ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 4, pp. 518–524. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © B.N. Shelimov, N.N. Tolkachev, G.N. Baeva, A.Yu. Stakheev, V.B. Kazanskii, 2011, published in Kinetika i Kataliz, 2011, Vol. 52, No. 4, pp. 529–535.

Photocatalytic Removal of Nitrogen Oxides from Air on TiO_2 Modified with Bases and Platinum

B. N. Shelimov*, N. N. Tolkachev, G. N. Baeva, A. Yu. Stakheev, and V. B. Kazanskii
Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia
**e-mail: bns@ioc.ac.ru*

Received July 9, 2010

Abstract—The efficiency of TiO_2 (Degussa P-25) modified with an alkaline admixture (urea, BaO), sulfuric acid, or platinum in the photocatalytic oxidation of NO (50 ppm) with a flowing 7% $O_2 + N_2$ mixture under UV irradiation in a flow reactor at room temperature and atmospheric pressure is reported. Because of the progressive blocking of active sites of the photocatalyst by the reaction products (NO_2, NO_3^-), it is impossible to realize prolonged continuous removal of NO_x ($NO + NO_2$) from air without catalyst regeneration at elevated temperatures. The efficiency of the photocatalysts is characterized by specific photoadsorption capacity (SPC) calculated from the total amount of NO_x adsorbed during 2-h-long irradiation. Modification of TiO_2 with 5% BaO or 5% urea raises the SPC of the catalyst by a factor of 2–3. Presumably, this promoting effect is due to the basic properties of these dopants, which readily sorb NO_2 and NO_3^-. A considerable favorable effect on SPC is also attained by adding 0.5% Pt to (5% BaO)/TiO_2. The SPC of the (0.5% Pt)/TiO_2 catalyst depends on the state of the platinum. The samples calcined in air at 500°C, which contain Pt^+ and Pt^{2+}, have an approximately 2 times higher SPC than unpromoted TiO_2 and ensure a much larger NO_2/NO ratio at the reactor outlet. Conversely, the samples reduced in an H_2 atmosphere at 200°C, whose platinum is in the Pt^0 state, show a lower SPC than the initial TiO_2 and cause no significant change in the NO_2/NO ratio.

DOI: 10.1134/S002315841104015X

Photocatalytic methods of removing organic and inorganic pollutants from air are being intensively developed now (see relevant reviews [1–7]). The most popular photocatalyst is titanium dioxide, which is catalytically very active, biologically and chemically inert, and fairly cheap. As TiO_2 is irradiated with UV light with a quantum energy exceeding its band gap (>3.0 eV for rutile and >3.2 eV for anatase), various organic atmospheric pollutants adsorbed on its surface are oxidized (mineralized) by atmospheric oxygen to CO_2 and water even at room temperature. When the initial organic pollutant molecule contains nitrogen, halogen, or sulfur atoms, there can be the undesired formation of oxides of these elements, which are toxic compounds. Both commercial TiO_2 brands and laboratory-made samples are used in photocatalysis. The latter are prepared by the hydrolysis of various organotitanium compounds followed by drying and calcination of the resulting TiO_2. The most active systems are those which have nanosized structure elements and, accordingly, are characterized by a developed surface and contain micropores. The syntheses of TiO_2-based nanomaterials, and their properties, modification methods, and applications are considered in recent reviews [8, 9].

The removal of nitrogen oxides, which are highly toxic compounds, from air is a challenging problem of environmental catalysis. It was demonstrated in a number of studies [10–16] that the irradiation of TiO_2 with UV light in air or in NO-containing O_2–N_2 mixtures yields NO_2. Part of the nitrogen dioxide remains adsorbed on the surface, and the rest of it is released into the gas phase. In addition, surface nitrate structures containing the NO_3^- fragment were identified by IR spectroscopy [17, 18]. At the early stages of UV irradiation, the concentration of NO_x ($NO_x = NO + NO_2$) at the outlet of the photocatalytic reactor is far below the initial NO concentration in the feed stream. However, the catalyst gradually loses activity with time because its active sites are blocked by the NO_2 and NO_3^- resulting from NO photooxidation, and the NO_x concentration at the outlet of the photocatalytic cell gradually approaches the initial NO concentration in the feed. The service life of the catalyst for NO_x removal from air depends on many factors, such as the initial NO concentration, the amount of TiO_2 in the reactor, the feed flow rate, and the humidity of the polluted air. TiO_2 fully restores its photocatalytic activity on being heat-treated in flowing air or inert gas at 400–500°C or washed with water. In the latter case, the adsorbed NO_3^- and NO_2^-, ions are washed off from the surface and the active sites become available for adsorption and subsequent photoreaction [12].

