3, the formula ratio of FeF₂ is FeF₃ (#33-0647) with minor FeF₂ (#45-1062).

Table II

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mass ratio: 2.5</th>
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<th>Mass ratio: 3.5</th>
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</tr>
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<tbody>
<tr>
<td>Phase</td>
<td>Mc</td>
<td>Mm</td>
<td>Phase</td>
<td>Mc</td>
</tr>
<tr>
<td>200°C</td>
<td>(NH₄)₃FeF₆+NH₄HF₂ 90%</td>
<td>88%</td>
<td>(NH₄)₃FeF₆+NH₄HF₂ 92.23%</td>
<td>71.1%</td>
</tr>
<tr>
<td>280°C</td>
<td>NH₄FeF₄</td>
<td>55.45%</td>
<td>NH₄FeF₄</td>
<td>43.13%</td>
</tr>
<tr>
<td>330°C</td>
<td>(NH₄)₀.₁₈FeF₃</td>
<td>52%</td>
<td>(NH₄)₀.₁₈FeF₃</td>
<td>33.42%</td>
</tr>
<tr>
<td>600°C</td>
<td>FeF₃+FeF₂</td>
<td>48.67%</td>
<td>FeF₃+FeF₂</td>
<td>32.08%</td>
</tr>
</tbody>
</table>
The fluorides become red at 550°C (Figure 9a). Clearly, the average particle size increases up to 500 nm. The EDS results in Figure 9b indicate that the fluorides consist of Fe and O with minor F. The atomic ratio of O:Fe is close to 3:2 of the formula ratio of Fe₂O₃. The XRD results in Figure 9c indicate that the fluorides consist mostly of Fe₂O₃ (#33-0664) with minor FeF₃ (#33-0647) and FeF₂ (#45-1062).

Discussion

The melting of NH₄HF₂ at 126.8°C (Carling and Westrum, 1976; House and Rippon, 1981; Resentera et al., 2020; White and Pistorius, 1972) leads to an endothermic peak in the DTA curve, as found in this work (Figure 3). This is why a clear peak is observed at 126.8°C for a mass ratio of 3.5 (Figure 4b). Even before the melting of NH₄HF₂, a minor mass loss occurs due to the decomposition of NH₄HF₂, as seen in Figures 3 and 4a. With the melting of NH₄HF₂ at 126.8°C, the mass loss increases sharply and a well-defined endothermic peak with large mass loss occurs at 178.4°C due to the fluorination of Fe₃O₄. According to Equations [1], [2], and [3], the fluorination of Fe₃O₄ should form (NH₄)₃FeF₆ and NH₄FeF₃. However, the results in Figures 5 and 6 indicate that only (NH₄)₃FeF₆ (#22-1040) with a comparable coarse faceted-

Figure 6—(a), (c), (e), (g) SEM images and (b), (d), (f), (h) the corresponding EDS data for Fe₃O₄/NH₄HF₂ mixtures (mass ratio: 2.5) after thermal treatment at different temperature for 1 hour. (a, b) 135°C; (c, d) 150°C; (e, f) 180°C; (g, h) 270°C.
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Grain morphology forms between 135 and 180°C. No NH₄FeF₃ was detected. The results suggest that divalent iron becomes trivalent through the oxidation of Fe₃O₄ or the involvement of oxygen during the fluorination progress (Laptash et al., 2000). In a word, oxygen is involved in the fluorination reaction according to the reaction:

\[
2\text{FeO} + 0.5\text{O}_2 + 18\text{NH}_4\text{HF}_2 \rightarrow 6(\text{NH}_4)_2\text{FeF}_6 + 9\text{H}_2\text{O} \tag{4}
\]

In this case, a minor mass gain should be observed. Figure 4b indicates that a minor mass gain occurs even at room temperature, suggesting fluorination may start at room temperature. To confirm this assumption, a Fe₃O₄/NH₄HF₂ mixture with mass ratio of 2.5 was prepared and kept for one week at room temperature, then analysed using XRD (Figure 10). Clearly, only (NH₄)₃FeF₆,
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Figure 10—XRD spectra of Fe₃O₄/NH₄HF₂ mixtures (mass ratio: 2.5) held at room temperature for one week

and no NH₄FeF₃ was detected, the same as at 135-180°C (Figure 5). Furthermore, the samples became warm during mixing, and a smell of ammonia was observed. The results suggest that the fluorination of Fe₃O₄ by NH₄HF₂ really begins at room temperature, the same as Fe₃O₄ (Wang et al., 2021).

