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The reaction of ammonium nitrate with pyrite

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Abstract

The reaction of ammonium nitrate with pyrite ore was studied using thermal analysis, qualitative and quantitative analyses of the reaction products, and combustion calorimetry. When the mixture of pyrite ore is heated in an argon atmosphere, an exothermic reaction takes place at about 190 °C. Reaction products when heated up to 300 °C are Fe_2O_3 and a small amount of $(NH_4)_2Fe(SO_4)_2$, and the main reaction is the oxidation of pyrite to Fe_2O_3 by ammonium nitrate as described by Eq. (4). The combustion reaction is somewhat different from the above thermal reaction. The combustion residue contained Fe_2O_3, Fe_3O_4 and $(NH_4)Fe(SO_4)_2$ as reaction products, and the overall combustion reaction for the equivalent mixture with regard to Eq. (3) is described by Eq. (5). Ammonium nitrate also reacts with pyrite ore at a relatively low temperature, even near room temperature. During long-term storage at around room temperature, the oxidation of pyrite proceeds gradually and $(NH_4)_3Fe(SO_4)_3$ is recognized as a reaction product.

1. Introduction

The reaction of pyrite ore and ANFO (Ammonium nitrate fuel oil explosive) has been studied in detail by many researchers. For example, Forshey et al. [1] studied the reaction of ANFO with pyrite ore and Miron et al. [2] studied the reaction of aluminized ANFO with pyrite ore. Miron et al. [3, 4] also studied the effect of weathering products and inhibitors on the reactivity of ANFO with pyrite ore. While an enormous amount of experimental results exist, there are few detailed descriptions about the reaction products, the reaction equation and the reaction process.

In this report, the reaction of ammonium nitrate (NH_4NO_3, AN) with pyrite ore (FeS_2) was studied mainly by thermal analysis, combustion calorimetry

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and chemical or instrumental analysis of the reaction products which were obtained under flowing argon gas by using a fixed-bed flow reactor in order to eliminate the heat of reaction. From the obtained results, the reaction products and reaction equation are described for the reaction at elevated temperature, the combustion reaction and the reaction at a relatively low temperature.

2. Experimental

2.1. Materials

Pyrite type iron disulfide was obtained from Yanahara Mine in Okayama Prefecture Japan. It contained 43.3 wt% iron and 49.9 wt% sulfur. After pulverization, pyrite was mixed with powdered ammonium nitrate in a dry box.

2.2. Analysis

Iron in pyrite ore and the ferric ion were analyzed by absorptiometry after dissolution in a hydrochloric acid solution and coloring with orthophenantororin.

Water-soluble ammonium, nitrate and sulfate ions in the reaction residue were analyzed by ion chromatography.

Water was determined by gravimetric analysis after being absorbed on silica gel. Unreacted ammonium nitrate and ammonium sulfate were determined by the analysis of NH_4^+, Fe^{3+} and NO_3^- ions. SO_2, N_2, O_2 and H_2 were not directly determined, but calculated from material balances of the reaction species.

Qualitative and quantitative analysis of iron oxide and unreacted pyrite were performed using common X-ray powder diffraction.

2.3. Apparatus and procedure

The thermal analysis was carried out under the conditions of a 5 mg sample weight, a heating rate of 20 °C/min and an argon gas flowing atmosphere using a Rigaku "Simultaneous DTA–TG analyzer".

The mixtures of ammonium nitrate with powdered pyrite were heated at a rate of 2 °C/min in a fixed-bed flow reactor with an argon gas stream. Reaction products were analyzed after being removed from the reactor and quenched.

A "Shimadzu Autocalculating Bomb Calorimeter" was used to measure the heat of combustion for 1 g sample in an argon gas atmosphere and combustion products were also analyzed by the same method described previously.

