Solid-State Thermal Transformations in a Mixture of Palladium Tetraammine Dichloride with Ammonium Chromate

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Abstract—Solid-state transformations of a $3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4$ mixture at temperatures from 40 to 550°C in various media have been studied by thermal analysis and mass spectrometry. The results demonstrate that the solid thermolysis product obtained in an argon atmosphere consists of a single phase: palladium-based Pd_{1-x}Cr_x solid solution isostructural with palladium and having a unit-cell parameter a = 3.897(2) Å. Its formation proceeds through the formation of metallic Pd and Cr, as evidenced by the absence of chromium oxide phases in all of the solid intermediate thermolysis products. The solid thermolysis product obtained in air consists of the phases Pd and PdO. A model has been proposed for the transformations of the $3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4$ mixture through the formation of metallic palladium and chromium.

Keywords: palladium, chromium, bimetallic particles, catalysts, thermolysis, solid solution **DOI:** 10.1134/S0020168518120038

INTRODUCTION

The preparation of bimetallic nanoalloys has been the subject of extensive studies and several reviews [1, 2], demonstrating that there is relentless research interest in this issue. The literature addresses modern theoretical approaches and unique techniques for the synthesis of novel, highly efficient materials, including palladium-based bimetallic catalytic systems. A number of examples of how a second metal influences the catalytic performance of palladium for the selective hydrogenation of unsaturated aliphatic hydrocarbons, aromatic compounds, and nitrogen-containing molecules, as well as for reactions involving CO and dehydrochlorination reactions, can be found in a review by Coq and Figueras [2].

Pd–Cr bimetallics are used, for example, as catalysts for the anodic oxidation of formic acid [3], sensor materials for high hydrogen concentrations [4], Pd– Cr/C and Pd–Cr/Si catalysts for the 1,3-butadiene hydrogenation process [5, 6], etc.

According to Iglesias-Juez et al. [7], the addition of chromium to palladium in the preparation of three-way catalysts (TWCs) is accompanied by a rise in the degree of NO conversion because of the formation of Pd–Cr alloys, and Pd–CrO_x particles promote CO

oxidation at reaction temperatures above 300° C. On the whole, the role of chromium in such bimetallic catalysts is interpreted in terms of geometric and electronic effects and the formation of mixed active centers, as well as in terms of a decrease in palladium– hydrogen bond strength [2, 5, 6] and the presence of valence *d*-electrons, which change the electron density of palladium, in the case of hydrogenation. It is well documented [8] that, in the presence of ammonia or an amine as a reducing agent, noble metal ions are capable of inducing the reduction of nonferrous metal ions to form a bimetallic nanoalloy.¹

One of the main, and the most technologically viable, approaches to the preparation of the systems under consideration is the thermolysis of complexes [9], mixtures of precursor compounds [10–13], or double complex salts (**DCS's**) [14–16]. Knowledge of the thermal stability of compounds in various gaseous atmospheres [17] makes it possible to properly choose conditions for the synthesis of a particular metallic phase, which is very important in preparing supported catalysts. The product of thermolysis of the double salt

¹ The method is known as noble metal induced reduction (NMIR).

 $[Cr(NH_3)_5Cl][PdCl_4]$ in a helium atmosphere (665°C) was shown to consist of two phases: Pd and Cr₂O₃. Thermolysis in a hydrogen atmosphere (450°C) yields Cr_{0.3}Pd_{0.7} and Cr₂O₃ [14]. As reported by Shubin et al. [14], the Cr_{0.5}Pd_{0.5} solid solution can be prepared by firing in hydrogen at 800°C, followed by prolonged holding, whereas metallic powders cannot be obtained even in a helium atmosphere.

Previously, we reported the key features of thermal solid-state reactions of $[Pt(NH_3)_4]Cl_2$ and $[Pd(NH_3)_4]Cl_2$ with NH_4ReO_4 [18] and of $[Pt(NH_3)_4]Cl_2$ with $(NH_4)_2CrO_4$ and $(NH_4)_2Cr_2O_7$ [19, 20] in air and an inert atmosphere.

As a continuation of our previous work, this paper addresses the key features of thermal solid-state reactions of $[Pd(NH_3)_4]Cl_2$ with $(NH_4)_2CrO_4$ in an inert (Ar) and an oxidizing (air) atmosphere.

