

# Pt Supported on Plasma-Chemical Titanium Nitride for Efficient Room-Temperature CO Oxidation

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## Abstract

Catalysts of carbon monoxide oxidation were synthesized by deposition of platinum on titanium nitride (TiN). Two substrates with an average particle size of 18 and 36 nm were obtained by hydrogen reduction of titanium tetrachloride in a stream of microwave plasma of nitrogen. The surface of the catalysts was studied by X-ray photoelectron spectroscopy (XPS). The data obtained by us in the present work indicate the presence of oxynitride as a transition layer between nitride and oxide. It was found that the CO oxidation rate on the 9 - 15 wt.% Pt loaded TiN catalysts is 120 times higher than that on the platinum black with a specific surface of 30 m<sup>2</sup>/g. Increase in the reaction rate of CO oxidation on Pt/TiN catalysts as compared to platinum black can be associated with both an increase in the concentration of CO molecules adsorbed and a decrease in the activation energy of the reaction. Catalysts are promising for use in catalytic air purification systems.

### **Keywords**

CO Oxidation, Titanium Nitride, Pt/TiN Catalysts, Carbon Monoxide, Microwave Plasma, Platinum Black, X-Ray Photoelectron Spectroscopy

## **1. Introduction**

Titanium nitride (TiN) is widely used due to its hardness, high electrical conductivity, corrosion resistance and high melting point [1] [2] [3], as well as its decorative properties, since its reflection spectrum is very similar to the reflection spectrum of gold [4] [5] [6] [7]. Recently, TiN has been used as a catalyst (electrocatalyst) for oxygen reduction reactions [8]-[13], and as a substrate for M/TiN catalysts, where M is a metal [14]-[21].

Catalytic oxidation of CO has received considerable attention in the related scientific literature (see, for example, publications [22]-[30] and references to them), due to its wide applications in exhaust gas after-treatment, CO oxidation for proton exchange membrane fuel cells and air purification systems. In this paper, we focus on low-temperature oxidation of CO in catalytic air purification systems. We hasten to note that the term "low-temperature oxidation" is rather a tribute to the tradition originating from the work of Haruta *et al.* [31], who reported that Au can be a highly active catalyst for the oxidation of CO at temperatures below 0°C. In principle, it is desirable to have catalysts in the air purification systems of residential premises, which work effectively at room temperature ( $15^{\circ}C - 25^{\circ}C$ ).

In this report, we present data on the synthesis and study of the properties of Pt/TiN catalysts for efficient room-temperature CO oxidation. Nano-sized TiN powder obtained by hydrogen reduction of titanium tetrachloride in a stream of nitrogen plasma was used as a substrate for the preparation of catalysts [32] [33] [34]. The study of the properties of catalysts in the oxidation of CO, which is contained in air at low concentrations (less than 100 mg/m<sup>3</sup>) at 295 K, showed that the CO oxidation rate on the 9 - 15 wt.% Pt loaded TiN catalysts is 120 times higher than that on platinum black with a specific surface of 30 m<sup>2</sup>/g.

There are many publications in the literature devoted to TiN, considering that it is of great practical interest, including investigation by XPS method [35]-[42]. However, the interpretation of experimental data obtained by XPS is somewhat different for different authors. This conclusion relates primarily to quantitative estimates which are connected both with different ways of subtracting the background in the XPS spectra and with the complexity of the object itself.

The fact is that titanium nitride exists as a homogeneous phase over a relatively wide range of compositions and has a tendency to oxidation. The composition and structure of the oxidized layer on the surface of titanium nitride depend on both the preparation method and storage conditions, and on the particle size.

#### 2. Materials and Methods

To obtain a catalyst based on titanium nitride nanoparticles, we used the method of reduction of catalytic metal (Pt) clusters on the surface of the support nanoparticles from an aqueous solution of  $H_2PtCl_6·6H_2O$  (99.9% (Cryochrom, St. Petersburg, Russia)) and a reducing agent (lithium formate-LiCOOH (99.9% (Cryochrom, St. Petersburg, Russia))) in the presence of support nanoparticles in solution. The catalyst was prepared as follows: an aqueous solution of  $H_2PtCl_6$   $6H_2O$  ( $10^{-3} - 10^{-2}$  mol/L) was mixed with an aqueous solution of lithium formate (0.02 - 0.2 mol/L). Then, the required amount of an aqueous solution of  $H_2PtCl_6·6H_2O$  and lithium formate was introduced into an aqueous suspension

