

Synthesis and Properties of a Carbon Monoxide Oxidation Catalyst Based on Plasma-Chemical Titanium Carbonitride, Titanium Dioxide, and Palladium

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Abstract—A CO oxidation catalyst based on plasma-chemical titanium carbonitride $\text{TiC}_{0.2}\text{N}_{0.8}$ and TiO_2 with a palladium content of 10 wt % has been synthesized. The dependence of the reaction rate of CO oxidation at room temperature and low CO concentrations ($<100 \text{ mg/m}^3$) on the $\text{TiC}_{0.2}\text{N}_{0.8}$ content has been studied. It has been found that, at $\text{TiC}_{0.2}\text{N}_{0.8}$ concentrations from 8 to 10 wt %, the catalyst exhibited a maximum rate of the CO oxidation reaction, which was 2.5 times higher than the rate of reaction on a catalyst based on pure TiO_2 that included palladium clusters. The catalysts are promising for use in catalytic and photocatalytic systems for air purification.

Keywords: CO catalyst, nanoparticles, titanium carbonitride, titanium dioxide, palladium

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Titanium dioxide is used as an active material in photocatalytic air purifiers for the removal of toxic gases, viruses, and bacteria [1–3]. The development of combined catalysts for photocatalytic devices with the efficient removal of both organic impurities and carbon monoxide (CO) from air is required because the photocatalytic removal of CO from air on pure titanium dioxide in a continuous mode is ineffective. Vershinin with coauthors studied CO catalysts based on nanomaterials and found that it is possible to form the nanoclusters of a catalytic metal (Pd or Pt) on the surface of nanodiamond (ND) [4, 5], β -SiC [6], and TiN [7], which are structurally similar to palladium and platinum. In this case, the cluster thickness is close to several lattice parameters of a catalytic metal; this ensures a high reaction rate of CO oxidation at room temperature and at low CO concentrations. The aim of this work was to synthesize a catalyst based on TiO_2 with the addition of plasma-chemical $\text{TiC}_{0.2}\text{N}_{0.8}$ nanoparticles including Pd clusters and to study its properties in the oxidation reaction of CO in order to assess the applicability of this catalyst to photocatalytic air purification systems.

EXPERIMENTAL

Titanium Carbonitride Synthesis Procedure

The $\text{TiC}_{0.2}\text{N}_{0.8}$ powder used in this work was obtained by the hydrogen reduction of titanium tetrachloride in a flow of microwave nitrogen plasma at atmospheric pressure. A mixture of titanium tetrachloride vapor with hydrogen and octane in a required ratio was introduced into a plasma nitrogen flow with an average bulk temperature of about 3000 K, which was obtained in a plasmatron using a microwave generator with a frequency of 2450 MHz and a maximum useful power of 5 kW. The volumetric flow rate of nitrogen was $2.5 \text{ m}^3/\text{h}$. The TiCl_4 feed rate was $3 \text{ g}/\text{min}$, and the flow rate of hydrogen was $0.4 \text{ m}^3/\text{h}$. The chemical interaction of the reactants and the condensation of $\text{TiC}_{0.2}\text{N}_{0.8}$ nanoparticles occurred in a tubular reactor 50 mm in diameter and 250 mm in length, the inner walls of which were lined with quartz. The particles formed in the reactor were separated from the gas phase by filtration on a bag filter after cooling the flow.

Catalyst Synthesis Procedure

Hombicat UV-100 TiO_2 (Sachtleben Chemie, Germany) and $\text{TiC}_{0.2}\text{N}_{0.8}$ obtained by the plasma-chemical method were used as a support for palla-