3. Results and discussion

3.1. The thermal reaction of ammonium nitrate with pyrite at elevated temperature

DTA and TG curves of pyrite, ammonium nitrate and their mixture (FeS_2/AN = 2/11 by weight) are shown in Fig. 1. Pyrite is oxidized in air in the

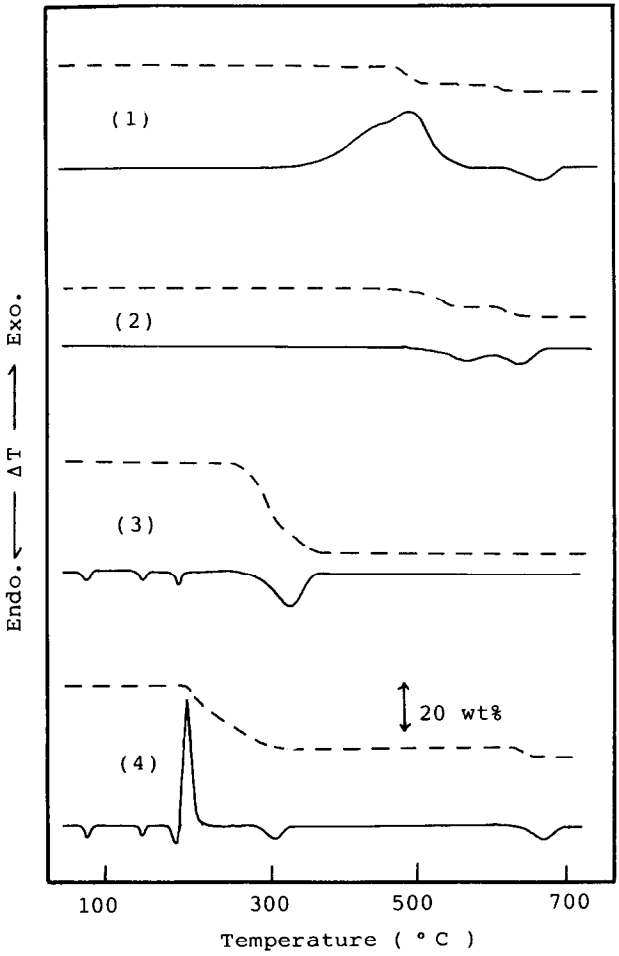

Fig. 1. Thermal analysis of pyrite, ammonium nitrate and their mixture: (1) pyrite in air, (2) pyrite in argon, (3) ammonium nitrate in argon, (4) the mixture containing pyrite and ammonium nitrate (molar ratio of 2:11) in argon. (------) TG, (——) DTA.

temperature range of 300–560 °C with a weight decrease of about 31%. In an argon atmosphere, it decomposes to ferrous sulfide (FeS) with a decrease of 21% in weight. Upon heating under a normal pressure of argon, ammonium nitrate begins to evaporate immediately after the melting accompanying the thermal decomposition.

The mixture of ammonium nitrate with pyrite reacts exothermally at 190–220 °C. However, pyrite and ammonium nitrate in the mixture do not thoroughly react. Namely, the unreacted ammonium nitrate begins to evaporate and decomposes above this temperature. Unreacted pyrite, on the other hand, decomposes to ferrous sulfide above 650 °C.

