ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 8, pp. 1333−1337. © Pleiades Publishing, Ltd., 2009.
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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Influence of the Amount of Ammonium Hydrogen Difluoride on the Degree of Fluorination of Mineral Raw Materials

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Received October 21, 2008

Abstract—The degree of fluorination and recovery of the main components from mineral raw materials were examined in relation to the amount of ammonium hydrogen difluoride NH_4HF_2.

DOI: 10.1134/S1070427209080023

Ammonium hydrogen difluoride NH_4HF_2 is a promising reagent for fluorination of mineral raw materials [1–6]. It was suggested [4–6] that NH_4HF_2 be introduced in understoichiometric amounts, so that the shortage of the reagent be filled by HF evolved during thermal decomposition of ammonium fluoride complexes of iron, titanium, and zirconium.

Earlier Miklailov et al. [7, 8] arrived at the conclusion that, when treated with ammonium fluorides (NH_4HF_2, NH_4F), metal oxides (Al_2O_3, Fe_2O_3) underwent "post-fluorination". At the same time, high degrees of fluorination of SiO_2, Al_2O_3, and Fe_2O_3 in those studies were achieved only when 108–140% stoichiometric amount of the fluorinating agent was taken [8, 9]. Menz [10] reported on possible repeated fluorination of oxofluorides as intermediates in thermal decomposition of ammonium fluoride complexes of zirconium.

Mel'nichenko et al. [6] described the so-called small ratio effect in break-down of zirconium concentrate with ammonium hydrogen difluoride, which consisted in acceleration of the process under NH_4HF_2 deficiency. This was suggested by the back titration data on the amount of ammonia evolved during fluorination. However, the rate of chemical reactions is known to increase with increasing concentration of the reactants. The yield of the product is typically increased by increasing the concentration of one of the reactants, i.e., by introducing a reagent excess. In breaking down mineral raw materials the knowledge of the reagent:concentrate ratio is essential for providing exhaustive fluorination and preventing raw material and reagent loss.

This study was aimed to elucidate how the amount of ammonium hydrogen difluoride affects breaking down of concentrates, in particular titaniferous concentrates, and determined the recovery of titanium compounds into the gas phase.

EXPERIMENTAL

The compositions of the concentrates used in the study are presented in Table 1. Fluorination was run with chemically pure-grade ammonium hydrogen difluoride in isothermal mode at 170°C without stirring the reaction mixture in two versions: in a tightly sealed Teflon beaker with a cover and an exhaust pipe [6] and in a platinum boat which was placed into a horizontal furnace vented with heated dry air. In the former case the evolved gas was absorbed with 0.1 N H_2SO_4, and this was followed by back titration with 0.1 N NaOH. In the latter case, the evolved vapor was absorbed with water, and the fluorine content was determined by titration with thorium nitrate in the presence of Alizarin Red S indicator [11]. The ammonium content was determined by the Kjeldahl method [12].

In the case of back titration the ammonium amount was calculated by the formula

$$W(NH_3) = \frac{E_{NH_3}\, a_a\, N_a\, (V_{alk.bl} - V_{alk})\, 100}{V_{alk.bl}\, 1000\, g}, \qquad (1)$$

where a_a is the H_2SO_4 aliquot; E_{NH3}, NH_3 equivalent;

Table 1. Composition of the concentrates (total)

Concentrate	Content, wt%									
	TiO_2	FeO	Fe_2O_3	SiO_2	$A1_2O_3$	CaO	MgO	MnO	ZrO_2	Na_2O
Ilmenite[a]	52.0	41.0 (total)		4.0	2.0	0.1	0.1	0.5	–	–
Zirconium		0.16 (total)		45.4	0.45				52.1	–
Titanium magnetite[b]	9.6	24.4	45.6	9.4	2.2	5.1	2.6	0.5	0.01	–
Rutile[c]	98.0	1.90 (total)		–	–	–	–	0.06	0.01	–
Sphene	36.3	2.50 (total)		30.1	1.4	28.0	0.7	0.06	–	0.7

[a] Contains P_2O_5, 0.2 %.
[b] The content of Co, Cr, Cu, Ni, V, and Zn elements is no greater than 0.3%.
[c] The content of Co, Cr, Cu, Ni, V, and Zn elements is no greater than 0.1%.

