COMPOSITE OF Pd OR Pt WITH CHROMIUM OXIDE(III) AS CATALYSTS IN CO PROX AND CO TOX PROCESSES

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Abstract

Thermal decomposition of complex salts $[M(NH_3)_4]A$ (M = Pt, Pd; A = CrO_4, Cr_2O_7) in oxygen atmosphere goes through the stage of formation of the phase $MCrO_2$ with delafossite structure and it's further decomposition and formation of the chromium oxide(III) and monometallic platinum or palladium. Thermal decomposition of complex salts $[M(NH_3)_4]A$ (M = Pt, Pd; A = CrO_4, Cr_2O_7) in hydrogen atmosphere proceeds with partial reduction of chromium to an metallic state and the formation of a metal solid solution M_xCr_{1-x} (M = Pt, Pd) with a chromium content up to 22 at.% and a chromium oxide(III). Catalytic properties of bimetallic Pt-Cr_2O_3 and Pd-Cr_2O_3 composites obtained by thermal decomposition in hydrogen atmosphere at the temperature 500 °C differs a lot from monometallic Pt and Pd in CO TOX and PROX processes. Addition of Cr_2O_3 boosted oxidative activity of metals probably due to appearance of metal-oxide interface, which is of crucial importance in catalysis.

Keywords: Platinum, palladium, chromium, catalysis, thermal decomposition

1.   INTRODUCTION

One of the actively developing areas of modern inorganic chemistry is the synthesis of complex salts - salts with complex cation and/or anion with different central atoms [1]. Depending on the conditions the thermal decomposition of such compounds leads to the formation of a variety of nanosized powders of metals and/or their oxides. Using the complex salts of metals is very convenient because the selection of suitable ligands and central metals makes it possible to uniquely set the composition of the final product and the ratio of metals, to obtain a single-phase metal and have only gaseous substances as by-products. The selection of the atmosphere and the temperature regime of the decomposition make it possible to control the morphology and the phase composition of the final products [2-4].

Hydrogen atmosphere predominantly results in formation of metallic systems, oxidative one - oxide systems, and inert - both metallic and oxide systems depending on the nature of the complex salt [3]. The products of such thermal decomposition are of great interest since they can have conductive and magnetic properties, e.g. using the Pt-Cr system as a coating for carbon electrodes increases conductivity and strength of electrodes [5] and two-layer films consisting of Cr_2O_3 and Pt have interesting magnetic behavior near the Neel point [6]. The products of the thermolysis can also be effective catalysts [7,8].

The use of alloy nanoparticles and metal-oxide nanostructures is a promising way to modify activity and selectivity, improve stability or at least partially substitute expensive noble metals in conventional supported metallic catalysts, such as Pt-, Pd- and Rh-based systems [9]. CO total oxidation (TOX) and CO preferential oxidation in the excess of hydrogen (PROX) are reactions in which the properties of conventional Pt- and Pd-based catalysts need to be improved. The CO TOX is important for low-temperature start of automotive catalysts. The CO PROX is considered to be a promising way for deep CO removal from hydrogen-rich gas mixtures for proton-exchange membrane fuel cells (PEMFCs) feeding [10]. Bimetallic Pt-M and Pd-M (M = Fe,

Co, Ni, Cu) systems showed a remarkable synergetic effect in CO TOX and PROX compared to Pt and Pd monometallic catalysts [11,12]. The origin of synergetic effect was mainly addressed to reaction occurrence at Pt(Pd)-M metallic or Pt(Pd)-MOx metal-oxide interface [5]. However the approaches for synthesis of Pt-Cr and Pd-Cr nanostructures as well as its catalytic properties are poorly studied. There were synthesized solid solutions and intermetallic compounds in the Cr-Pt, Cr-Pd systems in works [13] however their catalytic properties were not studied.

In the present work we report the thermal properties of complex salts $[M(NH_3)_4]A$ (M= Pt, Pd; A= CrO_4, Cr_2O_7). Thermal properties were examined by simultaneous thermogravimetry and differential scanning calorimetry with evolved gas analysis mass-spectrometry in the oxygen atmosphere. The products of the thermal decomposition were characterized by X-ray analysis. Catalytic properties of M-Cr_2O_3 (M = Pt, Pd) composites were studied in CO total (TOX) and preferential oxidation (PROX) reactions and compared with that of monometallic Pt and Pd nanopowders.