EXPERIMENTAL

The starting chemicals used were $[Pd(NH_3)_4]Cl_2$ synthesized from palladium dichloride (59.903% Pd, Russian Federation Purity Standard TU 2625-058-00196533-2002, AO Gulidov Krastsvetmet) as described elsewhere [18], $(NH_4)_2CrO_4$ (reagent grade, Russian Federation State Standard GOST 3774-76), and $(NH_4)_2Cr_2O_7$ (reagent grade, Russian Federation State Standard GOST 3763-76). The other chemicals used were of reagent grade or better purity. Appropriate ratios of weighed amounts of the palladium and chromium salts were dissolved in the minimum amount of distilled water needed. The resultant solutions were mixed in an evaporating dish and placed in a drying oven, where they were dried at a temperature of 100–110°C until complete water removal.

The mixtures were characterized by thermal analysis using a Netzsch STA 449 C Jupiter simultaneous thermal analysis system in combination with a QMS 403 C Aeolos mass spectrometer. A weighed amount of a mixture was placed in a corundum crucible and heated in flowing argon (40 mL/min) at a rate of 10°C/min or in air in a tube furnace at a heating rate of 10°C/min. Selective experiments aimed at obtaining solid intermediate thermolysis products at temperatures corresponding to endo- and exothermic peaks in differential scanning calorimetry (DSC) curves and determining their chemical and phase compositions were carried out in a flow-type quartz reactor inserted in a tube furnace (heating rate of 10°C/min), under flowing argon (40 mL/min) or in air.

X-ray diffraction patterns of all the samples containing mixture thermolysis products obtained at various temperatures were collected on an Arl X'tra diffractometer (Termo Fisher Scientific, Switzerland), using monochromatized Cu K_{α} radiation, with a wavelength of 1.54056 Å, and a linear correction for the wavelength 1.54433 Å (scan step of 2°, counting time per data point of 3 s, angular range $2\theta = 5^{\circ} - 80^{\circ}$). The phases present were identified by X-ray diffraction using the PCPDFWIN PDF2 automated database. Unit-cell parameters were refined using the DICVOL04 program [21].

The elemental composition of the thermolysis products obtained in argon and air was determined using a JEOL JED-2300 energy dispersive X-ray microanalysis system (accelerating voltage of 20 kV).

RESULTS AND DISCUSSION

First, we studied the behavior of the starting components $[Pd(NH_3)_4]Cl_2$ and $(NH_4)_2CrO_4$ during heating to 550°C in an argon atmosphere by analyzing the gaseous decomposition products. The $[Pd(NH_3)_4]Cl_2$ compound was found to be thermally stable during heating in the argon atmosphere to 190°C and then decompose in two steps (Fig. 1).

The endothermic peak centered at 191°C in its DSC curve is accompanied by a weight loss of 12.3% in the sample (Fig. 1). The gaseous decomposition products were found to include NH_3 . Thus, the initial stage of the thermal decomposition of the $[Pd(NH_3)_4]Cl_2$ salt (150–250°C) is the detachment of two ammonia molecules and the formation of *trans*-[Pd(NH_3)_2Cl_2], which is consistent with previous data [17]:²

$$[Pd(NH_3)_4]Cl_2$$

$$\rightarrow trans - [Pd(NH_3)_2Cl_2] + 2NH_3.$$
(1)

Subsequent decomposition of the *trans*- $[Pd(NH_3)_2Cl_2]$ formed is accompanied by a large endotherm at 328.9°C and a weight loss of 45.2% of the initial weight at a high rate (24.3%/min). In the gas phase at this stage, we observe the release of nitrogen as a product of ammonia oxidation with the Pd²⁺ central ion, which is in turn reduced to palladium metal. This is similar to data obtained by Smirnov et al. [17] in a helium atmosphere.³

According to X-ray diffraction data, the product of $[Pd(NH_3)_4]Cl_2$ thermolysis in argon at 500°C in this study consists of a single phase: cubic Pd with a unit-cell parameter a = 3.905(5) Å, corresponding to palladium with a unit-cell parameter a = 3.90 Å (PCPDFWIN PDF2 database, card no. 88-2335).

During heating in argon, $(NH_4)_2CrO_4$ is thermally stable up to 100°C. At higher temperatures, it decomposes in two steps. The first step is accompanied by an endotherm in the DSC curve, with a peak temperature of 157.5°C (Fig. 2). Mass-spectrometric analysis data indi-

² Smirnov et al. [17] presented thermal analysis data for $[Pd(NH_3)_4]Cl_2$ decomposition in nitrogen.

³ As pointed out by Smirnov et al. [17], the temperature of complete $[Pd(NH_3)_2Cl_2]$ decomposition to palladium metal in an ammonia atmosphere is 20°C lower than that in an inert atmosphere.