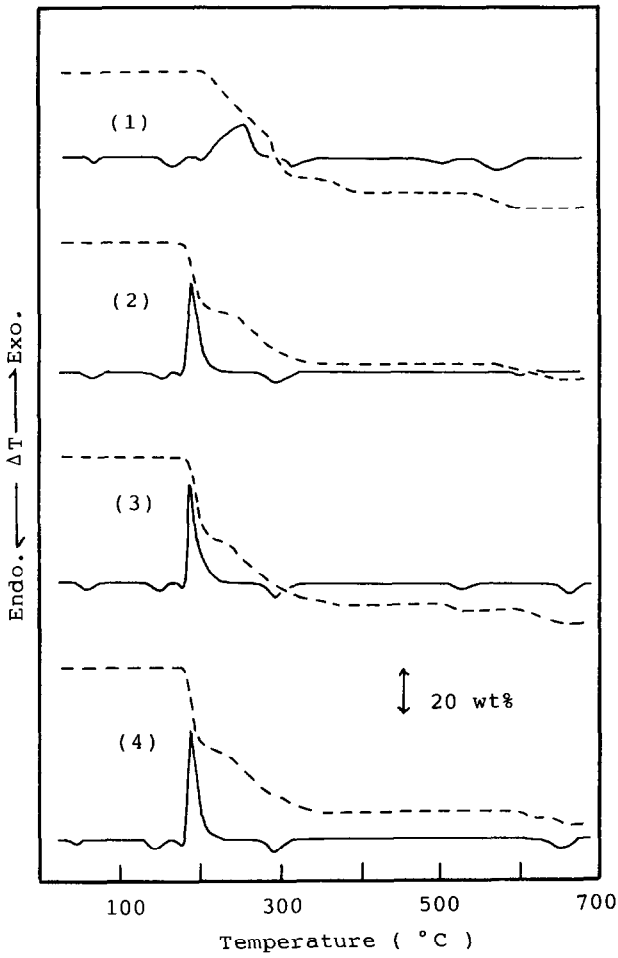

Fig. 2. Effect of particle size of pyrite on the thermal reaction of the mixture containing pyrite and ammonium nitrate (molar ratio of 2:11). (——) DTA, (-----) TG. (1) 149–297 μm, (2) 74–149 μm, (3) 44–74 μm, (4) under 44 μm.

3.2. Factors which have some effect on the thermal reaction of ammonium nitrate with pyrite

Kinetics of the thermal reaction of ammonium nitrate with pyrite, which proceeds heterogeneously, is markedly affected by some factors such as particle size, mixing ratio, atmospheric conditions, additives, and so on. Figure 2 shows the effect of pyrite particle size on the thermal reaction of ammonium nitrate with pyrite. The mixture which contains a small particle size pyrite shows a low reaction temperature and large heat release. This suggests that a diffusion process through a product layer on pyrite is the rate determining step for its oxidation by ammonium nitrate.

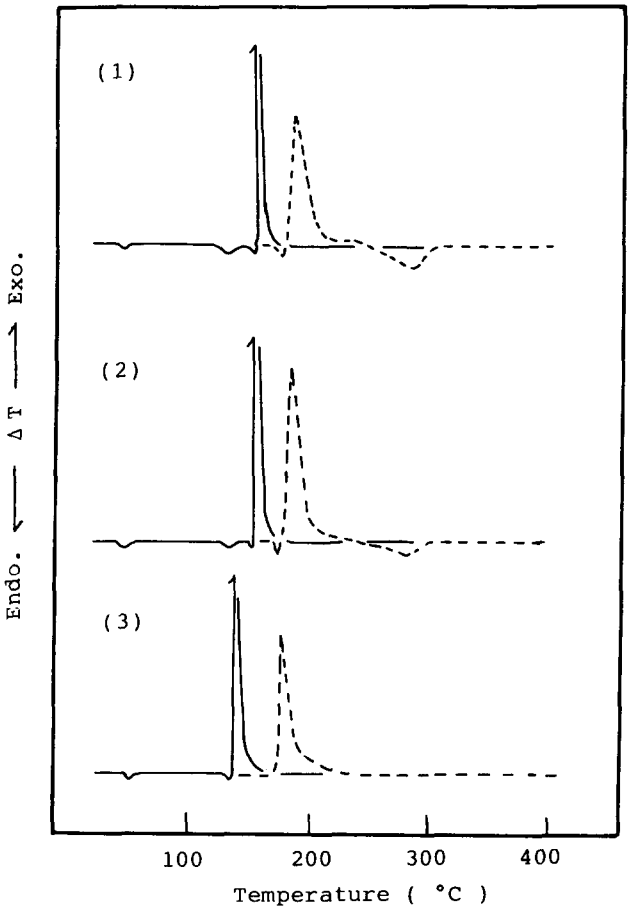

Fig. 3. Effect of pressure and composition on the thermal reaction of the mixture containing pyrite and ammonium nitrate. Composition: (1) pyrite:ammonium nitrate is equal to 2:20 (molar ratio), (2) 2:11, (3) equimolar mixture. Pressure: (------) 0 kgf/cm^2, (——) 50 kgf/cm^2 (gauge).

In Fig. 3, the pressure effects in the thermal reaction are shown for mixtures of various compositions. For each pressure, the reaction temperature changed with the composition, and the larger the content of pyrite in the mixture, the lower the reaction temperature. With regard to pressure effects, high pressure means a high reactivity. This is because the sublimation or evaporation of ammonium nitrate is suppressed under a pressurized condition.