Table 2. Amounts of ammonium and fluoride formed in fluorination at different ilmenite concentrate:NH_4HF_2 ratios 100:100 (stoichiometric amount)

Feed composition, concentrate:NH_4HF_2, %	Determined, g-ion		NH_4^+: F^-
	NH_4^+	F	
100 : 50	0.009	0.009	1 : 1
100 : 100 (stoichiometric amount)	0.022	0.013	1.7 : 1
100 : 150	0.021	0.032	1 : 1.5

N_a, H_2SO_4 normality; V_{alk}, volume of alkali spent for titration; $V_{alk.bl}$, volume of alkali in blank experiment; and g, weighed portion of the feed.

The amount of unchanged concentrate was estimated from the weight of the residue from aqueous leaching of the fluorination products, followed by decantation of suspensions of aluminum, magnesium, and calcium salts poorly soluble in water. The X-ray phase analysis showed that the residue was comprised by unchanged particles of the initial concentrate. The weight proportion of the residue was expressed as per cent of the amount of the concentrate contained in the weighed portion of the fluorination product.

Thermal decomposition of the fluorinated concentrate was carried out in a horizontal furnace under controlled heating in an argon atmosphere. Argon was additionally dried by passing through concentrated sulfuric acid and silica gel and supplied at a rate of 1–1.2 l h^{-1}. The setup comprised a controlled-temperature furnace and high- and low-temperature condensers for trapping gaseous products. The titanium recovery α into the gas phase was determined by the formula

$$\alpha = \frac{m_{in}W(TiO_2)_{in} - m_{sl}W(TiO_2)_{sl}}{m_{in}W(TiO_2)_{in}}, \qquad (2)$$

where $m_{in}W(TiO_2)_{in}$ is the weight of TiO_2 in the initial weighed portion of the fluorinated concentrate before thermal decomposition, and $m_{sl}W(TiO_2)_{sl}$, weight of TiO_2 in the thermal decomposition slime (residue).

The weight proportion of titania in the initial fluorinat-ed concentrate and in the slime was determined colorimetrically [13].

The products were identified by X-ray phase analysis at the scanning rate of 4 deg min^{-1} (DRON-3, Cu_α radiation).

The titrimetric data obtained by back titration of ammonia evolved in fluorination of the ilmenite concentrate were analogous to the earlier reported data [6]: The process tended to decelerate with increasing amount of the fluorinating agent and to accelerate with decreasing NH_4HF_2 amount in the feed. Evidently, an error was inherent in the experimental technique. The weight of the weighed portion in calculational formula (1) is composed of variable amounts of two reactants with different compositions. An increase in the weight of one of them will undoubtedly lead to a smaller resulting value, and vice versa. Also, fluorination yields a multicomponent system, and the gas phase contains not only ammonia but also decomposition products of NH_4HF_2 and, in

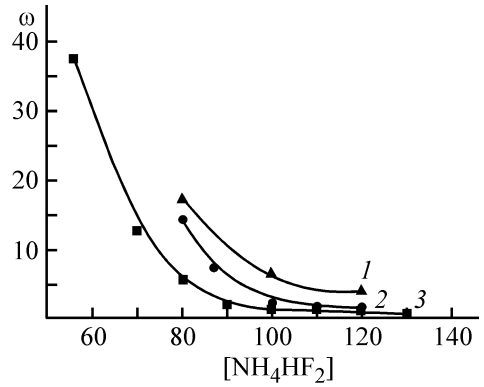
part, complex salts of the components of the concentrate. Formation of a deposit on the inner walls of the cover and the beaker nozzle suggests that decomposition actually takes place. The X-ray phase analysis showed that the deposit was essentially a mixture of NH_4HF_2, NH_4F, and $(NH_4)SiF_7$.

