April, 1985] © *1985 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 58, 1255—1258 (1985)*

Photocatalytic Oxidation of Sulfur on the Doped TiO_2 Catalysts

Yasumichi MATSUMOTO,* Yasuhide YAMAGUCHI, and Ei-ichi SATO
Department of Industrial Chemistry, Faculty of Engineering, Utsunomiya University, Ishi-icho 2753, Utsunomiya 321

(Received November 5, 1984)

TiO_2(anatase) doped with various elements was used as the photocatalyst in the production of sulfuric acid from sulfur in water into which O_2 was bubbled. The catalysts doped with typical elements having one and two valencies showed high catalytic activity, but some doped with typical elements having four and five valencies showed low activity. The intermediate, *i.e.*, $\dot{O}_2H$ radical, in the O_2 reduction produced by photoproduced electrons will probably play an important part in the production of sulfuric acid. Therefore, it was suggested that the Ti^{3+} ion in the TiO_2 lattice which contribute to direct O_2 reduction will inhibit sulfuric acid production. In the case of transition metal dopants, the transition metal cation in the TiO_2 lattice will directly affect the O_2 reduction. The catalyst doped (deposited) with Pt shows the highest catalytic activity of all the catalysts used in the present study.

Photocatalytic reactions are very important when using solar energy as a substitute for activation energy (downhill reaction), and in the chemical storage of solar energy (uphill reaction). We have discovered that sulfur is directly oxidized to SO_4^{2-}, *i.e.*, sulfuric acid, on a TiO_2 photocatalyst in water into which O_2 is bubbled.[1] This is a downhill reaction. Solar energy is used as a substitute for activation energy in this process. The direct production of sulfuric acid from sulfur by a photocatalyst is very important to the chemical industry.

However, the prodution rate of the sulfuric acid is very slow, if TiO_2 is used as the photocatalyst.[1] It is well known that the photocatalytic activity of TiO_2 is enhanced significantly by doping or deposition of some elements onto the TiO_2 surface.[2–11] Therefore, doped TiO_2 was used as the catalyst in the photocatalytic oxidation of sulfur in the present study. Some of the dopants gave higher activity, but others gave lower activity in this catalysis. In the present paper, we have discussed the catalysis bv doped TiO_2 as well as the mechanism for the photocatalytic oxidation of sulfur.

Experimental

Solid sulfur (99.99%, Rare Metallic Co. Ltd.,) and TiO_2 powder (99.6%, anatase, Merck) were used as the reactant and the catalyst, respectively. Unless otherwise stated, the doping was done by thermal decomposition of metal salts (nitrate, acetate, oxalate and chloride) on TiO_2 powder at 500 °C for 3 h, since the maximum catalytic activity was obtained at a heat treatment temperature of about 500 °C. Only TiO_2 (anatase) was detected for 1 atm% doped TiO_2 except for Pt doped TiO_2 by X-ray analysis. In the case of the latter sample, Pt metal as well as TiO_2 were detected. Pt probably is not doped into the TiO_2 lattice but is instead deposited on the surface.

Sulfur (0.4 g) was mixed with the doped TiO_2 (0.02 g) and water (50 ml). This suspension was poured into a quartz vessel and magnetically stirred with bubbling O_2 gas. It was then illuminated with an ultrahigh-pressure mercury lamp (500 W). A cutoff filter which transmits 50% of 290 nm of light, but completely cuts off light shorter than 240 nm was used in order to suppress the photoreaction of the sulfur itself, unless otherwise stated. The products were analyzed in the same manner as described in the previous paper.[1] When SO_4^{2-} ion could not be gravimetrically determined as $BaSO_4$ because it was present in a very small amount, the SO_4^{2-} was calculated from the pH value of the solution.