Because of the gradual poisoning of the TiO_2-based photocatalysts by the reaction products, it is impossible to carry out prolonged continuous photocatalytic NO_x removal from air without catalyst regeneration. However, the efficiency of the photocatalyst, i.e., the total amount of NO_x removed from air can be markedly increased by means of chemical modification. Some authors used mixtures of TiO_2 with adsorbents having a high adsorption capacity, such as type A and Y zeolites [19], montmorillonite [20], and activated carbon [21–23]. In these composite systems, part of the NO_2 desorbs from the TiO_2 surface and binds strongly to adsorption sites of the zeolite or carbon, thus vacating photocatalytic sites of TiO_2. Ichiura et al. [24] used thin composite plates prepared from a mixture of suspensions of TiO_2 and basic oxides (CaO, MgO) or $CaCO_3$. The nitrogen dioxide and HNO_3 that resulted from the photoreaction reacted with the oxides or carbonate. As a result, the amount of removed NO_x per unit weight of TiO_2 was substantially larger. We demonstrated earlier [25] that an efficient way of enhancing the specific photoadsorption capacity (SPC) of TiO_2 for nitrogen oxides is its dispersing on a support with a large specific surface area (e.g., Al_2O_3). The SPC of 50% TiO_2/Al_2O_3 per unit weight of titanium dioxide turned out to be >5 times higher than that of massive TiO_2. This effect is seemingly due to the fact that dispersion makes most of the TiO_2 atoms accessible to the adsorbing reactants and that part of the reaction products is captured by the support.

Thus, the problem of enhancing the specific activity, selectivity, and stability of titanium dioxide–based systems used in the photocatalytic removal of NO_x from air is still a challenge. Here, we report the preparation and testing of Degussa P-25 TiO_2 samples modified with alkaline admixtures and platinum, which is widely used as a promoter of various catalysts.

EXPERIMENTAL

Sample Preparation

The photocatalysts were unmodified and modified Degussa P-25 titanium dioxide samples ($S_{sp} = 48$ m^2/g). The BaO/TiO_2 sample (5% Ba) was prepared by incipient-wetness impregnation of TiO_2 with a solution of $Ba(NO_3)_2$ (analytical grade) followed by drying at 60°C and calcination in flowing air at 550°C for 2 h. The $Pt/BaO/TiO_2$ (0.5% Pt, 5% Ba) and Pt/TiO_2 (0.5% Pt) samples were prepared by incipient-wetness impregnation of BaO/TiO_2 (5% Ba) and TiO_2 with a solution of $[Pt(NH_3)_4]Cl_2$ (Aldrich) followed by calcination in air at 500°C.

$CO(NH_2)_2/TiO_2$ (5% urea) was obtained by incipient-wetness impregnation of TiO_2 with a urea solution and was dried at room temperature.

The SO_4/TiO_2 sample (2 wt % S) was prepared by double incipient-wetness impregnation of TiO_2 with 1 N H_2SO_4 followed by drying and calcination at 625°C for 4 h.

Determination of Photocatalytic Activity

The catalysts as a suspension of a fine powder in distilled water were applied onto the inner walls of a cylindrical, quartz, optically transparent, flow photoreactor (30 mm in diameter, 250 mm in height). Thereafter, the reactor was dried at 120°C overnight. The weight of the photocatalyst in the reactor was 0.2 g.

Photocatalytic activity in NO oxidation with oxygen was measured using a continuous-flow setup (Fig. 1) at atmospheric pressure near room temperature. The reactor, with a photocatalyst on its walls, was connected to the setup, and the photocatalyst was activated by heating it in flowing purified air at 500°C for 1 h. Next, the reactor was cooled to room temperature and a mixture modeling polluted air (45–50 ppm NO + 7 vol % O_2 + N_2) was passed through the reactor until the inlet and outlet NO concentrations were equal. The gas mixture flow rate was 440 cm^3/min.

The NO, NO_2, and NO_x (i.e., NO + NO_2) concentrations were measured in 5-s intervals on a luminescent NO_x analyzer (Eco Physics, Model CD70S) or on an IR analyzer (Temet Instruments, Model Gasmet^{TM} Dx-4000n). This IR analyzer was also used to determine the N_2O concentration in the gas.