To elucidate how the amount of ammonium hydrogen difluoride affects breaking down of the concentrates, fluorination of the ilmenite concentrate was carried out in a special setup by a modified technique. In these experiments the vapor evolved during fluorination of ilmenite was absorbed with water; the condensate formed in the connecting pipes was washed off into a receiver, and the content of ammonium and fluoride in the combined solution was determined.

The experiments at 170°C showed that the total amounts of ammonia evolved during fluorination are nearly identical in cases when the reagent in the feed was taken in the stoichiometric amount and with a 50% excess, which is quite understandable (Table 2). However, the content of fluorine in the latter case was 2.5 times higher, which suggests decomposition of the unchanged excess reagent and appearance in the gas phase of HF vapor.

With a 50% deficiency of NH_4HF_2 in the feed, the amount of the evolved ammonia was approximately half that in the case of the stoichiometric amount or of a 50% excess. This is quite understandable, since fluorination involved only one half of the concentrate. The fluoride content in this case was 1.4 times lower. A decrease in the amount of the reagent in the feed is responsible for a decrease in the HF vapor concentration in the gas phase, which results in a weaker binding by hydrogen fluoride of ammonia evolved during fluorination. This resulted in enhanced recovery of ammonia into the gas phase and an illusory acceleration of the reaction. Hence, the amount of ammonia evolved during fluorination exhibits no anomalies.

The HF vapor reacted with ammonia and was condensed on cold walls of the reactor cover and nozzle as a NH_4F– NH_4HF_2 mixture. Indeed, the most abundant deposit was detected in the case when the reagent in the feed was taken in an excess, while with understoichiometric amount of NH_4HF_2 the amount of the deposit was negligible. Moreover, the evolved HF vapor could get into the receiver with sulfuric acid, which leads to incorrect estimate of the amount of the evolved ammonia by back titration with alkali. Special tests showed that the receiving flasks contained fluorine.



Amount of unchanged ilmenite concentrate ω, %, at 170°C vs. amount of reagent [NH_4HF_2], % of the stoichiometric amount. Fluorination time, h: (*1*) 1; (*2*); and (*3*) 7.

Thus, the experiment showed that the amount of the ammonia evolved during the reaction tends to decrease with decreasing amount of the fluorinating agent. In other words, a NH_4HF_2 deficiency in the feed leads to inexhaustive fluorination of the concentrate.

This conclusion was supported by the measured weights of the unchanged ilmenite concentrate for different amounts of ammonium hydrogen difluoride. The figure shows that, in fluorination with the stoichiometric amount of NH_4HF_2 for 7 h at 170°C, up to 1% concentrate does not enter in the reaction. With the amount of fluorinating agent decreased to 55% of the stoichiometric amount, this is true of ca. 36% concentrate. In commercial applications

Table 3. Recovery of titanium(IV) from ilmenite concentrate at different amounts of the fluorinating reagent NH_4HF_2

Amount of NH_4HF_2	Decomposition temperature, °C (argon, 1 h)	Recovery	
		calculated[a]	found
120	600	0.99	0.99
100	600	0.98	0.94
80	600	0.86	0.77
60	600	0.64	0.60
100	500	0.98	0.87
60	500	0.64	0.41
100	400	0.98	0.61
80	400	0.86	0.47

[a] Calculated for exhaustive decomposition of the fluorinated concentrate.