In order to examine the moisture effect, the thermal analyses of the mixtures which contained water were performed. Figure 4 shows the DTA traces of the mixtures containing different amounts of water under the pressurized

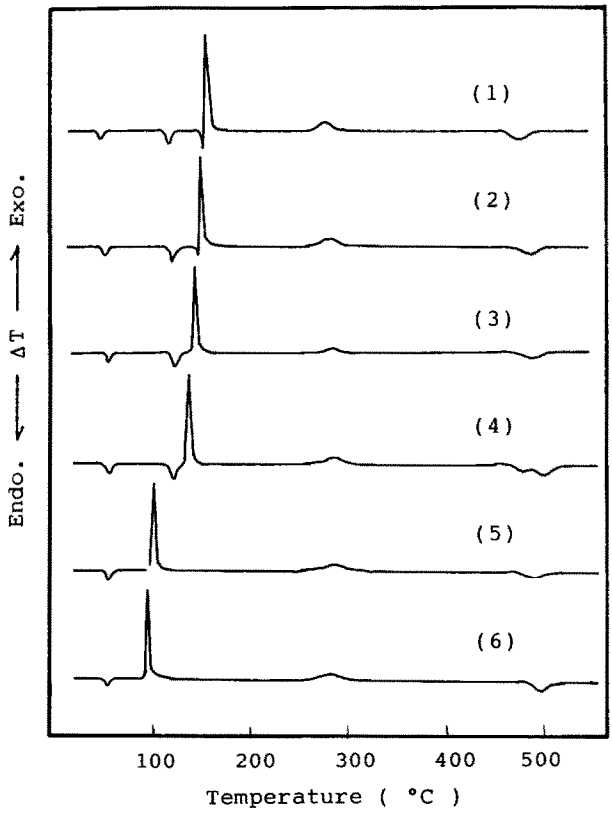

Fig. 4. Effect of moisture on the reactivity of the mixture containing pyrite and ammonium nitrate. Water content: (1) dried mixture, (2) 0.66 wt%, (3) 1.28, (4) 2.57, (5) 5.77, (6) 7.84.

condition of 20 kg/cm^2 of argon. Under the pressurized condition, water-containing mixtures show an exothermic reaction at temperature below 100 °C.

The additive effect on the thermal reaction of the mixtures of ammonium nitrate with pyrite is shown in Fig. 5. Urea, calcium carbonate and magnesium oxide are found to inhibit this reaction. Preliminary experiments, which were carried out for the mixtures of ammonium nitrate with these additives, showed the inhibiting effect of these additives on the thermal decomposition of ammonium nitrate.

3.3. Reaction equation of the thermal reaction of ammonium nitrate with pyrite

The oxidation of pyrite ore by oxygen gas and the perfect decomposition of ammonium nitrate are described by Eqs. (1) and (2):

