Reaction of [Pt(NH₃)₄]Cl₂ with NH₄VO₃ in an Alkaline Solution at 190°C in Autoclave

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Abstract—The reaction of $[Pt(NH_3)_4]Cl_2$ with NH_4VO_3 in alkaline solution in an autoclave at 190°C was studied. The solid autoclave thermolysis product was characterized by the methods of X-ray phase analysis, scanning electron microscopy, energy-dispersive X-ray spectroscopy, dynamic light scattering, and elemental analysis. The product is represented by two phases: Pt and a Pt₃V solid solution in the form of two types of particles of different morphology with a size less than 1 μ m. The reaction stoichiometry {9[Pt(NH_3)_4]Cl_2, 18NH_4VO_3, 18KOH} corresponds to the found amount of free ammonia (14NH₃) formed under the selected conditions.

Keywords: platinum, vanadium, autoclave thermolysis, elevated temperatures

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Platinum and platinum alloys are important components of catalysts used in chemical reactions, in the purification of automobile exhaust gases, fuel cell electrodes with a proton exchange membrane, materials for hightemperature and corrosion sensors, electronic and optical devices [1]. The catalytic properties of the Pt-V alloy are manifested in various processes [2-5]. Vanadium, which has a high affinity for oxygen and has a negative electrode potential, when added to platinum increases its activity as a catalyst in the reaction of oxygen electro-reduction [2, 3]. The Pt/V–TiO₂ catalyst is superior in its functional characteristics to the unalloyed TiO₂ and Pt/TiO₂ carrier in this reaction, and the Pt-V system is more durable than monometallic platinum. The addition of platinum and vanadium compounds to titanate nanotubes (TN) with subsequent processing under hydrothermal conditions leads to the formation of Pt-TN and V2O5-TN particles and to an increase in the number of Lewis and Bronsted acid centers, respectively, on the carrier surface, and, as a result, to an increase in the degree of advancement and selectivity of heterogeneous catalytic reactions [4]. The Pt–V–MCM-41¹ catalyst has a high catalytic activity over a wide temperature range in the reaction of NO selective catalytic reduction with propane [5].

To obtain Pt–V catalytic systems, hydrothermal (autoclave) synthesis is used [1–5], which has undoubted advantages over the most commonly used methods based on impregnation of a carrier with solutions of metal compounds, followed by drying at room temperature and calcination at 500°C in inert and reducing media [6]. When conducting processes in solutions at elevated temperatures in an autoclave, local overheating is absent and standardization of experimental conditions (temperature, reagent concentration, etc.) is facilitated.

Highly dispersed metal phases are formed on the autoclave thermolysis of ammines of platinum metals in alkaline solutions in the temperature range 110–220°C [7–10]. In alkaline aqueous solutions at 110–220°C in the autoclave tetraammineplatinum(II) dichloride is reduced [8]:

$$3[Pt(NH_3)_4]Cl_2 + 6KOH \rightarrow 3Pt^0 + N_2 + 10NH_3 + 6H_2O + 6KCl.$$

The study of chemical processes in solutions at elevated temperatures is important for the development of physical and chemical bases for the formation of polymetallic phases with precious metals [11].

In order to synthesize a bimetallic Pt–V alloy, we performed the reaction of the $[Pt(NH_3)_4]Cl_2$ and NH_4VO_3 salts in an alkaline solution in an autoclave at 190°C and obtained a gray powder. According to electron

¹ MCM-41—alumosilicates mesoporous material based on zeolite (Si : Al = 41).



Fig. 1. Histogram describing the size distribution of dispersed phase particles.

microscopic studies, the particles of the obtained sample are morphologically inhomogeneous: there are particles of regular spherical shape combined into voluminous porous formations and particles consisting of needle-like crystals (50–200 nm). The Pt–V–O atomic ratio found on the basis of EDX spectra is approximately 24 : 5 : 70, but the existence of oxide phases was not verified by X-ray phase analysis (XPA).