2. THERMAL PROPERTIES

2.1. Thermal properties of $[M(NH_3)_4]A$ (M = Pt, Pd; A = CrO_4, Cr_2O_7) in an oxidative atmosphere

Complex salts $[M(NH_3)_4]A$ (M= Pt, Pd; A= CrO_4, Cr_2O_7) has the same behavior during the thermal decomposition and differs only in the temperatures of the beginning and the end of decomposition. Therefore, the process of thermal decomposition will be discussed in details using the palladium salt as an example.

The decomposition of $[Pd(NH_3)_4]CrO_4$ in the oxygen atmosphere begins at the temperature 165 °C and accompanied by the main gas evolution: lines corresponding to nitrogen and water are presented on EGA-MS curves (**Figure 1a**).
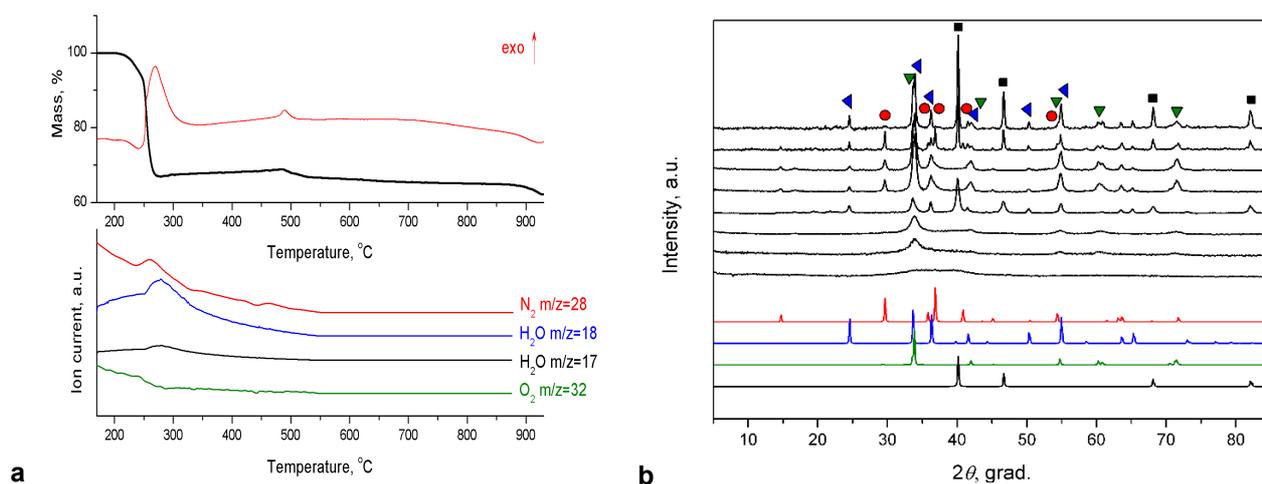
Figure 1 STA and EGA-MS curves for $[Pd(NH_3)_4]CrO_4$ in an oxygen atmosphere, 10 K min^{-1}(a) and XRD powder patterns of $[Pd(NH_3)_4]CrO_4$ thermolysis products in an oxygen atmosphere at different temperatures (b)

The evolution of ammonia was not detected, what indicates the occurrence of a redox reaction associated with the oxidation of the ammonia to nitrogen and the reduction of palladium to a metallic state and chromium to an oxidation state «+3». At the same time oxygen evolution is observed what can be related with the oxidation of the monometallic palladium. At a temperature 270 °C the residual mass is 66.9 %, what corresponds to the gross composition $PdCrO_{2.2}$ or $1/2Cr_2O_3$ + ½(1.4PdO + 0.6Pd). There are wide reflections of the amorphous phase on a diffractogram of the product obtained at this temperature (**Figure 1b**).

