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Reaction of Ammonium Chloride with the Copper(II) Sulfide and Oxide, and Identification of the Reaction Products

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Abstract—The processes and products of the reaction of copper(II) sulfide and oxide with ammonium chloride were studied. The process of the copper(II) compounds hydrochlorination was investigated with thermogravimetry and kinetic studies. Reaction products were studied by infrared spectroscopy and X-ray phase analysis.

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It is known that from aqueous solutions containing copper and ammonium chlorides ammonium chlorocuprates $(NH_4)_2CuCl_4$ and $(NH_4)_3CuCl_5$ can be obtained. Ammonium chloride reacts with metal oxides to form the corresponding chlorides [1]. In the reaction of copper oxide with ammonium chloride products are formed with physical and chemical parameters different from those of copper chloride [2, 3]. It was suggested that in the reaction of copper oxide with ammonium chloride ammonium chlorocuprates were formed.

The purpose of this work was to establish the mechanism of the reaction of copper oxide and sulfide with ammonium chloride and to identify the reaction products.

According to thermal analysis (Fig. 1) the process of hydrochlorination of the copper(II) compounds begins at 190ºC to form ammonium chlorocuprates, $(NH_4)_2CuCl_4$ in with copper oxide and NH_4CuCl_3 with copper sulfide, which at the temperature higher than 300ºC decompose affording $CuCl_2$ and then hydrolysis proceeds with water vapor to give copper(II) oxide.

The analysis of the differential scanning calorimetry (DSC) curves showed that the endothermic effect of dissociation of ammonium chloride is superimposed with the exothermic effect (190ºC) of the

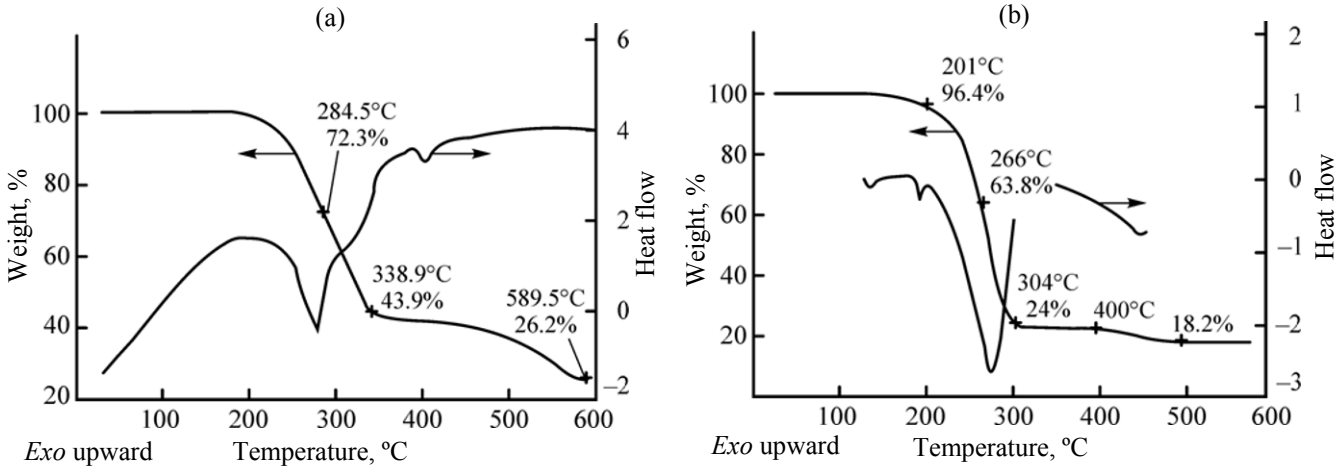

Fig. 1. Thermogravimetric analysis of the interaction of ammonium chloride with: (a) copper(II) oxide and (b) copper(II) sulfide.