A histogram describing the particle size distribution in the resulting solution, as given by dynamic light scattering (DLS) data, is shown in Fig. 1 (the average particle size is 708 nm).

The X-ray phase analysis confirmed the fact that the solid product of the $[Pt(NH_3)_4]Cl_2$ reaction with NH_4VO_3 under autoclave conditions is represented by two phases: metal platinum Pt^0 [a = 3.935(4) Å] and a solid solution based on platinum Pt_3V [a = 3.934(4) Å] (Table 1).

According to the results of the XPS study of the autoclave thermolysis product, the elemental composition of the surface can be expressed by the ratio $Pt : V : O \approx 42.1 : 7.5 : 50.4$ (at %), which is in satisfactory agreement with the EDX data. The X-ray photoelectron spectra (XPS) of vanadium and platinum in the autoclave thermolysis product (Fig. 2) characterize the chemical states of these elements.

The platinum spectrum (Fig. 2b) is represented by several spin-orbit doublets with a maximum at 71.2 eV.

The spectrum makes it possible to distinguished three states: Pt⁰ ($E_b = 71.2 \text{ eV}$), Pt²⁺ ($E_b = 72.3 \text{ and } 73.4 \text{ eV}$), and Pt⁴⁺ ($E_b = 74.9 \text{ eV}$). More than half of platinum found in the sample (56%) is in the metallic state.

Interpretation of the V2*p* line is complicated by the low vanadium content in the samples and the superposition of the Al $K_{\alpha3,4}$ satellite line from the O1*s* spectrum. The Pt4 $p_{3/2}$ line is also superimposed on the vanadium spectrum (Fig. 2a). The separation of the V2*p* XPE spectrum into doublets, $E_b = 516.7$ and 513.8 eV, points to the presence of V⁴⁺ and V²⁺, respectively. Consequently, the surface of the powder contains vanadium oxides VO and VO₂, which were not detected by X-ray phase analysis due to a small amount or a high dispersion.

The O1s oxygen spectrum can be represented by several components, $E_b(O1s) = 529.9$, 531.5, 533.3 eV. The first component refers to oxygen in the composition of oxides, and the second and third components—to the hydroxyl group and water, respectively; their presence is explained by the adsorption of water from air when preparing the sample for analysis.

During the autoclave experiments, the concentrations of platinum(II) and vanadium(V) in the solution decrease differently. The concentration of vanadium(V) in the alkaline solution after 150 min at 190°C decreases by half, and of platinum—almost to zero. Therefore, under these conditions, platinum(II) is completely reduced, and the vanadate ion—only by 50%, to form particles of metallic platinum and the Pt₃V solid solution. Their presence on the surface and in the sample volume is confirmed by the methods of XPA, XPS, SEM, and energy-dispersive microanalysis.

The fact of incomplete vanadium(V) reduction in the process under consideration raises the question of the form of its existence in the solution. Numerous data on the composition and structure of vanadates in solutions are often contradictory, and their formulas are not always sufficiently justified. Contradictions arise due to incorrect accounting for the ionic state of vanadium(V) [19]. In the pH = 7-11 region, along with monomers, there are

Table 1. Data of X-ray phase analysis of the autoclave thermolysis product

| Run no. | Experimental data | | | ICDD PDF-2 database | | | | | | |
|------------|-------------------|---------|--------|---|-----|--------------|---|-----|--------------|--|
| | <i>I</i> , % | 2θ, deg | d, Å | Pt, space group <i>Fm</i> -3 <i>m</i> (88-2343) | | | Pt_3V , space group $Fm-3m$ (65-8335) | | | |
| | | | | <i>d</i> , Å | hkl | <i>I</i> , % | d, Å | hkl | <i>I</i> , % | |
| 1 | 100 | 39.616 | 2.2729 | 2.2920 | 111 | 100 | 2.2228 | 111 | 100 | |
| 2 | 52 | 46.103 | 1.9670 | 1.9850 | 200 | 45.9 | 1.9250 | 200 | 46.3 | |
| 3 | 38 | 67.358 | 1.3889 | 1.4036 | 220 | 23.5 | 1.3611 | 220 | 22.6 | |