A further temperature increases to 485 °C leads to a mass increase up to 68.9 % that is associated with the gradual oxidation of metallic palladium. There are only PdO reflections on a diffractogram at the 400 °C and their intensity increases slightly upon heating to 450 °C. There is a mass loss step (~ 2 %) in the temperature range 485 - 525 °C that is associated with the crystallization of amorphous chromium oxide Cr_2O_3 and partial decomposition of palladium metal to metal (what is proved by oxygen evolution). It should be noted that the temperature of the decomposition of pure palladium oxide equals to 800 °C. There are reflections of metallic palladium and palladium oxide and chromium oxide in a diffractogram at the temperature 500 °C.

Over crystallization of chromium oxide particles local overheating occurs which leads to partial decomposition of palladium oxide to metal. The increase in temperature up to 890 °C is accompanied with a slow process of mass loss, that is corresponds to the gradual decomposition of palladium oxide to metal and the simultaneous formation of the phase of delafossite-like $PdCrO_2$. The diffractogram contain reflections of chromium oxide, palladium oxide and phase $PdCrO_2$ with a delafossite structure at temperatures 600 °C and 700 °C. There are no peaks of metallic palladium due to the entry of Pd atoms into the structure of $PdCrO_2$. In the temperature range 890 - 925 °C the last decomposition stage proceeds. Peaks of the metallic Pd appear at the temperature 900 °C and at the temperature 930 °C peaks of the $PdCrO_2$ disappear with the simultaneous increase in intensity of the metallic palladium. Thus, the $PdCrO_2$ phase with a delafossite structure exists in the temperature range 600 - 900 °C.

2.2. Thermal properties of $[M(NH_3)_4]A$ (M = Pt, Pd; A = CrO_4, Cr_2O_7) in hydrogen atmosphere

The decomposition of the main mass of the sample $[Pd(NH_3)_4]CrO_4$ occurs in the temperature range 110-175 °C and is accompanied by the release of water, nitrogen and ammonia, since in this case hydrogen is a main reducing reagent **Figure 2a**.
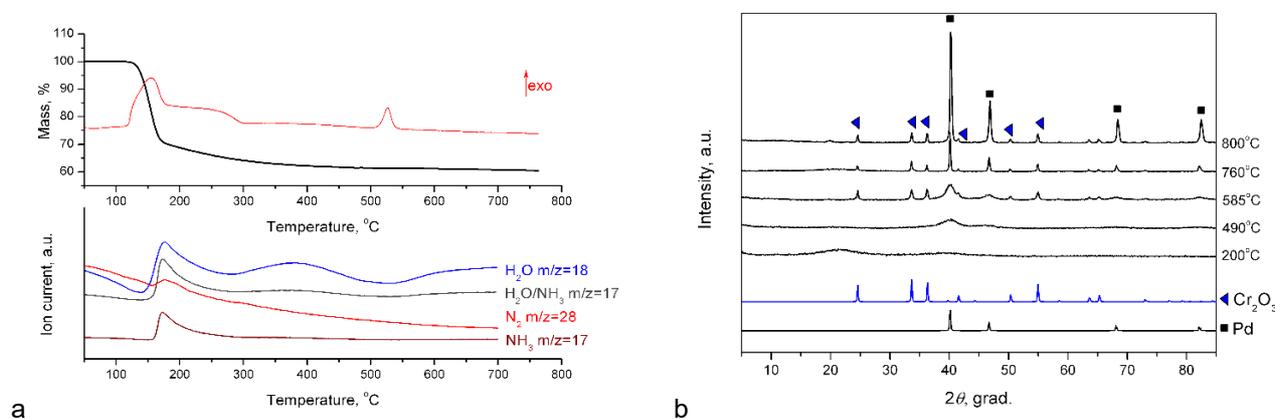
Figure 2 STA and EGA-MS curves for $[Pd(NH_3)_4]CrO_4$ in hydrogen atmosphere, 10 K min⁻¹(a) and XRD powder patterns of $[Pd(NH_3)_4]CrO_4$ thermolysis products in hydrogen atmosphere at different temperatures (b)

The product is amorphous at the temperature 175 °C (**Figure 2b**). Further process of decomposition slows down and the rate of mass loss decreases. Metallic palladium crystallization process starts at the temperature 490 °C and there are broad peaks of water on EGA-MS curves. There are wide reflections of the FCC phase on a diffractogram in this case (crystallite size 2-3 nm, residual mass is 61.5 % which corresponds to $PdCrO_{1.25}$). In temperature range 500-555 °C an exo effect associated with the crystallization of amorphous chromium oxide(III) is observed. Peaks of the Cr_2O_3 and finely dispersed palladium (crystallite size 3 - 5 nm) are observed in the diffractogram at the temperature 585 °C.

