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Photosensitized Oxidation of Ethanol on Alkoxy-Derived TiO_2 Powders

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In order to consider the factors affecting the photocatalytic properties of TiO_2, TiO_2 powders with controlled characteristics such as the crystalline phase, the crystallite size, and the specific surface area were prepared by hydrolyzing $Ti(Oi\text{-}C_3H_7)_4$. The photocatalytic property of the photo-oxidation of ethanol on the powder depended on the crystallite size and the microstructure. Ethanol was oxidized completely in the suspensions of the powders after illumination for 2 h while being bubbling with oxygen. The crystallite sizes of the powders were in the range of 20—30 nm. The microstructure of the powders consisted of the aggregation of fine and individual particles.

When a semiconductor is illuminated by light with energy greater than the bandgap energy, electron-hole pairs are generated and then separated by the electric field within the space charge region near the surface. These photogenerated species react with chemical species at the surface; the holes and the electrons are captured by reductants and oxidants, respectively. A number of the photocatalytic reactions have been studied especially for TiO_2 semiconductors with various shapes such as single crystals,[1,2] thin films,[3,4] and fine particles loading Pt, Ag, or RuO_2.[5-15] Many studies characterized the reactions by analyzing products and determining rates, but a few studies related the reactions with the characteristics of the semiconductor materials. The main process of the photocatalytic reaction consisted of the generation of electron-hole pairs by the absorption of light, the charge separation of the pairs and migration to the surface, and the capture of the electrons and the holes by chemical species. Each process depended on the characteristics of the materials such as the crystalline phase, the crystallite size, the specific surface area, and so on. Therefore, it is necessary to realize and control these characteristics, which are main factors determining the photocatalytic activity, for the development of the photocatalyst.

The sol–gel method of hydrolyzing a metal alkoxide and then heating is one of the progressive techniques for the synthesis of materials with controlled characteristics. Monosize powders, thin films and dense ceramic bodies of TiO_2 have been prepared by this method for application to electric devices.[16-20] We have presented the morphology and the photocatalytic properties of alkoxy-derived TiO_2 powders with various conditions for the preparation.[21] In this paper, we describe the preparation of TiO_2 fine powders with controlled characteristics by the alkoxide method and discuss the factors affecting the photocatalytic activity.

Experimental

Titanium tetraisopropoxide ($Ti(Oi\text{-}C_3H_7)_4$) was dissolved in absolute ethanol. A portion of deionized water was added to the solution while stirring. The concentration of the alkoxide was 0.1 mol dm^{-3}. The molar ratios of the water to the alkoxide (R) were 20, 100, or 1000. The solution was vigorously stirred for 2 h to complete the hydrolysis reaction. The precipitated powders were separated by a centrifuge, dispersed in basic aqueous solution (pH=11), freeze-dried and then heated at various temperatures for 1 h in air. The crystalline phase was determined by the X-ray diffraction method (XRD). The crystallite sizes were calculated from X-ray diffraction lines for anatase (d_{211}=0.16665 nm) and rutile (d_{211}=0.16874 nm) by using Scherrer's equation. The specific surface area was measured by the BET method. The absorption edge was determined from the absorption spectra of KBr tablets containing TiO_2 powders in the range of 500 to 300 nm.

The photocatalytic property of TiO_2 powders without loading metal was characterized by the photo-oxidation of ethanol (C_2H_5OH). The reaction proceeded as follows: C_2H_5OH was oxidized to acetaldehyde (CH_3CHO) and then acetic acid (CH_3COOH). CH_3COOH then decomposed to form carbon dioxide. The aqueous suspension (100 g) dispersing TiO_2 powder (1 g) and containing C_2H_5OH (0.5 mmol) was illuminated with a high pressure, 100 W mercury lamp while being stirred and being bubbled with oxygen at 25 °C. The organic species, which were contained in the solution (1 cm^3) sampled every 30 min, were analyzed quantitatively by gas chromatography. Blank tests were performed with the solution without TiO_2 powders, the suspension without being bubbled with oxygen, and the suspension without being illuminated.