Fig. 2. X-ray photoelectron spectra of (a) V2p and (b) Pt4f.

dimers, trimers, tetra-, and pentamers of vanadate ions. The equilibrium of vanadates in solutions is usually interpreted by the mathematical simulation method, but both the pH-metric method and the equilibrium simulation method are indirect and do not make it possible to determine directly the composition of vanadate ions and their structure in solutions. There are no effective direct physicochemical methods for the determination of the degree of hydrolysis of isopolyvanadate ions in solutions, so we can only assume that their existence in solution is more or less justified [20]. Therefore, taking into account the state diagram of the HVO₄^{2–} H₂O–NaOH system [20], it is safe to assume that the vanadate ion is present in the solution as the V₂O₄^{7–} dimer.

The amount of free ammonia released in the reaction was determined by acid-base titration (Table 2), which showed that its amount in the reaction mixture was 20–30% of the total amount of ammonia, and the average amount of free ammonia in the system was 24%. The amount of

free ammonia in the system, the formation of metallic platinum and a solid Pt_3V solution, and also incomplete (50%) reduction of vanadium give grounds to suggest variants of reactions (1)–(6) between $[Pt(NH_3)_4]Cl_2$ · H_2O and NH_4VO_3 in the aqueous alkaline solution in the autoclave at 190°C (Table 2).

Judging by the amount of free ammonia and the composition of the autoclave thermolysis products, Eqs. (2), (3), (5), and (6) are closest to the stoichiometric description of the process, whereas variants (1) and (4) do not meet these conditions. Since only half of vanadium is found in the solution after thermolysis, Eq. (2) also drops out. According to Eq. (3), the most part of vanadium is reduced, whereas only half of its initial amount was found in the solution. Equation (6) is more preferable in relation to the average value of the free ammonia amount (24%), but does not agree with the amount of vanadium remaining in the solution. Thus, the reaction of $[Pt(NH_3)_4]Cl_2$.

| Ea | | | Initial number | NH ₃ free | |
|-----|---|-------------|------------------|----------------------|------|
| no. | Possible reactions | Pt : V (at) | of ions NH_4^+ | number of molecules | % |
| 1 | $ [Pt(NH_3)_4]Cl_2 + 2NH_4VO_3 + 2KOH \rightarrow Pt^0 + 2V^0 + 2NH_3 + 2N_2 + 2KCl + 8H_2O $ | 1:2 | 6 | 2 | 33.3 |
| 2 | $3[Pt(NH_3)_4]Cl_2 + 6NH_4VO_3 + 6KOH \rightarrow 3Pt^0 + 3(NH_4)_4V_2O_7 + 4NH_3 + N_2 + 6KCl + 3H_2O$ | 3:6(1:2) | 18 | 4 | 22.2 |
| 3 | $9[Pt(NH_3)_4]Cl_2 + 18NH_4VO_3 + 18KOH \rightarrow 9Pt^0 + 12V + 3(NH_4)_4V_2O_7 + 16NH_3 + 13N_2 + 18KCl + 51H_2O$ | 9:18(1:2) | 54 | 16 | 29.6 |
| 4 | $6[Pt(NH_3)_4]Cl_2 + 12NH_4VO_3 + 12KOH \rightarrow 6Pt^0 + 6V + 3(NH_4)_4V_2O_7 + 10NH_2 + 3N_2 + 12KCI + 27H_2O$ | 6:12(1:2) | 36 | 2 | 5.5 |
| 5 | $9[Pt(NH_3)_4]Cl_2 + 18NH_4VO_3 + 18KOH \rightarrow 9Pt^0 + 6V + 6(NH_4)_4V_2O_7 + 12NH_2 + 9N_2 + 18KCI + 30H_2O$ | 9:18(1:2) | 54 | 14 | 25.9 |
| 6 | $6[Pt(NH_3)_4]Cl_2 + 12NH_4VO_3 + 12KOH \rightarrow 6Pt^0 + 2V + 5(NH_4)_4V_2O_7 + 26/3NH_3 + 11/3N_2 + 12KCI + 13H_2O$ | 6:12(1:2) | 36 | 10 | 24 |

Table 2. Variants of the reaction of [Pt(NH₃)₄]Cl₂·H₂O with NH₄VO₃ in aqueous alkaline solution in autoclave at 190°C

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 H_2O with NH_4VO_3 in an aqueous alkaline solution in an autoclave at 190°C is most consistent with Eq. (5).

