Synthesis of precious and non-ferrous metals in hydrothermal medium

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Abstract. This paper contains an overview of our results on platinum group metals disperse particles synthesis in water solutions in hydrothermal conditions. Metal phases (metal sols, powders and coatings) are formed in halogen and halogenammin complexes solutions in autoclave conditions at 110-230°C. The received materials are promising for the practical applications (catalysts, sensor controls, fuel elements, photonics and etc.).

1. Introduction

Nanoparticles are the basic material used in creating classical materials: powders, sols, films, coatings, composites, and other with unexpected properties [1]. To solve practical tasks it is necessary to ensure continuity of the entire sequence of synthesis’ stages of nanomaterial, namely:

- nanoparticles production,
- dimensional stabilization,
- insertion to the target system with non-fading and reproducible properties,

where relaxation processes of nanoparticles growth would have been kept idle.

According to academician M.V. Alfimov [2], it is the production of nanopowders that is one of the most rapidly growing areas of nanotechnology in the world.

From this point of view among all possible methods for obtaining nanoparticles, in our opinion, chemical methods have greater advantage over the physical ones. They essentially allow the influence of external environments to control the phase transition of condensation in the system and simultaneously influence the rate of small particles coagulation or coalescence. In chemical methods it is possible to deal with metastable states stabilization, for example, by adding SAS, cladding, microencapsulation by viscous dispersed medium, porous materials and other structurally-constrained medium.

The present report reviews our results on platinum group metals dispersed particles synthesis in aqueous solutions in autoclave conditions.
2. Experimental details
Experiments were carried out in fluoroplastic digester according to the methods previously described in papers [3-5].

3. Results and discussions
Reaction (1) of a reversible scrambling according to degrees of platinum oxidation occurs in acidic medium [3]:

\[
2 [\text{PtHal}_4]^2^- \rightarrow \text{Pt}^0 + [\text{PtHal}_6]^2^- + 2\text{Hal}^- (1)
\]

Reaction reversibility is the key characteristic of its use for platinum recrystallization in aqueous solution, for example, to change platinum particles dispersion. When various metals are inserted into the reaction system [3, 7] we can observe a reversible process of dissolution - crystallization, cementation (solid-phase exchange) and other (2, 3):

\[
\begin{align*}
\text{Pd}^0 + \text{Pt}^{2+} & \rightarrow \text{Pt}^{4+} + \text{Pd}^{2+} + \text{Pt}^0 \\
\text{Pd}^0 + \text{Ir}^{4+} & \rightarrow \text{Ir}^{3+} + \text{Pd}^{2+} + \text{Ir}^0 \\
\text{Rh}^0 + \text{Pd}^{2+} & \rightarrow \text{Pd}^0 + \text{Rh}^{3+}
\end{align*}
\] (2)

\[
\begin{align*}
M_0^0 \text{disp.} & \rightarrow M_n^0 \text{comp. (sol, powder)} \\
2\text{[PdX}_4]^{2-} & \xrightleftharpoons[\Delta G]{\Delta G} \rightarrow \text{[PdX}_6]^{2-} + 2\text{X}^+ + \text{Pd}^0
\end{align*}
\] (3)

The reaction products are binary metal deposits Pd-Pt, Pd-Ir, Rh-Pd in the form of solid solutions or mixtures. Dispersed deposits can spontaneously coarsen by equation (4) according to the small particles thermodynamics. This happens quite quickly at elevated temperatures in contact with the liquid phase.

For reaction (1) equilibrium with ultra compact and phases of platinum can be offered:

Figure 1(A) presents a graph of the function \( Q = \frac{C^2_{Pd^2+}}{C_{Pt^{4+}}} \), characterizing pseudoequilibrium (metastable) state of the system, depending on time. The graph resembles the classical dependence (Fig. 1(B)) of free energy change during the new phase particles (nuclei) formation.

For spherical particle formation with radius \( R \) the total change in free energy \( \Delta G \) is presented like [1]:

\[
\Delta G = \frac{4}{3} \pi \Delta g R^3 + 4 \pi \sigma R^2,
\]

where \( \Delta g \) - the difference between the specific free energies of two phases, \( \sigma \) - surface tension coefficient.

The maximum value of \( \Delta G \) (in our case, 7.5 kJ/mol) is the energy of critical nucleus formation. In the subcritical particle size nucleus formation has \( \Delta G > 0 \), and according to classical thermodynamics, it can not be spontaneous, new-phase particles dissolve. In the region where the particle sizes are more than \( R_{cr} \), spontaneous heterogeneous process of particle growth proceed up to
the balanced compact state. Such arguments are only of qualitative sense, since the macroscopic approaches of classical thermodynamics are not used here.