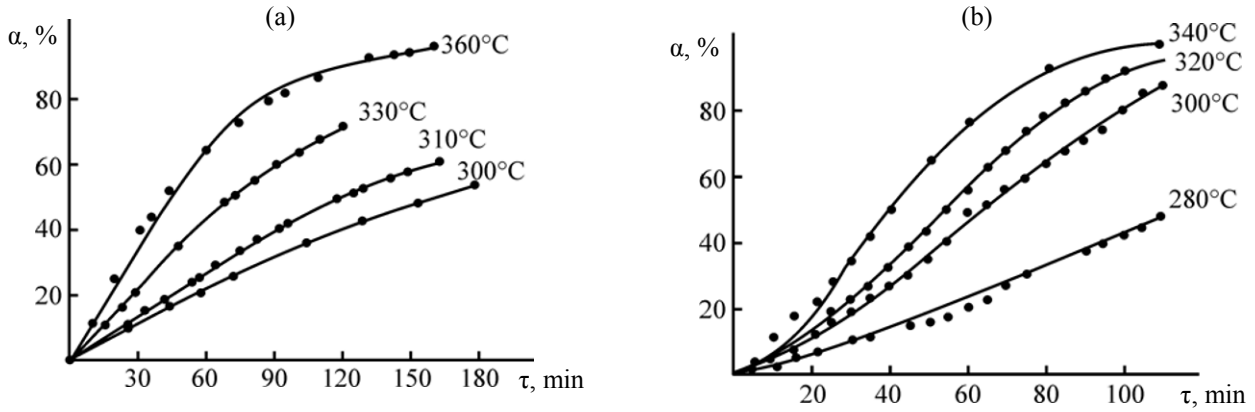

Fig. 2. The plots of the degree of conversion in time for the process of chlorination of (a) copper(II) oxide and (b) copper(II) sulfide.

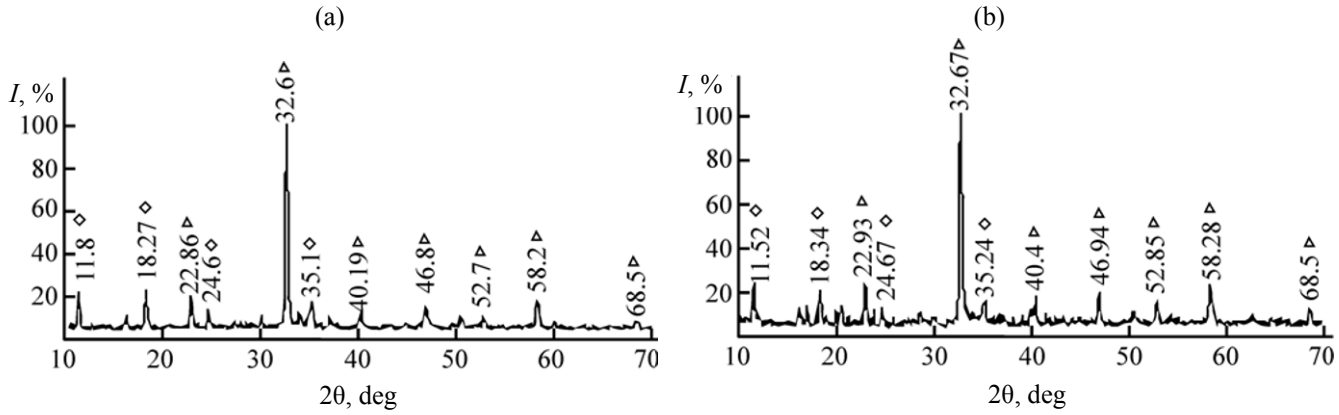

Fig. 3. Radiographs of the reaction products of ammonium chloride with: (a) copper(II) oxide and (b) copper(II) sulfide. (Rhombs) $(NH_4)_2CuCl_4$, (triangles) NH_4Cl.

chlorination of copper compounds, which is followed by the *endo* effect of removal of the reaction products. The whole process takes place with the heat consumption.

The sequence of reactions of the copper compounds chlorination with ammonium chloride can be represented as follows:

$$CuO + NH_4Cl \xrightarrow[-H_2O]{200^\circ C} (NH_4)_2CuCl_4 \xrightarrow[-NH_3,\ HCl]{340^\circ C} CuCl_2,$$

$$CuS + NH_4Cl \xrightarrow[-H_2S]{200^\circ C} NH_4CuCl_3 \xrightarrow[-NH_3,\ HCl]{300^\circ C} CuCl_2.$$

Mathematical treatment of kinetic data (Fig. 2) of the interaction of copper compounds with ammonium chloride was carried out using three equations: Gistling's, shrinking sphere, and Jander's. Experiental data of the processes are consistent with the equation of shrinking sphere. The following dependences of the degree of conversion (α) on time (τ) and temperature (*T*) for the interaction of ammonium chloride with copper oxide and sulfide were deduced:

with copper oxide

$$\alpha = 1 - \left(1 - 1.59e^{-\frac{51900}{8.31T}}\tau\right)^3, \quad (1)$$

with copper sulfide

$$\alpha = 1 - \left(1 - 0.0004e^{-\frac{9900}{8.31T}}\tau\right)^3. \quad (2)$$

The activation energy of the CuO chlorination is 51.9 kJ mol^{-1}, the limiting stage of the process is the kinetics of the chemical reaction, the way of accelerating the processes is the increase in the temperature. The activation energy of the interaction of copper sulfide with ammonium chloride was 9.9 kJ mol^{-1}. Rate-limiting step of the process is diffusion, to increase the reaction rate of chlorination the reaction mixture should be stirred vigorously.

