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Correlation of TiO_2 photocatalytic activity and diffuse reflectance spectra

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Abstract

Photocatalytic activity of TiO_2 samples prepared by aqueous hydrolysis of $TiCl_4$ and deposition with NH_3 in gaseous acetone photocatalytic oxidation has been found dependent on calcination temperature. The activity reaches its maximum at calcination temperature 450°C and then decreases, all the samples being anatase. The photocatalytic activity of the samples in a series of different calcination temperatures correlates well with reflectance of the samples in the visible light region. The increase in calcination temperature from 320 to 500°C results in the growth of TiO_2 crystallites, decrease in BET surface area, slight changes in lattice parameters, and removal of weak surface Bronsted acid centers that are speculated to be OH groups. TiO_2 prepared by deposition with NaOH exhibits much higher photocatalytic activity. The only paramagnetic species detected in the TiO_2 samples was NO that resulted from oxidation of lattice-captured NH_3. No NO was detected in TiO_2 prepared by deposition with NaOH. The concentration of NO increases steadily with calcination temperature as indicated by ESR spectra. The observed correlation of diffuse reflectance and photocatalytic activity was attributed to opposite effects of the increase of crystallinity and removal of surface water and hydroxyl groups. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TiO_2; Photocatalytic oxidation; Diffuse reflectance spectra

1. Introduction

Photocatalytic oxidation provides a unique opportunity for the purification of environment. The rate of oxidation is significant even at ambient temperature and very low concentrations of contaminants. Ultimate products of oxidation are usually innocuous inorganic compounds. A variety of organic compounds can be destructed by this method.

Development of photocatalytic methods of air purification requires elaboration of active photocatalysts. In order to prepare photocatalysts of sustained activity, it is desirable to know the mechanism how preparation influences photocatalytic activity of photocatalysts. This paper investigates how an important step of preparation, thermal treatment, influences activity and properties of resultant photocatalysts.

Titanium dioxide is widely known to be the best photocatalyst. It is usually prepared by hydrolysis of titanium compounds with subsequent thermal treatment (calcination) of the deposit formed. The temperature of the treatment is an important parameter that influences the activity of TiO_2. However, the conditions of measurement of TiO_2 photocatalytic activity can also markedly change the influence of calcination temperature. For photooxidation in gas phase, a peak in activity versus temperature dependence has already been reported for ethane [1], 1-butene [2], and methyl mercaptan [3]. For photocatalytic oxidation in liquid aqueous phase, some compounds do not demonstrate or demonstrate only a very weak peak in activity. Sparsely water-soluble organics, such as C_2HCl_3, C_6H_6, C_2Cl_4 [4,5] and cyclohexane [6] exhibited the highest oxidation rate over TiO_2 calcined at the highest temperature used. On the contrary, the rate of oxidation of highly water-soluble compounds such as C_6H_5COOH, C_6H_5OH and $CH_2ClCOOH$ has very weak maximum or just diminishes with the growth of calcination temperature [4]. This behavior was attributed to the change in adsorption properties of TiO_2 with the growth of calcination temperature: the surface contains less OH groups and is capable to adsorb higher quantities of hydrophobic compounds and lower quantities of hydrophilic compounds. However, Sclafani et al. [7] demonstrated a marked peak in the rate versus calcination temperature dependence for aqueous solution of phenol. They also showed that the decrease in activity at temperature above 500°C is not due to formation of rutile, since they prepared very active rutile.

In this paper, we study the influence of TiO_2 calcination temperature on its bulk and surface structure in connection to the rate of deep oxidation of highly water-soluble compound, acetone, in the gas phase.

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2. Experimental

Samples of TiO_2 were prepared by hydrolysis of $TiCl_4$ and deposition with aqueous solution of NH_3. The deposits were washed with distilled water and calcined in air for 3 h at certain temperature in the range 320–500°C.

Another sample of TiO_2 was made by aqueous hydrolysis of chemically pure $TiCl_4$ and precipitated by NaOH. The deposit was washed thoroughly with distilled water and calcined in air at 400°C for 3 h. Specific surface area of this photocatalyst is 120 m^2/g as determined by BET method. X-ray analysis showed presence of anatase phase only.

UV–VIS diffuse reflectance spectra of the catalysts were recorded using Shimadzu UV-300 spectrophotometer (Japan) equipped with integrating sphere appliance. MgO was a reference sample, and its reflectance was assumed 85% throughout the spectrum.