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2, \quad (1)$$

$$2NH_4NO_3 \rightarrow 4H_2O + 2N_2 + O_2. \quad (2)$$

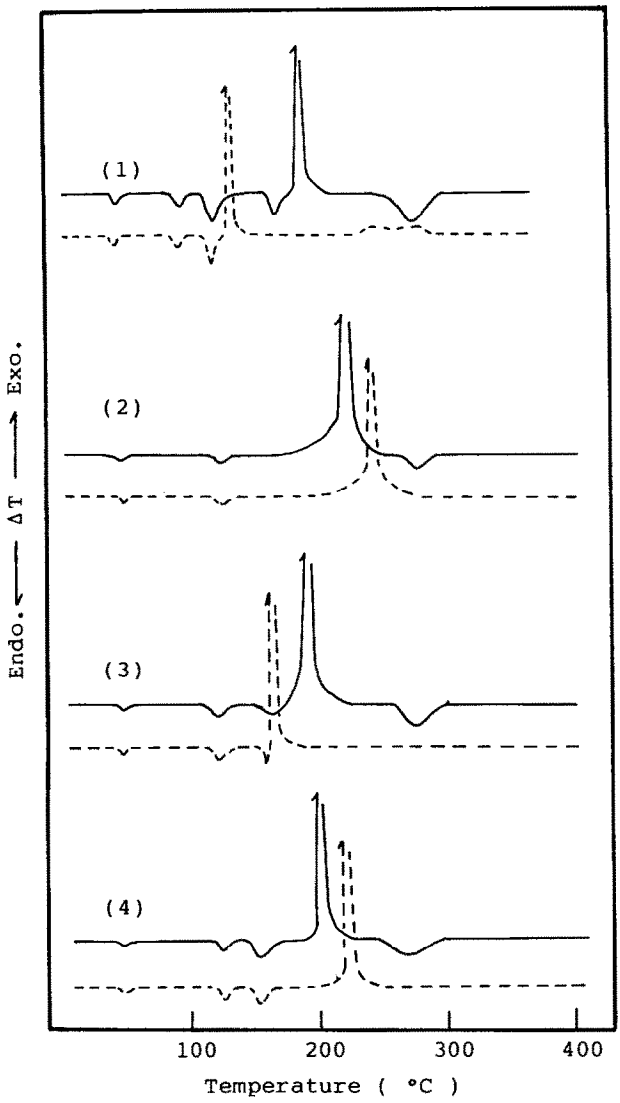

Fig. 5. Effect of additives on the reactivity of the mixtures containing pyrite and ammonium nitrate. Additive: (1) without additive, (2) urea, (3) calcium carbonate, (4) magnesium oxide. (——) under 0 kgf/cm^2 (gauge) of argon, (------) under 50 kgf/cm^2 (gauge) of argon.

The oxidation reaction of pyrite by ammonium nitrate based on Eqs. (1) and (2) is described below.

$$2FeS_2 + 11NH_4NO_3 \rightarrow Fe_2O_3 + 4SO_2 + 11N_2 + 22H_2O \quad (3)$$

From the qualitative and quantitative analyses, the reaction residue for the mixture of pyrite and ammonium nitrate of 2:11 molar ratio (the equivalent

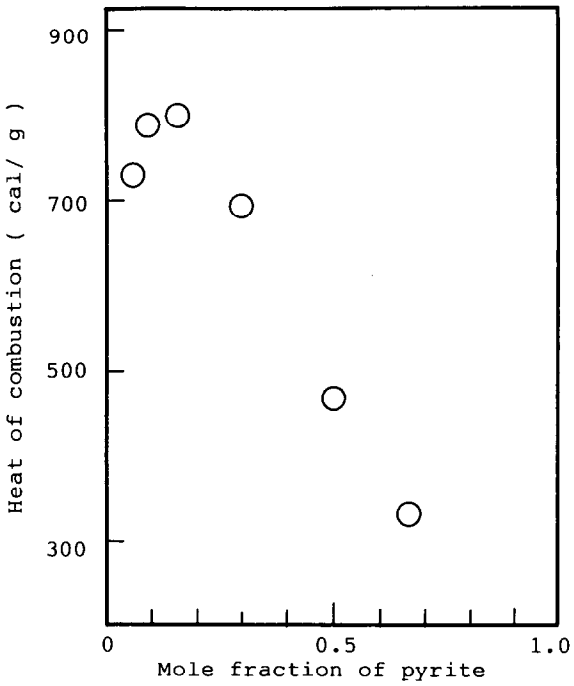

Fig. 6. Heat of combustion of the mixture containing pyrite and ammonium nitrate.

mixture according to Eq. (3)) upon heating to 300 °C contained Fe_2O_3, the water-soluble ferriferrous compound and $(NH_4)_2SO_4$, and a small amount of unreacted pyrite and NH_4NO_3. In order to confirm the soluble ferriferrous compound species, the reaction residue was separated into water-soluble and insoluble parts by adding purified water and filtering. The filtrate of the reaction residue contained ammonium ions, sulfate ions and iron ions. The molar ratio ammonium ions:iron ions:sulfate ion, other than ammonium nitrate and ammonium sulfate, is 1.07:1.00:2.13, and from these results a dissolved product is deduced as $(NH_4)Fe(SO_4)_2$. From the quantitative analysis of iron, 55% initial pyrite was converted to Fe_2O_3 and this indicates that Eq. (3) is the main reaction of the oxidation. In addition, 44% is determined as $(NH_4)Fe(SO_4)_2$ and 1% remained unreacted. According to these results, the following reaction which contains Eq. (3) as a main reaction is considered to take place in the course of the exothermic reaction up to 300 °C:

$$2FeS_2 + 11NH_4NO_3 \rightarrow 0.55\,Fe_2O_3 + 0.88\,(NH_4)Fe(SO_4)_2 + 2.02SO_2 + 19.25\,H_2O$$
$$+ 0.02\,FeS_2 + 0.10\,NH_4NO_3 + 0.18(NH_4)_2SO_4$$
$$+ 10.28\,N_2 + 0.43\,H_2 \qquad (4)$$

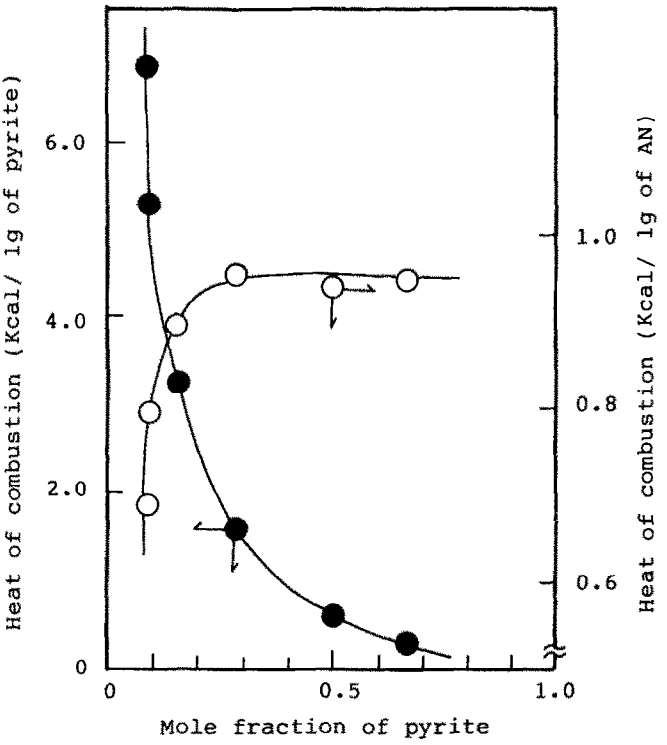

Fig. 7. Effect of composition on heat of combustion of the mixture containing pyrite and ammonium nitrate.

Weight loss from Eq. (4) for the mixtures of pyrite and ammonium nitrate (molor ratio 2:11) are calculated as 50.0 wt%. On the other hand, observed weight loss was 53.2 wt% from TG in Fig. 1 and corresponds well to Eq. (4) as the overall reaction.

3.4. Combustion of the pyrite and ammonium nitrate mixture

Figure 6 shows the heat of reaction for the various compositions of pyrite and ammonium nitrate determined by combustion calorimetry. The heat of combustion per 1 g pyrite and that of 1 g ammonium nitrate in Fig. 7 show an imperfect oxidation of pyrite and sufficient reaction of the ammonium nitrate. These results suggest that the rate-determining step of the combustion reaction is the oxidation step of pyrite.

Qualitative and quantitative analyses of the combustion product were carried out and the combustion residue contained Fe_2O_3, Fe_3O_4, $NH_4Fe(SO_4)_2$, $(NH_4)_2SO_4$, and unreacted FeS_2 and NH_4NO_3. The observed water in the combustion products amounted to 20.40 mol per 2.00 mol of pyrite for the mixture of pyrite and ammonium nitrate in a molar ratio 2:11. From

