Influence of humidity and acidity of the titanium dioxide surface on the kinetics of photocatalytic oxidation of volatile organic compounds

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The influence of the humidity and acidity of the TiO_2 surface on the kinetics of the photocatalytic processes of deep oxidation of volatile organic compounds was studied. At ~20 °C the rates of acetone and benzene oxidation are maximum at the coverages of TiO_2 with water close to monolayer and are 3—5 times higher than that in the dry atmosphere. The activation energy of benzene oxidation ($E_a = 6.3 \pm 0.4$ and 43.0 ± 3.2 kJ mol^{-1} at relative humidities of 8 and 70%, respectively) at a humidity higher than 30% decreases according to the exponential law with an increase in the surface acidity when multilayer water films are formed on the surface. Under the real conditions of operation of photocatalytic air purifiers, a TiO_2 particle is covered by water nanofilms. As in aqueous solutions, photoprocesses on the TiO_2 surface depend substantially on the solvation of the participants of the reaction, the formation of the double electric layer, and the concentration of the electrolyte (due to the dissociation of the surface acid-base groups).

Key words: titanium dioxide, photocatalysis, gas phase, surface acidity, air humidity, water adsorption.

The influence of the air humidity on the kinetics of photocatalytic oxidation of volatile organic compounds on TiO_2 has been studied by many authors.[1—7] The dependence of the rate of oxidation of organic compounds *vs.* humidity most often represents the curve with a maximum at the relative humidity from 3 to 26% at ~20 °C. The oxidation rate can increase several times with an increase in the humidity from 0 to 3—26%, whereas it decreases with a further increase in the water concentration.

For example, the rate of trichloroethylene oxidation at ~20 °C is independent of the water concentration at the relative humidity from 3 to 17%. However, with an increase in the latter (from 17 to 67%) the rate decreases substantially, and the observed reaction order with respect to water is equal to −3.[8]

The plots of the oxidation rates of ethylene and toluene *vs.* air humidity in a static reactor[4] have a maximum at the relative humidity ~21%.

Similar (in many respects) plots of the photooxidation rate *vs.* humidity were explained as follows. At a low humidity, the rate increase is related to an increase in the concentration of OH groups on the catalyst surface, resulting in an increase in the probability of capturing photogenerated holes and formation of $OH^{\bullet}$ radicals.[9] These radicals are further involved in the oxidation of adsorbed organic molecules on the TiO_2 surface. At a high humidity, the oxidation rate decreases due to the competition for the adsorption sites between the molecules of water and oxidized species and due to the hindered transport of the reactants to the TiO_2 surface because it is blocked with water molecules.

Meanwhile, it is well known that the formation of the dense-packed water monolayer on the TiO_2 surface is competed at the 20—30% humidity at ~20 °C.[10] Thus, under the conditions close to the ambient air when the relative humidity significantly exceeds 30%, we deal with the multilayer coverage of the catalyst surface with water molecules.

In this work, the processes on the photocatalyst surface were considered taking into account the formation of the multilayer water molecules, and the problems related to the influence of the acidity on the activity of titanium dioxide were discussed.

Experimental

Titanium dioxide Hombikat UV 100 (Sachtleben Chemie GmbH, 100% anatase, specific surface area 340 m^2 g^{-1}), H_2SO_4 (high-purity grade), NaOH (analytical grade), MeOH (high-purity grade), acetone (high-purity grade), benzene (analytical grade), and *n*-heptane (reference grade) were used. Benzoic

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† Deceased.

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acid was preliminarily purified by double recrystallization. Pyridine (analytical grade) was used without purification. Distilled water was used in experiments. Electroconductivity was measured with an OK-102/1 conductometer.