of titanium nitride with a concentration of solid particles of 0.4 g/L heated to  $60^{\circ}$ C. After an induction period (8 - 15 minutes), platinum clusters are deposited on the surface of titanium nitride nanoparticles. After keeping the solution for 24 hours at room temperature, the catalyst was washed with distilled water (5 - 6 times) to remove the reaction products. The catalyst was dried at 80°C for 24 hours. After drying the catalyst, the Pt clusters were additionally reduced by blowing the catalyst with a mixture of high-purity nitrogen (99.998% (LindeGas, Balashikha, Russia) and hydrogen (5 vol.%) for 1 hour at 100°C.

A similar method was described in detail earlier [34]. Two catalysts K18 and K36 with a platinum content of 12 wt.% were selected as the main objects of study. TiN with a particle size of  $18 \pm 2$  nm and  $36 \pm 2$  nm was used as a substrate in the K18 and K36 catalysts.

XPS spectra were obtained using a Specs PHOIBOS 150 MCD electron spectrometer with an Mg cathode. The vacuum in the spectrometer chamber did not exceed  $4 \times 10^{-8}$  Pa. The spectra were recorded in the constant transmission energy mode. For quantitative estimates, we used the table values of specific densities (4.24 g/cm<sup>3</sup> for TiO<sub>2</sub> and 5.44 g/cm<sup>3</sup> for TiN), as well as the following values of photoelectron escape depths [9]:  $\lambda_1 = \lambda_{TiO_2}^{TiO_2} = 3.08$  nm,  $\lambda_2 = \lambda_{TiO_2}^{TiN} = 1.73$  nm.

The kinetics of CO oxidation in air on the catalyst was studied according to the method described in detail earlier [10].

#### 3. Results and Discussion

**Table 1** lists the elemental content in the layer analyzed by XPS (2 - 4 nm). It is seen that the nitride particles are covered with a thick layer of contamination, the origin of which is associated with the high activity of titanium nitride nano-particles and the conditions of their sufficiently long storage in air. The presence of silicon and sulfur in the sample we associate with the features of the technology for producing titanium nitride.

It is known that the Ti2p spectrum of an individual titanium compound is a spin-orbit doublet, which is described by two peaks  $(Ti2p_{1/2} \text{ and } Ti2p_{3/2})$  with an intensity ratio of 1:2 and a distance between the peaks of 5.7 eV [11].

The experimental spectrum of Ti2p our titanium nitride is well described by 6 peaks or 3 doublets (**Figure 1(a)**) corresponding to titanium in nitride (1), oxynitride (2) and oxide (3). The positions and relative intensities of the  $Ti2p_{3/2}$  peaks are shown in **Table 2**.

Table 1. XPS composition of the samples under study.

Sample	Composition (at. %)						
	С	Ν	0	Pt	Si	Ti	S
TiN (36 nm)	58.8	6.3	23.3	-	2.5	7.1	1.8
K36	75.9	1.8	15.4	0.4	1.2	4.9	>0.1
K18	54.3	5.6	26.5	0.9	0.2	12.3	>0.1

Sample	Peak	$E_{b}$ eV	FWHM, eV	<i>I</i> , %	<i>d</i> , nm
TiN	1	455.7	1.8	15.1	
	2	457.3	1.7	6.9	3.7
	3	459.0	1.8	44.7	
K18	1	456.1	2.0	30.3	
	2	457.6	1.6	11.2	1.6
	3	459.1	1.7	25.1	
K36	1	455.8	1.9	29.4	
	2	457.4	1.7	13.1	1.5
	3	458.9	2.1	24.1	

**Table 2.** Peak positions, full width at half-maximum (FWHM) and intensities of the  $Ti2p_{3/2}$  peaks obtained by decomposing the Ti2p spectra of the samples under study. The designation of the parameter "*d*" see in the text.



**Figure 1.** Ti2p (a) and N1s (b) XPS spectra of the titanium nitride; (c)—Pt4f XPS spectrum of K32 catalyst after treatment with carbon monoxide; (d)—Kinetics of CO oxidation at T = 295 K, P = 101 kPa and 30% humidity on K18 (1), K36 (2) catalysts and on Pt black (3) (at the same platinum content in the samples).