Results and Discussion

Characteristics of Alkoxy-Derived TiO_2 Powders. Figures 1(a), (b), and (c) show XRD profiles of TiO_2 powders prepared with R=20, 100, and 1000, respectively, and heated in the range from 400 to 900 °C. It appeared that the critical temperature, below which the single phase of anatase developed, was 600 °C independent of R. There was a trace of diffraction lines due to the rutile phase in the profiles of the powders heated at 700 °C. The rate of the transformation of anatase to rutile depended on R. The powder prepared with R=20 and heated at 900 °C was the mixed phases of anatase and rutile, while the powder prepared with R=100 or 1000 was the single phase of rutile.

Figure 2 shows changes of the crystallite sizes of anatase and rutile in the powders with changing

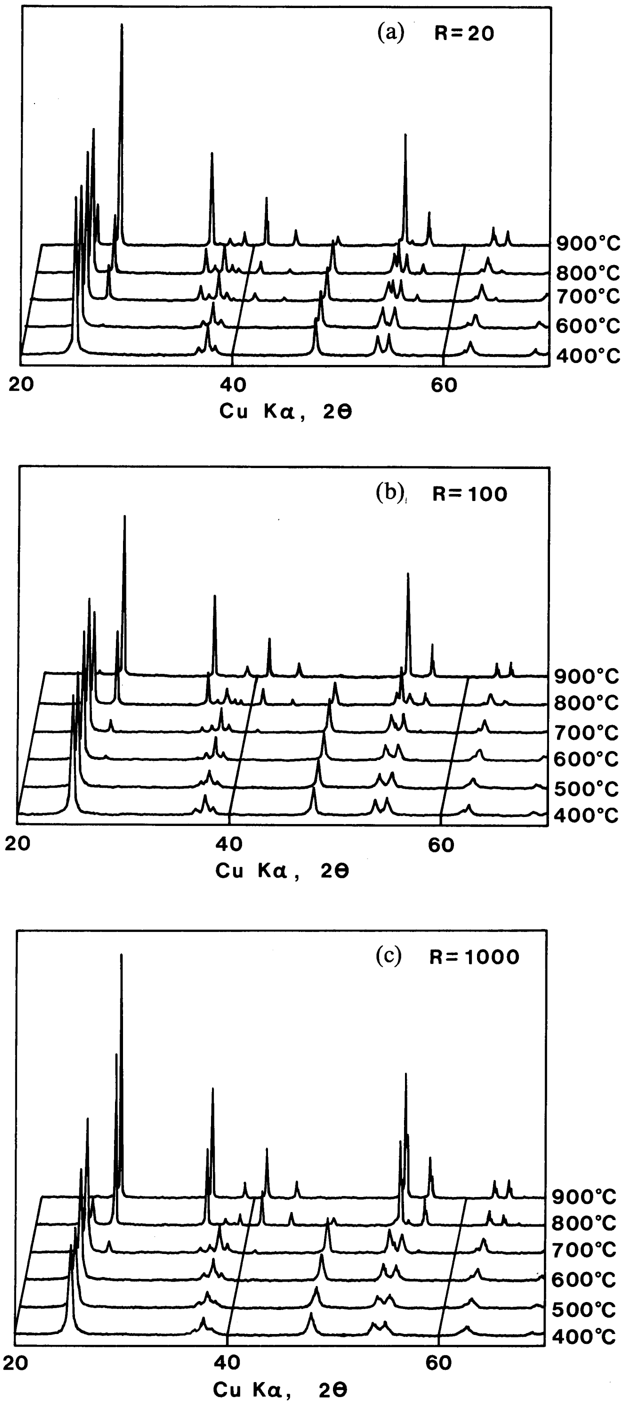

Fig. 1. XRD profiles of TiO_2 powders, which were prepared with R=20 (a), 100 (b), and 1000 (c), and heated at various temperatures.

