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Reaction of [Pd(NH₃)₄]Cl₂ with NH₄ReO₄ in Alkaline Water Solution at 190°C (Autoclave Process)

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Abstract—A reaction of tetraammine palladium(II) chloride with ammonium perrhenate in aqueous alkaline solution in the autoclave conditions was studied. The possible routes of the palladium and rhenium reduction with ammonia were suggested.

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The results of studies of chemical reactions of ammonia-chloride complexes of noble and nonferrous metals in water and alkaline solutions at elevated temperatures (above 100°C) gave rise to the development of a method of the autoclave thermolysis for the synthesis of metal systems (powders, sols, and the coatings of different materials) [1–4].

The process of autoclave thermolysis is based on an irreversible reduction of the complexing metal ion by its inner-sphere ammonia to afford the metal [5].

$$[M(NH_3)_{4-i}Cl_i]^{2-i} + 2 OH^{-}$$

$$\rightarrow M^0 + 1/3N_2 + (10/3-i)NH_3 + iCl^{-} + 2 H_2O, \qquad (1)$$

M = Pd, Pt, Rh, Ir, Ru, Co, Ni, Cu, etc.

The products of autoclave thermolysis of complex mixtures of different metal ammoniates are the solid polymetallic precipitates [6, 7]. Studies of solid-state thermal transformations of the double salts containing complex cations and anions of different metals performed in [8–10] resulted in obtaining metallic phases.

This paper presents the results of studying the reaction of $[Pd(NH_3)_4]Cl_2$ with NH_4ReO_4 in alkaline medium in the autoclave conditions at 190°C. We assumed that like the reaction (1), the ammonia in *statu nascendi*, as well as Pd^{2+} , may behave as reducing agents for rhenium.

The phase composition of the solid reaction product was determined by X-ray phase analysis. The results listed in Table 1 show that the solid product of the autoclave thermolysis of the mixture of $[Pd(NH_3)_4]Cl_2$ with NH₄ReO₄ contains three phases: palladium metal, rhenium metal, and rhenium dioxide.

Table 2 summarizes the experimental results of the determination of free ammonia and shows that its content in the system corresponds to 24–30% of the total value.

Based on product composition of this process, the following pathways of the oxidation–reduction reactions are presumable:

Reduction of rhenium

 $\begin{aligned} &\text{ReO}_4^- + 4\text{H}^+ + 3\overline{e} \rightarrow \text{ReO}_2 + 2 \text{ H}_2\text{O}, \\ &\text{ReO}_4^- + 8\text{H}^+ + 7\overline{e} \rightarrow \text{Re}^0 + 4 \text{ H}_2\text{O}. \end{aligned}$

Oxidation of ammonia

 $\begin{array}{c} 2 \operatorname{NH}_3 + 6\overline{e} \rightarrow \operatorname{N}_2 + 6\operatorname{H}^+, \\ \operatorname{NH}_3 + \operatorname{H}_2\operatorname{O} + 5\overline{e} \rightarrow \operatorname{NO} + 5\operatorname{H}^+, \\ \operatorname{NH}_3 + 2 \operatorname{H}_2\operatorname{O} + 7\overline{e} \rightarrow \operatorname{NO}_2 + 7\operatorname{H}^+. \end{array}$

Oxidation of ammonium

 $2 \operatorname{NH}_{4}^{+} + 6\overline{e} \rightarrow \operatorname{N}_{2} + 8\operatorname{H}^{+},$ $\operatorname{NH}_{4}^{+} + \operatorname{H}_{2}\operatorname{O} + 5\overline{e} \rightarrow \operatorname{NO} + 6\operatorname{H}^{+},$ $\operatorname{NH}_{4}^{+} + 2 \operatorname{H}_{2}\operatorname{O} + 7\overline{e} \rightarrow \operatorname{NO}_{2} + 8\operatorname{H}^{+}.$

These combined half-reactions can provide various modes of perrhenate ion reduction with ammonia, which differ by the products formed:

$$\begin{split} & \operatorname{NH_4ReO_4} \to \operatorname{NO_2} + \operatorname{Re} + 2\operatorname{H_2O}, \\ & 5\operatorname{NH_4ReO_4} \to 3\operatorname{NO} + 5\operatorname{ReO_2} + 7\operatorname{H_2O} + 2\operatorname{NH_3}, \\ & 2\operatorname{ReO_4} + 6\operatorname{NH_3} \to 2\operatorname{N_2} + \operatorname{ReO_2} + 6\operatorname{H_2O} + \operatorname{Re}. \end{split}$$