New phase particles nucleation in the subcritical (in size) conditionally homogeneous region has random nature stages; this must be shown in results non-reproducibility according to the allocated solid phase amount. Herein it is homogeneous nucleation stage, obviously, that is limiting in speed. Such facts were observed, for example, in paper [3]: only 1-2 mg of mohr platinum were extracted in 6 hours, and in the next 2.5 hours - 71.6 mg.

For the scrambling reaction we observed wave changes in time of platinum concentrations in various oxidation states. Figure 2 shows the experimental results for reaction (1) in the change of Pt (II) and Pt (IV) concentrations in process at 190°C and 210°C. This confirms the random nature of solid phase nucleation, which was discussed above.
For the following reactions:

\[ 2 \left[ \text{PtCl}_4 \right]^{2-} \rightarrow \text{Pt}^0 + \left[ \text{PtCl}_6 \right]^{2-} + 2\text{Cl}^- \quad \text{atm. CO}_2, \text{pH} = 7 \]

\[
\begin{align*}
\text{Pt}_{UPD}^{190^\circ C} & \rightarrow \text{Pt}_{comp}^0 \\
\text{Pt}^0_{UPD} & \rightarrow \text{Pt}^0_{comp}^{210^\circ C}
\end{align*}
\]

wave behavior allows to hypothesize about scrambling reaction mechanism. Figure 2 illustrates the mechanism of the heterogeneous process of scrambling in time at 190 °C, which has a wave character. At 210 °C fluctuations are smoothed out. This means that platinum quickly becomes compact. Wave process explains the given hypothesis.

The first two reactions are linked: the basic component of the first is the output of the second. Basic components of the second reaction are the outputs of the first. The third stage is the irreversible consumption of one component. This combination of stages fully complies with the conditions of oscillatory processes time, such as the famous Belousov-Zhabotinsky’s reaction. We consider important to point out a curious fact. At Chernyaevsk Chemistry, Analysis and Technology of platinum metals Conference, (2006), the report made by Distler V.V. [8] on ore genesis of grains of platinoids and gold ingrained in copper-nickel ores massive pieces in direct experiments the course of platinum and gold scrambling in the volcanic magma is proved. Currently, the study of scrambling autoclaving according to oxidation and crystallization degrees in the bimetallic system is being successfully developed in the ICCT SB RAS under the guidance of O.V. Belousov [9-11].

Autoclaving acquires a different character in alkali solution of halogen-ammonia complexes. The main reaction (6) - irreversible metal reduction with inner-ammonia:

\[
\left[ \text{M(NH}_3\text{)}_6\text{Cl}_4 \right]^{2+i} + 2\text{OH}^- \rightarrow \text{M}^0 + 1/3\text{N}_2 + + (10/3-\text{i}) \text{ NH}_3 + \text{iCl}^- + 2\text{H}_2\text{O}, \quad \text{(6)}
\]

where M - metal: Pt, Pd, Rh, Ir, Ru, Au, Ag, Cu, Ni, Co, etc.

State of solid metal phase (powder, mirror, sponge, weighed in solution in small portion, loose or dense coating on the substrate) depends on the composition and structure of the basic complexes, the composition and pH solution, temperature, time, agitation, etc. The dominating routes, which lead to the metallic phase, appear in the system depending on the conditions. Ammonia complexes irreversible restoration is realised for platinum, palladium, rhodium, ruthenium, cobalt, nickel, etc. [12-14]. The same processes (6) of autoclave thermolysis proceed in amin complex of platinum, where Amin is ethylenediamine, pyridine, glycine and other [15].

Carrying out the processes in a dispersion medium for metallic phase separation in structure-constrained conditions, which can control particle size, is of basic interest. Methods of sol-gel technology are widely used for the synthesis of hydroxides and oxides of amphoteric metals. A combination of sol-gel technology methods, autoclave methods producing metal dispersions in gelified medium of hydroxides allows to widen preparation possibilities for new catalyst systems, combining all the consistent technological operations. For example, boehmite crystalline modification of aluminum hydroxide is formed in autoclave conditions. Under the same conditions platinammine are restored to a metallic state. Combining these two processes, one can produce a suspension or coating.
on a thick substrate containing boehmite and platinum group metals. Drying and calcination will lead to the desired combination of metal on $\gamma$-$\text{Al}_2\text{O}_3$. With such a synthesis method even distribution of metal in hydroxide and then in aluminum oxide should be expected. Figure 3 shows micro photos of surface images of samples in the characteristic emission of ruthenium with its different content in the samples, which show that ruthenium is evenly distributed on the surface. In addition, metal reduction and crystallization of the metallic phase proceed in a "microreactor" of gel, which contributes to the high dispersion of platinum group metals particles.