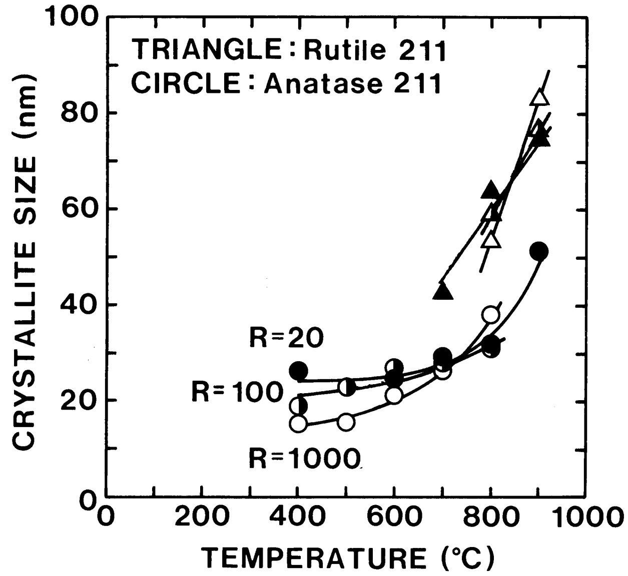

Fig. 2. Changes of the crystallite sizes of antase and rutile in the powders with temperature (●▲; R=20, ◑▲; R=100, ○△; R=1000).

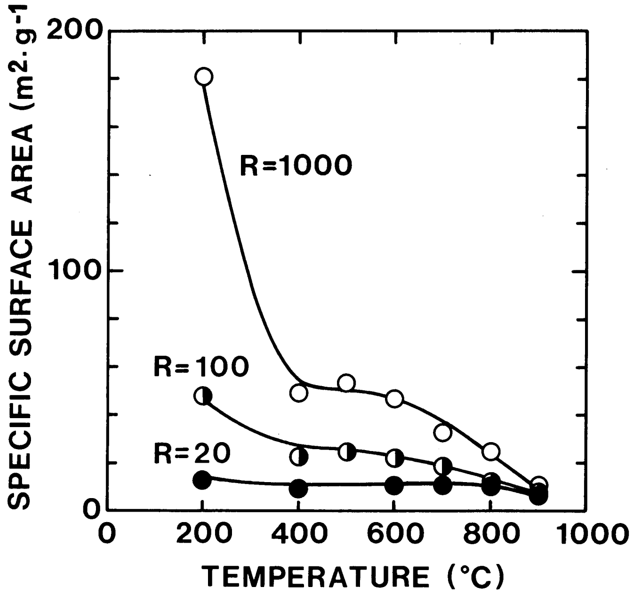

Fig. 3. Changes of the specific surface area of the powders with temperature.

temperature. The crystallite grew with increasing temperature. The crystallite size of anatase increased with the decrease of R and was less than 30 nm below 600 °C. The crystallite size of rutile was too small to calculate in the powders prepared with R=100 and 1000 and heated at 700 °C. The rate of the growth of the rutile phase with temperature increased with R. The size of the rutile in the powders heated at 900 °C was about 80 nm.

Changes of the specific surface area of the powders with temperature are shown in Fig. 3. The specific surface area decreased with increasing temperature. The more the value of R increased, the more the specific surface area increased and the change with temperature intensified. It was presented in our previous paper that the change of the specific surface area was related to the change of the microstructure of the powders during

Table 1. The Preparation Conditions and the Absorption Edge of Alkoxy-Derived TiO_2 Powders

R	Temperature/°C	Absorption edge/nm
20	600	375
20	900	390
100	600	370
100	900	395
1000	600	365
1000	900	400

Table 2. The Preparation Conditions, the Characteristics, and the Photocatalytic Property of Alkoxy-Derived TiO_2 Powders

R	Temp.	Cryst. size[a)]	Spec. surf. area	Loss of ethanol[b)]
	°C	nm	$m^2\ g^{-1}$	%
20	400	26^{A}	9.64	12.4
20	600	25^{A}	10.9	49.8
20	900	$51^{A},74^{R}$	6.68	52.7
100	400	19^{A}	22.6	41.4
100	500	23^{A}	24.7	65.6
100	600	27^{A}	22.3	100
100	700	28^{A}	18.5	100
100	800	$31^{A},59^{R}$	12.0	100
100	900	76^{R}	7.47	37.2
1000	400	15^{A}	49.4	67.6
1000	500	16^{A}	53.6	70.6
1000	600	21^{A}	47.1	93.8
1000	700	26^{A}	32.9	95.4
1000	800	$38^{A},53^{R}$	25.0	66.4
1000	900	83^{R}	11.1	44.8

a) A; anatase, R; rutile. b) Loss of ethanol after illumination of the powders for 2 h.

