Preparation of anhydrous FeF$_3$ by solid state reaction of iron oxide with ammonium hydrogen fluoride

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The preparation of anhydrous FeF$_3$ has been investigated by solid state reaction of Fe$_2$O$_3$ with NH$_4$HF$_2$. The reaction has been studied in both vertical and horizontal reactors. The difficulties encountered in carrying out the reaction upto 50g charge scale are discussed. The horizontal reactor provides better control of the kinetic factors than the vertical reactor.

The iron based alloys containing neodymium and boron, Nd$_2$Fe$_{14}$B, exhibit excellent permanent magnetic properties$^1$. One of the routes for preparation of these alloys is by calciothermic reduction of a mixture of NdF$_3$ and anhydrous FeF$_3$.$^2$ Thus anhydrous FeF$_3$ is an important intermediate required in the preparation of permanent magnets.

Iron fluoride can be prepared via aqueous route by treatment of a solution containing iron with aqueous HF solution$^3$. However, the product obtained by this process is the iron trifluoride trihydrate, FeF$_3$3H$_2$O, which is not a suitable intermediate for use in the preparation of Fe-Nd alloys by the calciothermic reduction route. This may be attributed to the difficulty encountered during the preparation of anhydrous FeF$_3$ from its trihydrate since the product obtained is invariably contaminated with Fe$_2$O$_3$ due to partial hydrolysis. Anhydrous FeF$_3$ can be prepared by the non-aqueous dry route involving hydrofluorination of Fe$_2$O$_3$ with anhydrous HF gas via the reaction:

$$\text{Fe}_2\text{O}_3 + 6\text{HF} \rightarrow 2\text{FeF}_3 + 3\text{H}_2\text{O},$$

$$\Delta F_{298} = -43.64 \text{ kcal}$$

However, in order to carry out this reaction, a special assembly made of monel alloy is required which can withstand the corrosive action of HF gas. Further, in order to avoid the reverse reaction, it is necessary to remove the water generated in the reaction as and when it is formed. This is done by maintaining the outlet gas pipe at a temperature > 120°C. This method of preparation of metal fluoride is, therefore, expensive. In contrast to anhydrous HF gas, ammonium fluoride (NH$_4$F) and ammonium hydrogen fluoride (NH$_4$HF$_2$) are cheaper and more convenient fluorinating agents$^4$-$^5$. Moreover, they can be used for the fluorination of metal oxides in solid state at lower temperatures (around 400°C). The methods involving use of these reagents are quite simple and do not require any special assembly. It has been reported that FeF$_3$ and FeF$_2$ can be prepared from Fe$_2$O$_3$ and NH$_4$F by heating the mixture in 1:12 mol ratio at 350 and 750°C, respectively$^4$. However, in order to prepare pure fluoride product without oxide contamination, it is necessary to use large excess of NH$_4$F. The present investigation deals with the preparation of anhydrous FeF$_3$ from $\alpha$-Fe$_2$O$_3$ by its reaction with NH$_4$HF$_2$ which is more reactive and is also required in less quantity than NH$_4$F.

**Experimental Procedure**

The chemicals used in the present study were $\alpha$-Fe$_2$O$_3$ (Qualigens) and ammonium hydrogen fluoride (Riedel de Haan) having a purity of 98%. The bifluoride was preheated at 60°C for one hour before use.

The reaction of iron oxide with ammonium bifluoride was carried out in vertical as well as horizontal reactors. The vertical reactor assembly consisted of an inconel retort of 100 mm diameter fitted with water cooled flange having arrangements for evacuation and gas flow. The reactor was heated in a pit type furnace. The horizontal reactor assembly was made of an alumina tube of 60 mm diameter fitted on both sides with flanges having provision for gas flow. The alumina reaction tube was heated in a resistance wire wound furnace placed in a horizontal position.

The iron oxide was mixed with required amount of NH$_4$HF$_2$ and the mixture was taken in an inconel container (crucible or boat) and heated to the required
temperature either in dynamic vacuum or in flowing high purity argon gas. The amount of NH₄HF₂ taken for reaction was 20% in excess of the stoichiometric requirement of 1:6 mol ratio. After each heating, the product was taken out, ground, mixed and subjected to the desired number of heating cycles. In order to ensure complete reaction, an additional 10% NH₄HF₂ was added to the charge after second heating cycle. The product after each heating cycle was examined by powder XRD analysis.

**Results and Discussion**

Preliminary studies carried on 0.1-0.5 g scale showed that the reaction of α-Fe₂O₃ with NH₄HF₂ proceeds via the following three stages:

100-150°C

\[ \text{Fe}_2\text{O}_3 + 6\text{NH}_4\text{HF}_2 \rightarrow 2(\text{NH}_4)_3\text{FeF}_6 \cdot 1.5\text{H}_2\text{O} \]

150-250°C

\[ (\text{NH}_4)_3\text{FeF}_6 \cdot 1.5\text{H}_2\text{O} \rightarrow \text{NH}_4\text{FeF}_4 + 2\text{NH}_4\text{F} + 1.5\text{H}_2\text{O} \]

300-400°C

\[ \text{NH}_4\text{FeF}_4 \rightarrow \text{FeF}_3 + \text{NH}_4\text{F} \]

Using these conditions, attempts were made to prepare anhydrous FeF₃ by increasing the scale of operation to 50g charge. The reaction was studied in vacuum as well as inert gas using vertical and horizontal reactors.