Modification of the TiO_2 surface. A loading of the catalyst (1 g) was placed in a 100-mL round-bottom flask, and an aqueous solution (50 mL) of NaOH or H_2SO_4 (C = 0.1, 1, 4, and 10 mol L^{-1}) was added. Then the flask was stored in a thermostat for 2 h at 50 °C and left for 12 h at ~20 °C. Thus treated samples were separated from the solution by centrifuging at 7000 rpm for 10 min. Then the conductivity of the separated solution was measured, and the TiO_2 precipitate was again mixed with distilled water (100 mL) followed by centrifuging. This procedure was repeated until the conductivity of the washing water became close to that of distilled water (10^{-5} S). Usually the number of TiO_2 washing cycles was 10—12. The samples prepared were dried in air for 2—3 h at 120 °C .

Measurements of isotherms of water adsorption on TiO_2. The process was carried out at 25 °C in a thermostatted static reactor with a catalyst loading (0.5 g), and dry air was purged through the reactor for 24 h. Water was added by portions (1—3 μL) until a constant concentration of water vapor in the reactor was established. The concentration was monitored with an LKhM-80 gas chromatograph equipped with a thermal conductivity detector. The amount of adsorbed water was calculated by the difference method. The adsorption isotherms obtained were processed using the Brunauer—Emmett—Teller (BET) equation

$$\frac{a}{a_{\mathrm{m}}} = \frac{C(p/p_0)}{(1-p/p_0)[1+(C-1)p/p_0)]},$$

where a is the amount of adsorbed water (mol g^{-1}), a_{m} is the amount of adsorbed water corresponding to the monolayer coverage of the surface (mol g^{-1}), p is the water vapor pressure (atm), p_0 is the pressure of saturated water vapor equal to $3.125 \cdot 10^{-2}$ atm at 25 °C,[11] and C is the constant.

Determination of the concentration of acid and basic sites on the TiO_2 surface. The procedure was carried out using a method described previously.[12] Solutions of benzoic acid and pyridine ($2 \cdot 10^{-3}$ *M*) in anhydrous heptane were prepared. The loadings (3 mg) of the TiO_2 samples under study were placed in vials with ground corks, a solution of benzoic acid or pyridine (5 mL) was added, and the mixtures were stored for 3 h until the adsorption equilibrium was established. Benzoic acid was adsorbed on the surface basic sites, and pyridine was adsorbed on the acid sites. Thus, by measuring the concentrations of the solutions before and after their contact with TiO_2 and knowing its specific surface area, one can estimate the number of the corresponding sites. Concentrations of benzoic acid and pyridine in solutions were measured using a Shimadzu UV-300 spectrophotometer. The typical values of the concentrations obtained for the acid sites were $(2—6) \cdot 10^{-4}$ mol g^{-1}, and those for the basic sites were $(0.6—1.4) \cdot 10^{-3}$ mol g^{-1}.

Measurement of oxidation rates of acetone and benzene. Experiments were carried out in a static reactor at ~20 °C. The TiO_2 samples were first prepared using the following procedure: the TiO_2 sample under study (300 mg) was added to water (20 mL), and the mixture was ultrasonicated with an UZDN-1 instrument for 15 min. Then this suspension (0.5 mL) was deposited on a glass support 2.5×3 cm in size and dried in air. The thus prepared sample was placed in a 434-mL static reactor with a quartz window, and air with the needed humidity was passed through the reactor for 3 h. Then the calculated amount of benzene or acetone (usually 0.5—2 μL) was injected with a liquid microsyringe, and the mixtures were left for 30 min for the establishment of stationary concentrations of vapors. Solutions were irradiated with a high-pressure DRSh-1000 mercury lamp using a combination of UFS-6 and SZS-23 light filters to separate the spectral line with λ = 365 nm. The radiation intensity was ~3—5 mW cm^{-2}. The oxidation rate was measured from the rate of CO_2 accumulation in the reactor. The concentrations of all substances were determined with an LKhM-80 gas chromatograph equipped with a flame-ionization detector. In order to determine CO_2, it was preliminarily passed through the methanation reactor, and CH_4 was analyzed.

