Improved Photocatalytic Activities by Loading Rutile TiO_2 Particles with Anatase or Amorphous Particles

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We have found that rutile TiO_2 particles exert strong oxidation power, when suitable electron acceptors are added to the reaction system. The power is strong enough to efficiently oxidize water to molecular oxygen [1]. However, they usually have low ability to reduce molecular oxygen. As a result, pure rutile particles show low photocatalytic activity for many kinds of reaction when oxygen is used as the electron acceptor. On the other hand, since anatase particles are active for reduction of molecular oxygen, they show high efficiency, especially, for oxidation of organic compounds using molecular oxygen as the electron acceptor.

Figure 1 shows the photographs of TiO_2 powders after photoirradiation in aqueous solution containing 2-propanol as the hole scavenger and NBT as the detector of superoxide ion generated from oxygen [2]. The rutile powders are strongly colored due to the deposition of formazan, which was produced by the reaction between NBT and superoxide ion. This result suggests that the main reduction product from oxygen on rutile particles is superoxide ion. On the other hand, on anatase particles, the main product was found to be hydrogen peroxide. Table 1 compares the production rates for acetone, hydrogen peroxide, and superoxide ion on several kinds of rutile and anatase powders. The results indicate that the high activity of anatase powders is related with its high production rate for hydrogen peroxide. Hence, the catalytic activity for reduction of oxygen to hydrogen peroxide is concluded to be the key to the efficient photocatalytic reaction using oxygen as the electron acceptor. In the case of amorphous particles, they have very poor photocatalytic activity due to very rapid electron-hole recombination in them. However, we found that the amorphous particles have very strong activity for reduction of molecular oxygen to hydrogen peroxide.

Based on the above findings, we have prepared photocatalysts by loading rutile particles with small amounts of fine anatase or amorphous particles by sonicating the mixed particles in solution. The amorphous particles were prepared by hydrolysis of titanium isopropoxide. Figure 2 indicates that the rutile powder loaded with amorphous particles show improved photocatalytic activity for the oxidation of 2-propanol. On this mixed photocatalyst, the oxidation power, which is necessary for the oxidation of 2-propanol, is supplied from the holes produced in the rutile particles. The reduction of oxygen probably takes place on amorphous particles; the electron produced in the rutile particles are considered to be transferred from the rutile particles to the amorphous particles across a small energy barrier. It should be emphasized that the photocatalytic activity is improved by depositing rutile particles with amorphous particles that are photocatalytically inactive. Similar improvement in the activity was also observed by loading rutile particles with fine anatase particles [3].

References:
[1] T. Ohno, D. Haga, K. Fujihara, K. Kaizaki, M. Matsumura, *J. Phys. Chem.B*, **101** (1997) 6415; errata, **101** (1997) 10605.
[2] H. Goto, Y. Hanada, T. Ohno, M. Matsumura, *J. Catal.*, in press.
[3] T. Ohno, K. Tokieda, S. Higashida, M. Matsumura, *Appl. Catal. A*, **244** (2003) 383.

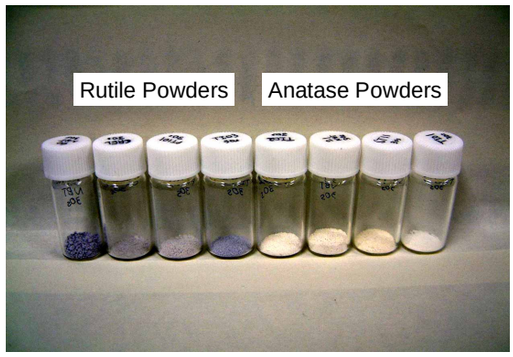

Figure 1. Photographs of TiO_2 powders after photoirradiation in 4 vol% 2-propanol containing NBT for 30 s.

Table 1. Production rates for acetone, hydrogen peroxide, and superoxide ion using different TiO_2 powders. R and A in the parentheses stand for rutile and anatase, respectively.

TiO_2 powder	Acetone	H_2O_2	O_2^-
NS90 (R)	0.5	0.0	1.0
CR-EL(R)	0.8	0.1	0.9
TIO-3(R)	0.8	0.0	1.6
TIO-2(A)	3.3	2.9	0.4
ST-21(A)	5.4	5.3	0.2
ST-11(A)	2.8	2.7	0.5

Units: 10^{-7} mol/min

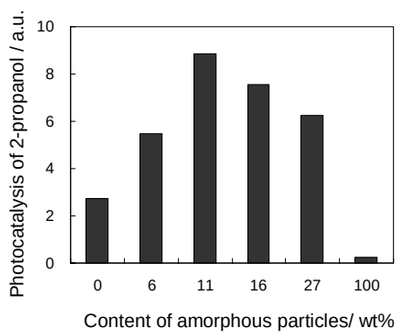

Figure 2. Photocatalytic activity of rutile TiO_2 particles loaded with fine amorphous particles at different contents. The photocatalytic activity was evaluated by the production rate of acetone from aqueous solution of 4 vol% 2-propanol which was bubbled with oxygen.