The thickness of the oxide film d can be calculated by a simple formula (see, for example, [12]):

$$\frac{I_{3}}{I_{1}} = \frac{I_{\text{Ti2p}}^{\text{TiO}_{2}}}{I_{\text{Ti2p}}^{\text{TiN}}} = \frac{\sigma_{\text{Ti2p}}^{\text{TiO}_{2}}}{\sigma_{\text{Ti2p}}^{\text{TiN}}} \frac{n_{\text{Ti}}^{\text{TiO}_{2}}}{n_{\text{Ti2}}^{\text{TiN}}} \frac{\lambda_{\text{Ti2p}}^{\text{TiO}_{2}}}{n_{\text{Ti2p}}^{\text{TiN}}} \left[ \exp(d/\lambda_{\text{Ti2p}}^{\text{TiO}_{2}}) - 1 \right],$$
(1)

where  $I_1$  and  $I_3$  are the intensity of the peaks in **Table 2**,  $\sigma_{\text{Ti2p}}$  is ionization cross section of Ti2p level,  $\lambda_{\text{Ti2p}}^{\text{TiO2}}$  is the escape depth of Ti2p photoelectrons from the oxide layer on the surface of the nitride.

Formula (1) for nanoparticles gives an overestimated value of d (Table 2), since it is derived for a flat infinite sample coated with an oxide film, and does not take into account the contributions to the intensity  $I_3$  of the oxide film from the side surfaces of the TiN nanoparticles.

In the spectrum of N1s (**Figure 1(b**)), in addition to the main peak related to nitrogen in the mononitride lattice ( $E_b$  = 397.1 eV), we can distinguish also 2 peaks with  $E_b$  = 399.2 and 401.6 eV (**Table 3**). According to the literature data [13], the peak with  $E_b$  = 399.2 eV can be associated with nitrogen atoms in the lattice of the oxynitride Ti(N,O). The peak with  $E_b$  = 401.6 eV in the literature is often attributed to molecular nitrogen [14], which is formed during the oxidation of nitride.

Thus, the particles of initial titanium nitride are covered with a rather thick film of titanium oxide, which contains nitrogen atoms. Between the nitride and the oxide on its surface is a thin layer of oxynitride.

The contents of elements (in atomic percent) in the near-surface layer of catalysts are presented in **Table 1**. It can be seen that, as in the initial TiN, a rather thick hydrocarbon film is present on the catalyst surface. It can be noted that in the process of preparing catalysts, the  $[N/Ti]_{at}$  ratio, calculated from the integrated intensities of the N1s and Ti2p lines, decreases by a factor of 2.

It can be seen (**Table 2**) that the ratio of  $I_3/I_1$  in catalysts is lower than that in the initial titanium nitride. Consequently, the thickness of the oxide film on the surface of TiN in the catalyst is less than that in the initial TiN.

Sample	Peak	$E_b$ , eV	FWHM, eV	<i>I</i> , %
TiN	1	397.1	2.3	71.3
	2	399.2	2.5	19.3
	3	401.6	2.8	9.2
K18	1	397.1	2.0	18.1
	2	399.4	2.6	80.1
	3	401.6	1.9	1.7
K36	1	397.1	2.7	30.8
	2	399.4	2.3	61.4
	3	401.6	2.7	7.7

**Table 3.** Positions, half-widths and intensities of peaks obtained by decomposing the N 1s spectra of the initial titanium nitride and catalysts.

The direct contact of platinum with oxinitride cannot be excluded either, since the oxide layer does not have to be continuous. Consequently, the properties of the contact between the catalytically active metal (Pt) and the substrate in the catalyst under study differ significantly from the Pt/TiO<sub>2</sub> contact.

The spectrum of Pt4f is well described by two doublets  $Pt4f_{7/2}$  and  $Pt4f_{5/2}$  (**Figure 1(c)**), one of which, with  $E_b(Pt4f_{7/2}) = 71.4 \text{ eV}$ , corresponds in its position to metallic platinum, the second (with  $E_b(Pt4f_{7/2}) = 74.3 \text{ eV})$ -Pt<sup>4+</sup> oxide. It should be noted here that the treatment of the catalyst with carbon monoxide does not lead to the complete reduction of platinum.