![Micro photos of sample surfaces](image)

**Figure 3.** The image of the sample surface in a characteristic radiation:

a) Ruthenium 5% Ru / AlO (OH); b) ruthenium, 10% Ru / AlO (OH)

We studied the reaction of the ions interaction $[\text{Pt(NH}_3\text{)}_4\text{]}^{2+}, [\text{Pd(NH}_3\text{)}_4\text{]}^{2+}$ with $\text{NH}_4\text{ReO}_4$ in alkaline solutions under hydrothermal conditions.

In paper [16] the stoichiometry of tetraamminplatinic (II) and ammonium perrhenate interaction is studied and proved:

$$3[\text{Pt(NH}_3\text{)}_4\text{]}\text{Cl}_2 + 6\text{NH}_4\text{ReO}_4 + 6\text{KOH} \rightarrow 3\text{Pt}^0 + 6\text{Re}^0 + 8\text{N}_2\uparrow + 2\text{NH}_3\uparrow + 6\text{KCl} + 30\text{H}_2\text{O}$$  \hspace{1cm} (7)

Table 1 shows the experimental and theoretical data on XPA of solid product reaction product (7), which is a solid solution or a mixture of metallic phases of platinum and rhenium.

**Table 1.** X-ray characteristics of the solid product of an autoclaved thermolysis mixture of $[\text{Pt(NH}_3\text{)}_4\text{]}\text{Cl}_2$ and $\text{NH}_4\text{ReO}_4$.

| Product of autoclave thermolysis - Pt phase | Product of autoclave thermolysis – Re phase |
|-------------------------------------------|-------------------------------------------|
| $2\theta$, deg | I, % | d/n, Å (exp.) | d/n, Å (ASTM) | $2\theta$, deg | I, % | d/n, Å (exp.) | d/n, Å (ASTM) |
|----------------|------|----------------|----------------|----------------|------|----------------|----------------|
| 50.7           | 100  | 2.261          | 2.27           | 47.4           | 30   | 2.408          | 2.388          |
| 59.3           | 85   | 1.957          | 1.956          | 54.7           | 100  | 2.107          | 2.105          |
| 88.8           | 84   | 1.383          | 1.385          | 56.5           | 11   | 1.254          | 1.626          |
| 110.2          | 100  | 1.180          | 1.179          | 67.8           | 22   | -              | 1.380          |
| 117.8          | 60   | 1.130          | 1.130          | 82.1           | 20   | -              | 1.173          |
Experiments have been carried out to prove the stoichiometry of this reaction and to quantify the free ammonia by the method described in the experimental part of this paper.

Data from Table 2 show good agreement between the experimental and theoretical values of free ammonia. Thus, the interaction in autoclave conditions proceeds according to equation (7).

**Table 2.** The results of the NH₃ content determination in solutions after autoclave experiments completion (150 min, 190° C).

| Weighed portion, g | m NH₃, (theor.), g | m NH₃, (exp.), g | % of theoretical value |
|-------------------|-------------------|-----------------|----------------------|
| [Pt(NH₃)₄]Cl₂•H₂O | 1.036             | 0.789           | 0.101                | 0.0969               | 95.9               |
| NH₄ReO₄            |                   |                 |                      |                     |                    |
| (0.55 Pt) (0.55 Re)| 1.036             | 0.789           | 0.101                | 0.0942               | 93.3               |
|                   | 0.776             | 1.181           | 0.025                | 0.0241               | 96.0               |
| (0.43 Pt) (0.82 Re)|                   |                 |                      |                     |                    |

Similarly, the interaction of [Pd(NH₃)₄]Cl₂ and NH₄ReO₄ mixture in platinum-rhenium system has been studied. The phase composition of the solid reaction product was determined by XFA. The results given in Table 3 show that the solid product of autoclave thermolysis of this mixture contains three phases - the metal palladium, the metal rhenium and rhenium dioxide.

**Table 3.** X-ray characteristics of the solid product of an autoclaved thermolysis mixture of [Pd(NH₃)₄]Cl₂ and NH₄ReO₄.

| Product of autoclave thermolysis - Pd phase | Product of autoclave thermolysis - phase ReO₂ | Product of autoclave thermolysis - phase Re |
|--------------------------------------------|---------------------------------------------|--------------------------------------------|
| 20, degr I, % d/n, Å (exp.) d/n, Å (AST M)| 20, degr I, % d/n, Å (exp.) d/n, Å (AST M)| 20, degr I, % d/n, Å (exp.) d/n, Å (AST M)|
| 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 | 40.2 5 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 | 82.3 20 1.17 1.173 |
Table 4 summarizes the experimental results of free ammonia determination, which show that its quantity in the system corresponds to 24-30% of the total.