Table 4. Amount of the unchanged concentrate in relation to the amounts of reagent NH_4HF_2. Fluorination time 5 h

Amount of NH_4HF_2, % of the stoichiometric amount	Amount of unchanged concentrate, %			
	zirconium, 170°C	titanium-magnetite, 180°C	rutile, 160°C	sphene, 160°C
60	46.8	–	–	–
90	11.2	41.7	–	–
100	5.4	33.7	19.6	10.8
110	–	29.6	–	–
130	0.52	–	–	–

this would complicate the processing, entail additional expenses for repeated fluorination, and decrease the recovery of titanium compounds into the gas phase.

This was corroborated by the titanium(IV) recoveries from ilmenite concentrate, obtained with different amounts of the fluorinating reagent NH_4HF_2 (Table 3). The recovery of titanium(IV) compounds into the gas phase was monitored via determining the content of titanium(IV) in the residue from thermal decomposition. The ilmenite concentrate was fluorinated with different amounts of NH_4HF_2 under identical conditions.

Table 3 shows that the titanium recovery in the same temperature mode tends to decrease with decreasing amount of the fluorinating agent, which is associated with inexhaustive fluorination of the concentrate.

For the other concentrates examined the degree of fluorination varies with the amount of ammonium hydrogen difluoride in a similar manner (Table 4).

The theoretical recovery of titanium(IV) was calculated under the presumption of exhaustive decomposition of the resulting fluoro complex of titanium(IV). The titanium(IV) recovery calculated with the amount of nonfluorinated concentrate taken into account, i.e., without "post-fluorination", and the experimental data obtained at 600°C are fairly close. Hence, under the actual conditions at a small layer thickness, additional fluorination of ilmenite with the HF vapor evolved in decomposition of ammonium fluorometallates is negligible. An excess of reagent is required for exhaustive fluorination, but in decomposition of large amounts of concentrates additional fluorination cannot be excluded.

At 400 and 500°C the calculated and experimental recoveries of titanium(IV) are different because of a decrease in the temperature of the process and, hence, inexhaustive decomposition. Examination of the kinetic features of thermal decomposition showed that the titanium(IV) recovery is at a maximum at ≥600°C.

Excessive reagent typically complicates stirring of the feed whose viscosity can be decreased, and solidification, prevented, by introducing the reagent in portions, as it is consumed in the reaction.

The X-ray phase analysis suggests that, in thermal decomposition of ilmenite concentrate fluorinated with insufficient amount of NH_4HF_2, the slime contains a part of titanium, represented by off-stoichiometric compound $Fe_{0.5}Ti_{0.5}O_{1.5}F_{0.5}$. In a dry inert atmosphere in this case the titanium recovery into the gas phase is not increased. Oxofluoride with this composition was prepared by heating an α-Fe_2O_3, FeF_3, and TiO_2 mixture for 6 h at 700–950°C [14]. In fluorination with insufficient amount of the reagent the slime contains unchanged ilmenite which, when heated, apparently reacts with fluorometallates to form $Fe_{0.5}Ti_{0.5}O_{1.5}F_{0.5}$. When thermal decomposition of ilmenite concentrate fluorinated with the stoichiometric or excessive amount of the reagent is run in a dry argon atmosphere, the amount of $Fe_{0.5}Ti_{0.5}O_{1.5}F_{0.5}$ is negligible, which decreases the titanium loss.

CONCLUSIONS

(1) The degree of breaking down of titanium and zirconium concentrates was examined in relation to the amount of ammonium hydrogen difluoride. It was found that fluorination of titaniferous and zirconium concentrates should be run with at least stoichiometric amount of ammonium hydrogen difluoride (NH_4HF_2), which increases the degree of reaction when introduced in some excess (10–25%).

(2) Decomposition of the concentrate fluorinated with an NH_4HF_2 excess causes the titanium recovery into the gas phase to increase. It attains a maximum with the

reagent taken in a 10–25% excess with respect to the stoichiometric amount.

(3) Fluorination of the concentrate with understoichiometric amounts results in a titanium loss by binding into nonvolatile $Fe_{0.5}Ti_{0.5}O_{1.5}F_{0.5}$.

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