Taking into account the presented results, we can assume that the interaction of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ with NH₄VO₃ in the aqueous alkaline solution in the autoclave at 190°C proceeds to form a mixture of Pt₃V [a=3.934(4) Å] and Pt⁰ [a = 3.936(5)Å]. Under these conditions, incomplete (50%) reduction of the vanadate ion and the formation of bimetallic Pt₃V particles take place. The results obtained demonstrate the advantages of autoclave synthesis, which makes it possible to obtain in one stage bimetallic powders promising for use as catalysts in industrially important reactions.

EXPERIMENTAL

We used $[Pt(NH_3)_4]Cl_2 \cdot H_2O$, synthesized from $H_2[PtCl_6] \cdot 6H_2O$ (technic specifications 2612-059-00196533-2002, V. N. Gulidov "Krastsvetmet" JSC) according to the standard method [21], and NH₄VO₄ (CAS no. 7803-55-6, chemically-pure grade). Other reagents were of grade not lower than chemically-pure.

The experiments were performed under conditions similar to those previously described [15, 16]. Weighted samples of the $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ and NH_4VO_3 salts were added to 0.1 M KOH solution, the reaction mixture was poured into a fluoroplastic autoclave and saturated with nitrogen to prevent the occurrence of side oxidation reactions. The autoclave with the alkaline solution of the salt mixture was sealed and continuously shaken for 150 min at 190°C (optimal conditions for salt reduction). The autoclave was then rapidly cooled to room temperature, then the solution was frozen to reduce the loss of free ammonia from the system. The resulting gray powder was filtered through a glass filter, washed with distilled water, and dried to a constant weight at 90–100°C.

The amount of free ammonia in the reaction system after autoclave thermolysis was determined by acid-base titration. The solutions were analyzed by atomic emission spectroscopy using an optical emission spectrometer iCAP 6300 Duo (Thermo Scientific USA) with inductively coupled plasma. The elemental composition and the microphotograph of the thermolysis product were obtained by X-ray spectral microanalysis (XMA) on a Jeol JSM 6390A scanning electron microscope with an EDS attachment Jeol JED-2200. The particle size of the resulting powder was studied by dynamic scattering using a 90plus/BI-MAS particle size analyzer (Brookhaven). The morphology of the samples was studied using a scanning electron microscope (Carl Zeiss NVision 40, Japan). The chemical composition of the surface was studied using an appropriate attachment for energy-dispersive X-ray analysis (EDX). The phase composition of the solid product was studied using an ARL X'TRA diffractometer (TermoFisherScientific, Switzerland) (Cu K_{α} , $\lambda = 1.54056$ Å, angle range $2\theta = 5^{\circ}-80^{\circ}$). The phases were identified using the PCPDFWIN pdf2 automated database. The unit cell parameters were refined using the DICVOL04 program [22].

Photoelectron spectra of the studied powders were obtained using an Omicron ESCA+ X-ray photoelectron spectrometer (OMICRON nanoscience, Germany) with excitation by monochromatic Al radiation with energy of 1486.6 eV and power of 252 W. The pressure in the analyzer chamber did not exceed 10^{-9} torr. The transmission energy of the analyzer is 20 eV. The position of the lines of elements that make up the surface layer was standardized according to the C1s spectrum of hydrocarbon pollutants precipitated from the atmosphere and during the synthesis. The peak bond energy was assumed to be 285.0 eV.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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