Reduction of palladium from its complex compounds with ammonia proceeds in an alkaline

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Pd phase				ReO ₂ phase				Re phase			
2θ, deg	I, %	d, Å (exp)	d, Å(ASTM)	20, deg	I, %	d, Å (exp)	d, Å(ASTM)	2θ, deg	I, %	d, Å (exp)	d, Å(ASTM)
40.25	100	2.238	2.23	26.3	40	3.386	3.401	37.1	30	2.421	2.388
46.7	50	1.943	1.94	31.4	80	2.846	2.865	40.25	30	2.238	2.226
68.4	30	1.37	1.371	46.7	50	1.943	1.946	42.7	100	2.116	2.105
82.3	30	1.17	1.17	53.0	30	1.726	1.701	68.4	20	1.37	1.38
86.8	10	1.121	1.12	76.4	20	1.245	1.262	76.4	20	1.245	1.262
				81.4	30	1.181	1.203	82.3	20	1.17	1.173

Table 1. X-ray characteristics of the solid autoclave thermolysis product of the [Pd(NH₃)₄]Cl₂-NH₄ReO₄ mixture

 Table 2. Experimental values of the initial amount of reactants (based on metal and ammonia) and free ammonia experimentally measured

Run no.	D 1	D -	Pd:Re	NHI .	Fre	e NH ₃	Assumed equation in Table 3	
	Pđ, g	Re, g	(atomic)	ΣNH ₃ , g	g	%		
1	0.057	0.1	1:1	0.0459	0.0140	30.5	4, 6	
2	0.057	0.1	1:1	0.0459	0.0113	24.6	The same	
3	0.057	0.1	1:1	0.0459	0.0121	26.4	"	
4	0.057	0.1	1:1	0.0459	0.0121	26.4	"	
5	0.057	0.066	1.5:1 (3:2)	0.0425	0.0090	21.2	5	
6	0.1	0.1	1.75:1	0.0728	0.019	26.1	(4), (6)	
7	0.1	0.1	1.75:1	0.0728	0.0224	30.8	The same	
8	0.1	0.1	1.75:1 (7:4)	0.0728	0.020	27.5	"	

medium in the autoclave conditions according to the equation:

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$$3[Pd(NH_3)_4] + 6KOH \rightarrow 3Pd + N_2 + 10NH_3 + 6H_2O + 6KCl.$$

The fact that the reaction products are palladium and rhenium metals, and rhenium dioxide, suggest many versions of equation for the processes of reduction of the $[Pd(NH_3)_4]Cl_2-NH_4ReO_4$ mixture in alkaline medium in the autoclave conditions. The most plausible, as we believe, are the equations listed in Table 3. Table 3 shows also the atomic ratio of metals, the total number of ammonia molecules before the reaction, the number of molecules of free ammonia and its percentage with respect to the total number of molecules in the corresponding reaction.

As seen from the data of Table 3 the hypotheses described by Eqs. (4)–(6) match the experimental data

the most closely, as the amount of free ammonia (%) agrees well with experimental data obtained after titration of free ammonia (Table 2).

Comparing the data in Tables 1–3, we assume that two probable reaction equation are the most appropriate to describe the process of autoclave thermolysis of the mixture of complex salts $[Pd(NH_3)_4]Cl_2-$ NH₄ReO₄: (i) Autoclave reduction at the parallel occurrence of reactions (4) and (5). (ii). Autoclave reduction along Eq. (6).

Based on the above experimental data we give preference to the reaction Eq. (6).