After the removal of the furnace, the catalyst in the reactor was irradiated with UV light from two 26-W black light lamps. The radiant intensity of the lamp, measured with a Photex radiometer and a set of light filters, was distributed as follows:

Wavelength range, nm	420–390	390–370	370–350	350–320	320–290
Fraction of radiant intensity in the range, %	3.5	19.5	47.0	25.6	5.0

For a more uniform irradiation of the photocatalyst, the UV lamps were placed on both sides of the reactor; in addition, the reactor and lamps were surrounded with an aluminum shield.

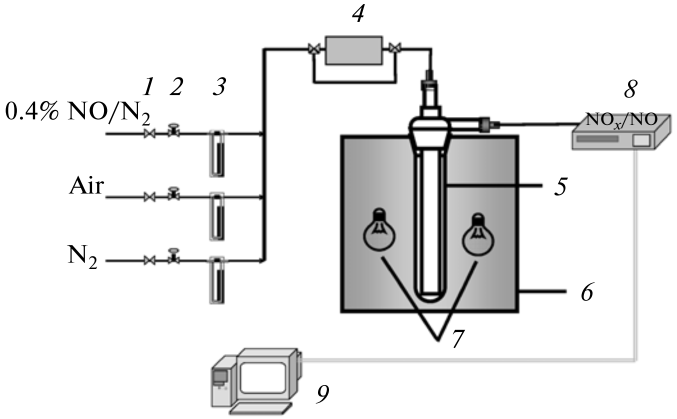


Fig. 1. Setup for photocatalytic activity measurements: (*1*) valve, (*2*) needle valve, (*3*) flow meter, (*4*) water separator, (*5*) quartz reactor, (*6*) aluminum shield, (*7*) UV lamps, (*8*) NO$_x$ analyzer, and (*9*) personal computer.

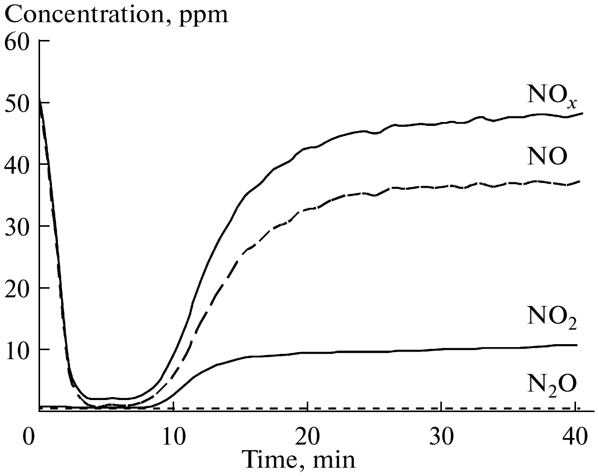


Fig. 2. Outlet NO, NO$_2$, NO$_x$, and N$_2$O concentrations as a function of the UV irradiation time for the TiO$_2$ (Degussa P-25) photocatalyst.

The state of supported platinum was determined by diffuse reflectance IR spectroscopy of adsorbed CO. Spectra were recorded on a Nicolet Protégé 460 IR spectrophotometer using a diffuse reflectance attachment. Before taking the spectra, the samples were heat-treated for 1 h at 500°C and a residual gas pressure of 0.01 Pa. The IR spectra were recorded at room temperature in the presence of CO (8 Torr) and after pumping the samples at 20°C (30 min) and 100°C (1 h).

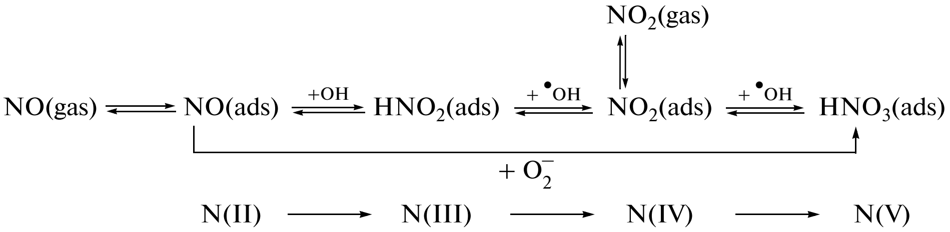
RESULTS AND DISCUSSION

It was established by preliminary experiments that, without UV irradiation, the NO concentration in the NO–O$_2$–N$_2$ stream at the inlet and outlet of the photoreactor with TiO$_2$ remains invariable for at least 2 h. After UV light is switched on, the outlet NO concentration falls sharply, and, after some period of time, whose length depends on the sample, NO$_2$ appears at the outlet, whose concentration then varies with time. No other products of the photoreaction were observed. Figure 2 presents the typical plots of the NO, NO$_2$, and NO$_x$ concentrations as a function of the irradiation time for the TiO$_2$ photocatalyst. The zero point corresponds to the beginning of irradiation.