Table 4. The experimental values of the basic amount of reactants (for metal and ammonia) and of free ammonia in the reaction products.

| Pd, g  | Re, g  | Pd:Re (atomical) | \( \sum \text{NH}_3 \), (basic quantity), g | Quantity of free \( \text{NH}_3 \) g | % |
|--------|--------|------------------|-------------------------------------------|---------------------------------|----|
| 0.057  | 0.1    | 1:1              | 0.0459                                   | 0.0140                          | 30.5 |
| 0.057  | 0.1    | 1:1              | 0.0459                                   | 0.0113                          | 24.6 |
| 0.057  | 0.1    | 1:1              | 0.0459                                   | 0.0121                          | 26.4 |
| 0.057  | 0.1    | 1:1              | 0.0459                                   | 0.0121                          | 26.4 |
| 0.057  | 0.066  | 1:5:1            | 0.0425                                   | 0.0090                          | 21.2 |
|        |        | (3:2)            |                                          |                                 |     |
| 0.1    | 0.1    | 1.75:1           | 0.0728                                   | 0.019                           | 26.1 |
| 0.1    | 0.1    | 1.75:1           | 0.0728                                   | 0.0224                          | 30.8 |
| 0.1    | 0.1    | 1.75:1           | 0.0728                                   | 0.020                           | 27.5 |

Specified as the reaction products, metallic states of palladium, rhenium and rhenium dioxide allow to assume a significant variety of equations for the recovery processes of mixture [Pd(NH\(_3\))\(_4\)]Cl\(_2\) - NH\(_4\)ReO\(_4\) in an alkaline environment in the autoclave conditions. Here are the atomic ratios of metals, the total number of ammonia molecules before the reaction, the number of molecules of free ammonia and its percentage of the total number of molecules for the corresponding reactions:

Table 5. Presumptive variants of recovery processes of mixture [Pd(NH\(_3\))\(_4\)]Cl\(_2\) - NH\(_4\)ReO\(_4\).

| Possible reactions | Pd:Re | \( \sum \text{NH}_3 \) | Quantity of free \( \text{NH}_3 \) |
|-------------------|-------|-------------------------|-------------------------------------|
| 2NH\(_4\)ReO\(_4\)+2[Pd(NH\(_3\))\(_4\)]Cl\(_2\)+4KOH \( \rightarrow \) 2Pd\(_8^0\)+2Re\(_0^0\)+3N\(_2^0\)+4NH\(_3^0\)+4KCl+12H\(_2^0\)O | 2:2   | 14                       | 4                                  |
|                   |       |                         | 28.                                 | 6                                 |
| 12NH\(_4\)ReO\(_4\)+6[Pd(NH\(_3\))\(_4\)]Cl\(_2\)+12KOH \( \rightarrow \) 6Pd\(_8^0\)+10Re\(_0^0\)+13N\(_2^0\)+8NH\(_3^0\)+12KCl+2ReO\(_2^0\)+54H\(_2^0\)O+2NO | 6:12  | 36                       | 8                                  |
|                   |       |                         | 22.                                 | 2                                 |
| 7NH\(_4\)ReO\(_4\)+4[Pd(NH\(_3\))\(_4\)]Cl\(_2\)+8KOH \( \rightarrow \) 4Pd\(_8^0\)+6Re\(_0^0\)+8N\(_2^0\)+6NH\(_3^0\)+8KCl+ReO\(_2^0\)+33H\(_2^0\)O+NO | 4:7   | 23                       | 6                                  |
|                   |       |                         | 26.                                 | 1                                 |
Data given in table 5 shows that the most close to the description of the experimental results are hypothesis, described by equations (8), (9) and (10) as the quantity of free ammonia (%) agrees well with experimental data obtained after titration of free ammonia. Based on the above experimental data, in our opinion, we should give preference to the reaction equation (10).

4. Conclusion

- On an example of binary metal systems results of researches of the processes proceeding in hydrothermal conditions which products are disperse phases are resulted;
- The observable reactions aren't typical for processes of coordination chemistry under normal conditions it is noticed.
- For the first time it is experimentally proved that under hydrothermal conditions redox interaction processes of tetraamines platinum (II) and palladium (II) with perrenatum of ammonia proceed;
- For the first time results of research of autoclave thermolysis processes ruthenium ammines chlorides in the depressive environment of hydroxide aluminum suspensions are resulted.
- In the products of these reactions metallographic phases of platinum, palladium and rhenium were discovered;
- Studied processes in the platinammine (II) and palladium (II) systems with perrenatum of ammonia liberalize the autoclave thermolysis method and allow to deliberately perform the dispersed bimetallic materials synthesis in solutions and the dispersion medium.

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