Procedure of determination of the photocatalytic activity of TiO_2 from the rate of acetone oxidation in a flow-type reactor has been described previously.[13] The conditions of tests were as follows: temperature of the reactor, 40 °C; partial pressures of water and acetone vapors, $4 \cdot 10^{-3}$ and $5 \cdot 10^{-4}$ atm, respectively; incident light intensity, 20—30 mW cm^{-2} (λ = 334 nm). Samples for the determination of the activity were prepared in the same manner as those for measuring the rates of benzene and acetone oxidation in a static reactor. The incident light intensity was determined with an LM-2 power meter. The quantum yield φ (the fraction of electron-hole pairs involved in oxidation) was calculated from the formula $\varphi = 16 \cdot (W_{\mathrm{a}}/I)$, where W_{a} is the rate of acetone oxidation (mol s^{-1}), and I is the incident light intensity (mol-quantum s^{-1}). This corresponds to the following empirical reaction of acetone mineralization:

$$\mathrm{MeCOMe} + 4\,\mathrm{O_2} \xrightarrow{16\,h\nu} 3\,\mathrm{H_2O} + 3\,\mathrm{CO_2}.$$

Conductivity of TiO_2 powders was measured with an OK-102/1 conductometer. Air with a humidity of 63% was passed through the sample under study for 12 h. Then, the powder was placed in the measuring unit of the conductometer, and the conductivity was measured.

Results and Discussion

Influence of humidity on the rate of photocatalytic oxidation of acetone and benzene vapors. Under the real conditions of TiO_2 operation, water is one of the components that is permanently present in the gas phase and interacts with the catalyst surface. Therefore, the first part of our work is devoted to studying the influence of the humidity on the rate of oxidation processes.

The plots of the initial rates of acetone and benzene oxidation *vs.* air humidity are presented in Figs. 1 and 2, respectively. They contain the characteristic maxima at the relative humidity from 17 to 32%. This plot of the oxidation rate *vs.* humidity has previously been explained by the fact that the adsorption of water at the initial stage increases the number of OH groups on the TiO_2 surface. These groups efficiently capture holes on the surface to form $OH^{\bullet}$ radicals, and the photooxidation rate increases. However, with a further increase in the humidity water forms multilayer coatings on the surface, and the reaction rate decreases. This has previously been explained by the

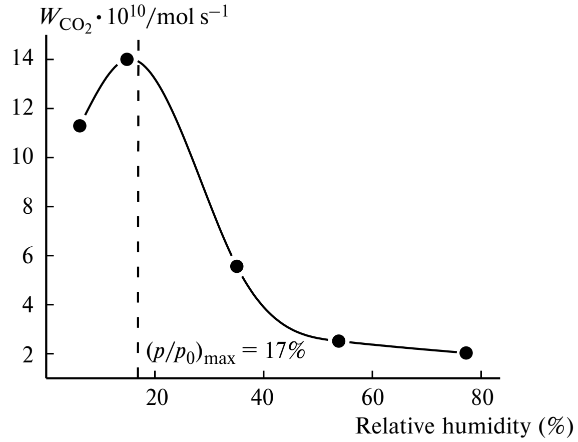

Fig. 1. Rate of CO_2 accumulation (W_{CO_2}) in the photocatalytic oxidation of acetone vapor as a function of the relative air humidity in the static reactor (T = 25 °C, initial concentration of acetone vapor $5 \cdot 10^{-4}$ atm, I = 5 mW cm^{-2} (λ = 365 nm), $p_0 = 3 \cdot 10^{-2}$ atm).

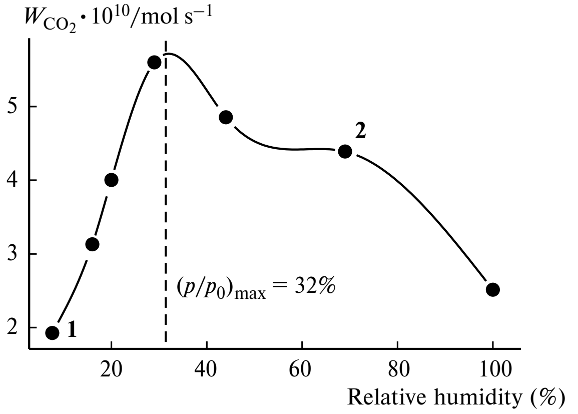

Fig. 2. Rate of CO_2 accumulation (W_{CO_2}) in the photocatalytic oxidation of benzene vapor as a function of the relative air humidity in the static reactor (T = 17 °C, I = 5 mW cm^{-2} (λ = 365 nm), $p_0 = 3 \cdot 10^{-2}$ atm): E_a = 6.3 (**1**) and 42 kJ mol^{-1} (**2**).