The NO photooxidation reaction can be divided into three stages. At the initial stage, immediately after irradiation is started, the outlet NO concentration decreases rapidly to its minimum (near-zero) value and stays at this level for some time (Fig. 2). As this takes place, the NO$_2$ concentration in the gas is very low and almost invariable. According to ion chromatography data, the most abundant ion in the water that was used to wash irradiated TiO$_2$ is NO_2^- [12]. Therefore, at this stage, NO is mainly oxidized to HNO$_2$(ads). At the second, transitional stage, NO$_2$ appears in the gas phase and its concentration increases with time. Therefore, HNO$_2$ is further oxidized to NO$_2$, which can subsequently be oxidized to HNO$_3$. This is accompanied by a marked increase in the outlet NO concentration. At the third stage, the reaction reaches a steady state in which the NO$_x$ concentration is nearly equal to the inlet NO concentration; however, two nitrogen-containing components—NO and NO$_2$—are observed at the outlet. At this stage, nitrogen oxides are practically not removed from the gas. Moreover, since the single-exposure maximum allowable NO$_2$ concentration in the air for inhabited areas is 4.7 times lower than the NO concentration, according to sanitary regulations, this "purified" air is even more toxic than the initial air.

The washings obtained from the catalyst that is in the steady state are dominated by NO_3^- ions [12], whose concentration varies insignificantly with time at this stage. Therefore, NO is oxidized to NO$_2$, while HNO$_3$ remains on the surface, blocking active sites. Note that, once the steady state is reached, the outlet NO concentration is well below the inlet NO concentration. Hence, NO photooxidation does not cease at this stage, but the process is at equilibrium so that the NO$_2$ formation rate is equal to the rate of TiO$_2$ desorption from the photocatalyst surface. After the termination of the photoreaction, the initial activity of TiO$_2$ can be fully restored by removing the NO oxidation products via the heat treatment of the catalyst in flowing nitrogen at 650–773 K.

Thus, the overall NO photooxidation process can be represented as follows:



In this process, the oxidation state of nitrogen increases progressively from +2 (NO) to +5 (HNO_3).

The mechanism of NO photooxidation on TiO_2 was discussed in a number of publications [12, 24–29]. All researchers, based on the analogy between this process and gas-phase free-radical processes, agree that the key role in photooxidation is played by the $^{\bullet}OH$ radicals that result from the capture of holes photogenerated in TiO_2 by surface hydroxyl groups and adsorbed water molecules:

$$TiO_2 \xrightleftharpoons{h\nu} h^+ + e^-, \quad \text{(I)}$$

$$OH^- + h^+ \rightleftharpoons {}^{\bullet}OH, \quad \text{(II)}$$

$$H_2O + h^+ \rightleftharpoons {}^{\bullet}OH + H^+, \quad \text{(III)}$$

where h^+ is a hole and e^- is an electron site.

Reaction (III) was unlikely under our experimental conditions because the photocatalysts were pre-heat-treated in flowing air at 500°C.

The oxidation of NO with the $^{\bullet}OH$ radical takes place via the following consecutive reactions:

$$NO + {}^{\bullet}OH \rightleftharpoons HNO_2, \quad \text{(IV)}$$

$$HNO_2 + {}^{\bullet}OH \rightleftharpoons NO_2 + H_2O, \quad \text{(V)}$$

$$NO_2 + {}^{\bullet}OH \rightleftharpoons HNO_3. \quad \text{(VI)}$$

The electrons liberated in reaction (I) are likely captured by the electron acceptor molecules of oxygen:

$$O_2 + e^- \rightleftharpoons O_2^-. \quad \text{(VII)}$$

The subsequent fate of O_2^- is not usually discussed in the literature. It is quite obvious, however, that this species is involved in the photocatalytic process; otherwise, the catalytic cycle would be unrealizable.