EXPERIMENTAL

We used tetraammine palladium(II) dichloride synthesized as described in [11], ammonium per-

Equations no.	Possible reactions	Pd:Re	$\Sigma \mathrm{NH}_3$	Free NH ₃		
(1)	NH ₄ ReO ₄ + 3 [Pd(NH ₃) ₄]Cl ₂ + 6 KOH → 3Pd ⁰ + Re ⁰ + N ₂ + 10 NH ₃ + 8 H ₂ O + NO ₂ + 6 KCl	1:3	13	10	73	
(2)	$6 \text{ NH}_4 \text{ReO}_4 + 3 [\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 + 6 \text{ KOH} \rightarrow 3\text{Pd}^0 + 6\text{Re}^0 + 8\text{N}_2 + 2 \text{ NH}_3 + 30 \text{ H}_2\text{O} + 6 \text{ KCl}$	3:6 (1:2)	18	2	11	
(3)	$11 \text{ NH}_{4}\text{ReO}_{4} + 6 [\text{Pd}(\text{NH}_{3})_{4}]\text{Cl}_{2} + 12 \text{ KOH} \rightarrow 6\text{Pd}^{0} + 5 \text{ ReO}_{2} + 6\text{Re}^{0} + 9\text{N}_{2} + 14 \text{ NH}_{3} + 43 \text{ H}_{2}\text{O} + 3 \text{ NO} + 12 \text{ KCl}$	6:11	35	14	40	
(4)	$2 \text{ NH}_{4}\text{ReO}_{4} + 2 [\text{Pd}(\text{NH}_{3})_{4}]\text{Cl}_{2} + 4 \text{ KOH} \rightarrow$ $2\text{Pd}^{0} + 2\text{Re}^{0} + 3\text{N}_{2} + 4 \text{ NH}_{3} + 4 \text{ KCl} + 12 \text{ H}_{2}\text{O}$	2:2 (1:1)	14	4	28.6	
(5)	$12 \text{ NH}_4\text{ReO}_4 + 6 [Pd(\text{NH}_3)_4]\text{Cl}_2 + 12 \text{ KOH} \rightarrow 6\text{Pd}^0 + 10\text{Re}^0 + 13\text{N}_2 + 8 \text{ NH}_3 + 12 \text{ KCl} + 2 \text{ ReO}_2 + 54 \text{ H}_2\text{O} + 2 \text{ NO}$	6:12 (1:2)	36	8	22.2	
(6)	$7 \text{ NH}_4 \text{ReO}_4 + 4 [\text{Pd}(\text{NH}_3)_4] \text{Cl}_2 + 8 \text{ KOH} \rightarrow$ $4 \text{Pd}^0 + 6 \text{Re}^0 + 8 \text{N}_2 + 6 \text{ NH}_3 + 8 \text{ KCl} + \text{ReO}_2 + 33 \text{ H}_2\text{O} + \text{NO}$	4:7	23	6	26.1	

Table 3. Presumed versions of the reduction process in [Pd(NH₃)₄]Cl₂-NH₄ReO₄ mixture

rhenate and potassium hydroxide (reagent grade) were commercial chemicals.

Experiments were carried out in fluoroplastic autoclaves according to the methods previously described in [1-5]. Weighed samples of salt [Pd(NH₃)₄]Cl₂ and NH₄ReO₄ were added to a solution of potassium hydroxide of required concentration, which is then saturated with nitrogen to prevent side reactions with oxygen. The autoclave with the alkaline solution of a mixture of salts [Pd(NH₃)₄]Cl₂ and NH₄ReO₄ was sealed and kept at a temperature of 190°C for 150 min while stirring. After the specified time the autoclave was quickly cooled to room temperature, and the solution was frozen to reduce the loss of free ammonia contained in the system. Content of ammonia after the reaction was determined by acid-base titration. The procedure is described in detail in [12]. The amount of free ammonia in the system was calculated from the results of titration and compared with the theoretical amount of ammonia calculated according to the assumed reaction equation. The close values of the theoretical and experimental masses of free ammonia indicate the validity of the suggested stoichiometry of the reaction of palladium and rhenium salts.

In the autoclave after opening a gray solid with metallic luster was found. It was isolated from the solution by filtration through filter paper ("blue ribbon"), washed with distilled water, and dried. The phase composition of the solid product of the autoclave process was studied by X-ray diffraction (XRD) on a DRON-2.0 diffractometer ($\lambda CoK_{\alpha} = 1.79$ Å, $U_a = 20$ kV, $I_a = 20$ mA, $v_{count} = 2^{\circ}/\text{min}$). The diffraction pattern assignment was carried out using the ASTM database [13].

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