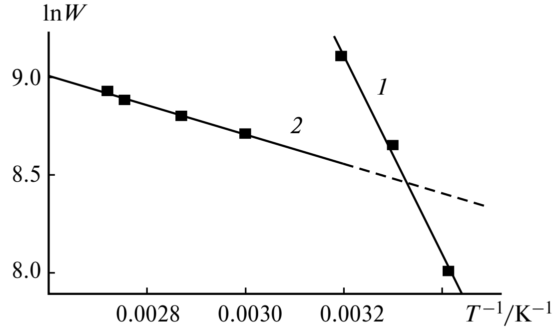

Fig. 3. Temperature plots of the rates of photocatalytic oxidation of benzene vapor (W) in the Arrhenius coordinates at the concentration of water vapor in the gas phase $1.2 \cdot 10^{-2}$ atm (I = 5 mW cm^{-2}, irradiation with the light at λ = 365 nm): E_a = 42 (*1*) and 6.3 kJ mol^{-1} (*2*).

retardation of the transport of the reactants to the photocatalyst surface upon the formation of the multilayer coatings. At the same time, the water films on the photocatalyst surface can result in the solvation of the participants of the reaction and can considerably change the energy characteristics of the process.

In order to confirm this assumption, we measured the activation energies of benzene photooxidation at different concentrations of water vapor. In the dry atmosphere, we have E_a = 7.6 kJ mol^{-1}. At the concentration of water vapor in the gas phase equal to $1.2 \cdot 10^{-2}$ atm, two linear regions can easily be distinguished in the temperature dependence of the reaction rate in the Arrhenius coordinates (ln$W$—$1/T$) (Fig. 3). In the first region (in the 20—40 °C temperature interval), $E_a = 42 \pm 3.2$ kJ mol^{-1}; in the second region (in the 55—90 °C temperature interval), $E_a = 6.3 \pm 0.4$ kJ mol^{-1}, *i.e.*, this value coincides with the activation energy in the dry atmosphere. Thus, the activation energy of benzene photooxidation decreases more than sevenfold with the temperature increase by 40 °C, which can be explained by a change in the coating of the TiO_2 surface with water molecules.

In order to verify this assumption, we measured the isotherms of water adsorption on TiO_2 Hombikat UV 100 at 30 and 70 °C. These temperatures were chosen for measuring the adsorption isotherms because they are placed in the centers of the linear regions of the ln$W$—$1/T$ plot (see Fig. 3). The results of the measurements are presented in Fig. 4. The values presented below for the partial pressures of water vapors are recalculated to the temperature 25 °C. The final humidity corresponds to the temperatures of measurement of the adsorption isotherms. The amount of water corresponding to the monolayer coating of the TiO_2 surface and the relative humidity at which monolayer formation is competed were calculated in the framework of the BET theory. It turned out that at 30 °C the monolayer coating with $a_m = (7.2 \pm 0.3) \cdot 10^{-3}$ mol g^{-1} is formed at $(p/p_0)_m$ = 0.22 or $p_{H_2O} = 9.2 \cdot 10^{-3}$ atm, and at 70 °C for $a_m = (4.4 \pm 0.14) \cdot 10^{-3}$ mol g^{-1} it is formed at $(p/p_0)_m$ = 0.22 or $p_{H_2O} = 6.765 \cdot 10^{-2}$ atm. These data suggest that at the concentration of water vapor in air equal to $1.2 \cdot 10^{-2}$ atm and at the temperature of the reactor of 30 °C the amount of water on the photocatalyst surface is greater than the monolayer coating, whereas at the temperature of the reactor of 70 °C and the same concentration of water vapor in the gas phase water does not form a monolayer coating.