Results

Figure 1 shows the production rates of SO_4^{2-} and H_2S on the doped TiO_2 as a function of the concentration of the dopants. Similar tendencies to those in this figure were observed for other dopants. The production rates of SO_4^{2-} and H_2S show the maximum and the minimum at about 1 atm% concentration of the dopants, respectively. This result suggests that the elements, except for Pt, are doped into anatase lattice up to about 1 atm% but not above this range, as described in the latter section. No other products, for example $S_2O_3^{2-}$ or SO_3^{2-}, were detected for all catalysts. Photoreaction products were scarcely detected when doped rutile powder was used as the catalyst. Therefore, the anatase structure is very important for catalysis in the photooxidation of sulfur in the case of the doped TiO_2 as well as nondoped TiO_2.[1]

Figure 2 shows the relationship between the production rate of SO_4^{2-} and the ionic valency of the dopant in the TiO_2 lattice. The ionic valencies of the dopants used in this figure are those of their oxides which are the most stable under ordinary conditions. Pt was classified for convenience as a zero value, because Pt metal was detected by X-ray analysis as stated above. In general, the catalytic activity decreases with the increase in the ionic valency of the dopant. This tendency is especially clear for the typical element. Typical element dopants, having ionic valencies of one, two and three, will lead to a decrease in the amount of Ti^{3+}, while those having an ionic valency of five will lead to an increase of Ti^{3+} in the TiO_2 lattice, if the amounts of the oxygen anion vacancies are constant in the lattice. The catalytic activity of the nondoped anatase (SO_4^{2-} production rate$=0.2\times10^{-4}$ mol h^{-1}) is almost the same as those doped with typical elements having ionic valencies of three and four. This will be in agreement with the fact that the Ti cation exists as Ti^{3+} or Ti^{4+} in the TiO_2 lattice. It may be concluded from the above results that the existence of Ti^{3+} in the TiO_2 lattice will inhibit the produc-

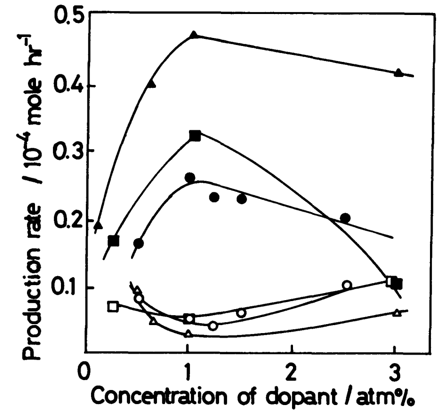

Fig. 1. Production rates of SO_4^{2-} and H_2S as a function of the concentration of dopants. Closed symbols represent the production rates of SO_4^{2-}, while open symbols represent the production rates of H_2S. Circles, squares and triangles represent TiO_2 catalysts doped with Ru, Na, and Pt, respectively.

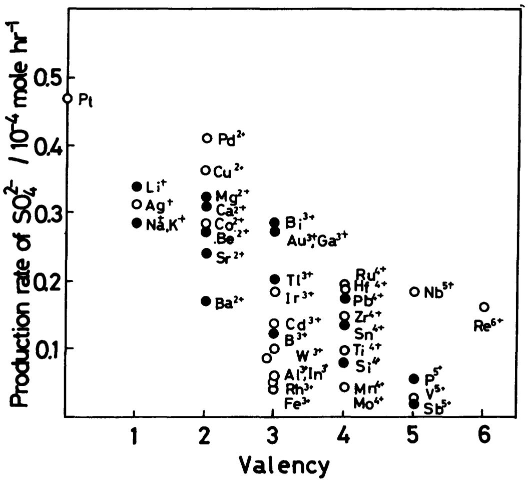

Fig. 2. Relationship between the production rate of SO_4^{2-} and the ionic valency of the dopant. Closed symbols represent typical elements and open symbols represent transition metals.

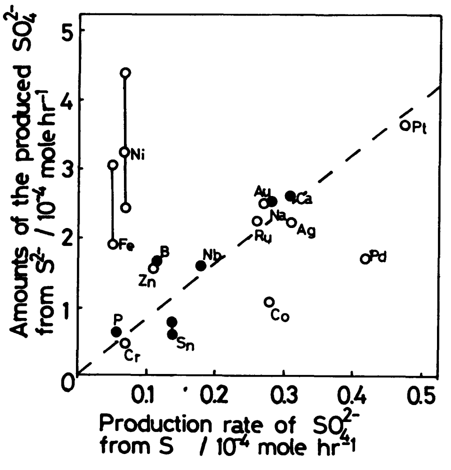

Fig. 3. Relationship between the production rate of SO_4^{2-} from sulfur and the amounts of SO_4^{2-} produced from S^{2-}.

