Correlation between Photocatalytic Activities and Structural and Physical Properties of Titanium(IV) Oxide Powders

Orlando-Omar Prieto-Mahaney,[1] Naoya Murakami,[1] Ryu Abe,[1,2] and Bunsho Ohtani*[1,2]
[1]*Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810*
[2]*Catalysis Research Center, Hokkaido University, Sapporo 001-0021*

(Received November 14, 2008; CL-081076; E-mail: ohtani@cat.hokudai.ac.jp)

Correlation between structural and physical properties and photocatalytic activities for five kinds of reactions of 35 titania samples was obtained through multivariable analyses: photocatalytic activities were empirically reproduced by a linear combination of six properties with fair reliability. While a portion of results could be interpreted using a conventional mechanism, significant activity dependence on properties, not disclosed yet, was suggested.

Photocatalytic reaction is induced by photoexcited electrons (e^-) and positive holes (h^+) generated in a solid photocatalyst followed by redox reaction with surface-adsorbed substrates. Titanium(IV) oxide (titania) is one of the most promising photocatalysts because of its high chemical stability, sufficient energy of its e^- and h^+ to drive various photocatalytic reactions, negligible toxicity, inexpensiveness, and ease of preparation. Only one plausible weakness of the titania photocatalyst is that it absorbs only ultraviolet light, though such transparency is preferable when titania is coated on colored materials. It is known that the photocatalytic activity, i.e., rate of photocatalytic reaction, depends on the structural and physical properties of titania. It is believed that there is a relationship between properties and activities, i.e., a structure–activity correlation. It has often been claimed that the smaller the particle size, i.e., the larger the specific surface area, the higher the photocatalytic activity or that anatase is better than rutile.[1] However, such discussion on the correlations has been limited to a certain series of samples prepared in a similar way or small number of commercial samples,[2] and there seem no comprehensive correlations.

The present study aims at obtaining the structure–activity correlations for a large number of titania photocatalysts covering commercially available titania samples in Japan (see Table S1)[14] by statistical multivariable analysis. Five representative reactions were chosen, and their relative rates were analyzed using six properties,[3] specific surface area (BET), density of lattice defects (DEF), primary (PPS) and secondary (SPS) particle size, and existence of anatase (ANA) and rutile (RUT) phases, to obtain intrinsic dependence of photocatalytic activities on the properties.

Five test photocatalytic reactions were as follows: **a**, Oxygen (O_2) liberation and silver deposition from a deaerated aqueous silver sulfate solution; **b**, Dehydrogenation of methanol in a deaerated aqueous solution; **c**, Oxidative decomposition of acetic acid to liberate carbon dioxide (CO_2) from an aerated aqueous solution; **d**, Decomposition of acetaldehyde into CO_2 in air; and **e**, Synthesis of pipecolinic acid from L-lysine in a deaerated aqueous solution (see SI).

First, the rates of reactions were compared with each structural property. In general, there were no significant relations between them, while, in some cases, dependence of the rate on a parameter was observed (see SI, Tables S2 and S4). This seems reasonable since the titania samples used in this study were of a wide range and synthesized or treated in different ways. Then, the data were analyzed statistically by solving the following matrix equation, $[\text{rate}]_{35\times1} = [\text{property}]_{35\times6} \times [\text{coefficient}]_{6\times1}$, for each reaction. The experimental results, rates and properties, were standardized using mean of data and standard deviation in order to make the calculated coefficients have the same weight being independent of properties, i.e., enabling direct comparison of partial regression coefficients (k).