With a decrease in the CO concentration in the test chamber, an increase in the  $CO_2$  concentration occurs at the same time due to the irreversible oxidation reaction of CO with air oxygen. As can be seen from Figure 1(d) the time dependence of the CO concentration in the test chamber with a catalyst is described by Equation (2):

$$C_{\rm CO}\left(t\right) = C_{\rm CO}\left(0\right) {\rm e}^{-kt}, \qquad (2)$$

where  $C_{CO}(t)$  is the measured value of the concentration of CO in the test chamber,  $C_{CO}(0)$  is the value of the concentration of CO at the initial (zero) time, *k* is the reaction rate constant, *t* is the time.

From the experimental data shown in Figure 1(d), it was found that the reaction rate constant on K18 is  $120 \pm 20$  times higher than that of Pt black with a specific surface of 30 m<sup>2</sup>/g. It should also be noted that the reaction rate constant on K18 is  $1.5 \pm 0.1$  times higher than that on K36.

**Table 4** shows the comparative characteristics of the catalysts. The ratio of the reaction rates  $V_{18}/V_x$  per unit mass of Pt in the catalyst was determined, where  $V_{18}$  is the rate of the CO oxidation reaction on a catalyst with a TiN 18 particle size and a Pt content of 12 wt %, and  $V_x$  is the reaction rate on a catalyst with a TiN particle size 36 nm or Pt-black. The investigation of the CO oxidation reaction of these samples was carried out according to the procedure described above.

To determine the adsorption properties of platinum in the catalysts and in platinum black, the absorption of CO from the gas phase was measured. After processing the experimental results, it was found that the ratio of  $N_{CO}(Pt/TiN)/N_{CO}(Pt-black)$  is equal to 3.8 ± 0.4 for K18 and to 2.5 ± 0.3 for K36. The measurements were carried out at T = 295 K and P = 101 kPa.

**Table 4.** Comparative characteristics of catalysts at  $C_{CO}(0) = 100 \text{ mg/m}^3 T = 295 \text{ K}$ , P = 101 kPa, RH = 30%.

Catalyst	Particle SizePt, nm	Particle SizeTiN, nm	Pt content in catalyst, wt %	V <sub>18</sub> / V <sub>x</sub>
TiN/Pt	$8 \pm 1$	$18 \pm 2$	12	1
TiN/Pt	$12 \pm 1$	$36 \pm 4$	12	$1.0 \pm 0.1$
Pt-black	9 ± 1	-	100	$120 \pm 20$

#### 4. Conclusions

Thus, an increase in the reaction rate of CO oxidation on Pt/TiO<sub>2</sub>/TiN catalysts as compared to platinum black can be associated with both an increase in the concentration of CO molecules adsorbed and a decrease in the activation energy of the reaction. The reaction rate increases only by  $3.8 \pm 0.4$  times due to increase in the concentration of CO molecules on the surface of platinum. Therefore, the main reason for the increase in the reaction rate is possibly associated with a decrease in the activation energy of the CO oxidation reaction. From the Arrhenius equation, it follows that with a  $32 \pm 5$  times increase in the reaction rate, the calculated value of the decrease in activation energy will be from 8.1 kJ/mol to 8.5 kJ/mol. The reason for the decrease in the activation energy can be, for example, the formation of oxide layers of platinum on the surface of the Pt cluster [43] [44] or the influence of support (as in the case of support doping [45] [46]).

New catalysts of carbon monoxide oxidation were synthesized by deposition of platinum on titanium nitride with an average particle size of 18 nm and 36 nm. It was established that: 1) as a result of catalyst synthesis, the oxide film on the surface of titanium nitride is enriched with nitrogen, and its thickness decreases; 2) surface content of Pt is less than volume content; 3) treatment of the catalyst with carbon monoxide does not lead to the complete reduction of platinum.

The catalytic properties of Pt/TiN samples in the oxidation of CO at room temperature and low CO concentrations (less than 100 mg/m<sup>3</sup>) were studied. The reaction rate constant of CO oxidation on the 9 - 15 wt.% Pt loaded TiN catalysts was found to be 120 times higher than that on platinum black with a specific surface of  $30 \text{ m}^2/\text{g}$ .

The developed Pt/TiN catalyst is promising for use in catalytic and photo-catalytic air purification devices at low CO concentrations, subject to further research.

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#### **Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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