Measurements of photocatalytic activity were performed in a flow–circulation system described previously in detail [8]. The flow–circulation system includes quartz reactor, membrane circulation pump and stainless steel connection pipes. The reactor is placed in a temperature controlled box to maintain temperature of 40°C. The circulation rate provided by the pump was about 8 l/min, that is over 100 times higher than the maximum input flow rate used. Therefore, the reactor can be considered as a perfect stirring reactor and there are no concentration and temperature gradients in it. Samples were deposited on glass plates and formed films non-transparent for UV light.

Specimens in the quartz reactor were irradiated by the light of 1000 W Xenon lamp transmitted through 313 nm interference filter. Incident light intensity was 7 mW/cm^2, feed acetone concentration 500 ppm, feed water vapor concentration 4500 ppm.

Quantum yields of the samples in acetone oxidation were calculated on the basis of incident light intensity, because Fig. 1 shows that almost all the incident UV light with $\lambda = 313$ nm is absorbed. For the calculation, it was assumed that 16 photons are required to completely oxidize each molecule of acetone. Rates of acetone consumption and CO_2 production were in good stoichiometric agreement.

X-ray diffraction patterns were obtained on a URD-63 diffractometer (Germany) using Cu Kα radiation. ESR spectra were recorded using Bruker ER 200D instrument at 77 K.

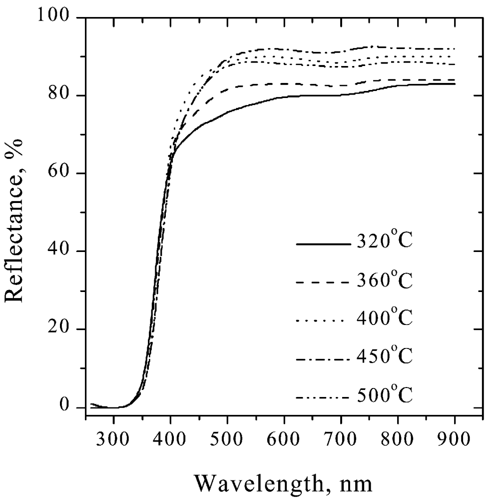

Fig. 1. Diffuse reflectance spectra of TiO_2 samples calcined at different temperatures.

3. Results and discussion

Fig. 1 depicts diffuse reflectance spectra of photocatalysts of the series with different calcination temperature. These spectra are noticeably different in the visible light region. One can see that the reflectance in the visible light region grows with the rise of calcination temperature (for samples calcined at 320–450°C) and then diminishes (for the sample calcined at 500°C). Average reflectance of a sample can be expressed quantitatively as an integral of diffuse reflectance spectrum on wavelength in the limits of 260–900 nm. This characteristic together with specific surface area and catalytic activity of the photocatalysts in complete acetone oxidation is represented in Table 1. Specific surface area of the samples steadily decreases with the increase in temperature of thermal treatment. This is obviously due to progressive aggregation of small crystallites into larger particles. In spite of the fact that the specific surface area diminishes, the catalytic activity increases until the temperature attains 450°C and decreases only then. The catalytic activity of the samples is represented in Table 1 as quantum yield. We are inclined to think that it is more sound to use quantum yield rather than reaction rate per unit of surface area [7] as characteristic of photocatalysts' activity because it is very difficult to determine the surface area that actually takes part in the reaction. Quantum yield or total rate of oxidation under constant light intensity is also of higher practical importance.

Hydroxyl groups on the surface of TiO_2 are often regarded as active sites for photocatalytic oxidation [2]. Hydroxyl groups are also adsorption sites for compounds tending to form hydrogen bond. Such compounds are usually water-soluble. On the contrary, water-insoluble compounds would tend to adsorb on hydrophobic adsorption sites. Hydroxyl groups are progressively removed

Table 1
Characterization of TiO_2 samples calcined at different temperature and their activity in gaseous acetone photocatalytic oxidation

Calcination temperature (°C)	Specific surface (m^2/g)	Integral of spectrum (nm)	Quantum yield (%)
320	120	41200	15
360	114	42700	19
400	108	45870	30
450	96	46200	41
500	88	44700	32

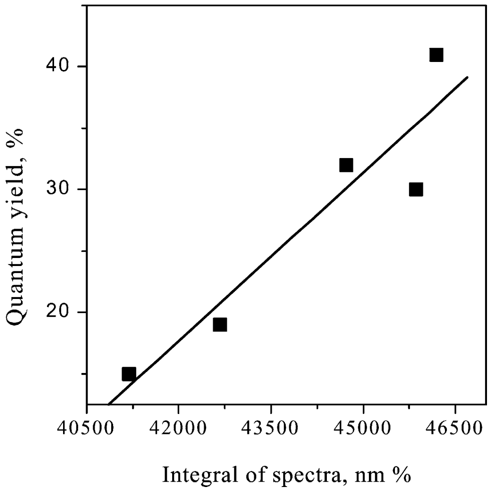

Fig. 2. Correlation of activity in acetone oxidation and integral of diffuse reflectance spectra in the visible region.

