

## Dependence of photocatalytic activity of anatase powders on their crystallinity

Michio Inagaki <sup>a,\*</sup>, Rie Nonaka <sup>a</sup>, Beata Tryba <sup>a</sup>, Antoni W. Morawski <sup>b</sup>

<sup>a</sup> Faculty of Engineering, Aichi Institute of Technology, Yakusa, Toyota 470-0392, Japan

<sup>b</sup> Institute of Chemical and Environmental Engineering, Technical University of Szczecin, ul. Pulaskiego 10, 70-322 Szczecin, Poland

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### Abstract

Structural changes in anatase phase in four TiO<sub>2</sub> photocatalysts with annealing at high temperatures were followed by evaluating crystallite size and lattice strain of anatase phase separately and measuring the content of anatase. The rate constant *k* for the decomposition of methylene blue in its aqueous solution under UV irradiation was determined as a measure of photocatalytic activity. Marked dependences in crystallinity improvement, i.e., the growth of crystallite and the decrease in lattice strain, and in phase transformation from anatase to rutile phases of TiO<sub>2</sub> on annealing temperature was observed above 500 °C, depending on starting photocatalysts used. The phase transformation to rutile started after reaching of crystallite size to about 32 nm and of lattice strain to about  $0.5 \times 10^{-3}$ . Rate constant *k* was found to depend on both crystallite size and lattice strain of anatase; it increased with increasing crystallite size up to about 32 nm and decreasing lattice strain down to about  $0.5 \times 10^{-3}$ . Further increase in crystallite size and decrease in lattice strain induced the decrease in rate constant *k*, mainly due to the partial transformation of anatase to rutile. The present results showed that the activity of the photocatalysts was possible to be improved by annealing at a high temperature, by selecting an optimal condition of annealing for getting a high crystallinity in anatase phase and no phase transformation to rutile phase.

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### 1. Introduction

Photocatalyst anatase-type TiO<sub>2</sub> has been attracted attention for the remediation of global environment (Ollis and Al-Ekabi, 1993). Even though so many works were carried out on the preparation, modification and fixation of anatase powders and some of their results were transferred to practical applications (Fujishim, 1996; Ohko et al., 2001), a great effort was still devoted in order to improve the performance of photocatalysts. Different methods for the preparation of anatase powders were proposed; hydrolysis under hydrothermal condition of titanium tetraethoxide above 250 °C giving the particles of 20–

30 nm size (Yanagisawa et al., 1998), anatase powders with relatively high crystallinity and high photoactivity for water purification being synthesized from TiOSO<sub>4</sub> under hydrothermal condition at 180 °C (Inagaki et al., 2001; Toyoda et al., 2004), vapor hydrolysis of titanium tetraisopropoxide at 260 °C resulting in nano-sized particles (Chan et al., 1999), destabilization of aqueous titanium lactate below 100 °C giving thin films on various substrates (Baskaran et al., 1998), decomposition of titania-hydrate coated on hollow glass spheres (Shin and Kimura, 1999), etc. Doping of different metal ions into anatase structure was tried, in order to improve photocatalytic performance (Anderson and Bard, 1997; Okada et al., 2001; Hirano et al., 2002). Mounting of anatase particles on mesoporous silica and silica beads was reported with certain success (Takeda et al., 1995; Chun et al., 2001; Nishikawa and Takahara, 2001). Performance of anatase-mounted activated carbons was

\* Corresponding author. Tel.: +81 565 48 8121; fax: +81 565 48 0076.  
E-mail address: ina@aitech.ac.jp (M. Inagaki).

also studied in detail (Herrmann et al., 1997; Torimoto et al., 1997; Tryba et al., 2003; Toyoda et al., 2003a). Recently we developed new photocatalyst, carbon-coated anatase, which could have certain advantages, better photocatalytic activity than anatase itself, high adsorptivity, the ability to inhibit the interaction with organic binders, etc. (Izumi et al., 2001; Tsumura et al., 2002a,b; Toyoda et al., 2003b, 2005; Tryba et al., 2004a,b).