At ~20 °C and the relative humidity >30% the TiO_2 surface is covered by the water film, and the activation energy of benzene oxidation should be close to the value obtained for an aqueous suspension of TiO_2. In fact, the activation energy of benzene photooxidation measured for an aqueous suspension of TiO_2 in the 19—40 °C temperature interval turned out to be 51.5 ± 6.0 kJ mol^{-1},

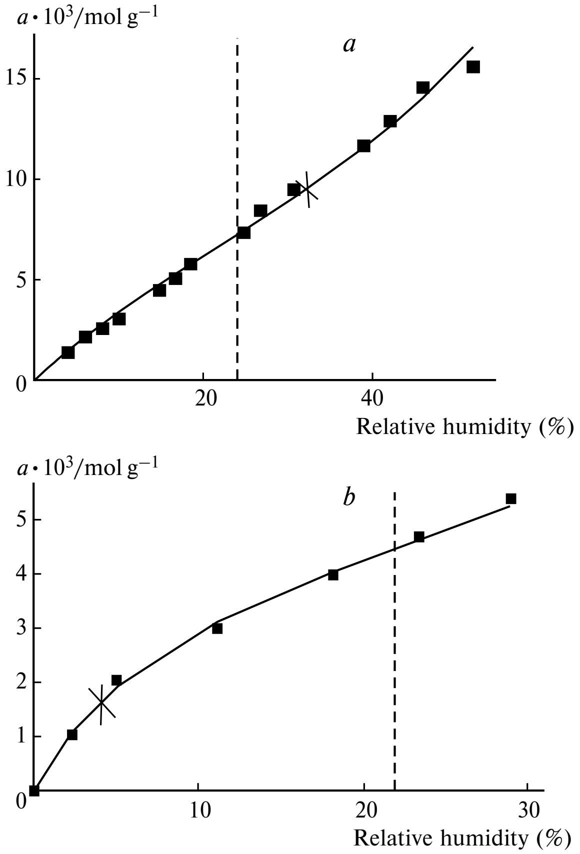

Fig. 4. Isotherms of water adsorption on TiO_2 measured at 30 (*a*) and 70 °C (*b*) (solid lines are the isotherms of BET adsorption, and dotted lines are the boundary of the monolayer coating of the TiO_2 surface by water molecules; the cross marks the concentration of water vapor equal to $1.2 \cdot 10^{-2}$ atm recalculated to 25 °C; *a* is the amount of adsorbed water).

which is close to $E_a = 42\pm3.2$ kJ mol^{-1} for the multilayer coating of the catalyst by water molecules.

The plot of the activation energy of benzene oxidation *vs.* concentration of the sulfuric acid used for the treatment of TiO_2 is shown in Fig. 5 (for the measurement of the surface acidity and modification of the sample, see below). The data obtained show that E_a decreases with an increase in the acidity of the TiO_2 surface. It cannot be excluded that this is related to a change in the electrolyte concentration in water nanofilms on the titanium dioxide surface. This assumption is confirmed by the following experiment. Two TiO_2 Hombikat UV 100 samples treated with 1 and 4 *M* solutions of $NaNO_3$ using the same procedure as that for sulfuric acid were prepared. Then the activation energy of benzene photooxidation on these samples was measured under the conditions of multilayer coating of the surface with water molecules. It turned out that for a 1 *M* solution of $NaNO_3$ $E_a = 38\pm3$ kJ mol^{-1}, and for a 4 *M* solution of $NaNO_3$ $E_a = 32\pm3$ kJ mol^{-1}, *i.e.*, E_a also decreases with an increase in the electrolyte concentration as in the case of sulfuric acid.