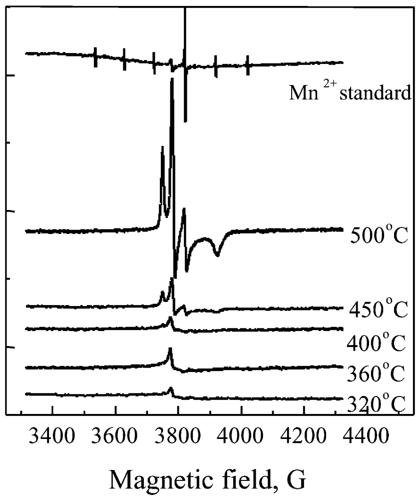

Fig. 3. ESR spectra of TiO_2 samples calcined at different temperatures. Taken at 77 K, samples weight 20 mg, modulation 10 Gs.

in the calcination of TiO_2. Thus, using such type of argumentation [4] one could predict the decrease of photocatalytic activity for water-soluble compounds with the increase of TiO_2 calcination temperature. Table 1 shows that this is not the case. Probably, adsorption properties of TiO_2 are not the only factor that determines the dependence of activity on calcination temperature. Gas–solid oxygen isotopic exchange (GSOIE) has been demonstrated to stop if organics is admitted to TiO_2 and starts again after full consumption of organics [9]. This fact testifies the existence of common surface oxygen intermediate of oxidation and GSOIE, probably O^-. The rate of GSOIE peaks over TiO_2 calcined at 500°C [1]. Therefore, the peak in rate versus calcination temperature dependence can be related to the peak of the rate of production of active surface oxygen species.

Fig. 2 demonstrates photocatalytic activity of TiO_2 plotted against integral of diffuse reflectance spectra. There is a correlation between these values that is close to linear, i.e. the higher the reflectance the higher the activity. This correlation can be used for choosing the best photocatalyst among series of TiO_2 treated at different temperatures without carrying out actual measurements of activity. The absorption in visible light region of the spectrum is probably caused by some bulk or surface defects in TiO_2 structure. We attempted to detect such possible defects using ESR method.

Fig. 3 shows ESR spectra of all the samples calcined at 320–500°C and the spectrum of Mn^{2+} used as a standard. The parameters of all the TiO_2 spectra are similar: $A_\perp = 32\,\text{Gs}$, $g_\perp = 2.002$, $g_{||} = 1.927$. The intensity of the spectra increases steadily with the increase in TiO_2 calcination temperature. This type of spectrum is characteristic for adsorbed or absorbed molecules NO. Similar spectra were observed for NO adsorbed on TiO_2 surface [10] and NO in TiO_2 matrix [11]. There are two types of NO in TiO_2 matrix, π with $A_\perp = 32\,\text{Gs}$ and σ with $A_\perp = 16\,\text{Gs}$ [11]. The difference in their ESR spectra results from different distribution of density of unpaired electron along the N–O axis due to different geometry of adsorption. The $A_\perp$ parameter remains unchanged for many instances of π form [12–14]. The parameter $g_{||}$ for π form of adsorbed NO lies within 1914 and 1943 [10,11,13,14]. Therefore, the detected ESR spectrum corresponds to isolated π NO molecules.

The sample of TiO_2 prepared by deposition with NaOH did not demonstrate any ESR signal. Thus, appearance of NO is associated with the deposition with NH_3. Obviously, ammonia molecules captured in TiO_2 lattice during preparation were oxidized by lattice oxygen during high temperature thermal treatment. Ammonia adsorbed on TiO_2 surface would probably be removed during washing and thermal treatment. Since the concentration of NO steadily increases with the increase in calcination temperature, the behavior of diffuse reflectance cannot be associated with these NO molecules and should be attributed to some other causes.