Table 1 shows the summary of results of analyses. Squared multiple correlation coefficient, R^2, was also listed. It was found that the best R^2 values were obtained when ANA and RUT were defined to be 1 or 0 (dummy variables) when the most intensive peak of anatase and rutile was detected in the XRD patterns and otherwise, respectively. Although it is known that increase in the number of variables improves the fitting, i.e., makes R^2 to be close to unity, no other appropriate properties have been found to be added to the list. As a general trend, **a** and **e** gave relatively larger R^2s, i.e., higher reproducibility of the results fitting to a linear combination of properties, while those for the others were also fairly high.[4] Figure 1 shows this linearity for **a** as an example; the calculated (predicted) relative activities of each sample using obtained coefficients (k) were plotted against the observed activity. Another significant feature is that coefficient of k_{ANA} has large positive value in all the cases except for **a**. This is the first example, within the authors' knowledge, of support for a general understanding in this field that anatase is more active than rutile, since previously reported data were of only a limited number of samples and neglected the influence of the other properties. On the other hand, k_{RUT} was relatively small and it was negative in **d** suggesting that rutile phase in the photocatalysts is rather inert compared with anatase. Although large positive and negative k_{BET} and k_{DEF}, respectively, are expected since large surface area is advantageous to adsorb reaction substrate(s) and defective sites accelerate recombination of e^- and h^+, large positive k_{BET} was observed only for **b** and even large positive k_{DEF} was obtained for **c**, **d**, and **e** as discussed later. k_{PPS} and k_{SPS} depended on the type of reactions.

Table 1. Squared multiple correlation coefficient (R^2) and partial regression coefficients (k)

Coefficient	a	b	c	d	e
R^2	0.86	0.52	0.58	0.60	0.85
k_{BET}	−0.01	0.43	−0.09	0.13	0.19
k_{DEF}	−0.15	−0.25	0.19	0.43	0.32
k_{PPS}	0.12	−0.20	−0.18	−0.20	−0.52
k_{SPS}	0.57	0.08	−0.20	−0.04	−0.07
k_{RUT}	0.14	0.28	0.11	−0.06	0.02
k_{ANA}	0.04	0.40	0.57	0.55	0.63

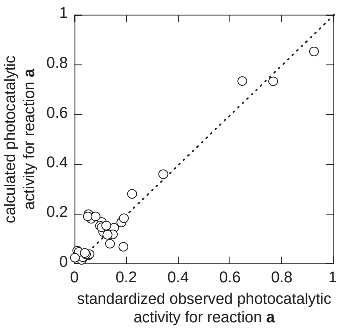

Figure 1. Relation between standardized photocatalytic activities for reaction **a** observed and calculated using obtained partial regression coefficients in Table 1. This linearity indicates that the activity of samples can be estimated from their physical properties.

For **a**, k_{ANA} was small but positive, which means that anatase does not prohibit the reaction, while k_{RUT} was not so large, suggesting that it is not indispensable to be rutile for higher activity. It seems that large secondary particles (large positive k_{SPS}) composed of large primary particles of less crystalline defects (negative k_{DEF}) are preferable, which agrees with the general recognition reported so far.[5] A significant point, which has been revealed in this study first, is that the reported higher activity of rutile powders[6] for **a** is mainly attributable to their secondary particle size[7] but not to rutile crystal, and it is expected that anatase would be active when its secondary particle size is large.

Reaction **b** was performed using in situ platinized titania particles, since bare samples show negligible activities.[4] The positive k_{RUT} and k_{ANA} coefficients seem reasonable, since the bottom of the conduction band (CB) of anatase (-0.20 V vs. NHE) and rutile ($+0.04$ V) crystals is reported[8] to be almost the same or a little negative compared with the standard electrode potential of hydrogen evolution (H^+/H_2; 0 V). k_{ANA}, a little larger than k_{RUT}, might be related to a slightly more negative CB level of anatase. Comparable activity of rutile phase has been shown previously through action spectrum analyses.[9] It has been shown for hydrogenation of 2-propanol that the rate depends on the amount of surface-adsorbed alcohol.[10] Large positive k_{BET}, as well as negative k_{PPS}, and large negative k_{DEF} suggested that this reaction requires both a large amount of adsorbed methanol and less probability of e^-–h^+ recombination.