According to Equation [4], the fluorination of Fe₃O₄ at room temperature also causes the formation of H₂O, which is absorbed by the fluorides. The loss of absorbed H₂O between 100 and 150°C (Wang et al., 2020) plus the decomposition and removal of NH₄HF₂ between 126.8 and 160.2°C (Mukherjee et al., 2011; Resentena et al., 2020; White and Pistorius, 1972) might cause the formation of another weak peak at 144.9°C, as seen in Figure 4a. The peak at 144.9°C will be overlapped by the fluorination of Fe₃O₄ at 178.4°C at a high mass ratio of 3.5, as seen in Figure 4b.

With the melting of NH₄HF₂ at 126.8°C, the reaction rate increases sharply due to the faster liquid-solid reaction rate compared to the slower solid-solid reaction rate. Based on the above analysis, the peak at 178.4°C at mass ratio 3.5 is mainly due to the fluorination of Fe₃O₄ according to Equation [4]. However, according to Equation [4], the mass ratio of NH₄HF₂ to Fe₃O₄ for complete fluorination is 2.2140. Therefore, fluorination should be completed for both mass ratios. However, results in Figures 5a and 5b indicate that minor Fe₃O₄ and NH₄HF₂ are still detected between 135 and 180°C even after 1 hour, suggesting a slow fluorination rate of Fe₃O₄.

With increasing temperature, the further fluorination of unreacted Fe₃O₄ plus the decomposition/sublimation of NH₄HF₂ will consume all or part of the NH₄HF₂. In this case, the products at 200°C should consist of (NH₄)₃FeF₆ with minor NH₄FeF₄. Theoretical calculation indicates that the product masses at 200°C for mass ratios of 2.5 and 3.5 are 81.77–90% and 55.42–92.23%, in fair agreement with the measured values of 88% and 41%, as seen in Table II. There are three reasons for this. The first is the measurement error, as seen in Table II. The second is the release of NH₄F from NH₄FeF₄ (#20-0503), which results in the further fluorination of Fe₃O₄ residues according to following reaction:

\[
2\text{Fe}_3\text{O}_4 + 0.5\text{SO}_2 + 24\text{NH}_4\text{F} = 6\text{NH}_4\text{FeF}_4 + 9\text{H}_2\text{O} + 18\text{NH}_3 \uparrow
\]

There is no direct evidence for this. However, the XRD results in Figure 5 indicate that the complete fluorination of Fe₃O₄ is a lengthy process. Therefore, the assumption that fluorination of Fe₃O₄ is incomplete before 327°C during TG-DTA analysis is reasonable (Wang et al., 2021). The third reason is the slower release rate of NH₄F from NH₄FeF₄ at 327°C during TG-DTA analysis. To confirm this assumption, a Fe₃O₄/NH₄HF₂ mixture with mass ratio of 2.5 was prepared and heated at 330°C for 10 minutes, then analysed using SEM/EDS and XRD. The results are shown in Figure 11. Clearly, only minor (NH₄)₃FeF₆ (#747-0646) was detected, with major NH₄FeF₄ (#20-0503). The results indicate that the complete release of NH₄F from NH₄FeF₄ takes a long time, even at 327°C.

With a further increase in temperature, (NH₄)₃FeF₆ will gradually lose all its NH₄F to form FeF₄ with minor FeOF due to the partial reduction of Fe (II) to Fe (III) by ammonia at 400°C (Alexeiko et al., 2008; Bentrup and Menz, 1990; Pourroy and Poix, 1989; Laptash and Polyshchu, 1995; Laptash et al., 2000; Wang et al., 2021), as seen in Figure 8b. After 400°C, the mass loss is negligible, as seen in Figure 4. Therefore, the measured residue at 600°C is closed to the theoretical value after consideration the measurement error and the adsorption of F, N, and NH₃ by FeF₃ during TG-DTA analysis.