heating.[21)] The ratio of the specific surface area of the powder heated at 900 °C (S_{900}) to that of the powder heated at 200 °C (S_{200}) seemed to characterize the degree of sintering. For the powders prepared with R=20, 100, and 1000, the ratios (S_{200}/S_{900}) were 2.02, 6.43, and 16.3, respectively. The powders prepared with R=1000 had a large specific area and a high sintering activity. It was found that necking between particles and densification were promoted significantly in the powder prepared with R=1000 and heated at 900 °C.[21)]

The absorption edges of the powders are shown in Table 1. The values of the absorption edges of the powders heated at 600 and 900 °C were in the range of 365 to 375 nm and 390 to 400 nm, respectively. For the anatase powders heated at 600 °C, the absorption edge shifted to a shorter wavelength with a higher value of R. For the rutile powders heated at 900 °C, the absorption edge also shifted to a shorter wavelength with a lower value of R. The shifts of the absorption edges, blue-shifts, were related to the sizes of the powders and were interpreted by the so-called quantization effect.[7,13)]

Photocatalytic Property of Alkoxy-Derived TiO_2 Powders. Figures 4(a), (b), and (c) show the progress of the photo-oxidation of ethanol on the TiO_2 powders, which are prepared with R=20, 100 and 1000, respectively, and heated at various temperatures during the illumination. For the powders with R=20 (Fig. 4(a)), the photocatalytic activity was enhanced with increased temperature. The loss of ethanol after illumination for 6 h on the powders heated at 400, 600, and 900 °C were 21.6, 77.0, and 93.6%, respectively. On the powders heated at 400 °C, the oxidation of ethanol was too slow to detect the generation of acetic acid even after illumination for 6 h. For R=100 (Fig. 4(b)), the loss of ethanol after illumination for 6 h on the powders heated at 400 and 500 °C was 79.2 and 98.2%, respectively. On the powders heated at temperatures in the range of 600 to 800 °C, ethanol was oxidized effectively after 2 h and then acetic acid was oxidized completely after 3 h. The loss of ethanol after illumination for 6 h on the powder heated at 900 °C was 73.6%. For R=1000 (Fig. 4(c)), the loss of ethanol after illumination for 6 h on the powders heated at 400 and 500 °C was 90.6 and 99.0%, respectively. Ethanol and acetic acid were oxidized completely in 3 and 4 h, respectively, on the powder heated at 600 or 700 °C. The loss of ethanol after illumination for 6 h on the powders heated at 800 and 900 °C were 97.8 and 69.0%, respectively. Neither the change of content of ethanol nor the generation of acetaldehyde and acetic acid was detected in the solutions that did not contain TiO_2 powders, were not bubbled with oxygen or were not illuminated. It was thus determined that the diminution of ethanol was due to the photocatalytic oxidation.

Table 2 shows the preparation conditions such as R and temperature, the characteristics such as the crystallite size and the specific surface area, and the photocatalytic property (the loss of ethanol after illumination for 2 h). In the range of temperatures from 400 to 600 °C, the enhancement of the photocatalytic activity was related to the development of the anatase phase and was independent of R. The crystallite sizes of the powders, which were heated at temperatures from 600 to 800 °C and showed a good photocatalytic property, were about 20—30 nm. It appeared that the values were below the width of the space charge layer, in which photogenerated electrons and holes diffuse without recombination. There was a remarkable difference between the photocatalytic activities of the powders, which were prepared with R=100 and 1000, and heated at 800 °C. It should be noted that the difference was due to the microstructure of the powders as mentioned in the section describing the specific surface area. Figure 5(a) and (b) show the SEM photographs of the powders, which were prepared with R=100 and 1000, respectively, and heated at 800 °C. Individual particles were not observed in the photograph (Fig. 5(b)) of the agglomeration of the powder prepared with R=1000, but were observed in the photograph of the aggregation of the powder prepared with R=100. The values of the specific surface area did not affect the photocatalytic