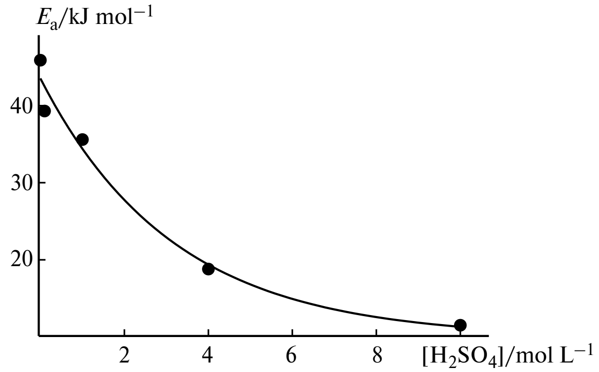

Fig. 5. Activation energy (E_a) of benzene photooxidation as a function of the concentration of sulfuric acid used for the modification of TiO_2 (T = 25—40 °C, I = 5 mW cm^{-2}, λ = 365 nm, relative humidity 63% at 25 °C).

One more proof for the change in the electrolyte concentration in the water film upon the treatment of TiO_2 with sulfuric acid or $NaNO_3$ is the dependence of the conductivity of the TiO_2 powders in the humid atmosphere on the concentration of H_2SO_4 and $NaNO_3$, which were used for the modification of TiO_2. The results of measurements of the conductivity at the relative humidity 63% are presented in Table 1. It is noteworthy that after the treatment of titanium dioxide with H_2SO_4 and $NaNO_3$ the catalysts were washed until the conductivity of the washing water reached the value of distilled water. This means that the conductivity of the powders is not the result of the residual amount of an acid in the water films but is caused by the dissociation of surface acid-base groups.

Thus, it can be concluded that the presence of adsorbed water at the photocatalyst surface has a substantial effect on the photocatalytic oxidation of benzene. Probably, the participants of the process are solvated in the water nanofilms, which results in a change in the activation energy compared to that in the dry atmosphere.

By analogy to the processes in aqueous suspensions, we can consider several reasons for which the activation energy can decrease with an increase in the electrolyte concentration in the water nanofilms.

Table 1. Conductivities of the TiO_2 samples treated with solutions of H_2SO_4 and $NaNO_3$ with different concentrations at ~20 °C and relative humidity 63%

Treatment of sample	Conductivity/μS
0.1 *M* solution of H_2SO_4	5.5
1 *M* solution of H_2SO_4	7.5
4 *M* solution of H_2SO_4	8.0
10 *M* solution of H_2SO_4	9.5
0.1 *M* solution of $NaNO_3$	12.5
1 *M* solution of $NaNO_3$	47.0
4 *M* solution of $NaNO_3$	185.0

First, when the electrolyte concentration increases, the potential drop in the Helmholtz layer increases at the water—TiO_2 surface interface. The activation energy of the interphase charge transfer also decreases according to the equation $E_a = E^* - \alpha \cdot \psi_H$, where E^* is the activation energy of the interphase charge transfer in the absence of the double electric layer, α is a coefficient, and Ψ_H is the potential drop in the Helmholtz layer. Note that the processes of organic species oxidation on the titanium dioxide surface are directly related to the electron transfer at the TiO_2—water interface.

Second, the change in the electrolyte concentration (ionic strength) changes the activity of the charged reactants. When the limiting step is the interaction of two species with opposite charges (for example, $C_6H_6^+$ and O^-), the activation energy decreases.

In addition, it should be taken into account that the acid treatment of TiO_2 changes the strength of the surface acid sites. This affects the adsorption energy of the participants of the reaction and, probably, influences on the measured activation energy.

Acidity of the TiO_2 surface. As shown previously,[14,15] the treatment of TiO_2 with sulfuric acid can enhance its photoactivity, although the mechanism of this effect remains unclear. Therefore, it was of interest to determine how the acid-base pretreatment of TiO_2 influences its photocatalytic activity.

The resulting dependence of the quantum efficiency of the photocatalytic oxidation of acetone vapor on the preliminary treatment of TiO_2 with sulfuric acid or NaOH is presented in Fig. 6, where the number of acid sites, which changes due to this treatment, on the TiO_2 surface is put on the abscissa.