We hypothesized earlier [25] that the radical anion $O_2^{-\bullet}$ directly oxidizes NO into the nitrate ion:

$$NO + O_2^{-\bullet} \rightleftharpoons NO_3^-. \quad \text{(VIII)}$$

As was mentioned above, the nitrate ion results from contact between TiO_2 and NO in the presence of oxygen. It was identified by IR spectroscopy [17, 18] and was also detected in the washings from TiO_2 after NO photooxidation.

Other NO oxidation mechanisms involving $O_2^{-\bullet}$ are also possible. Initially, $O_2^{-\bullet}$ may react with the proton liberated by adsorbed water via reaction (III):

$$O_2^{-\bullet} + H^+ \rightleftharpoons HO_2^{\bullet}. \quad \text{(IX)}$$

Next, the $HO_2^{\bullet}$ radical may oxidize NO to HNO_3:

$$NO + HO_2^{\bullet} \rightleftharpoons HNO_3. \quad \text{(X)}$$

Figure 3 plots the NO_x concentration at the outlet of the photoreactor versus the UV irradiation time for modified TiO_2-based catalysts. The time dependence of the NO_x concentration for the initial TiO_2 is also presented here for comparison. These dependences are similar in character for all catalysts, but they differ significantly in two parameters, namely, the minimum NO_x concentration attained soon after the beginning of irradiation and the time to reach the steady state. The efficiency of the photocatalysts in the removal of nitrogen oxides from air was estimated as the total amount of NO_x adsorbed by the photocatalyst during 2-h-long irradiation, which was determined by integrating the kinetic curves shown in Fig. 3. The calculated SPCs per gram of catalyst are listed in the table.

The modification of TiO_2 by impregnation it with an aqueous $Ba(NO_3)_2$ or urea solution followed by drying and heat treatment yields BaO/TiO_2 and $(NH_2)_2CO/TiO_2$ samples having, respectively, a 2 and 3.2 times higher SPC than unmodified TiO_2 (table). This promoting effect is likely due to the alkaline admixtures efficiently sorbing the resulting NO_2 and HNO_3. A significant increase in the SPC is also attained by adding 1% Pt to (5% BaO)/TiO_2. However, this leads to a marked increase in the NO_2/NO ratio under steady-state conditions. This is an undesired side effect in view of NO_2 being more toxic than NO.

The "acidic" TiO_2 prepared by impregnating the initial titanium dioxide with H_2SO_4 shows low efficiency in NO oxidation (Fig. 3). The causes of this greatly decreased efficiency of TiO_2/H_2SO_4 were not studied in this work because this photocatalyst is of no practical interest. Apparently, its low activity is due to the lower yield of $^{\bullet}OH$ radicals in reaction (II) because of the blocking of hydroxyl groups by H_2SO_4 molecules

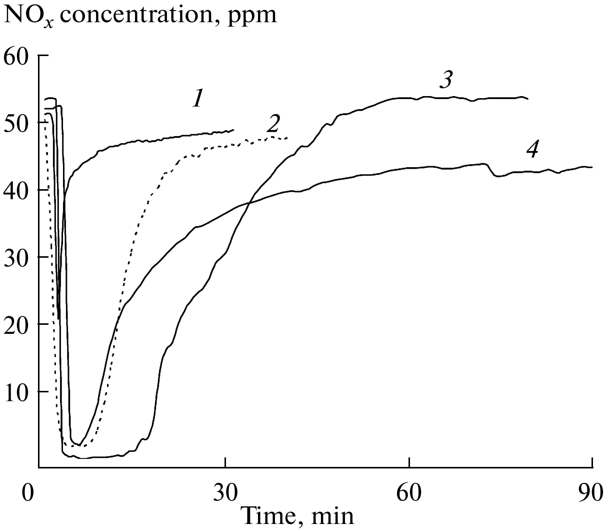


Fig. 3. Outlet NO_x concentration as a function of the UV irradiation time for the (*1*) SO_4^{2-}/TiO_2, (*2*) TiO_2, (*3*) BaO/TiO_2, and (*4*) $(NH_3)_2CO/TiO_2$ photocatalysts.