Fig. 1. Thermal analysis results for $[Pd(NH_3)_4]Cl_2$ decomposition in an argon atmosphere and mass spectra of the gaseous decomposition products.

cate the presence of NH_3 and H_2O in the gas phase. The process can be described by a reaction scheme corresponding to the polymorphic transformation of ammonium chromate into a dichromate [22].⁴

In air, this reaction occurs in the temperature range $110-170^{\circ}$ C:

$$\frac{2(NH_4)_2 CrO_4 \to (NH_4)_2 Cr_2O_7}{+ 2NH_3 + H_2O.}$$
(2)

Subsequent thermal transformation of $(NH_4)_2Cr_2O_7$ involves two steps. The first step is characterized by a small exotherm at 232.2°C and evolution of ammonia and water at 248.2°C (Fig. 2). The process can be represented by the following scheme:

$$(NH_4)_2 Cr_2 O_7 \rightarrow 2CrO_3 + 2NH_3 + H_2 O.$$
 (3)

In the second step, we observe a large exotherm at a temperature of 269.1°C and nitrogen release (m/z = 28) in the gas phase, with a maximum at 289.0°C. The process is related to the oxidation of the ammonia by the chromium trioxide formed in the first step and follows the reaction scheme

$$3CrO_3 + 2NH_3 \rightarrow 3CrO_2 + N_2 + 3H_2O.$$
 (4)

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The exothermic decomposition of ammonium chromate in this temperature range, with maxima at 240.0 and 260.0°C, was described previously [22]. It is worth noting that, at a temperature of 243.2°C, we observe release of a small amount of oxygen (m/z = 32) (Fig. 2), which is an intermediate product of chromium trioxide decomposition:

$$2CrO_3 \rightarrow 2CrO_2 + O_2. \tag{5}$$

The mass spectrum of the gas phase in this temperature range indicates the presence of NH₃, H₂O, O₂, N₂, and other oxidation products (nitrogen oxides, m/z = 30). It should be emphasized that N₂ release is observed at a higher temperature than is NH₃ release, probably because of its oxidation by the chromium trioxide formed previously according to scheme (3) (exothermic peak at 269.1°C), as represented by scheme (4) [22].⁵

Thermal transformations of a $3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4$ mixture were studied by simultaneous thermal analysis (Fig. 3). Unlike the distinct compounds considered above, the mixture undergoes three steps of conversion.

⁴ Thermal analysis results for (NH₄)₂CrO₄ decomposition in air were presented in Ref. [22].

⁵ Thermal analysis results for (NH₄)₂CrO₄ decomposition in air were presented in Ref. [22].



Fig. 2. Thermal analysis results for $(NH_4)_2CrO_4$ decomposition in an argon atmosphere and mass spectra of the gaseous decomposition products.

In the first step, which occurs in the temperature range 190–260°C and is represented by two broad endotherms, with maxima at 234.9 and 259.5°C, we observe a small weight loss of 7.4% ($\Delta m_{\text{meas}} = 7.4\%$), $\Delta m_{\text{calc}} = 7.4\%$), which is probably due to the polymorphic transformation of ammonium chromate to ammonium dichromate and structural changes in [Pd(NH₃)₄]Cl₂. These effects are accompanied by the release of gaseous products: H₂O, 2NH₃, and 1/2N₂ (Fig. 3). The thermal analysis and mass spectrometry data for the 3[Pd(NH₃)₄]Cl₂ + (NH₄)₂CrO₄ mixture and the assumed overall compositions of the solid intermediate products are presented in Table 1.

The X-ray diffraction data for the thermolysis products corresponding to these endothermic events indicate the presence of two phases: $[Pd(NH_3)_2Cl_2]$ and a cubic phase isostructural with Pd. The unit-cell parameters of the cubic phases isostructural with Pd $(a = 3.9068(2) \text{ Å at } 234.9^{\circ}\text{C} \text{ and } a = 3.907(3) \text{ Å at } 259.5^{\circ}\text{C})$ coincide to within the present experimental uncertainty with the unit-cell parameter of pure Pd (a = 3.905(5) Å) prepared by us through the thermal decomposition of palladium(II) tetraammine dichloride (Fig. 4).