TABLE 1. PHOTOPRODUCTS FROM S, S^{2-}, $S_2O_3^{2-}$, AND SO_3^{2-} ON TiO_2/Pt

Reactants	Products/10^{-4} mole				
	H_2S	S^{2-}	$S_2O_3^{2-}$	SO_3^{2-}	SO_4^{2-}
S(0.4 g)	0.05	0	0	0	0.47
S^{2-}(1×10^{-3} mol)	0.03	—	1.10	2.12	3.64
$S_2O_3^{2-}$(1×10^{-3} mol)	0.08	0	—	0	4.16
SO_3^{2-} (1×10^{-3} mol)	0.01	0	0	—	9.93
(10×10^{-3} mol)	0.04	0	0	—	76.70

tion of SO_4^{2-}.

Figure 3 shows the relationship between the production rate of SO_4^{2-} from sulfur and the amount of photoproduced SO_4^{2-} from S^{2-} (Na_2S) in one hour. The initial concentration of S^{2-} in the solution was 10^{-3} mol/50 ml in this test. With the exceptions of Ni and Fe dopants, it was found that catalytic activity of the doped anatase for both reactions had almost the same tendency. Other ions, for example $S_2O_3^{2-}$ and SO_3^{2-}, were also produced when the S^{2-} ion was used as the starting reactant. On the other hand, amounts of less than 50% $S_2O_3^{2-}$ ($Na_2S_2O_3$) were also photooxidized to SO_4^{2-} on doped TiO_2 under illumination, but the tendency of the activity did not agree with that from sulfur to SO_4^{2-}, and no SO_3^{2-} was detected. When SO_3^{2-} (Na_2SO_3) was used as the reactant, large amount of SO_4^{2-} were obtained even in the dark. Under illumination, 90—100% of the SO_3^{2-} was changed to SO_4^{2-}, but no $S_2O_3^{2-}$ was detected. Table 1 shows typical results for the above tests on Pt-doped TiO_2. Thus, S^{2-} and $S_2O_3^{2-}$ will not be the intermediates in the mechanism of photocatalytic oxidation of sulfur on TiO_2, because no $S_2O_3^{2-}$ was detected in this process.

Figure 4 shows the wavelength dependencies of the photocatalytic production rate of SO_4^{2-} from sulfur on the doped TiO_2. These results show that the photocatalytic oxidation in this process is based on the hole and the electron produced by the bandgap photon of anatase (<390 nm). Figure 5 shows the photocatalytic production rate of SO_4^{2-} from sulfur on the Pt-doped TiO_2 as a function of the light intensity. Linear relationships of $\log V/\log I$ were observed, and the slope was about 1.0, where I denotes the light intensity. The same dependencies of the photoproduction of SO_4^{2-} from S^{2-} and from $S_2O_3^{2-}$ on the wavelength and the light intensity were also observed for the doped TiO_2.

Discussion

Figure 6 illustrates the process of photooxidation of sulfur to SO_4^{2-} on a TiO_2 catalyst. Sulfur is directly converted to $S_2O_3^{2-}$, SO_3^{2-}, and H_2S (S^{2-}) by the catalyst under illumination, and a small amount of S^{2-} in the solution are oxidized to $S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-} as described in the previous section. In practice, a large portion of the produced S^{2-} is evolved from the solution as H_2S gas, because the solution changes to the acid due to the production of SO_4^{2-}. Therefore, neither $S_2O_3^{2-}$ nor SO_3^{2-} is detected in the solution. If SO_3^{2-}

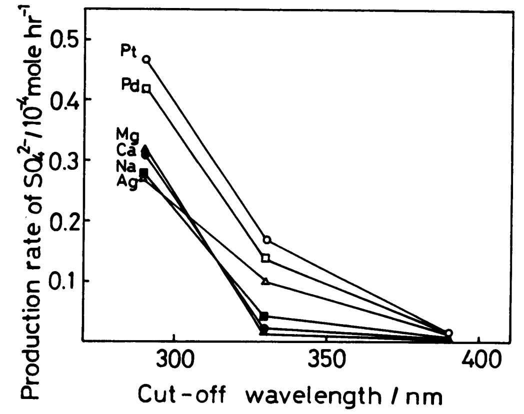

Fig. 4. Wavelength dependence of the photoproduction ate of SO_4^{2-} from sulfur.