Thus, the highest activity (76%) is observed for the sample treated with a 10 *M* solution of H_2SO_4 (the amount of acid sites is $6.1 \cdot 10^{-4}$ mol g^{-1}). Then the activity decreases with a decrease in the H_2SO_4 concentration and achieves 62% for nontreated TiO_2 Hombikat UV 100 (the amount of acid sites is $3.7 \cdot 10^{-4}$ mol g^{-1}). The activity continues to decrease with an increase in the concentration of a NaOH solution, which was used for treatment, and achieves the lowest value (17%) for 10 *M* NaOH (the amount of acid sites is $1.7 \cdot 10^{-4}$ mol g^{-1}). Such a significant difference in the activity cannot be explained by the different specific surface areas of the samples prepared because, as follows from Table 2, the specific surface areas and characteristic pore sizes determined by the nitrogen adsorption method for four samples are close.

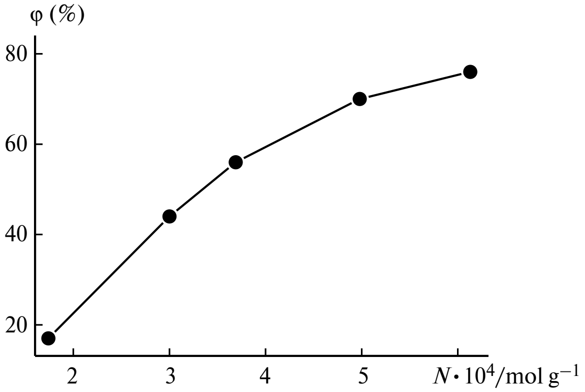

Fig. 6. Quantum efficiency of the photocatalytic oxidation of acetone vapor (φ) as a function of the number of acid sites (N) on the TiO_2 surface (the number was changed by the pretreatment of TiO_2 with H_2SO_4 or NaOH).

Table 2. Specific surface area and pore diameter of the Hombikat UV 100 TiO_2 samples prepared by low-temperature nitrogen adsorption

Pretreatment of catalyst	Specific surface area /m^2 g^{-1}	Diameter of pores /nm
4 *M* solution of H_2SO_4	341	5.0
1 *M* solution of H_2SO_4	306	5.2
Nontreated Hombikat UV 100	340	4.9
4 *M* solution of NaOH	355	5.0

According to the data in Ref. 14, the presence of Na^+ ions on the TiO_2 surface can suppress its photocatalytic activity. On the one hand, this could explain the decrease in the activity of the TiO_2 samples treated with NaOH, although the samples were thoroughly washed during preparation. On the other hand, this cannot explain the difference in the activities of the sulfated samples because the content of Na^+ ions in these samples should be the same.

The regularities of the photocatalytic oxidation of ethanol vapor on the TiO_2 samples prepared by hydrolysis of $TiCl_4$ at different pH have previously[16] been studied. It was shown that the activity of TiO_2 was related to the acidity of its surface. Therefore, we characterized our modified samples of titanium dioxide by measuring the concentrations of the acid and basic sites on the surface.

The results of measurements of the total amount of the acid and basic sites are presented in Fig. 7, *a* and *b*, respectively. Comparing these data on the amount of the acid and basic sites with the data on the activity of the TiO_2 samples (see Fig. 6), we can conclude that the photocatalytic activity correlates explicitly with the concentration of the acid sites on the TiO_2 surface. We believe that this dependence of the photocatalytic activity of TiO_2 on its acid-base characteristics can be related to a change in the adsorption of the initial reactants and products of their oxidation on the TiO_2 surface.

