Synthesis and properties of nanomaterial based catalyst for air purifiers

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Abstract. Catalyst based on nanosized titanium dioxide (5-7 nm) and nanodiamod (5 nm) has been synthesized. The catalyst contains 94 mass% of TiO₂, 3 mass% of ND and 3 mass% of Pd. The average size of Pd cluster is 4 nm. The catalyst has been analyzed by TEM, XRD and XPS methods. Kinetics of catalytic and photocatalytic oxidation of CO, ethanol, acetone and formaldehyde has been studied at room temperature and low concentration of impurities in air (< 40 mg/m³). A ratio of reaction rate constants for impurities to the reaction rate for ethanol has been determined. It has been shown that photocatalytic oxidation rate for ethanol is close to oxidation rate for CO. Oxidation rate for CO on the synthesized catalyst is three times higher than that for CO on an ND free catalyst. The catalysts synthesized by us are promising to be used in catalytic and photocatalytic in domestic air purifiers.

1. Introduction

The most efficient method of air purification in homes, offices and medical clinics used now is photocatalytic method. Photocatalytic method for air purification is studied to be modified [1-3]. The method is based on destruction of molecular impurities by air oxygen on the surface of semiconducting catalyst (titanium dioxide) under UV radiation. Main oxidation products are carbon dioxide and water. The photocatalytic method provides both elimination of toxic organic impurities and efficient disinfection of air from pathogenic microorganisms. However, some gases are not oxidized effectively on pure titanium dioxide under UV radiation. Particularly, photocatalytic method of air purification from carbon monoxide (CO) on pure titanium dioxide is not efficient. Moreover, if concentration of alcohols, ketones, other organic impurities, viruses and bacteria in air is high, their oxidation is not full, and side toxic products such as CO and aldehydes form. We found that thin clusters of catalytic metals (Pd, Pt) can form on nanodiamond (ND) and silicon carbide (β–SiC) surface. Previously, we showed that catalytic metal cluster thickness is close to 1-3 parameters of catalytic metal lattice (0.4-1.2 nm). Thus, high ratio of surface atoms to atoms in the bulk of cluster is provided. As a result, high catalytic activity of CO oxidation is attained at room temperature and low concentration characteristic of homes and offices [4-9]. The goal of this work is to study catalytic and photocatalytic oxidation of CO and organic impurities on a hybrid catalyst composed of ND and nanostructured titanium dioxide which contain Pd clusters, to estimate efficiency of usage in photocatalytic air purifiers in homes and offices.
2. Experimental

2.1 Synthesis of catalysts

TiO$_2$ of Homcat UV-100 (Sachtlichen Chemie GmbH, Germany) and nanodiamond of SDND trademark (Plasmochem, Germany) were used as supports. ND average size was 5±1 nm, and specific surface of TiO$_2$ was close to 380±15 m$^2$/g. Average size of crystallites was 5-7 nm. The catalyst was synthesized as described in [4]. Aqueous solution of PdCl$_2$ (10$^{-3}$-10$^{-2}$ mole/l) was mixed with aqueous solution of lithium formate (0.02-0.2 mole/l) at 20$^\circ$C. Then the calculated amount of aqueous solution of PdCl$_2$ and lithium formate was added to water suspension of ND and TiO$_2$ heated to 50$^\circ$C. Concentration of solid particles was 2 g/l. In 5-10 minutes of induction period Pd clusters precipitated on the surface of ND and TiO$_2$ particles. The solution was cooled down to room temperature during 6 hours, and catalyst was washed 5-6 times with distilled water to remove reaction products and dried for 24 hours at 80$^\circ$C. When the catalyst was dried, Pd clusters were reduced. By blowing the catalyst with nitrogen-hydrogen mixture (5 v/v, %) for 1 hour at 100$^\circ$C. Aqueous suspension of ND and TiO$_2$ was prepared in a HD 3200 ultrasonic homogenizer. Then 1 portion of the catalyst containing 82 mass.% TiO$_2$ + 9 mass.% ND + 9 mass.% Pd was mixed with 2 portions of pure TiO$_2$. So-homogenized mixture was applied to a porous plate 40×40×6 mm in size sintered from glassy balls 1 mm in diameter and dried for 24 hours at 80$^\circ$C.