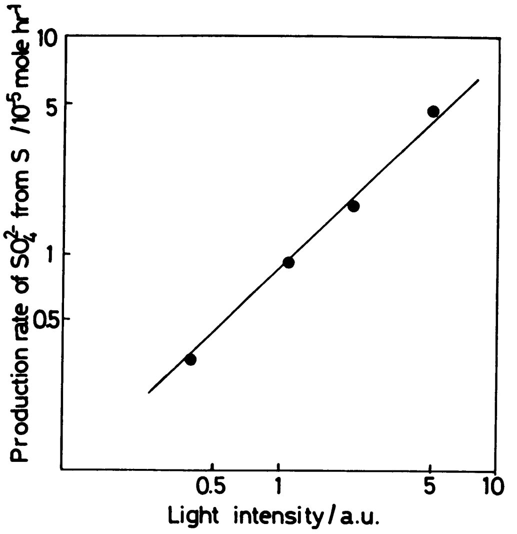

Fig. 5. Photocatalytic production rate of SO_4^{2-} from sulfur on the Pt-doped TiO_2 as a function of light intensity.

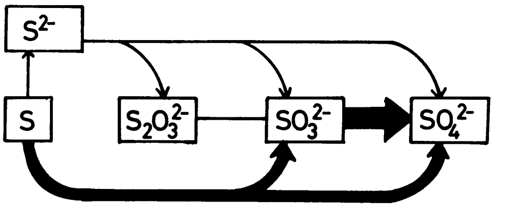

Fig. 6. Photocatalytic oxidation process of sulfur on TiO_2 catalyst.

is photoproduced in the solution, this is immediately oxidized to SO_4^{2-}.

Figure 7 shows the ratio of the rate/H_2S production rate as a function of the SO_4^{2-} production rate in the photocatalytic oxidation of sulfur on the doped TiO_2. It was found that the ratio increases with the increase in the production rate of SO_4^{2-}. If we assume the linear relationship in the figure, it can be seen that the production rate of H_2S (about 0.05×10^{-4} mol h^{-1}) is constant for all samples. It should also be noted that the minimum value of the ratio is about one.

The following reaction will proceed on the catalyst surface under illumination:

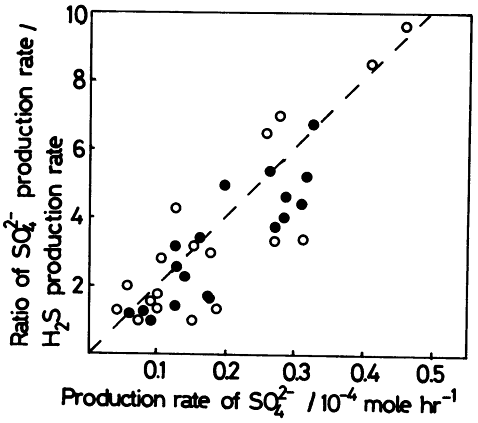

Fig. 7. Relationship between the ratio of SO_4^{2-} production rate/H_2S production rate and the production rate of SO_4^{2-}.