**Vertical reactor** — In the vertical assembly, the charge was taken in an inconel crucible (50 mm diameter) and subjected to three cycles of heating at 300, 400 and 400°C for 4-5 h each in dynamic vacuum. Such a procedure gave a product which was not homogenous. It had brown colour on the top layer and grey yellow on the lower portions. This was because decomposition of the complex could take place only from the top surface and not from the bulk of the charge. Increasing the temperature to 450°C also did not help. These experiments were repeated in flowing argon gas instead of dynamic vacuum. But the results obtained were similar. Thus it was evident that complete decomposition of the complex into FeF₃ was not possible because of the kinetic factors. The kinetic factors that control the solid state reactions are particle size of the reactants, mixing and packing of reactants, formation of the complexes, (NH₄)₃FeF₆ and NH₄FeF₄, thermal decomposition of the complexes, removal of decomposition products from the reaction zone and back reaction. In the vertical reactor, the exposed surface area is less and bed height of the charge is more. Both these factors hinder the release of decomposition products and hence prevent the reaction from proceeding in the forward direction. Further experiments were carried out so that the exposed surface area was increased and bed height was reduced. This was done by using a smaller charge of 35g (10g Fe₂O₃ + 25g NH₄HF₂) taken in a larger crucible (70 mm diameter). Such a charge was heated three times at 350, 375 and 375°C for 10-14 h each in flowing argon gas. The product obtained under these conditions was found to be uniform having brown colour and was identified as FeF₃ powder XRD. Thus in a vertical system, it was possible to prepare anhydrous FeF₃ from a charge containing upto 10g Fe₂O₃ in flowing argon gas using a crucible of 70 mm diameter. The operation in flowing argon gas is simpler and does not require constant attention as in the case of dynamic vacuum.

**Horizontal reactor** — In the horizontal reactor, a charge of 35g was taken in an inconel boat and subjected to four heating cycles at 115, 250, 350 and 350°C for 4-5 h each. The results of weight change and phase analysis of the products obtained after each heating cycle are presented in Table 1. It is evident that (NH₄)₃FeF₆ complex is formed at 115°C. This complex starts decomposing at 250°C leading to the formation of a mixture of (NH₄)₃FeF₆ and NH₄FeF₄ in the second heating campaign. Heating of these complexes upto 350°C in the third and fourth stages results in complete decomposition to FeF₃. Decomposition of the complex, when carried out

<table>
<thead>
<tr>
<th>Heating cycle</th>
<th>Temperature, °C</th>
<th>Weight of product, g</th>
<th>Colour of product</th>
<th>Phases identified by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>115</td>
<td>32</td>
<td>Light grey</td>
<td>(NH₄)₃FeF₆</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>24</td>
<td>Light grey yellow</td>
<td>(NH₄)₃FeF₆ + NH₄FeF₄</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>15</td>
<td>Brown on top surface, Greyish green in bulk</td>
<td>FeF₃ + complex</td>
</tr>
<tr>
<td>IV</td>
<td>350</td>
<td>14</td>
<td>Brown</td>
<td>FeF₃</td>
</tr>
</tbody>
</table>
above 400°C, was found to yield a product containing some Fe₂O₃. This could be because the water formed during decomposition reaction reacted with FeF₃ above 400°C. The soaking period of 4-5 h at each temperature was found to be adequate for the completion of reaction for 35g charge. Based on the results of weight change obtained at different temperatures, the percentage conversion of Fe₂O₃ to FeF₃ was found to be > 99%.

The XRD patterns of samples containing (NH₄)₃FeF₆, NH₄FeF₄ and FeF₃ matched well with the standard charts available in JCPDS Cards 7-9. In the case of FeF₃ product prepared by this method, no additional unidentified lines were observed. Since the products were evaluated for their phase purity by the XRD method, the purity of FeF₃ obtained under optimum conditions was > 95% (X-ray limit). The aim of the process was to prepare anhydrous FeF₃ free of Fe₂O₃. This was ensured by using 20% excess of NH₄HF₂ in the first stage of heating and another 10% NH₄HF₂ in the third stage of heating. The final product obtained was found to be free of Fe₂O₃ phase and the conversion efficiency of the process under optimum conditions was > 99%.

In the horizontal system, the charge placed in a boat had comparatively lower bed height and more exposed area to the flowing argon gas. This helped in sweeping away the products of decomposition from the reaction zone. The product obtained after each heating cycle was found to be more uniform as compared to the case in a vertical system. Thus the kinetic factors in a horizontal system could be controlled better than in vertical system. The horizontal system is, therefore, preferable to the vertical one.

Conclusions

The present study has provided information regarding optimum conditions for the preparation of anhydrous FeF₃ from Fe₂O₃ and NH₄HF₂ on 35-50g charge scale by solid state reaction. The vertical system provides kinetic hindrance to the decomposition of the [NH₄]₃FeF₆ and NH₄FeF₄ complexes formed in the first stage of reaction. These kinetic factors can be overcome if sample bed height is reduced and exposed surface area is increased. Both these conditions are better achievable in a horizontal reactor than in the vertical one.

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References