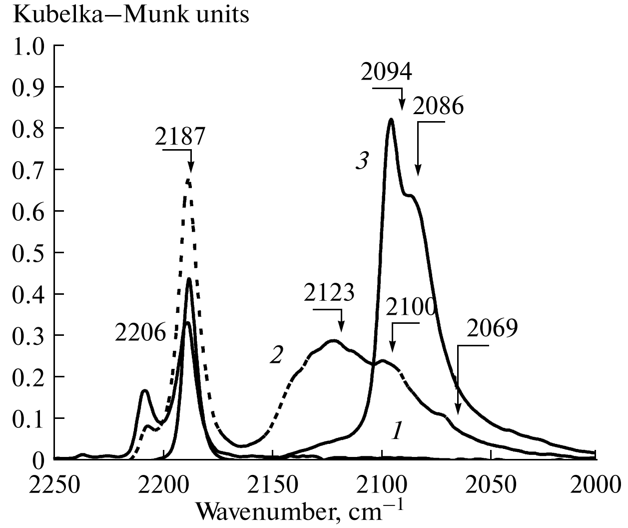


Fig. 4. IR spectra of CO adsorbed (*1*) on TiO_2 and (*2*, *3*) on Pt/TiO_2 after (*2*) heat treatment in air at 500°C and (*3*) subsequent reduction in an H_2 atmosphere at 200°C. $P_{CO} = 8$ Torr; room temperature.

and/or because equilibrium (III) shifts to the left with an increasing proton concentration.

The table also presents data illustrating the effect of Pt on the SPC of TiO_2. Clearly, the SPC depends on the state of platinum in TiO_2, which was monitored by recording the IR spectra of adsorbed carbon monoxide (Fig. 4). The spectrum of platinum-free TiO_2 after CO adsorption shows absorption bands at 2206 and 2187 cm^{-1} (Fig. 4, curve *1*), which disappear entirely upon the pumping of the sample at room temperature. These bands occur at lower frequencies than the band of free CO molecule ($\nu_{(CO)} = 2143$ cm^{-1}) and are due to the stretching vibrations of the C–O bond in weakly bonded Ti^{4+}–CO complexes [30]. The IR spectrum of Pt/TiO_2 preheated in air at 500°C and brought into contact with CO shows, along with the above absorption bands (which are assignable in this case to Pt^{2+}–CO complexes as well), an absorption band at 2123 cm^{-1} (Fig. 4, curve *2*). This band is characteristic of Pt^+–CO complexes. The lower frequency bands are conventionally assigned to complexes between CO and Pt^0 [30]. The changes in the intensity of absorption bands of adsorbed CO caused by pumping of the samples at different temperatures are illustrated in Fig. 5. At room temperature, the absorption bands of Pt^{2+}–CO (2206 and 2187 cm^{-1}) disappear entirely, while the band due to the Pt^+–CO complexes (2123 cm^{-1}) disappears only partially. These complexes decompose completely

Specific NO_x photoadsorption capacity of TiO_2-based photocatalysts

Photocatalyst	Inlet NO concentration, ppm	SPC		NO_2/NO in the steady state
		$\frac{\mu\text{mole } NO_x}{g_{Cat}}$	$\frac{\text{mol } NO_x}{\text{mol } TiO_2} \times 10^{-2}$	
TiO_2 (“Degussa P25”)	55	60	0.48	0.25
5% BaO/TiO_2	53	121	1.02	0.35
0.5% $Pt/5\%BaO/TiO_2$	55	194	1.56	5.09
5% $(NH_2)_2CO/TiO_2$	52	190	1.60	0.27
0.5% Pt/TiO_2 (oxidized)	50	110	0.88	4.49
0.5% Pt/TiO_2 (reduced)	50	44	0.35	0.20

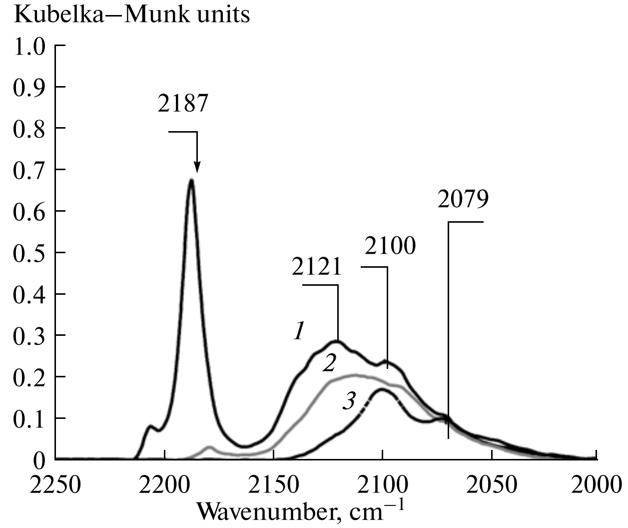


Fig. 5. IR spectra of CO adsorbed on the oxidized Pt/TiO_2 sample (*1*) after CO adsorption at room temperature and P_{CO} = 8 Torr and (*2*, *3*) after subsequent pumping of the sample containing adsorbed CO at (*2*) room temperature and (*3*) 100°C.