The presence of many-dimensional bulk defects could also cause increased absorption of visible light. X-ray diffraction is a good method to detect them. Results of X-ray diffraction study on TiO_2 of the series with different calcination temperature are given in Table 2. All the samples consist of 100% anatase. Lattice constants of TiO_2 do not undergo substantial changes with the increase in calcination temperature. However, as it could be expected from data on specific surface area, there is a significant increase of the size of crys-

Table 2
X-ray characterization of TiO_2 anatase calcined at different temperatures

Temperature of calcination (°C)	Lattice constants (Å)		Crystallite size (Å)
	A	*c*	
360	3.790(2)	9.503(5)	110
400	3.792(2)	9.489(6)	140
450	3.791(1)	9.495(3)	150
500	3.788(2)	9.505(6)	170

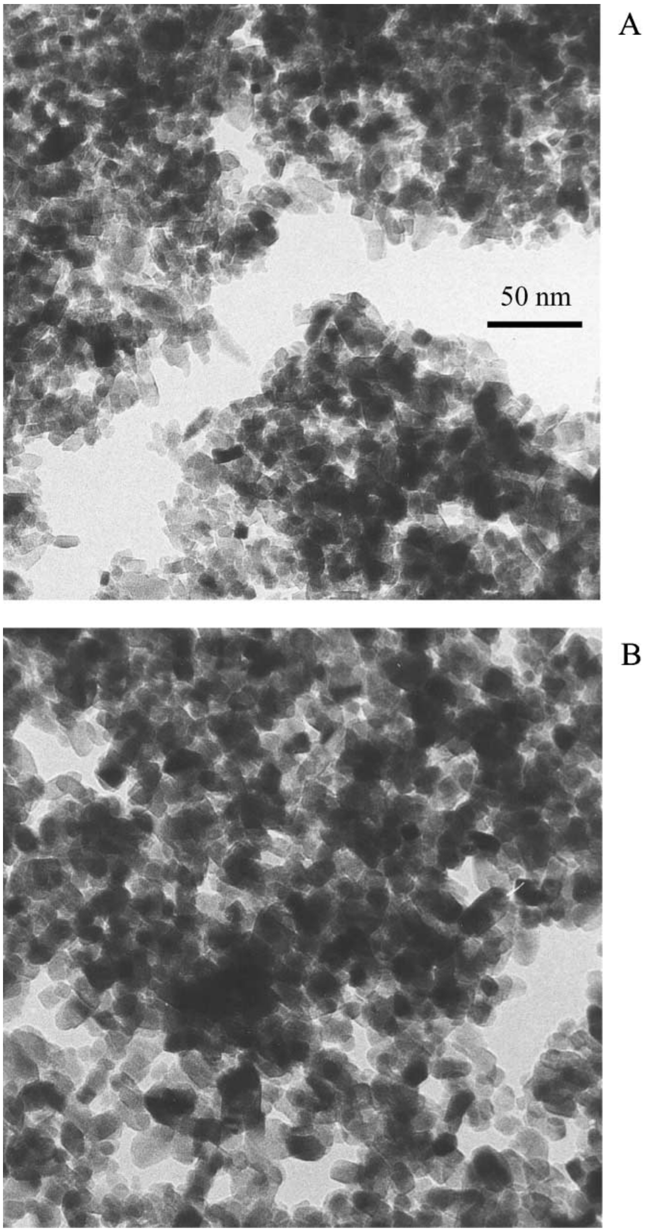

Fig. 4. Photomicrographs of TiO_2 calcined at 320°C (A) and 500°C (B).

tallites. Thus, no new phases were detected, all the samples having been of good crystallinity. This conclusion is corroborated by TEM images of TiO_2 calcined at 320 and 500°C (Fig. 4). The average size of crystallites in TEM pictures is in satisfactory agreement with the data obtained by X-ray diffraction. Two-dimensional defects (dislocations) are not observable in TEM. They are scarce most probably.

Cao et al. [2] reported that discoloration of TiO_2 was developed during photocatalytic oxidation of 1-butene at low humidity levels. They discovered only carbonate species on the surface after the reaction. Thus, the discoloration can be attributed to removal of water or hydroxyl groups. Excessive quantities of water species on the TiO_2 surface have detrimental effect on photocatalytic gas phase oxidation, but small quantities are essential for sustained reaction rate [2,15]. Therefore, the peak in photocatalytic activity at calcination temperature 450°C could be attributed to optimal quantity of water on the TiO_2 surface. However, the decrease in specific surface and growth of crystallinity should not be disregarded because these factors are also important for photocatalytic activity [16]. The increase of crystallinity could also increase reflectance of TiO_2.

Sample of TiO_2 prepared by deposition with NaOH exhibits much higher activity in acetone oxidation. Its quantum yield is 72%.

4. Conclusion

Calcination temperature of TiO_2 has been demonstrated to markedly influence its properties and photocatalytic activity in gaseous acetone oxidation. Calcination at 450°C produces TiO_2 with the highest activity. Diffuse reflectance spectra of TiO_2 calcined at different temperature and photocatalytic activity were found to correlate. This correlation may be used for quick estimation of photocatalytic activity without real photocatalytic measurements. It was supposed that the quantity of surface OH groups and crystallinity of TiO_2 determine the existence and position of the peak of photocatalytic activity.

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