SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Reaction of Magnesium Oxide and Magnesium Silicates with Ammonium Hydrodifluoride

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Abstract—The reactions of magnesium oxide and magnesium silicates (forsterite and serpentines) with ammonium hydrodifluoride is studied using DTA, X-ray powder diffraction, and IR spectroscopy. The conditions for the formation of intermediate phases are determined. The structure of the silicate mineral does not significantly affect the fluorination.

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Ammonium hydrodifluoride is a solid product of utilization of fluorine-containing industrial gases; it is highly reactive and can be regenerated from either solution or gas. Reactions with ammonium hydrodifluoride yield, apart from simple fluorides, coordination compounds with various ammonium and fluorine contents, as well as nonvolatile oxyfluorides; the extent to which the latter are understood determines whether NH_4HF_2 is used successfully in fluoride metallurgy [1].

According to Rakov [2], NH_4HF_2 , approaching hydrogen fluoride in reactivity, has several strengths: it is readily dehydrated, and fluorination reactions do not require complicated equipment.

Systematic investigations of the reactions of NH_4HF_2 with minerals and concentrates are now underway in the Far East of Russia [1, 3–7]. However, the fluorination of minerals contained in raw material is not fully described in the literature.

Here, we report on the reaction of NH_4HF_2 with magnesium oxide and with two varieties of magnesium silicates, namely forsterite (an island silicate, i.e., a mineral with isolated tetrahedra; its simplified formula is Mg_2SiO_4) and serpentines (serpophite and antigorite; sheet minerals with the simplified formula $Mg_6(OH)_8[Si_4O_{10}]$).

The forsterite structure is built of MgO_6 octahedra that share their edges to form zigzag chains and are linked through SiO₄ tetrahedra. Each oxygen atom is at the same time a corner of three octahedra and one tetrahedron.

Serpentines are built of two-layer sheets: one (tetrahedral) layer is built of silicon–oxygen tetrahedra and the other (octahedral, brucite) layer contains magnesium cations in octahedral voids that are formed by oxygen ions and hydroxide groups. Octahedral and tetrahedral layers in serpentines can be stacked in several modes. The most distinctive mode is when a complex sheet is bent with the tetrahedral structural element on the inner side of the bend. The antigorite unit cell includes one complex sheet, which is folded in such a way that the polarity at each bend line inverts.

Serpophite is a serpentine variety characterized by fine-crystalline and cryptocrystalline ophitic aggregates. Serpophites tend to structure disorder.

EXPERIMENTAL

The starting materials used were reagent grade magnesium oxide; native monomineral samples of magnesium silicates: forsterite Mg_2SiO_4 and serpentines (serpophite and antigorite) $Mg_6(OH)_8[Si_4O_{10}]$; and doubly crystallized analytical grade ammonium hydrodifluoride NH_4HF_2 .

The starting materials, taken in stoichiometric proportions, were carefully ground, placed into a platinum crucible (sample sizes were 200–400 mg), and heated at 2.5 K/min in a Q-1500 derivatograph.

The X-ray powder diffraction analysis of reaction products was carried out on a DRON-2 diffractometer using CuK_{α} radiation.

IR-spectroscopic investigations were performed on a UR 20 instrument.

RESULTS AND DISCUSSION

Reaction of Magnesium Oxide with Ammonium Hydrodifluoride

Rakov indicated in his review [2] that magnesium with ammonium hydrodifluoride forms the following compounds: $(NH_4)_2MgF_4 \cdot 2H_2O$, $(NH_4)_2MgF_4$, and NH_4MgF_3 . The dihydrate is dehydrated at 110°C.



Fig. 1. Thermoanalytical traces for the reaction between magnesium oxide and ammonium hydrodifluoride in the molar ratio 1 : 2.

Researchers who investigated the heating behavior of $(NH_4)_2MgF_4$ and NH_4MgF_3 report conflicting data: the $(NH_4)_2MgF_4$ undergoes thermal decomposition to NH_4MgF_3 and MgF_2 at 215–230 and 260–400°C [2].

The reaction route and the formation temperatures of intermediates and magnesium fluoride were refined in additional experiments.

Thermoanalytical traces for a MgO plus NH_4HF_2 mixture (1 : 2 mol/mol) is displayed in Fig. 1. A strong exotherm with a peak at 86°C is observed; it masks the endotherm due to melting of ammonium hydrodifluoride. The appearance of the next endotherm at 180°C is due to the end of $(NH_4)_2MgF_4$ formation by the reaction

$$MgO + 2NH_4HF_2 = (NH_4)_2MgF_4 + H_2O.$$
 (1)

This compound rapidly decomposes upon further heating to yield a new diammoniumtetrafluoromagnesium complex at 215°C:

$$(NH_4)_2MgF_4 = NH_4MgF_3 + NH_3 + HF.$$
 (2)

Temperature elevation induces NH_4MgF_3 decomposition (the associated DTA endotherms are seen in Fig. 1). The process finishes at 315°C by MgF_2 formation:

$$NH_4MgF_3 = MgF_2 + NH_3 + HF.$$
 (3)

Calculated weight losses for the reaction stages correlate with the values found from the TG traces. The intermediates and the final product were synthesized at these temperatures and verified using X-ray powder diffraction.



Fig. 2. IR spectra for (1) (NH₄)₂MgF₄ and (2) MgF₂.

Figure 2 displays IR absorption spectra for $(NH_4)_2MgF_4$ and MgF_2 in the frequency range from 400 to 1800 cm⁻¹. Bands at 400–500 cm⁻¹ are associated with Mg–F stretching vibrations. Bands at 1440 and 1230 cm⁻¹ in the $(NH_4)_2MgF_4$ spectrum are associated with bending vibrations in NH_4^+ and HF_2^- .