dium. The average size of $\text{TiC}_{0.2}\text{N}_{0.8}$ particles was close to 32 ± 4 nm, and the specific surface area and the average crystallite size of TiO_2 were about 380 ± 15 m^2/g and 5–8 nm, respectively. To obtain catalysts, we used the formation of palladium clusters on the surface of support particles in an aqueous solution containing palladium chloride and a reducing agent, lithium formate LiCOOH , according to a previously patented method [8]. The catalyst was prepared as follows: an aqueous solution of PdCl_2 (10^{-3} – 10^{-2} mol/L) was mixed with an aqueous solution of lithium formate (0.02–0.2 mol/L) at 20°C . Then, a required amount of the aqueous solution of PdCl_2 and lithium formate was introduced into an aqueous suspension of $\text{TiC}_{0.2}\text{N}_{0.8}$ and titanium dioxide with a solid particle concentration of 2 g/L heated to 45 – 50°C . After an induction period (5–10 min), palladium clusters were deposited on the surface of $\text{TiC}_{0.2}\text{N}_{0.8}$ and titanium dioxide particles. Then, the solution was cooled to room temperature for 6 h, and the catalyst was washed with distilled water (five or six times) to remove reaction products and dried at 80°C for 24 h. An HD 3200 ultrasonic homogenizer was used to prepare an aqueous suspension of TiO_2 and $\text{TiC}_{0.2}\text{N}_{0.8}$. After preparing the catalyst, we obtained an aqueous suspension of the catalyst once again, applied it to a porous plate ($40 \times 40 \times 6$ mm) sintered from glass beads 1 mm in diameter, and then dried it at 80°C for 24 h.

Instruments Used for Physicochemical Catalyst Characterization

Nitrogen adsorption/desorption isotherms and BET specific surface areas of titanium nitride samples were measured at liquid nitrogen temperature (77 K) using a Quantachrome Quadrasorb SI analyzer. The $\text{TiC}_{0.2}\text{N}_{0.8}$ samples were conditioned at 573 K in an atmosphere of helium using a FloVac Degasser for 3 h immediately before measurements. The X-ray diffraction spectra were recorded with a DRON ADP-2-02 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154056$ nm). A JEOL JEM 2100 transmission electron microscope and a SPECS PHOIBOS 150 MCD-9 electron analyzer with a magnesium anode X-ray source (Mg $\text{K}\alpha$ radiation, 1253.6 eV) were used to study the structure and composition of the catalyst surface with Pd clusters. An Acculab ALC-80d4 electronic balance was used for weighing the reagents and samples.

Procedure for Studying Catalytic Properties

The kinetics of CO oxidation in air on the catalyst was studied according to a procedure described earlier [6]. The study of the catalytic properties was carried out as follows: a test chamber was blown with a gas mixture of carbon monoxide with air with a CO concentration of 150 mg/m^3 for 600 s at a flow rate of 50 cm^3/s . Then, the inlet and outlet valves of the test

chamber were closed and a flow booster located in the test chamber was turned on to ensure gas mixture circulation through the sample with the catalyst at a rate of 30 cm^3/s . After a decrease in the concentration of CO a level of 100 mg/m^3 due to the catalytic reaction, a digital stopwatch was turned on and the readings of sensors were recorded. The test chamber with a volume of 0.3 ± 0.003 dm^3 was equipped with CO, CO_2 , and humidity and temperature (RH/T) sensors. A microprocessor-based converter was used for the processing of sensor signals. The following sensors were used: a NAP-505 CO sensor (Nemoto), an MSH-P/ CO_2 / $\text{NC}/5/\text{V}/\text{P}$ optical CO_2 sensor (Dynamont), and an SHT75 humidity and temperature sensor (Sensirion).

Results of Studying the Physicochemical Properties of the Catalyst

Figure 1 shows the results of X-ray diffraction analysis of the catalyst containing 81 $\text{TiO}_2 + 9$ $\text{TiC}_{0.2}\text{N}_{0.8} + 10$ wt % Pd. From the X-ray diffraction data, it was found that the coherent scattering region (CSR) of Pd clusters was close to 6 nm. Earlier, Vershinin et al. [6] found that the CSR of Pd clusters was close to 3.5 nm for a catalyst based on pure TiO_2 containing 10 wt % Pd.

Figure 2 shows the results of XPS studies of the catalyst (81 $\text{TiO}_2 + 9$ $\text{TiC}_{0.2}\text{N}_{0.8} + 10$ wt % Pd) using the decomposition of the Pd3d photoelectron spectra into individual components as an example.