2.2. Physical-chemical properties of catalyst

Physical-chemical properties of the synthesized catalyst were studied. Specific surface of the samples was measured by BET method from isotherms of adsorption/desorption of nitrogen at 77 K using a Quantachrome Quadrasorb SI analyzer. X-ray diffraction spectra were registered with a DRON ADP-2-02 diffractometer using Cu K$\alpha$ irradiation ($\lambda$ = 0.154056 nm). Morphology of catalyst and Pd cluster surface applied to a nanosized support was analyzed by TEM using a JEOL JEM 2100 microscope and a SPECS Phoibos 150 MCD spectrometer. Reagents and samples were weighed with an ALC-80d4 Acculab balance.

2.3. Analysis of catalytic properties

Photocatalytic and catalytic properties of the catalyst were analyzed as described in [6, 10]. A 300 liter test chamber was filled with air-impurity (CO or ethanol or acetone or formaldehyde) mixture. Then a blower was switched on, which provided 1 l/s air circulation rate through a plate with applied catalyst. A Phillips PL L 36 W lamp was used in photocatalytic experiments. Radiation power of the lamp was 9 W in the UV-A range. The lamp was located at a distance of 20 mm from the plate with applied catalyst. The test chamber was equipped with gas (CO, CO$_2$ and CH$_x$), humidity and temperature sensors (RH/T). Concentration of formaldehyde was determined with a HalTech Hal-HFX105 instrument. Sensor signals were processed with a microprocessor converter A NAP-505 (Nemoto) CO sensor, a MSH – P/CO$_2$/NC/5/V/P (Dynamet) CO$_2$ optical sensor, a TGS 2602 (Figaro) CH$_x$ sensor, and a SHT75 (Sensirion) humidity and temperature sensor were used.

3. Experimental results on analysis of catalytic and photocatalytic properties

The data on analysis of catalytic and photocatalytic oxidation of CO and ethanol and acetone and formaldehyde, respectively, are shown in figures 1 and 2. Catalyst mass was 1.8 g in all experiments.
Figure 1. Kinetics of catalytic oxidation of CO (1, 2) and photocatalytic oxidation of CO (3) and Et(OH) (4) at T= 296 K, RH =30 %, P= 1013 kPa, 1: 3 mass.% Pd + TiO$_2$, mass was 1.8 g. 2,3,4: 3 mass.% Pd +3 mass.% ND + TiO$_2$, sample mass was 1.8 g.

Figure 2. Kinetics of catalytic oxidation of HCOH (1) and photocatalytic oxidation of HCOH (2) and C$_3$H$_6$O (3) at T= 296 K, RH =30 %, P= 1013 kPa, sample mass was 1.8 g.
The time dependence of concentration of impurity in a test chamber filled with a catalyst is described by Eq. (1) characteristic of an irreversible process:

\[ C(t) = C_0 e^{-kt} \]  

(1)

\( C(t) \) is concentration of CO in a test chamber, \( C_0 \) is concentration of impurity at initial moment, \( k \) – reaction rate constant, \( t \) – время. The experimental data allowed reaction rate constants to be calculated for both catalytic and photocatalytic oxidation of CO, ethanol, formaldehyde and acetone. The ratio of reaction rate constant for oxidation of impurity to that for ethanol is presented in Table 1. It is seen that the constants of photocatalytic oxidation of ethanol and CO are close for the above-mentioned catalyst. Since the reaction rate is directly proportional to the reaction rate constant, reaction rates must be close at equal concentration. It was found from the experimental data presented in Figure 1 that oxidation reaction rate for CO on the catalyst with added ND is three times higher than on ND free catalyst.