The data on CO_2 adsorption on the TiO_2 Hombikat UV 100 samples (Fig. 8) confirm that the adsorption parameters change at different acidities. It is seen from the isotherms presented that the amount of adsorbed CO_2 decreased fivefold. Thus, the isotherms of CO_2 adsorp-

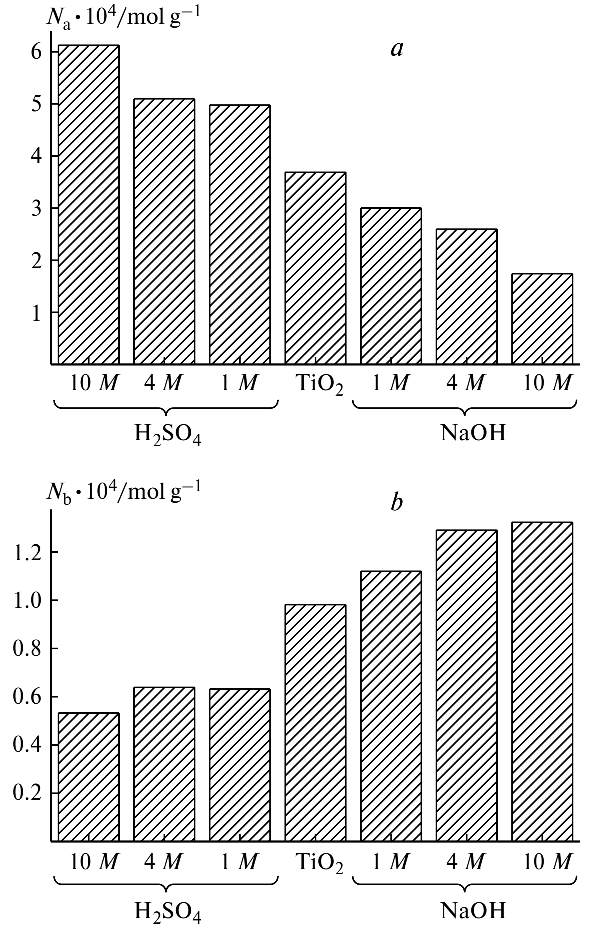

Fig. 7. Total number of acid (N_a) (*a*) and basic (N_b) (*b*) sites on the surface of the catalysts obtained by the treatment of TiO_2 Hombikat UV 100 (measured using the methods of adsorption of pyridine and benzoic acid, respectively) in anhydrous heptane.

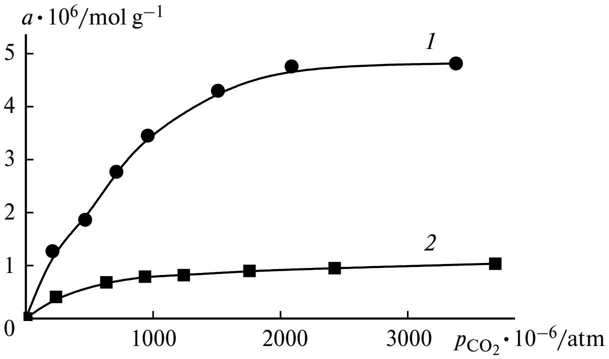

Fig. 8. Isotherms of CO_2 adsorption on TiO_2 Hombikat UV 100 nontreated (*1*) and treated with a 1 *M* aqueous solution of H_2SO_4 (*2*) at 25 °C.

tion on TiO_2 show that the interaction with the acidic sample surface is much weaker. This can be a reason for the enhancement of the photocatalytic activity of TiO_2 due to a lower degree of blocking the surface of the acidic samples by adsorbed carbon dioxide.

Thus, we studied the photocatalytic oxidation of acetone and benzene. The reaction rate is shown to depend substantially on the air humidity and achieves the maximum value when the coating of the surface with water molecules is close to monolayer.

The activation energies of benzene photooxidation at different humidities were determined: E_a = 6.3 and 42.0 kJ mol^{-1} in the dry and humid atmospheres, respectively. This difference is related, most likely, to the formation of the water nanofilms on the surface of the TiO_2 particle. The photocatalytic reactions on the titanium dioxide surface are affected by the solvation of the reactants and formation of the electrolyte in the water films due to the dissociation of the surface groups.

It is established that the TiO_2 samples characterized by strong acidity of the surface are more active in the photocatalytic oxidation of organic substances. This is probably related to the change in the adsorption energy of the reactants on their surface.

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