Effect of the acidity of TiO_2 surface on its photocatalytic activity in acetone gas-phase oxidation

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The effect of the surface acidity of modified TiO_2 samples on the rate of photocatalytic decomposition of acetone vapor was studied. The TiO_2 activity was shown to depend strongly on the concentration of acid and basic sites on the surface. It was 1.23 times greater for TiO_2 treated with 10 M H_2SO_4 solution than for the untreated sample. This dependence may be related to changes in the adsorption energy of the reagents.

KEY WORDS: titanium dioxide; acetone; photocatalytic degradation; surface acidity.

1. Introduction

In recent decades, the problem of industrial contamination of the atmosphere with volatile organic compounds has become very important. In this connection, photocatalytic methods of air purification to remove organic impurities seem to be promising. Numerous researchers have shown that in heterogeneous photocatalytic processes almost any organic substance may be oxidized [1,2]. As indicated earlier [3,4], TiO_2 treatment with sulfuric acid could increase its photoactivity, although the mechanism is not completely clear.

In this work, we studied the effect of treatment of Hombikat UV 100 TiO_2 catalyst with sulfuric acid or sodium hydroxide on its activity in the photocatalytic decomposition of acetone vapor.

2. Experimental

The Hombikat UV 100 catalyst (Sachtleben Chemie, 100% anatase with specific surface area $340\,m^2/g$) was modified by the following method. A 1 g catalyst sample was placed in a 100 ml round-bottomed vessel with 50 ml of NaOH or H_2SO_4 aqueous solutions of concentration 1, 4 and 10 M and the vessel was placed in a thermostat and kept at 50 °C for 2 h. The vessel was then kept at room temperature for 12 h and the treated samples were separated from the solution by centrifugation. The electrical conductivity of the separated solution was measured, and TiO_2 precipitate was stirred in 100 ml of distilled water with subsequent centrifugation. This operation was repeated until the conductivity of the washed off water approached that of the initial distilled water (10^{-5} Siemens). Conductivity was measured with an OK-102/1 conductivity meter (Russia). The number of washing cycles was normally 10–12. Finally, the samples were dried in air at 120 °C for 2–3 h.

The specific surface areas and pore diameters of several samples were measured by the low-temperature nitrogen adsorption method with an ASAP-2400 instrument (Micromeritics, USA). All the data obtained are presented in table 1.

The method for determining the TiO_2 photocatalytic activity from the rate of acetone oxidation was elaborated in our laboratory by Vorontsov and reported earlier [5]. The experimental conditions were as follows: reactor temperature, 40 °C; concentrations of water and acetone vapor, 4000 and 500 ppm, respectively; and intensity of incident light, 20–30 mW/cm^2 ($\lambda = 334$ nm).

Samples preparation was carried out as follows: 30 mg of TiO_2 sample were added to 20 ml of water and subjected to ultrasonic treatment with a UZDN-1 device (Russia) for 15 min. Then 0.5 ml of this suspension was deposited over a 2.5 × 3 cm glass support and dried in air. The intensity of the incident light was measured with an LM-2 power meter (Russia). The quantum yield (the part of electron–hole pairs involved in the reaction) was calculated with the equation $\varphi = 16(W_a/I)$, where W_a is the rate of acetone oxidation (mol/s) and I is the intensity of incident light (mol/s). The multiplication by a factor of 16 indicates that we need 16 quanta of light (assuming that one quantum generates one electron–hole pair) to oxidize completely one acetone molecule to CO_2 and H_2O according to the following reaction:

$$CH_3COCH_3 + 4O_2 \xrightarrow{16h\nu} 3H_2O + 3CO_2$$

The quantities of acid and basic sites were determined as the quantities of pyridine and benzoic acid (BA)

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Table 1
Specific surface areas and pore diameter of catalyst samples