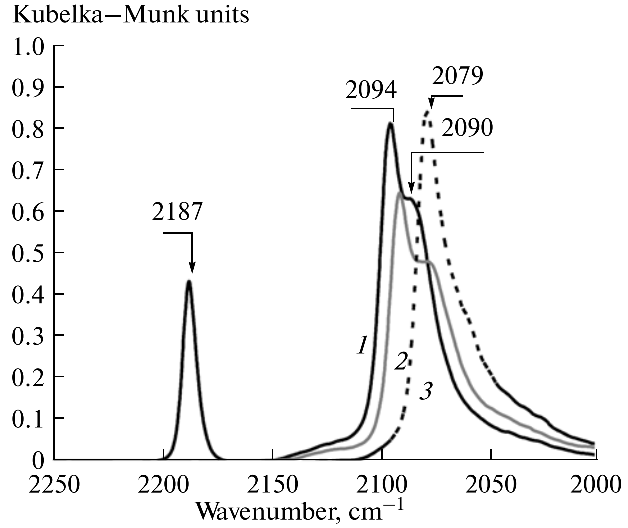


Fig. 6. IR spectra of CO adsorbed on the reduced Pt/TiO_2 sample (*1*) after CO adsorption at room temperature and P_{CO} = 8 Torr and (*2*, *3*) after subsequent pumping of the sample containing adsorbed CO at (*2*) room temperature and (*3*) 100°C.

upon pumping at 100°C. The Pt^0–CO complexes are thermally more stable and survive partially upon pumping at 100°C. Thus, the CO–Pt/TiO_2 system provides another example of the familiar correlation between the strength of the CO–Pt bond and the ν_{CO} of the adsorbed carbon monoxide molecule [30].

In the IR spectrum of the Pt/TiO_2 sample prereduced with hydrogen at 200°C (Fig. 4, curve *3*), the absorption band of the Pt^+–CO complexes is missing, indicating that the entire Pt^+ is reduced, and the absorption bands of the Pt^0–CO complexes (2094 and 2086 cm^{-1}) are much stronger than the same bands in the spectrum represented by curve *2*. The band at 2187 cm^{-1} is likely due to Ti^{4+}–CO. The Pt^0–CO complexes possess the highest thermal stability and decompose upon pumping at 100°C (Fig. 6).

Now we will discuss the effect of different forms of Pt in TiO_2 on its photocatalytic properties. The presence of Pt^+ and Pt^{2+} in the oxidized samples affords a nearly twofold enhancement of the SPC (table). In addition, the NO_x leaving the reactor in this case is dominated by NO_2. This is possibly due to the more intensive direct NO oxidation by oxygen adsorbed on the Pt ions. Conversely, after the reduction of platinum to Pt^0 in an H_2 atmosphere at 200°C, the SPC of this sample is lower than the SPC of unpromoted TiO_2 and the NO_2/NO ratio is practically unchanged. Presumably, the inhibiting effect of platinum is due to the capture of electrons generated in TiO_2 by absorbed light quanta. This slows down the chain of conversions depicted in the above scheme. Note, however, that the effect of Pt^0 is not as significant as the effect of the platinum ions.

It was reported that the Pt/TiO_2 photocatalyst prepared by impregnation of titanium dioxide with a $Pt(NH_3)_4(NO_3)_2$ solution followed by calcination at 200–500°C exhibits appreciable activity in NO oxidation into NO_2 and HNO_3 under irradiation with visible light (up to λ = 546 nm) and that the reaction rate decreases markedly upon the reduction of platinum to platinum metal [31].

Thus, the data presented here suggest that the photocatalytic activity of titanium dioxide in the removal of nitrogen monoxide from air can be substantially enhanced by introducing a basic promoter or platinum. The presence of more oxidized platinum species affords a significant increase in SPC, while the reduced platinum species diminish SPC.