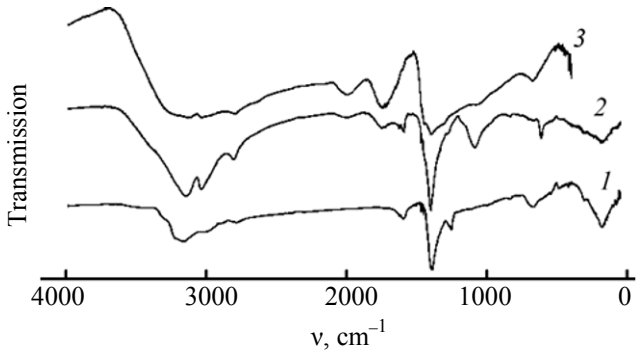

Fig. 4. IR spectra of (*3*) ammonium chloride and the products of its reaction (*2*) with the copper(II) oxide **I** and (*1*) sulfide **II**.

Chemical analysis of the products of NH_4Cl reaction with CuO (**I**) and CuS (**II**) showed the compositions of **I** $CuCl_2 \cdot 3.11\ NH_4Cl$, of **II** $CuCl_2 \cdot 5.43\ NH_4Cl$. At the synthesis temperature 320°C compound **I** is fluid, and **II** is a solid.

Compound	**I**	**II**
Formula	$CuCl_2 \cdot 3.11\ NH_4Cl$	$CuCl_2 \cdot 5.43\ NH_4Cl$
Content, %:		
Cu	21.23	24.50
Cl	60.19	58.95
NH_4	18.58	16.55

According to X-ray phase analysis (Fig. 3), the main component of both the products is ammonium tetrachlorocuprate, and there are the peaks of ammonium chloride. The background signal is weak, indicating a high degree of crystallinity of the products obtained.

In the IR spectra of products **I**, **II** and NH_4Cl (Fig. 4) there are the bands in the region of 4000–400 cm^{-1} characteristic for the ammonium ion, at 669, 2800, 3000 cm^{-1}, and 3100–3300 cm^{-1}, of same shape for all three substances. Common for them peak at 1400 cm^{-1} is split and broaden due to the deformation of the ammonium ion in NH_4Cl by the chloride ion. In the chloroammoniun copper complexes the ammonium ion is associated with a large complex ion $CuCl_4^{2-}$ and therefore is less deformed, that results in a narrow and sharp peak at 1420 cm^{-1}. The spectra of both products contain a weak peak at 1612 cm^{-1} characteristic of ammonia in the ammoniacate complexes. In the spectra of the reaction products of ammonium chloride with copper(II) oxide and sulfide in the region of 400–50 cm^{-1} there are the peaks at 295 and 170–110 cm^{-1} characteristic of the tetrahedral ion $CuCl_4^{2-}$ [4].

Based on the results of chemical analysis, X-ray diffraction and IR spectroscopy, we can argue that the reaction of ammonium chloride with the copper(II) oxide and sulfide in the temperature range 200–300ºC affords $(NH_4)_2CuCl_4$, which at further heating decomposes to $CuCl_2$.

EXPERIMENTAL

Thermogravimetric (TGA) analysis and differential scanning calorimetry (DSC) were carried out on a combined TGA/DSC/ DTA analyzer TA instruments Universal V4.2E SDT Q600 with programmed data treatment, the balance sensitivity 0.1 μg. Heating rate 5 deg min^{-1}. For the analysis were used mixtures of 12.5 mg of CuO with 42.7 mg of NH_4Cl or 9.0 mg of CuS with 40.0 mg NH_4Cl [4].

The kinetic experiment was performed by continuous weighing the reacting mixture with automatic weight registration. The degree of conversion was determined from the mass loss due to the formation of gaseous compounds. Preliminary the rate of decomposition of ammonium chloride at the same temperatures was experimentally determined, and the corresponding corrections were added to the final results. The temperature was maintained with the accuracy within 2ºC [5].

Chloride ion content was determined by titration with standardized $AgNO_3$ solution in the presence of $KCrO_4$ as the indicator. The copper content in the compounds was determined colorimetrically. The content of ammonium ion was determined photometrically by the absorption of its colored complex with the Nessler reagent.

The IR spectra were recorded in a nitrogen flow on a NICOLET 6700 Fourier spectrometer of Thermo Electron Corporation in the wavenumber range 50–4000 cm^{-1}, the allowable error of the wave numbers scale ±0.5 cm^{-1}. For the region 4000–400 cm^{-1} the samples were prepared by compression of tablets, the ratio of test substance:KBr is 1:300. For the measurements in the region of 400–50 cm^{-1} mineral oil was used [6].

The X-ray diffraction analysis was performed on a DRON-3M instrument with a copper anticathode. Conditions of the measuing: $I = 25$ A, $V = 35$ kV.

Compound I. A mixture of copper oxide, 6.67 g, and ammonium chloride, 17.61 g, was calcined at a temperature of 320ºC for 12 h.

Compound II. Prepared similarly from 5.46 g of copper sulfide and 18.04 g of ammonium chloride at a temperature of 320ºC for 12 h.

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