Catalyst	Specific surface area (m^2/g)	Pore diameter (nm)
4 M H_2SO_4 treated	341	5.0
1 M H_2SO_4 treated	306	5.2
Hombikat UV 100	340	4.9
4 M NaOH treated	355	5.0

adsorbed on the TiO_2 surface, respectively [6]. Benzoic acid was preliminarily purified via double recrystallization, whereas pyridine of analytical grade was used without preliminary purification; 2×10^{-3} M solutions of these substances in anhydrous heptane were prepared. A 3 mg amount of the TiO_2 under study was placed in vessels with ground stoppers, and 5 ml solution of BA or pyridine were added. By measuring the absorbance of the solutions before and after their contact with TiO_2, the number of appropriate sites can be estimated according to the equation

$$\nu_{\mathrm{ads}} = \frac{D_0 - D}{\varepsilon l m} V$$

where D_0 and D are the absorbance of the solutions before and after their contact with TiO_2, respectively (dimensionless), V is the solution volume (l), l is the cell pathlength (cm), ε is the absorption coefficient (l/cm/mol) and m is the catalyst mass (g). Absorption coefficients for BA and pyridine in heptane are 1.15×10^4 ($\lambda = 230$ nm) and 1.73×10^3 ($\lambda = 251$ nm), respectively.

The BA and pyridine concentrations were measured with a Shimadzu (Japan) UV-300 spectrophotometer. Typical concentrations of acid and basic sites were $(2–6) \times 10^{-4}$ and $(0.6–1.4) \times 10^{-3}$ mol/g, respectively.

3. Results and discussion

Figure 1 shows the dependence of the quantum yield of the photocatalytic oxidation of acetone vapor on TiO_2 pretreated with sulfuric acid or sodium hydroxide. The highest activity (76%) is observed for the sample treated with 10 M H_2SO_4. The activity decreases with decreasing concentration of sulfuric acid and attains 62% for the untreated Hombikat UV 100 TiO_2 catalyst. Further, the activity decreases with increasing concentration of sodium hydroxide solution, which was used for pretreatment, and attains its lowest value, 17%, for 10 M NaOH.

Such a wide variation in activity could not be attributed to the differences in the specific surface areas of the prepared samples, since it is evident from table 1 that the specific surface areas and typical pore sizes of four samples, determined by nitrogen adsorption, were similar.

According to the data reported by Yu *et al.* [3], the presence of Na^+ ions at the TiO_2 surface could decrease its photocatalytic activity. This could explain the decrease in activity of TiO_2 samples treated with NaOH, although the samples were thoroughly washed during the synthesis. On the other hand, this could not explain the difference in the activities of sulfated samples, since the concentrations of Na^+ ions in these samples should be similar.

Previously, we studied the photocatalytic oxidation of ethanol vapor over TiO_2 samples, obtained by $TiCl_4$ hydrolysis at various pH values, and showed that the

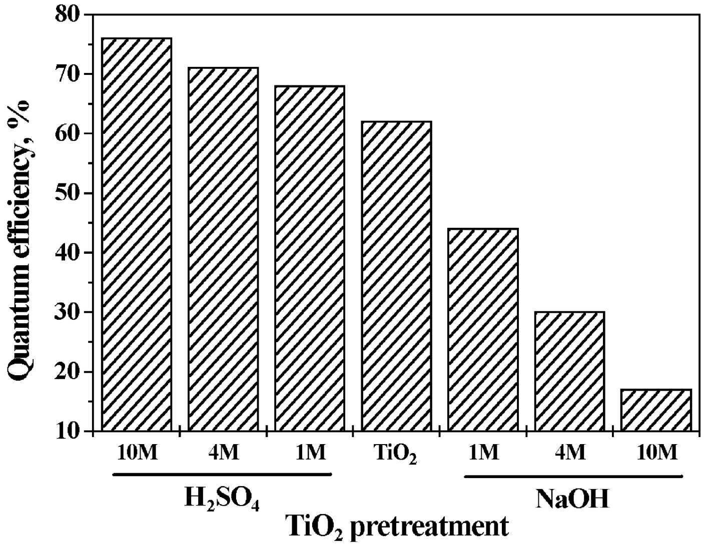

Figure 1. Dependence of the quantum efficiency of photocatalytic oxidation of acetone vapor on the TiO_2 pretreatment with sulfuric acid or sodium hydroxide.

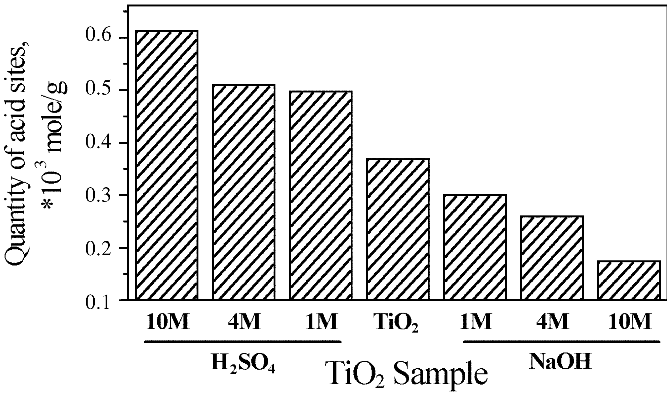

Figure 2. Total number of acid sites on the surface of modified TiO_2 catalysts measured by pyridine adsorption in anhydrous heptane.