An increase in temperature to 800 °C leads to an increase in particles size (crystallite size 28 - 39 nm) and a shift of reflections of the FCC phase of palladium to the region of smaller angles, what can be related with the incorporation of chromium atoms into the palladium structure and the formation of a solid solution in Pd-Cr system. Refining the parameters of the unit cell of the FCC phase by full-profile method gives the following values: space group Fm-3m, a = 3.881 Å, V/Z = 14.6 Å^3. The obtained V/Z value corresponds to a $Pd_{0.85}Cr_{0.15}$ solid solution.

The decomposition of $[Pd(NH_3)_4]Cr_2O_7$ proceeds in a similar pathway to the palladium complex. There is an exo effect corresponded to the chromium oxide crystallization in the temperature range 505 - 570 °C. The diffractogram shows reflections of the FCC phase at 600 °C. The refinement of the crystal cell parameters of the crystal cell of the FCC gives the following values: space group Fm-3m, a = 3.881 Å, V/Z = 14.6 Å^3, which corresponds to a $Pd_{0.85}Cr_{0.15}$ solid solution. Further temperature increase leads to an increase in particles size.

In case of platinum salts the product at 600 °C is $Pt_{0.78}Cr_{0.22}$ solid solution. The product after temperature increase up to 800 °C is a mixture of intermetallic compound with a structure of Pt_3Cr and Cr_2O_3.

3.   CATALYTIC PROPERTIES

Catalytic properties of $Pd-Cr_2O_3$ and $Pt-Cr_2O_3$ systems were studied in CO total (TOX) and preferential oxidation (PROX) processes as model reactions for activity and selectivity testing, respectively. The data on CO TOX is presented at **Figure 7a**.
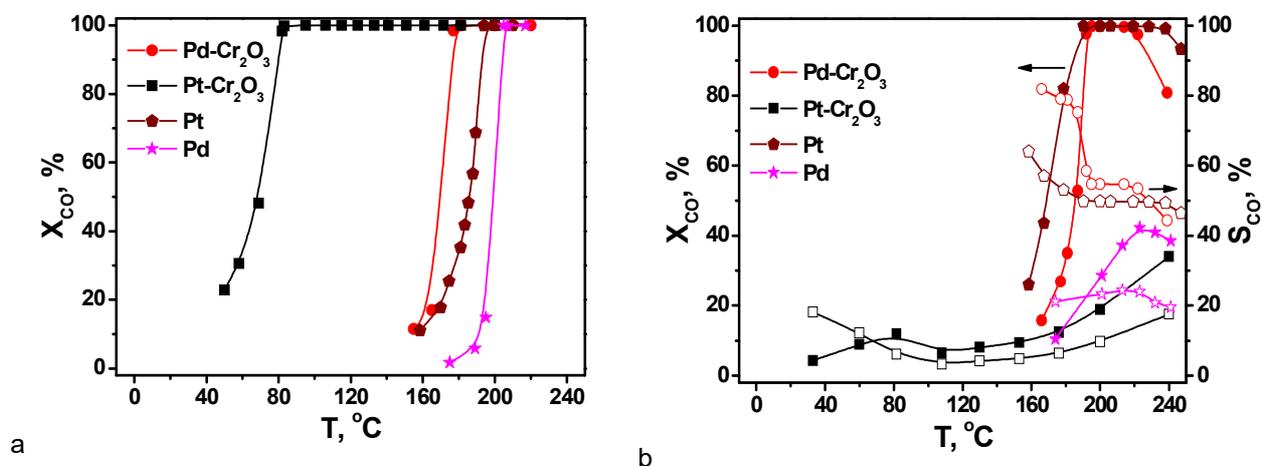
Figure 7 The temperature dependences of CO conversion (X_{CO}) for CO TOX (a) over the Pt, Pd, $Pd-Cr_2O_3$ and $Pt-Cr_2O_3$ nanopowders. Feed gas composition (vol.%): 1.0 CO, 1.0 O_2 with He as balance. WHSV: 120 000 cm^{3}g^{-1}h^{-1} (STP) (a) and the temperature dependences of CO conversion (X_{CO}) and selectivity (S_{CO}) for CO PROX over the Pt, Pd, $Pd-Cr_2O_3$ and $Pt-Cr_2O_3$ nanopowders. Feed gas composition (vol.%): 1.0 CO, 1.0 O_2 with H_2 as balance. WHSV: 120 000 cm^{3}g^{-1}h^{-1} (STP) (b)