$$H_2O + h^+ \longrightarrow \dot{O}H + H^+ \quad (1)$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad (2)$$

$$OH^- + h^+ \longrightarrow \dot{O}H \quad (3)$$

$\dot{O}H$ will be produced from both H_2O and OH^-, which are produced from the direct reduction process of O_2 (Eq. 3). After all, sulfur reacts with $\dot{O}H$ as follows, leading to unity as the value of the ratio of the SO_4^{2-} production rate/H_2S production rate:

$$2S + 4\dot{O}H \longrightarrow H_2S + H_2SO_4 \quad (4)$$

This reaction process is suitable for the catalysts which give unity for the value of the above ratio. If a relatively stable intermediate, for example $\dot{O}_2H$ is produced in the O_2 reduction process, this species will contribute to the direction production of SO_3^{2-} or SO_4^{2-} as follows:

$$O_2 + e^- \longrightarrow O_2^- \quad (5)$$

$$O_2^- + H_2O \longrightarrow \dot{O}_2H + OH^- \quad (6)$$

$$\dot{O}H + \dot{O}_2H + S \longrightarrow H_2SO_3 \quad (7)$$

$$3\dot{O}H + \dot{O}_2H + S \longrightarrow H_2SO_4 + H_2O \quad (8)$$

Many other reaction processes in which the intermediate $\dot{O}_2H$ is contained, will exist in the photocatalytic oxidation process of sulfur as a matter of course. However, this intermediate must surely contribute to the reaction process on the catalysts which gives values of more than unity in the ratio of the SO_4^{2-} production rate/H_2S production rate. Because the values of the ratio are always unity, if only the process (4) occurs in the photocatalytic oxidation of sulfur. In conclusion, only small amounts of SO_4^{2-} will be produced on the catalysts on which O_2 is immediately reduced to OH^-, but large amounts of SO_4^{2-} will be produced on the catalysts on which O_2 is not immediately reduced to OH^-.

The former catalysts are TiO_2 doped with the typical elements having ionic valences of five; therefore, relatively large amount of Ti^{3+} exist in the lattice. On the other hand, the latter catalysts have only small amounts of Ti^{3+} in the lattice, because the catalysts are doped with the typical elements having valencies of one, two and three. That is, the Ti^{3+} ion probably will take part in the immediate reduction of O_2. In the case of doping with a transition metal, the transition metal cations in the TiO_2, as well as the titanium cations, will directly affect the O_2 reduction.

This doped area which affects the O_2 reduction will be dotted on the TiO_2 surface. When the amounts of the dopants increase beyond about 1 atm%, the dopants will deposit on the doped area as oxides. Therefore, the doped area decreases and the doped TiO_2 becomes like that of the nondoped TiO_2. The results shown in Fig. 1 are explained by this phenomenon. In the case of the Pt dopant, Pt metal on the TiO_2 will act as the site which produces the intermediate $\dot{O}H$ in the O_2 reduction. However, the increase of the deposited Pt metal will bring about inhibition of the illumination on the TiO_2 surface, leading to a decrease in the production rate of SO_4^{2-} as shown in Fig. 1. As a matter of course, the deposited oxides will cause the light passing to the TiO_2 surface to be disturbed as in the case of the other dopants.

References

1) Y. Matsumoto, H. Nagai, and E. Sato, *J. Phys. Chem.*, **86**, 4664 (1982).

2) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 2239 (1978).

3) H. Reiche and A. J. Bard, *J. Am. Chem. Soc.*, **101**, 3127 (1979).

4) C. D. Jaeger and A. J. Bard, *J. Phys. Chem.*, **83**, 3146 (1979).

5) I. Izumi and F. R. F. Fand, and A. J. Bard, *J. Phys. Chem.*, **85**, 218 (1981).

6) S. Sato and J. M. White, *J. Phys. Chem.*, **85**, 336 (1981).

7) M. Gräzel, *Ber. Bunsenges. Phys. Chem.*, **84**, 981 (1980).

8) R. H. Baker, J. Lilie, and M. Gräzel, *J. Am. Chem. Soc.*, **104**, 442 (1982).

9) J. M. Lehn, J. P. Sauvage, and R. Ziessel, *Nouveau Journal de Chimie* **4**, 623 (1980).

10) T. Kawai and T. Sakata, *Nature*, **286**, 474 (1980).

11) K. Domen, S. Naito, M. Soma, T. Onishi, and K. Tamaru, *J. Chem. Soc., Chem. Commum.*, **543**, (1980).