REFERENCES

1. Linsebigler, A.L., Lu, G., and Yates, J.T., Jr., *Chem. Rev.*, 1995, vol. 95, p. 735.
2. Peral, J., Domenech, X., and Ollis, D.F., *J. Chem. Technol. Biotechnol.*, 1997, vol. 70, p. 117.
3. Mills, A., Le Hunte S, *J. Photochem. Photobiol., A*, 1997, vol. 108, p. 1.
4. Zhao, J. and Yang, X., *Build. Environ.*, 2003, vol. 38, p. 645.
5. Fujishima, A. and Zhang, X., *C.R. Chim.*, 2006, vol. 9, p. 750.
6. Fujishima, A., Zhang, X., and Tryk, D.A., *Surf. Sci. Rep.*, 2008, vol. 63, p. 515.
7. Vorontsov, A.V., *Usp. Khim.*, 2008, vol. 77, p. 973.

8. Thompson, T.L. and Yates, J.T., Jr., *Chem. Rev.*, 2006, vol. 106, p. 4428.
9. Chen, X. and Mao, S.S., *Chem. Rev.*, 2007, vol. 107, p. 2891.
10. Ibusuki, T. and Takeuchi, K., *J. Mol. Catal.*, 1994, vol. 88, p. 93.
11. Hashimoto, K., Wasada, K., Toukai, N., Kominami, H., and Kera, Y., *J. Photochem. Photobiol., A*, 2000, vol. 136, p. 103.
12. Devahasdin, S., Fan, C., Jr., Li, K., and Chen, D.H., *J. Photochem. Photobiol., A*, 2003, vol. 156, p. 161.
13. Inagaki, M., Inai, T., Yoshkawa, T., and Tryba, B., *Appl. Catal., B*, 2004, vol. 51, p. 247.
14. Li, F.B., Li, X.Z., Ao, C.H., Hou, M.F., and Lee, S.C., *Appl. Catal., B*, 2004, vol. 54, p. 275.
15. Matsuda, S. and Hatano, H., *Powder Technol.*, 2005, vol. 151, p. 61.
16. Ohko, Y., Nakamura, Y., Negishi, N., Matsuzawa, S., and Takeuchi, K., *J. Photochem. Photobiol., A*, 2009, vol. 205, p. 28.
17. Alekseev, A.V. and Filimonov, V.N., *Zh. Fiz. Khim.*, 1984, vol. 58, p. 2023.
18. Nakamura, I., Sugihara, S., and Takeuchi, K., *Chem. Lett.*, 2000, vol. 29, p. 1276.
19. Hashimoto, K., Wasada, K., Osaki, M., Shono, E., Adachi, K., Toukai, N., Kominami, H., and Kera, Y., *Appl. Catal., B*, 2001, vol. 30, p. 429.
20. Zhang, A., Zhang, R., Zhang, N., Hong, S., and Zhang, M., *Kinet. Catal.,* 2010, vol. 51, p. 529.
21. Ao, C.H. and Lee, S.C., *Appl. Catal., B*, 2003, vol. 44, p. 191.
22. Ao, C.H. and Lee, S.C., *J. Photochem. Photobiol., A*, 2004, vol. 165, p. 131.
23. Ao, C.H. and Lee, S.C., *Chem. Eng. Sci.*, 2005, vol. 60, p. 103.
24. Ichiura, H., Kitaoka, T., and Tanaka, H., *Chemosphere*, 2003, vol. 51, p. 855.
25. Shelimov, B.N., Tolkachev, N.N., Tkachenko, O.P., Baeva, G.N., Klementiev, K.V., Stakheev, A.Yu., and Kazansky, V.B., *J. Photochem. Photobiol., A*, 2008, vol. 195, p. 81.
26. Dalton, J.S., Janes, P.A., Nicholson, J.A., Hallam, K.R., and Allen, G.C., *Environ. Pollut.*, 2002, vol. 120, p. 415.
27. Kuo, C.-S., Tseng, Y.-H., Huang, C.-H., and Li, Y.-Y., *J. Mol. Catal. A: Chem.*, 2007, vol. 270, p. 93.
28. Yu, Q.L. and Brouwers, H.J.H., *Appl. Catal., B*, 2009, vol. 92, p. 454.
29. Ballari, M.M., Hunger, M., Hüsken, G., and Brouwers, H.J.H., *Appl. Catal., B*, 2010, vol. 95, p. 245.
30. Davydov, A.A., *IK-spektroskopiya v khimii poverkhnosti okislov* (IR Spectroscopy Applied to the Chemistry of Oxide Surfaces), Novosibirsk: Nauka, 1984.
31. Lin, Y.-M., Tseng, Y.-H., Huang, J.-H., Chao, C.-C., Chen, C.-C., and Wang, I., *Environ. Sci. Technol.*, 2006, vol. 40, p. 1616.