Reactions **c** and **d**, exhibiting a similar trend of coefficients, were conducted under aerated conditions, and their mechanism must contain O_2 reduction by e^-. Preference of anatase crystallites (large positive k_{ANA}) may be caused by the above-mentioned CB position. The potential of one-electron reduction of O_2, $O_2^{\bullet-}/O_2$ (-0.05 V) or HO_2/O_2 (-0.28 V) is a little more negative than that for H_2 evolution, and thereby small difference (ca. 0.16 V) in CB position may be decisive. Another feature of these oxidative decompositions was a relatively large positive k_{DEF}, which must accelerate the e^-–h^+ recombination. A possible interpretation for this inconsistency is that the defective sites act as an adsorption site for organic compounds and/or O_2 and the influence of enhanced e^-–h^+ recombination on the rate was small, presumably owing to efficient radical chain reaction.[11] Taking into account negative k_{DEF} for **b**, in which organic compound, methanol, is also oxidized, enhanced adsorption of O_2 at the defective sites might occur, though at present we have no evidence supporting this hypothesis. Positive k_{BET} for **d**, in contrast to the negative value for **c**, suggests that this gas–solid phase reaction requires diffusion of substrates, acetaldehyde and O_2, and, therefore, the larger the surface area, the faster the diffusion for **d**.

Reaction **e** has been known to proceed through redox-combined mechanisms; Lys is oxidized by h^+ and hydrolyzed and cyclized to a Schiff base intermediate which undergoes reduction, at surface-loaded Pt deposits, by e^- to yield PCA.[12] Similarity of the trend with **b** suggests that the reaction rate is also governed by the first oxidation step. The positive k_{DEF} is attributable to the preferable adsorption of Lys at the defective sites. The larger and smaller k_{ANA} and k_{RUT}, respectively, compared with **b** might reflect a difference in reduction process between **b** and **e**; reduction of the Schiff base intermediate[13] is thought to require a little more negative potential of e^- than that for H_2 liberation.

In conclusion, statistical multivariable analyses of photocatalytic activities depending on the properties of titania powders supported the conventional wisdom, e.g., anatase is more active than rutile especially for photocatalytic oxidative decomposition of organic compounds, and lattice defects reduce activity in reactions conducted under deaerated conditions. On the other hand, unexpected results were also observed; e.g., lattice defects are beneficial especially for reactions under aerated conditions, and the activity for O_2 liberation is governed by secondary particle size rather than crystal form. Since each property changes depending on each other to some extent (see Tables S2 and S3), e.g., rutile crystallites are often large compared with anatase, intrinsic dependence of activity on each property has been ambiguous. The intrinsic dependence of activity as shown in this study could be demonstrated, for the first time, by statistical multivariable analyses.

References and Notes

1 Problems appearing in such discussions have been pointed out in a recent article: B. Ohtani, *Chem. Lett.* **2008**, *37*, 216.
2 A recent paper has reported the activity of 6 samples depending on the type of organic compounds to be degraded in aerated aqueous solutions: J. Ryu, W. Choi, *Environ. Sci. Technol.* **2008**, *42*, 294.
3 Some of the properties have been already reported: N. Murakami, O. O. Prieto-Mahaney, R. Abe, T. Torimoto, B. Ohtani, *J. Phys. Chem. C* **2007**, *111*, 11927.
4 Relatively small R^2 for reaction **b** might be due to possible differences in size and morphologies of platinum deposits and this will be discussed elsewhere.
5 For example: S. Nishimoto, B. Ohtani, H. Kajiwara, T. Kagiya, *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 2685.
6 For example: S. Nishimoto, B. Ohtani, H. Kajiwara, T. Kagiya, *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 61.
7 Nosaka et al. reported a relation between secondary particle size and rate of photocatalytic superoxide anion radical production, but the reason has not been fully clarified yet: Y. Nosaka, M. Nakamura, T. Hirakawa, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1088.
8 G. Rothenberger, J. Moser, M. Grätzel, N. Serpone, D. K. Sharma, *J. Am. Chem. Soc.* **1985**, *107*, 8054.
9 T. Torimoto, N. Nakamura, S. Ikeda, B. Ohtani, *Phys. Chem. Chem. Phys.* **2002**, *4*, 5910.
10 S. Nishimoto, B. Ohtani, T. Kagiya, *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 2467.
11 B. Ohtani, Y. Nohara, R. Abe, *Electrochemistry* **2008**, *76*, 147.
12 B. Ohtani, S. Tsuru, S. Nishimoto, T. Kagiya, K. Izawa, *J. Org. Chem.* **1990**, *55*, 5551.
13 B. Ohtani, K. Iwai, S. Nishimoto, S. Sato, *J. Phys. Chem. B* **1997**, *101*, 3349.
14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.