Three main peaks with Pd3d_{5/2} binding energies of 335.4, 336.5, and 337.8 eV can be distinguished in the Pd3d spectra. The signals in the spectra are in good agreement with published data, and they characterize palladium in a metallic state with a Pd⁰ binding energy of 335.4 eV (Pd3d_{5/2}). The spin–orbital splitting between Pd3d_{5/2} and Pd3d_{3/2} sublevels is 5.26 eV. The peak of palladium with a binding energy of ~ 336.5 eV, which was observed in the spectra of a catalyst sample with titanium carbonitride, can be attributed to palladium(II) oxide, which was probably formed in the course of sample storage in air. The peak with a binding energy of 337.8 eV belongs to the state Pd⁴⁺, for example, in the composition of PdO₂ or to clusters localized at defects on the support surface [9, 10].

Results of Testing the Catalytic Properties of the Catalyst

Figure 3 shows the results of a study of the catalytic properties of the following catalysts: catalyst 1, 90 $\text{TiO}_2 + 10$ wt % Pd and catalyst 2, 81 $\text{TiO}_2 + 9$ $\text{TiC}_{0.2}\text{N}_{0.8} + 10$ wt % Pd. The concentration of CO_2 increased simultaneously with a decrease in the concentration of CO in the test chamber due to the irreversible reaction of CO oxidation by atmospheric oxygen ($\text{CO} + 1/2 \text{O}_2 = \text{CO}_2$) on the catalyst surface.

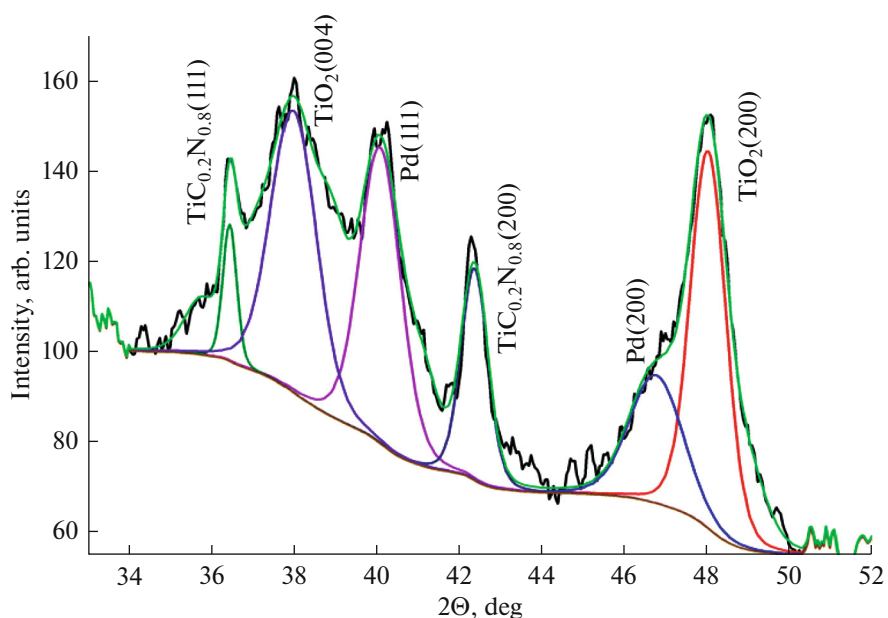


Fig. 1. Diffraction pattern of the catalyst containing 81 TiO₂ + 9 TiC_{0.2}N_{0.8} + 10 wt % Pd.