The second step of the thermal transformation is observed in the range $260-340^{\circ}$ C and is the decomposition of the components of the mixture under consid-

eration. The first to decompose is the chromium salt: at a temperature of 278.5°C, the DSC curve (Fig. 3a) shows an exothermic peak, which is due to the highly exothermic reactions observed for $(NH_4)_2CrO_4$ at 269.1°C (Fig. 2). The decomposition process is accompanied by a weight loss of 9.0% and the release of H₂O, NH₃, N₂, and O₂ gases. The exothermic reaction at 278.5°C, accompanied by heat release, initiates the decomposition of the *trans*- $[Pd(NH_3)_2Cl_2]$ formed in the first step of the thermolysis process. The decomposition is an exothermic process and requires energy. The thermal destruction of this component is responsible for a large endothermic doublet in the DSC curve, with maxima at 308.8 and 328.8°C. In this process, the weight loss is 26.6% of the initial weight and the average weight loss rate is 6%/min. According to mass spectrometry data, at 331.6°C the gas phase contains not only H₂O, NH₃, N₂, and O₂ but also HCl (Fig. 3). In our opinion, this can be interpreted as evidence for predominant decomposition of the palladium salt in this step. The total weight loss in the second step is 35.6% ($\Delta m_{\text{meas}} = 35.6\%$, $\Delta m_{\text{calc}} = 35.0\%$), and this corresponds to the removal of H₂O, 5NH₃, 1/2N₂, 4HCl, and 3/4O₂. According to X-ray diffraction data, the solid products of the thermal transformations at 308 and 328°C consist of two phases, $[Pd(NH_3)_2Cl_2]$ and a cubic phase isostructural with



Fig. 3. (a) Thermal analysis results for a $3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4$ mixture in an argon atmosphere and mass spectra of the gas phase formed.

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Step	Temperature range, °C	$t_{\rm event}, {}^{\circ}{\rm C}$		$\Delta m, \%$		/C	Overall composition	
		DTG	DSC	experiment	calculation	<i>m</i> /Iormula	gas phase	solid phase
1	190–260	235	"—" 234.9 "—" 259.5	7.4	7.4	17/NH ₃ 18/H ₂ O 28/N ₂	2NH ₃ H ₂ O 1/2N ₂	$Pd_{3}CrCl_{6}-O_{3}N_{11}H_{36}$
2	260-340	279.4 327.4	"—" 278.5 "—" 308.8 "—" 328.8	35.6	35.0	17/NH ₃ 36/HCl 18/H ₂ O 28/N ₂ 32/O ₂	5NH ₃ 4HCl H ₂ O 1/2N ₂ 3/4O ₂	Pd ₃ CrCl ₂ - O _{0.5} N ₅ H ₁₅
		$\Sigma \Delta m_{1-2}$		43	42.4			
3	340-425	384 397	372.5 385.2 398.6	16.3	18.5	36/HCl 17/NH ₃ 18/H ₂ O 28/N ₂	2HCl 4NH ₃ 1/2H ₂ O 1/2N ₂	Pd ₃ Cr
		$\Sigma \Delta m_{3-4}$		59.3	60.9			
		<i>m</i> _{solid residue}		40.7	39.1			

Table 1. Thermal analysis and mass spectrometry data for the $3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4$ mixture and assumed overall compositions of the solid intermediate products [reaction (6)]

Pd (Fig. 5a), like the samples obtained at 235 and 260°C. At the same time, the unit-cell parameters of the cubic phases isostructural with Pd (a = 3.896(1) Å at 308°C and a = 3.894(3) Å at 328°C) are smaller than that of pure Pd (a = 3.905(5) Å) with allowance for experimental uncertainty (Fig. 4). The slight decrease in unit-cell parameter indicates the formation of palladium-based solid solutions, Pd_{1-x}Cr_x, in the samples, because r(Cr) = 1.27 Å is smaller than r(Pd) = 1.37 Å [23]. This fact correlates well with results reported by Korenev et al. [16], which confirm the formation of a Pd_xCr_y solid solution as a result of the thermolysis of the [Cr(NH₃)₅Cl][PdBr₄] · H₂O double salt in a hydrogen atmosphere.

Next, in the third step, the thermolysis of the mixture in the range 340–425°C is accompanied by a series of endotherms peaking at 372.5, 385.2, and 398°C. The gaseous thermolysis products include H₂O, NH₃, N₂, and HCl, but in much smaller amounts than in the preceding decomposition step. The weight loss in this step is 16.3% ($\Delta m_{\text{meas}} = 16.3\%$, $\Delta m_{\text{calc}} = 18.5\%$), which corresponds to the removal of 1/2H₂O, 4NH₃, 1/2N₂, and 2HCl.

According to X-ray diffraction data, the reaction product obtained at 372°C contains two isostructural cubic phases (Fig. 5): Pd (a = 3.894(9) Å) and a Pd_{1-x}Cr_x solid solution (its unit-cell parameter, a = 3.889(2) Å, is smaller than that of pure Pd, a = 3.905(5) Å (as represented by points t = 372(1) and t = 372(2), respectively, in Fig. 4). It should be emphasized that the Cr

content of the solid solution obtained at 372°C exceeds that of the solid solutions obtained at 308 and 328°C.