It can be seen that Pt and Pd have similar properties in CO TOX: CO is oxidized at T = 160 - 200 °C. The presence of Cr_2O_3 with Pd slightly increases activity, possibly due to an increase in the dispersion of the metal. The presence of Cr_2O_3 with Pt significantly increased activity; a complete conversion of CO was already observed at 80 °C. It is known that Pt catalysts are inactive in CO oxidation at T <150 °C due to surface blocking by strongly adsorbed CO molecules and the absence of a free surface required for O_2 dissociation. Most likely, the Cr_2O_3 surface can participate in O_2 activation by analogy with other variable-valence oxides of other metals, and opens up the possibility of a reaction at the $Pt-Cr_2O_3$ phase boundary, which leads to high low-temperature activity.

The properties of Pt, Pd, Pd-Cr_2O_3 and Pt-Cr_2O_3 nanopowders have also been studied in the preferential oxidation of CO in excess of H_2 (PROX). It can be seen in the **Figure 7b** that Pd is active in the oxidation of CO at T = 160 - 240 °C, but has a low selectivity, mainly oxidizing H_2. The maximum conversion of CO was only 40%. The presence of Cr_2O_3 with Pd significantly increased the activity in the oxidation of CO and, accordingly, the selectivity of the catalyst in the temperature range 160 - 240 °C. At T = 195 - 215 °C, a complete conversion of CO was achieved. The oxidation of CO on Pt began at T > 150 °C, and the selectivity for CO did not exceed 65 %.

Such properties of Pt are explained by the fact that at low temperatures the filling of the Pt surface with adsorbed CO molecules is close to saturation, and the oxidation reactions of CO and H_2 do not proceed. With an increase in temperature, CO desorption occurs, empty Pt surface appear on which dissociative adsorption occurs, and thereby the oxidation of CO and H_2 is "triggered", therefore, high selectivity is not achievable on Pt. The presence of Cr_2O_3 with Pt radically changed the properties of the catalyst, increasing its activity in the oxidation of H_2 and reducing the selectivity below 20 %. A slow increase in CO conversion at T = 120-240 °C is probably associated with the course of the steam reforming of CO due to H_2O obtained during the oxidation of H_2.

4. CONCLUSION

It was shown that the process of thermal decomposition of synthesized compounds in an oxygen atmosphere is multistage and is accompanied by sequential reactions of the formation of platinum metal oxide, its decomposition at temperatures of 490 - 520 °C (which is significantly lower than the decomposition temperature of pure platinum metal oxide - 800 °C), the formation of the $MCrO_2$ phase with the structure of delafossite and its subsequent decomposition to metallic platinum or palladium and chromium oxide(III). For the first time, the existence of a phase of a delafossite-like compound containing platinum, $PtCrO_2$, has been shown experimentally.

It was established that thermal decomposition in hydrogen atmosphere undergoes with the partial reduction of chromium oxide into metallic state and simultaneous formation of a metal solid solution with chromium content up to 22 at %.

It has been shown that catalytic properties of bimetallic Pt-Cr_2O_3 and Pd-Cr_2O_3 differ a lot from monometallic Pt and Pd in CO TOX and PROX processes. Addition of Cr_2O_3 boosted oxidative activity of metals probably due to appearance of metal-oxide interface, which is of crucial importance in catalysis.

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