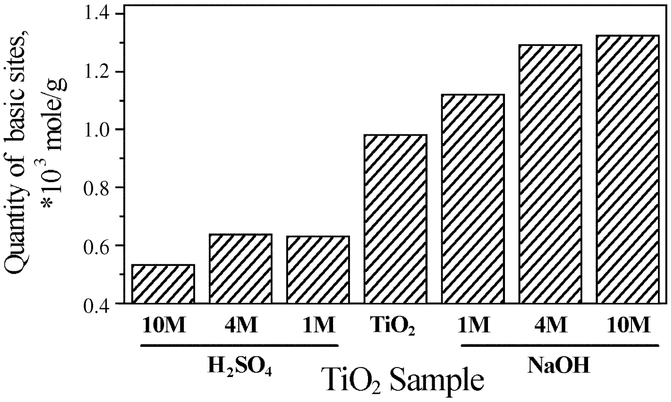

Figure 3. Total number of basic sites on the surface of modified TiO_2 catalysts measured by benzoic acid adsorption in anhydrous heptane.

TiO_2 activity is related to its surface acidity [7]. Therefore, the concentrations of acid and basic sites were measured on the surface of all synthesized TiO_2 samples.

The total numbers of acid and basic sites are presented in figures 2 and 3, respectively. Comparison of the number of acid and basic sites with the activity of TiO_2 samples (figure 1) indicates that photocatalytic activity is higher for samples with a larger number of acid groups and a smaller number of basic groups on the TiO_2 surface.

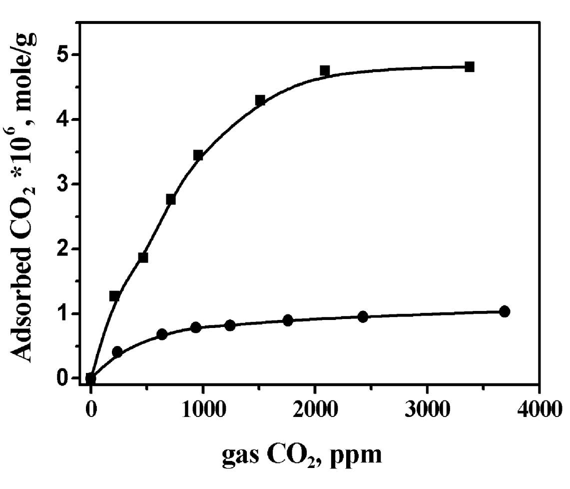

Figure 4. CO_2 adsorption isotherms on the commercial Hombikat UV 100 TiO_2 (■) and on Hombikat UV 100 treated with 1 M H_2SO_4 (●). Temperature, 25 °C.

The dependence of TiO_2 photocatalytic activity on its acidic properties is caused by changes in the adsorption constants of the reagents, intermediates and products of photooxidation on the TiO_2 surface. Indeed, most of the intermediates of photooxidation have an acidic nature [7,8]. Such species may be adsorbed on the surface of TiO_2, which has a high basicity, and prevent further reaction occurrence. At the same time, owing to a lower adsorption of organic acids, the surface of more acidic TiO_2 samples remains free for interaction with the reagents. The method of treatment with sulfuric acid could be used for activation of TiO_2 catalysts making their activity higher by about 20–30%.

The following experiment indicates that adsorption of reagents is different on acid and non-acid catalysts (figure 4). The adsorption isotherms of carbon dioxide were measured on the commercial Hombikat UV 100 TiO_2 catalyst and on this catalyst treated with 1 M H_2SO_4. The adsorption on the acid catalyst is about five times lower. It must be emphasized again that we attribute such behavior to the increase in the number of acid sites on the catalyst surface.

4. Conclusion

The treatment of TiO_2 with sulfuric acid enhances its photocatalytic activity in acetone vapor photooxidation by 20–30%. Such an enhancement could be explained by the increase in the number of acid sites on the catalyst surface. The nature of the acid sites is still unclear and requires further investigation.

Acknowledgments

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