X-ray diffraction data demonstrate that the samples obtained at temperatures of 385 and 398°C and the final solid reaction product (500°C) consist of a palladium-based Pd_{1-x}Cr_x solid solution. The unit-cell parameters of the cubic phases in these samples, a = 3.8939(4) Å (385°C), a = 3.895(1) Å (398°C), and a = 3.897(2) Å (500°C), are smaller than the unit-cell parameter of pure Pd: a = 3.905(5) Å. It should be stressed that, with increasing temperature, the amount of Cr in the samples decreases: the largest amount of chromium was found in the sample obtained at a temperature of 372°C.

Attention should be paid to the fact that, according to Savitskii et al. [24], annealing of palladium—chromium alloys containing 24–26 at % chromium at temperatures below 500°C leads to the formation of an ordered $L1_2$ phase, which was not detected in this study.

The total weight loss of the mixture is 59.3% $(\Delta m_{\text{meas}} = 59.3\%, \Delta m_{\text{calc}} = 60.9\%)$ and the weight fraction of the solid residue is 40.7% ($m_{\text{solid residue calc}} = 39.1\%$), which corresponds to the overall formula of the residue Pd₃Cr. The total weight fraction of the metals in the mixture is 41.8%. We detected no reflections from other phases, in particular, no reflections from oxides. The chemical composition of the final product can be represented by the formula Pd₈Cr_{0.2}O_{0.7}. The observed oxygen content of the samples can be interpreted as evidence that the trace amounts of chromium not



Fig. 4. Unit-cell parameters (with allowance for experimental uncertainty) of the cubic phases isostructural with Pd in the $3[Pd(NH_3)_4]Cl_2-(NH_4)_2CrO_4$ system.

incorporated into the solid solution are rapidly oxidized by atmospheric oxygen when the samples are withdrawn from the reactor.

Thus, taking into account all of the above, the thermal transformation of the $3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4$ mixture at 500°C in an inert gas (argon) flow can be represented by the following scheme:

$$3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4
\rightarrow Pd_3Cr + 3/2N_2 \uparrow + 11NH_3 \uparrow (6)
+ 6HCl \uparrow + 2.5H_2O \uparrow + 3/4O_2 \uparrow.$$

According to X-ray diffraction data, the product of the thermal transformation of the $3[Pd(NH_3)_4]Cl_2 +$ $(NH_4)_2CrO_4$ mixture at 500°C in air consists of two phases: Pd (whose unit-cell parameter, a = 3.903(3) Å, coincides to within the present experimental uncertainty with that of pure Pd, a = 3.905(5) Å, Fig. 4) and PdO. No reflections from other phases were detected. Elemental analysis data indicate that the composition of the thermolysis product is Pd_{7.4}Cr_{1.5}O_{1.0}. The absence of reflections from chromium correlates well previous results [25].

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The solid-state reaction in the mixture in air at 500° C can be represented by the scheme

$$3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4 \rightarrow 2Pd + PdO + 1/2Cr_2O_3 + 12NH_3^{\uparrow} + N_2^{\uparrow} (7) + H_2O^{\uparrow} + 3/4O_2^{\uparrow} + 6HCl.$$

CONCLUSIONS

The thermal stability of a $3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4$ mixture is determined by the onset temperature for $(NH_4)_2CrO_4$ decomposition (150°C), which is accompanied by one endotherm (157.5°C) and two exotherms: small (232.2°C) and large (269.1°C).

The product of $3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4$ thermolysis in argon at 500°C in this study consists of a single phase: palladium-based $Pd_{1-x}Cr_x$ solid solution isostructural with palladium and having a unitcell parameter a = 3.897(2) Å.

The formation of the final solid product in argon proceeds through the formation of metallic palladium and chromium, as evidenced by the formation of a



Fig. 5. X-ray diffraction data for the solid decomposition products of a $3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4$ mixture; (a) samples obtained at 328 and 372°C; (b) peak at $2\theta \sim 40^\circ$ in the X-ray diffraction pattern of the sample prepared at 372°C.

 $Pd_{1-x}Cr_x$ solid solution and the absence of chromium oxide phases in all of the solid intermediate thermolysis products.

largest amount of chromium was found in the sample obtained at a temperature of 372°C.

The amount of chromium in the samples varies during heating: first increases and then decreases. The

The product of the thermolysis of the $3[Pd(NH_3)_4]Cl_2 + (NH_4)_2CrO_4$ mixture at 500°C in air consists of the phases Pd and PdO.

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