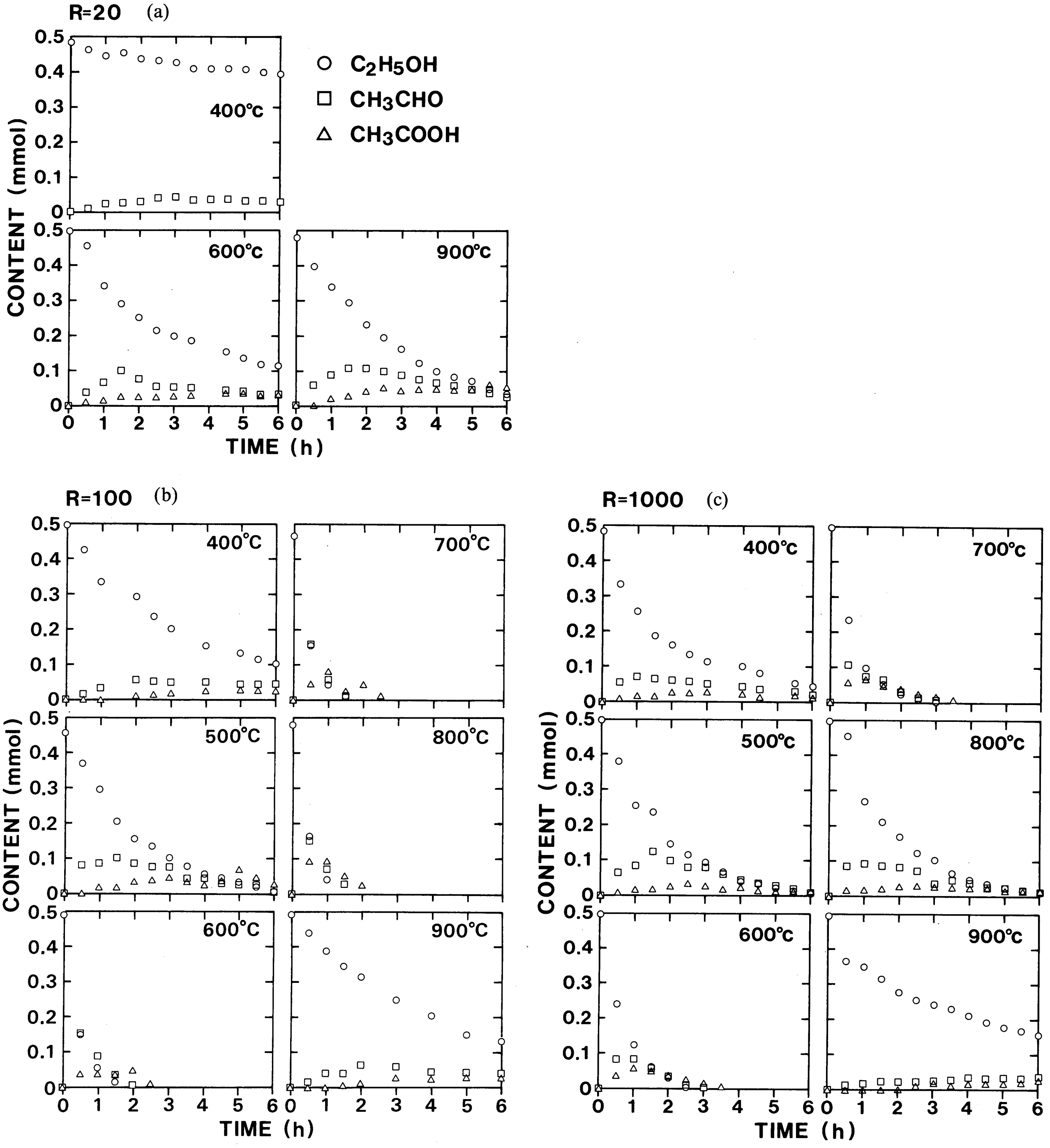

Fig. 4. Changes of the contents of ethanol, acetaldehyde, and acetic acid in the suspensions of the powders, which were prepared with *R*=20 (a), 100 (b), and 1000 (c) and heated at various temperatures, with time of illumination.