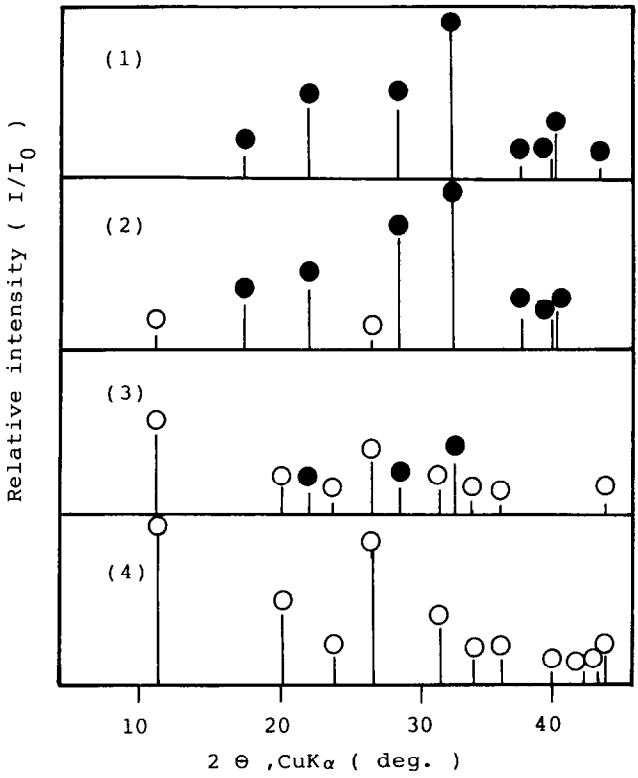

Fig. 8. X-ray diffraction patterns of the reaction product of the mixture containing pyrite and ammonium nitrate at room temperature. Composition (molar ratio of pyrite/AN) and intensity: (1) 2/20, 8000 CPS, (2) 2/15, 8000 CPS, (3) 2/7, 1000 CPS, (4) equimolar mixture, 1000 CPS. (●) ammonium nitrate, (○) $(NH_4)_3Fe(SO_4)_3$.

these results, we can conclude that the net combustion reaction is represented by Eq. (5):

$$2FeS_2 + 11NH_4NO_3 \rightarrow 0.13Fe_2O_3 + 0.31Fe_3O_4 + 0.61(NH_4)Fe(SO_4)_2 + 2.30SO_2 + 20.40H_2O + 0.20FeS_2 + 0.03NH_4NO_3 + 0.08(NH_4)_2SO_4 + 10.59N_2 + 0.54O_2 \quad (5)$$

3.5. The reaction of ammonium nitrate with pyrite at low temperature

In Fig. 4, it was stated that the thermal reaction of ammonium nitrate with pyrite was greatly accelerated by moisture. This indicates that there exists a low-temperature reaction of ammonium nitrate with pyrite along with the participation of water. When the mixtures of ammonium nitrate with pyrite are stored for 3 days under a relative humidity of 70% at room temperature, an yellowish product forms. The X-ray powder diffraction of this product after drying shows the existence of $(NH_4)_3Fe(SO_4)_3$ (see Fig. 8). The reaction

product for the equimolar mixture was separated into water-soluble and insoluble parts by adding purified water and then filtering. The filtrate of the reaction products contained NH_4^+, Fe^{3+}, SO_4^{2-} and NO_3^-. After subtracting the amount of unreacted NH_4NO_3, the molar ratio $NH_4^+ : Fe^{3+} : SO_4^{2-}$ is 2.70:1.00:3.00, which corresponds well to the formation of $(NH_4)_3Fe(SO_4)_3$.

4. Conclusions

An exothermic reaction takes place when heating a mixture of ammonium nitrate with pyrite at about 190 °C. This reaction is affected by the particle size of the pyrite, the composition of the mixture, water, additives and atmospheric pressure.

The reaction residue when heating up to 300 °C contained Fe_2O_3 and a small amount of $(NH_4)Fe(SO_4)_2$, ammonium nitrate and ammonium sulfate. The overall reaction is described by Eq. (4).

Combustion residue for the mixture (pyrite and ammonium nitrate in the molar ratio of 2:11) contained Fe_2O_3, Fe_3O_4, $NH_4Fe(SO_4)_2$, and unreacted pyrite and NH_4NO_3. The combustion reaction is described by Eq. (5).

Under the conditions of high humidity, the mixture of ammonium nitrate with pyrite can react even at room temperature to form $(NH_4)_3Fe(SO_4)_3$.

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