### Table 1. Oxidation reaction rate constant ratio

| Formula | \( \text{C}_2\text{H}_5\text{OH} \) | CO | \( \text{CH}_2\text{O} \) | \( \text{C}_3\text{H}_6\text{O} \) |
|---------|-----------------|----|-----------------|-----------------|
| Ratio   | 1.00 | 0.90 | 1.10 | 0.60 |

### 4. Results and discussion

The two conditions at the least are to be fulfilled for preparation of a low-thickness cluster (1-3 parameters of Pd lattice) and its reliable adhesion to a support:

1. Support structure must be similar to that of catalytic metal (Pd) with lattice parameters differing no more than by 10%. Table 1 shows parameters of face-centered cubic lattice of diamond, silicon carbide and some metals. We chose diamond as support. Another suitable support is silicon carbide of cubic modification.

2. Necessary conditions for the synthesis of catalytic metal cluster on support surface are to be provided. We found that the best results are provided by lithium formate (reductant) for synthesis in the presence of support nanoparticles in water and the usage of salts/acids of palladium or platinum. Optimal conditions for synthesis were found as well. This allows Pd and Pt clusters of 0.4-1.2 nm thickness and 3-5 nm in diameter to be formed on ND and \( \beta \)-SiC surface [5, 6, 8, 9]. It was found by XPS method that Pd oxides form on the Pd cluster surface [9].

### Table 2. Parameters of cubic lattice of support and catalytic metal

| Formula | C - diamond | \( \beta \)-SiC | Pd | Pt | Au |
|---------|-------------|----------------|----|----|----|
| Lattice parameter a, nm | 0.357 | 0.436 | 0.389 | 0.392 | 0.408 |

Such approach was applied by us for the first time in patent [4]. It is reported in [11] on that conditions were determined in which thin Pt clusters can be formed on the surface of Au which is isostructural to Pt, and it is shown in [12] that Pt clusters on Cu-Au alloy nanoparticles show improved catalytic
properties in hydrogen-oxygen fuel cells. ND additives promote the formation of Pd cluster of low thickness with high active surface that results in higher reaction rate of CO oxidation. A 1.5-fold increase of oxidation reaction rate for CO under UV irradiation can be due to both higher temperature of catalyst surface and the effect of UV irradiation. Now it is impossible to evaluate unambiguously the effect of surface heating or the effect of UV. The catalytic oxidation reaction of CO can be written as follows:

\[
2\text{PdO} + 2\text{CO} \rightarrow 2\text{CO}_2 + 2\text{Pd}, \\
2\text{Pd} + \text{O}_2 \rightarrow 2\text{PdO},
\]

Net reaction on the catalyst is the following:

\[
2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2,
\]

Photocatalytic reactions for some impurities are listed below:

\[
\text{CH}_3\text{CH}_3 + 8 [\text{O}] \xrightarrow{h \nu \text{TiO}_2} 3\text{CO}_2 + 3\text{H}_2\text{O}, \\
\text{C}_2\text{H}_5\text{OH} + 6 [\text{O}] \xrightarrow{h \nu \text{TiO}_2} 2\text{CO}_2 + 3\text{H}_2\text{O}, \\
\text{HCHO} + 2 [\text{O}] \xrightarrow{h \nu \text{TiO}_2} \text{CO}_2 + \text{H}_2\text{O},
\]

5. Conclusion

Catalyst containing 94 mass.% TiO\textsubscript{2}, 3 mass.% ND and 3 mass.% Pd with average size of Pd cluster of 4 nm has been synthesized based on nanosized titanium dioxide (5-7 nm) and nanodiamond (5 nm). Kinetics of catalytic and photocatalytic oxidation of CO, ethanol, acetone and formaldehyde has been studied at room temperature and low concentration of impurities in air (< 40 mg/m\textsuperscript{3}). A ratio of reaction rate constants for oxidation of impurities and ethanol has been determined. It has been shown that photocatalytic oxidation rate for ethanol is close to oxidation rate for CO. Oxidation rate for CO on the synthesized catalyst is three times higher than that for CO on an ND free catalyst. The catalysts synthesized by us are promising to be used in catalytic and photocatalytic in domestic air purifiers.

6. References

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