Reaction of Magnesium Silicates with Ammonium Hydrodifluoride

Our goal was to determine the fluorination parameters and the synthesis temperatures for intermediates and to elucidate how the structural features of the silicates affect the fluorination.



Fig. 3. Thermoanalytical traces for the reaction between forsterite and ammonium hydrodifluoride in the molar ratio 1 : 7.5.

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY Vol. 51 No. 5 2006



Fig. 4. X-ray diffraction patterns for mixtures of forsterite with ammonium hydrodifluoride exposed at (1) 180, (2) 250, and (3) 300° C.

Forsterite. Figure 3 displays thermoanalytical traces for a Mg_2SiO_4 plus NH_3HF_2 mixture (1 : 7.5 mol/mol). Several features are observed in the DTA trace: an endotherm at 125°C, associated with NH_4HF_2 melting, transforms to a strong exotherm with a peak at 135°C. Then, weak features at about 180°C manifest the end of formation of intermediate complex fluorides by the scheme

$$Mg_{2}SiO_{4} + 7.5NH_{4}HF_{2} = (NH_{4})_{3}SiF_{7} + 2(NH_{4})_{2}MgF_{4} + 4H_{2}O + 0.5NH_{3}.$$
(4)

Further temperature elevation induces the decomposition of fluoro complexes (NH₄)₃SiF₇ and (NH₄)₂MgF₄ to $(NH_4)_2SiF_6$ and NH_4MgF_3 , respectively. The reaction involved is

$$(NH_4)_3 SiF_7 + (NH_4)_2 MgF_4$$

= (NH_4)_2 SiF_6 + NH_4 MgF_3 + 2NH_3 + 2HF. (5)

The set of exo- and endotherms observed in the range 290–330°C is due to the final fluorination stage: NH_4MgF_3 decomposes to MgF_2 , and $(NH_4)_2SiF_6$ sublimes. The $(NH_4)_2SiF_6$ sublimation mechanism is a point of discussion. Kurilenko [6] suggested a stagewise formation of adduct $SiF_4 \cdot 2NH_3$, followed by its transformation into amine-bridged $Si_2F_7N_2H_5$. Mel'nichenko and colleagues showed later [7] that, when $(NH_4)_2SiF_6$ is heated between 220 and 460°C, the

Absorption

formation of pentafluoroammonium salt NH_4SiF_5 occurs along with sublimation; the pyrohydrolysis of this salt yields ammonium oxofluorosilicates of variable composition, which reduce the $(NH_4)_2SiF_6$ sublimation temperature. From gas, $(NH_4)_2SiF_6$ is deposited in two polymorphs: hexagonal and cubic [7].

The weight loss by a Mg_2SiO_4 plus NH_4HF_2 mixture, heated to 330°C, corresponds to the formation of magnesium fluoride and removal of volatiles.

The above scenario of the reaction was validated by X-ray powder diffraction. Figure 4 displays the X-ray diffraction patterns for samples of Mg_2SiO_4 plus NH_4HF_2 mixtures exposed at 180, 250, and 300°C. The products identified are $(NH_4)_3SiF_7$ and $(NH_4)_2MgF_4$, $(NH_4)_2SiF_6$ and NH_4MgF_3 , or MgF_2 , respectively.

The IR spectra of the products of intermediate reaction stages are shown in Fig. 5. Qualitatively the spectra are alike. Bands at 730 and 480 cm⁻¹ are due to the vibrations of SiF_6^{2-} octahedra. Bands in the range 400– 500 cm⁻¹ are associated with the Mg–F stretching vibrations. The strong band at 1440 cm⁻¹ is due to the bending vibrations of NH_4^+ ion.

Serpophite and antigorite. Figure 6 shows the thermoanalytical curves for a mixture of antigorite $Mg_6(OH)_8Si_4O_{10}$ and NH_4HF_2 (1 : 26 mol/mol). The endotherm at 110°C in the DTA trace is associated with melting of ammonium hydrodifluoride. Compounds $(NH_4)_3SiF_7$ and $(NH_4)_2MgF_4$ are formed up to 220°C according to the reaction

$$Mg_{6}(OH)_{8}Si_{4}O_{10} + 26NH_{4}HF_{2}$$

= 4(NH₄)₃SiF₇ + 6(NH₄)₂MgF₄ (6)
+ 18H₂O + 2NH₃.

Subsequent rise in temperature brings about the thermal decomposition of the products of reaction (6) with the formation of $(NH_4)_2SiF_6$ and NH_4MgF_3 , respectively. The endotherm with a minimum at 302°C is due to the end of NH_4MgF_3 decomposition and $(NH_4)_2SiF_6$ sublimation to yield the final product MgF_2 .

Note that the structural-order features of serpentines do not affect the reaction kinetics or the formation temperature of the synthesis products: the fluorination of antigorite and serpophite by NH_4HF_2 follows identical scenarios.

In summary, we have refined the route of the reaction of magnesium oxide with ammonium hydrodifluoride. We have found that fluorination ends at 315°C **Fig. 6.** Thermoanalytical traces for the reaction between antigorite and ammonium hydrodifluoride in the molar ratio 1 : 26.

with magnesium fluoride formation. Our results correlate with those of Ikrami and colleagues [8].

Our investigations of reactions between magnesium silicates and NH_4HF_2 show that the reagents are fully fluorinated and the final products are magnesium fluoride MgF₂ and volatile (NH_4)₂SiF₆.

Island silicates are stripped with the greatest difficulty [6]. The complete fluorination of such minerals with NH_4HF_2 was achieved in Teflon autoclaves at 200°C. We found that the structure of the silicate mineral does not affect fluorination noticeably: intermediate ammonium compounds are observed at identical temperatures regardless of whether NH_4HF_2 reacts with island or sheet silicates.

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