Reaction of \([\text{Pt(NH}_3\text{)}_4]\text{Cl}_2\cdot\text{H}_2\text{O} \text{ and NH}_4\text{ReO}_4 \text{ in Alkaline Aqueous Solution at 190°C (under Pressure)}\)

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Abstract—Reactions of thermolysis under pressure of tetraammineplatinum(II) chloride and ammonium perrhenate in alkaline aqueous solution were studied. The products formed at the thermolysis in a pressure reactor were investigated. A model of platinum and rhenium ions reduction to metallic state by inner sphere ammonia from \([\text{Pt(NH}_3\text{)}_4]\text{Cl}_2\) is suggested.

The results obtained in the chemical reactions of ammonium–chloride complexes of noble metals in aqueous alkaline solution at elevated temperature (above 100°C) gave rise to development of the method of thermolysis under pressure of metallic systems (powders, sols, coatings on various materials) that found application, e.g., for producing catalysts [1–4].

The method is based on the irreversible reduction of the complexing metal ion by the inner sphere ammonia with liberation of the metal [5].

\[
\text{[M(NH}_3\text{)}_4\text{Cl}_2\text{]}^{\text{2+}} + 2\text{OH}^- \rightarrow \text{M}^0 + 1/3\text{N}_2 + (10/3-i)\text{NH}_3 + i\text{Cl}^- + 2\text{H}_2\text{O}, \quad (1)
\]

\[
\text{M} = \text{Pt, Pd, Rh, Ir, Ru, Co, Ni, Cu, and others.}
\]

Heating of solid ammonia compounds also leads to formation of metal as a result of solid phase thermolysis [6, 7]. Thus certain analogy can be traced between the processes of autoclave and solid phase thermolysis of ammonia complexes. The products of autoclave thermolysis of the complex ammoniates containing different metals are polynmetallic solid precipitates. A series of investigations [8, 9] has been carried out on solid phase thermal transformations of double salts with complex cations and anions containing different metals, and the corresponding metallic phases were obtained.

In this work we present results of the study of reaction of \([\text{Pt(NH}_3\text{)}_4]\text{Cl}_2\cdot\text{H}_2\text{O} \text{ with NH}_4\text{ReO}_4 \text{ in alkaline medium at heating in autoclave at 190°C. We presumed that by analogy with the reaction (1) the ammonia “in statu nascendi” as well as Pt}^{\text{2+}} \text{can behave as reducing agents for rhenium.}

The results listed in Table 1 show that the solid product contains two phases, metallic platinum and rhenium.

The established fact of formation of platinum and rhenium in metallic state at the reaction of \([\text{Pt(NH}_3\text{)}_4]\text{Cl}_2\cdot\text{H}_2\text{O} \text{ and NH}_4\text{ReO}_4 \text{ allows to suggest the following equation for this reaction:}

\[
3[\text{Pt(NH}_3\text{)}_4]\text{Cl}_2 + 6\text{NH}_4\text{ReO}_4 + 6\text{KOH} \rightarrow 3\text{Pt}^0 + 6\text{Re}^0 + 8\text{N}_2 \uparrow + 2\text{NH}_3 \uparrow + 6\text{KCl} + 30\text{H}_2\text{O}. \quad (2)
\]

To prove the stoichiometry of this reaction we carried out experiments on quantitative determination of liberated ammonia. The results of typical experiments are listed in Table 2.

The experiments 1–4 were carried out at an excess of tetraammineplatinum(II) chloride with respect to the calculation accounting for stoichiometry in keeping with Eq. (2). For these experiments the theoretical amount of free amminia was calculated as a sum of two values: that based on Eq. (2) assuming a complete consumption of rhenium salt, and based on Eq. (1) corresponding to the consumption of excess tetraammineplatinum(II). In exp. no. 5 the ratio of platinum and rhenium was taken according to the stoichiometry of Eq. (2). The data in Table 2 show good consistence of experimental values and theoretical amounts of free

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ammonia. Thus, reaction of salts in autoclave conditions proceeds according to Eq. (2).

The results of this work allow obtaining bimetallic platinum–rhenium systems without further reduction operations, e.g., by hydrogen, at the production of platinum–rhenium catalysts.

EXPERIMENTAL

In the work was used tetraammineplatinum(II) dichloride synthesized along the procedure in [10], commercial ammonium perrhenate, and KOH of "chemically pure" grade.

The experiments were carried out in fluoroplastic autoclaves by the procedures described in [1–7]. The weighed samples of [Pt(NH₃)₄]Cl₂·H₂O and NH₄ReO₄ were added to a solution of potassium hydroxide of required concentration, and the mixture was then saturated with nitrogen to avoid side reactions with air oxygen. The autoclave with alkaline solution of mixture of [Pt(NH₃)₄]Cl₂·H₂O and NH₄ReO₄ was sealed and kept at temperature 190°С for 150 min with stirring. After that the autoclave was rapidly cooled to room temperature, and the solution within was frozen for minimization of loss of free ammonia by the system. The content of ammonia after reactions was measured by the method of acid-base titration along the procedure in [11]. Analysis was carried out according to following sequence. The autoclave with frozen at –15°С solution was placed to a tubular furnace equipped with reflux microcondenser and receiver containing 0.1 N solution of hydrochloric acid. The autoclave was heated to 130–150°С, and ammonia was distilled off. The distillation was stopped when 2/3 by volume of liquid was passed to the receiver containing acid. The acid excess was titrated with potassium hydroxide solution (0.1 N) against methyl orange indicator. The mass of free ammonia in the system was calculated from the results of titration, and it was compared with the theoretical amount of ammonia calculated from the assumed reaction equation. Close theoretical and experimental mass values point to the reliability of the assumed stoichiometry of reaction of platinum and rhenium salts.

In the autoclave after opening a solid product of grey color with metallic luster was found. It was isolated from solution by filtration through a glass frit, washed with distilled water, and dried. Phase composition of the solid products obtained in the autoclave process was examined by the method of X-ray phase analysis (XRPA) on a DRON-2.0 diffractometer (FeKα-radiation, λα = 1.937 Å, Uα 20 kV, Iα 20 mA,