At 550°C without gas protection, Fe oxides (Figure 9) form due to the oxidation of FeF₃ (Alexeiko et al., 2008; Juneja et al., 1995; Sophronov et al., 2016). In order to analyse the oxidation progress, a Fe₃O₄/NH₄HF₂ mixture with mass ratio of 2.5 was prepared and heated at 550°C for 10 minutes, then analysed using SEM/EDS and XRD. The results are shown in Figure 12. Clearly, the fluorides contain a major component of FeF₂ with minor FeOF (#18-0648). FeF₂ is either absent or below the detection limit of XRD. Combined with the results in Figure 9, it can be concluded

\[
\text{(NH₄)₃FeF₆} \rightarrow \text{NH₄FeF₄} + 2\text{NH₃} \uparrow
\]

Theoretical calculation show that NH₄FeF₄ residues at 280°C for mass ratios of 2.5 and 3.5 are 55.45% and 43.13%, in fair agreement with the measured values of 48% and 47% from the TG curve after consideration of the measurement error, as listed in Table II.

With increasing temperature, NH₄FeF₄ (#20-0503) will lose NH₄F to form FeF₄ at temperature above 330°C (Alexeiko et al., 2008; Juneja et al., 1995; Sophronov et al., 2016). However, Figure 4 shows that there exists another peak at 327-327.6°C. Figures 7a and 8a suggest that the fluoride at 330°C is not FeF₃, but (NH₄)₃FeF₆ (#47-0646) with minor N (Bentrup and Menz, 1990). The fluoride of (NH₄)₃FeF₆ is a different colour (green) to that formed at 270°C (white). Furthermore, the particle size increases up to 150 nm with significant agglomeration (Figure 7a). From the above results, it could be concluded that NH₄FeF₄ lost only part of its NH₄F to form a new intermediate phase of (NH₄)₃FeF₆ at 327°C. According to theoretical calculation, the residue masses at 330°C for mass ratios of 2.5 and 3.5 are 49.26% and 33.42%. These values are lower than the measured values of 52% and 41%, as seen in Table II. There are three reasons for this. The first is the measurement error, as seen in Table II. The second is the release of NH₄F at 327°C, which results in the further fluorination of Fe₃O₄ residues according to following reaction:

\[
(NH₄)₃FeF₆ = NH₄FeF₄ + 2NH₃ \uparrow
\]
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that oxidation proceeds through the following stages: FeF₃ → FeOF → Fe₂O₃. Furthermore, oxidation is faster than reduction under these conditions, which is why no FeF₂ is detected (Figure 12), and the fluorides after 1 hour consist of a major proportion of Fe₂O₃ and only minor FeF₂ (Figure 9).

Conclusions
The thermal and microstructural analysis of the fluorination of magnetite (Fe₃O₄) with NH₄HF₂ at different mass ratios of NH₄HF₂ to Fe₃O₄ (2.5 and 3.5) was carried out by means of TG-DTG-DTA, SEM/EDS, and XRD. The results indicate that the mass ratio of NH₄HF₂ to Fe₃O₄ has no influence on the fluorination reaction progress and the corresponding temperature. The fluorination of Fe₃O₄ starts at room temperature, dominates at 178.4°C, and is completed at 200°C with the formation of (NH₄)₃FeF₆. No NH₄FeF₄ forms due to the involvement of oxygen. As the temperature increases above 180°C, the unreacted NH₄HF₂ decomposes and is removed from the system. Furthermore, (NH₄)₃FeF₆ decomposes sequentially through a three-step reaction by the formation of NH₄FeF₄ at 259.2-259.9°C, then (NH₄)FeF₃ at 320°C, and finally FeF₃ with minor FeF₂ at 400°C. At 550°C in air, FeF₃ is oxidized to FeOF/Fe₂O₃.
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