activity so much as the thermal catalytic activity. The bandgap energy of anatase is larger than that of rutile.[5] Rutile should show a higher quantum yield. However, the rutile powders, which were prepared by heating at a high temperature, began to sinter, grew to be large grains, and had a relatively large crystallite size. This is the reason that the rutile powders showed low photocatalytic activity. A study on the preparation of fine and dispersed rutile powders without necking to each other for the photocatalyst is in progress. The results will be presented in the near future.

Conclusion

TiO_2 powders with controlled characteristics such as the crystalline phase, the crystallite size, the specific surface area, and the microstructure were synthesized by

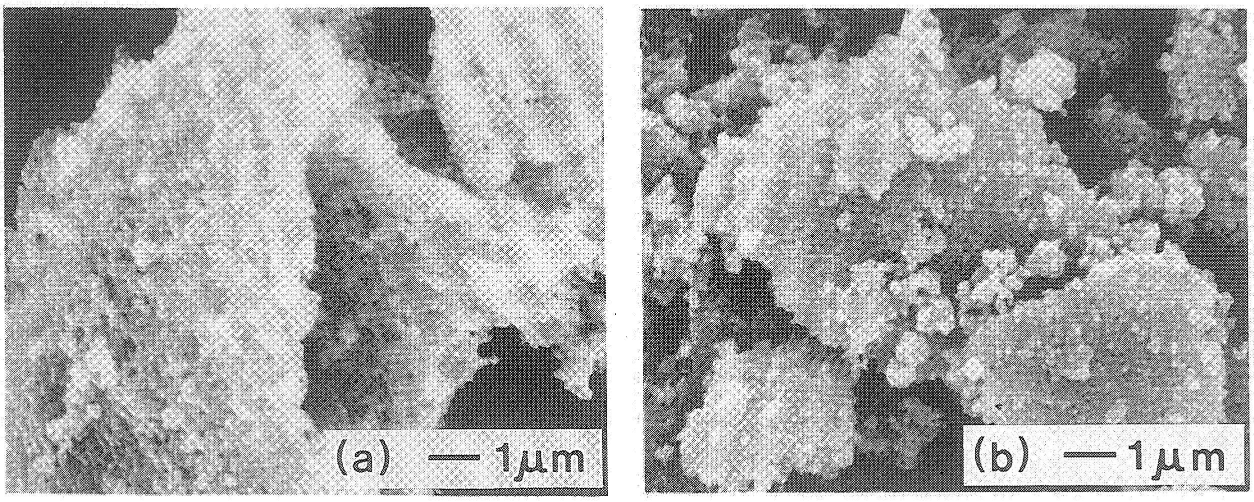

Fig. 5. SEM photographs of the powders, which were prepared with R=100 (a) and 1000 (b), and heated at 800 °C.

hydrolyzing $Ti(Oi\text{-}C_3H_7)_4$ with various molar ratios (R) of water to the alkoxide and heating at various temperatures. The photocatalytic property of the photooxidation of ethanol on the powder was affected by the crystallite size and the microstructure. The powders, of which the crystallite sizes were in the range of 20—30 nm, showed a good photocatalytic property. It was found that photogenerated electrons and holes could diffuse to the surface of the powder in the distance of 20—30 nm without recombination. The microstructure was required to consist of fine and individual particles without necking for the capture of the electrons and holes by the chemical species at the surface and the desorption of the products from the surface. The value of the specific surface area was not so important for the photocatalytic reaction as for thermal catalytic reactions. On the powders, which were prepared with R=100 and heated at temperatures in the range of 600 to 800 °C, ethanol oxidized completely after illumination for 2 h.

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