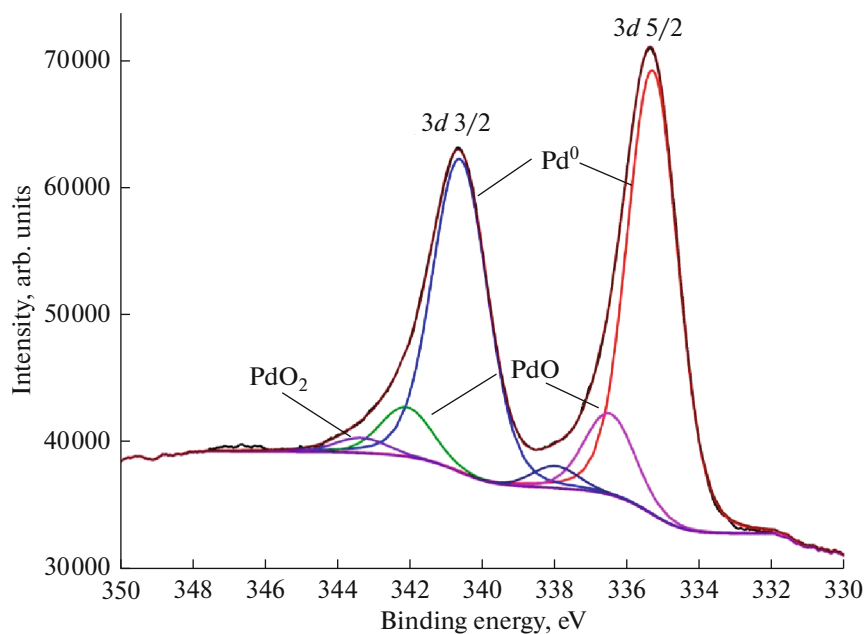


Fig. 2. The Pd3d XPS spectra of the surface of a Pd cluster in the catalyst containing 81 TiO₂ + 9 TiC_{0.2}N_{0.8} + 10 wt % Pd.

As can be seen in Fig. 3, the time dependence of the concentration of CO in the test chamber with a catalyst is described by the equation

$$C_{\text{CO}}(t) = C_{\text{CO}}(0)e^{-kt}, \quad (1)$$

where $C_{\text{CO}}(t)$ is the measured concentration of CO in the test chamber, $C_{\text{CO}}(0)$ is the concentration of CO at

the initial (zero) point in time, k is the reaction rate constant, and t is time.

To study the effect of catalyst composition on the catalytic properties, we synthesized and tested ten catalyst samples based on titanium carbonitride and titanium dioxide with a palladium content of 10 wt %, and the concentration of titanium carbonitride was varied from 0 to 30 wt %. The weight of Pd in each of the test

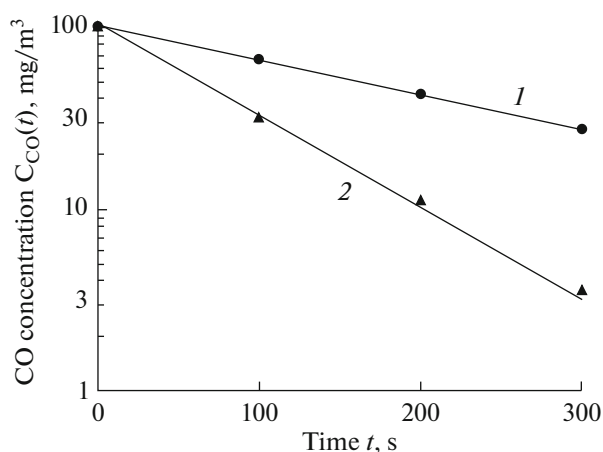


Fig. 3. Kinetics of CO oxidation on catalysts 1 and 2 at $T = 295$ K and RH = 30%

samples was close to 1.5 mg. The reaction rates of CO oxidation were determined for each sample after processing the experimental data based on Eq. (1). Then, the ratio between reaction rates V_x/V_0 was determined, where V_0 is the rate of CO oxidation at a concentration of 100 mg/m³ for a composition containing 0 wt % TiC_{0.2}N_{0.8}, and V_x is the rate of CO oxidation at a concentration of 100 mg/m³ for a catalyst containing x wt % TiC_{0.2}N_{0.8}. Figure 4 shows the results of the experimental studies.

To determine the adsorption properties of palladium in catalyst 1 and catalyst 2, the absorption of CO by a catalyst from the gas phase was measured. For this purpose, the sample with a catalyst was placed in a 50-cm³ stainless steel test chamber equipped with inlet and outlet valves for supplying a gas mixture. The test chamber was purged with dry nitrogen at a rate of 50 cm³/s for 100 s; then, it was purged with a mixture of CO and N₂ for 5 s at a rate of 50 cm³/s. Then, the inlet and outlet valves were closed and the volume fraction of CO was determined after 10 min. It was experimentally found that a nearly equilibrium volume fraction of CO in the test chamber was established within 10 min. For the analysis of CO, 3-cm³ samples were taken from the test chamber after 10 min; then, the sample was injected into a 300-cm³ measuring chamber filled with air. The volume fraction of CO in the measuring chamber was analyzed with a NAP-505 CO sensor (Nemoto). The amount of CO molecules adsorbed by the surface of Pd per unit weight of Pd in the catalyst can be calculated using the following formula:

$$N_{\text{CO}} = (C_{\text{ic}} - C_{\text{fc}})V_0 N_A / 100m_{\text{Pd}}V_M, \quad (2)$$

where C_{ic} is the initial volume fraction of CO in %, C_{fc} is the final volume fraction of CO in %, V_0 is the volume of the test chamber in dm³, N_A is the Avogadro number, m_{Pd} is the weight of palladium in the catalyst

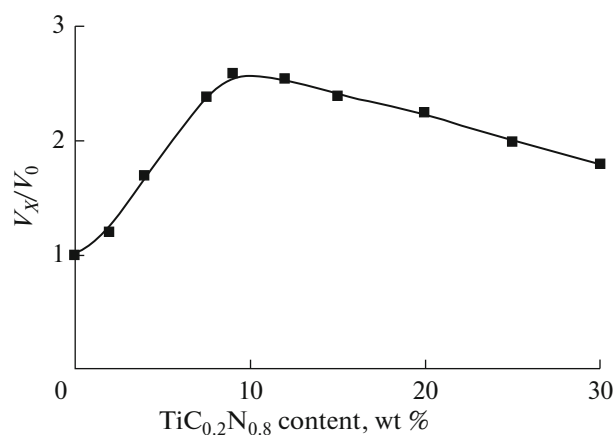


Fig. 4. Dependence of V_x/V_0 on the TiC_{0.2}N_{0.8} content of the catalyst at $T = 295$ K and RH = 30%.

in g, and V_M is the molar volume of gas in dm³. The weight of the catalyst was chosen to provide the final concentration in a range from 0.45 to 0.55 of the initial volume fraction of 1% CO. After the processing of experimental results, it was found that the ratio N_{CO} (Pd in catalyst 1)/ N_{CO} (Pd in catalyst 2) was close to 1.0 ± 0.15 . The measurements were carried out at a temperature of 295 K and a gas mixture pressure of 101 kPa in the test chamber.

DISCUSSION

From the experimental results, it was found that the catalysts were similar in the adsorption properties of palladium. From the data on the kinetics of CO oxidation, which are shown in Figs. 3 and 4 (per unit weight of Pd), it was found that the maximum rate of CO oxidation on palladium supported onto titanium dioxide with titanium carbonitride additives was higher by a factor of 2.5 than the rate of CO oxidation on palladium supported onto pure titanium dioxide. In this case, an increase in the reaction rate of CO oxidation can be associated with a decrease in the activation energy of the reaction rate. From the Arrhenius equation, it follows that the activation energy decreases by 2.2 ± 0.3 kJ/mol as the reaction rate increases by a factor of 2.5. Similar results were obtained in a study of silicon carbide additives [6]. At an optimal concentration of titanium carbonitride (8–10 wt %), TiC_{0.2}N_{0.8} acts as a center for the formation of palladium clusters with a low activation energy in the CO oxidation reaction and, hence, a maximum rate of the oxidation reaction. Preliminary tests of the catalyst in the photocatalytic oxidation of ethanol showed that the catalyst also efficiently oxidizes ethanol; therefore, the catalyst is also promising for use in catalytic and photocatalytic air purification systems for domestic applications.

CONCLUSIONS

A CO catalyst was synthesized on the basis of plasma-chemical $\text{TiC}_{0.2}\text{N}_{0.8}$ and TiO_2 . As a result of studying the reaction rate of CO oxidation as a function of the $\text{TiC}_{0.2}\text{N}_{0.8}$ content at room temperature, it was found that the catalyst exhibited a maximum rate of the CO oxidation reaction at a titanium carbonitride concentration of 8 to 10 wt %. At low CO concentrations ($<100 \text{ mg/m}^3$), the reaction rate of CO oxidation on the developed catalyst was higher by a factor of 2.5 than the reaction rate on the catalyst based on pure TiO_2 including palladium clusters. The catalysts are promising for use in catalytic and photocatalytic air purification systems.

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