The effect of size of primary particles (crystallite size) was also studied. For the decomposition of  $C_2HCl_3$  gas, the maximum decomposition rate was observed on the primary particles with the size of about 8 nm and the rate decreased gradually with increasing particle size (Maira et al., 2000). Among the powders with different crystallite sizes, anatase with the size of 11 nm was shown to have the highest photoactivity for the decomposition of  $CHCl_3$  gas (Wang et al., 1997). For methylene blue ( $C_{16}H_{18}N_3S$ , MB) in water, however, anatase particles with average size of 30 nm were reported to have the highest decomposition rate (Xu et al., 1999). Degradation rate of  $C_2HCl_3$  in its aqueous solution was reported to increase with increasing crystallite size up to about 15 nm (Rivera et al., 1993). In a series of our works, crystallinity of anatase was shown to govern its photoactivity through the evaluation of the crystallinity by the full width at half maximum intensity (FWHM) of the 101 diffraction line of X-ray powder pattern (Inagaki et al., 2001; Toyoda et al., 2004). Using the anatase powders prepared through sol–gel process with different aging times and different annealing temperatures, it was clearly shown that maximum rate constant for the decomposition of methylene blue in aqueous solution was obtained for the sample having the FWHM of around  $0.6^\circ$  in  $2\theta$  ( $CuK\alpha$ ) (apparent crystallite size of about 10 nm), but maximum decomposition fraction of diluted NO gas was given by the samples with FWHM of about  $1.5^\circ$  (apparent crystallite size of about 5 nm) (Inagaki et al., 2004). These experimental facts were qualitatively consistent with the experimental results reported before (Rivera et al., 1993; Wang et al., 1997; Xu et al., 1999; Maira et al., 2000), which did not base on a large number of experimental points. In our previous paper on anatase powders synthesized under hydrothermal condition from  $TiOSO_4$ , a similar dependence of the rate constant for the methylene blue decomposition on FWHM of 101 diffraction line of anatase was observed, the maximum rate constant for the sample with FWHM of around  $0.22^\circ$  (apparent crystallite size of about 35 nm) (Toyoda et al., 2004). For carbon-coated anatase, which were recently developed by our group, the same dependences of the rate constant of different pollutants in their diluted aqueous solutions, methylene blue, reactive black 5, phenol and iminocadin triacetate, on FWHM were observed, though the values of the rate constants were different depending on the pollutants (Tsumura et al., 2002; Tryba et al., 2004a, 2004b; Toyoda et al., 2005). However, the broadening of X-ray diffraction line is well

known to be due to at least two factors, i.e., crystallite size and lattice strain, and so a simple calculation of crystallite size from the observed values of FWHM of diffraction line is ignoring lattice strain.

In the present work, crystallite size and lattice strain in anatase crystallites were separately evaluated from the dependence of FWHM values observed on different diffraction lines on  $\sin\theta$  according to so-called Hall's equation (Hall, 1949). The relations of the rate constant for methylene blue decomposition in aqueous solution to crystallite size and lattice strain were discussed on different anatase samples. Marked dependence of rate constant on crystallinity of anatase phase was observed. In order to get a high rate constant, it was clearly shown that high crystallinity, i.e., large crystallite size and small lattice strain in anatase was desired, which could be obtained just before the phase transformation to rutile phase.

## 2. Experimental

### 2.1. Samples

The sample ST-01 (Ishihara-Sangyo, Japan) is a single phase of anatase, of which the size of primary particles was determined to be 7 nm by X-ray diffraction and that of aggregated secondary particles was about 60 nm by transmission electron microscope. It has a large BET surface area of about  $300\text{ m}^2\text{ g}^{-1}$ . The powders were annealed at different temperatures from 400 to 800 °C for different periods in air. Heating rate to each temperature was  $200\text{ }^\circ\text{C h}^{-1}$ .

The anatase powder A11 (Police, Poland), which was a single phase of anatase and a high crystallinity, was used as a sample to study on the modification by carbon doping by our group (Janus et al., 2004; Morawski et al., in press). In the present work, the precursor of this A11 powder supplied by Police, Poland, (hereafter A11 precursor), which showed very broad and weak diffraction lines of anatase phase, was annealed at different temperatures from 400 to 800 °C for different periods in air.

For comparison, two powders of  $TiO_2$  with fine particles were used, which were prepared through sol–gel process from titanium tetraisopropoxide in its ethanol solution with different aging times (10 min and 24 h) and then annealed at different temperatures from 100 to 900 °C for 1 h in air. As-prepared  $TiO_2$  powder with 10 min aging (hereafter sol–gel-10 min) was composed of a single phase of anatase, even though its diffraction lines were very broad, and that prepared with 24 h aging (sol–gel-24 h) was identified as amorphous from its X-ray powder pattern. Both of them were composed of the aggregates of fine particles with less than 10 nm size. Details of the preparation, the structural changes with annealing and the photoactivity of those samples were reported in our previous paper (Inagaki et al., 2004). Annealing of these  $TiO_2$  powders was carried out by the exactly the same procedure as ST-01 and A11 precursor.

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