## Photocatalytic Oxidation of Cyanide on Platinized TiO<sub>2</sub>

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The photocatalytic oxidation of cyanide on platinized  $TiO_2$  was studied mainly from the standpoint of semiconductor electrochemistry to elucidate the role of platinum deposited on  $TiO_2$  photocatalysts. It was found that platinization enhances the rate of the oxygen reduction which constitutes a partial process of the photocatalytic reaction, but suppresses the rate of photosensitized oxidation as the counter partial process in which cyanide is oxidized competitively with water. The activities of single crystal and powder  $TiO_2$  catalysts for photocatalytic reaction were compared for cases with and without 50 monolayers of Pt. They were found comparable in spite of a large surface area of the latter, suggesting that the number of photons striking the catalyst surface entirely controls the rate of photocatalytic reaction. Effects of platinization on the electrochemical properties of  $TiO_2$ , evaluation of the rate of photocatalytic reaction by electrochemical analyses, and effects of illumination on the photocatalytic process are discussed.

## Introduction

Heterogeneous reactions at semiconductor photocatalysts are interesting from the viewpoint of solar energy utilization. It has been shown that several photocatalytic or photoelectrosynthetic reactions are governed by electrochemical mechanisms<sup>1–7</sup> and can be developed by using the construction principles of photoelectrochemical cells.<sup>8–14</sup> However, there is a marked difference in the reaction mode between the photoelectrochemical cell with a semiconductor electrode and the heterogeneous reaction on a semiconductor photocatalyst.

The open circuit voltage as the driving force of the photoelectrochemical cell reaction is equal to the potential difference between the flat-band potential of the semiconductor electrode and the redox potential of an electrochemical process which occurs at a metal counterelectrode.<sup>15</sup> In the case of photocatalytic reactions, however, a different situation will usually arise. Both the oxidation and reduction processes have to occur on the same semiconductor catalyst, although reaction sites for these pro-cesses may be different.<sup>16</sup> Desirable situations of the energy band of the semiconductor for these processes are quite opposite. For n-type semiconductor photocatalysts, for example, an upward bending of the band is feasible for the photosensitized oxidation process, while a downward bending is desirable for the reduction process. As a result, the photocatalytic reaction may occur under a condition close to the flat-band, resulting in a relatively poor efficiency for solar energy conversion as compared to the photoelectrochemical cell systems.<sup>10</sup>

As a mean to enhance the rate of heterogeneous reactions on semiconductor photocatalysts, platinization was recently shown to be effective for n-type  $\text{TiO}_2$  in photocatalytic synthesis of methane from acetic acid<sup>17</sup> and in amino acid photosynthesis,<sup>18</sup> and for n-type  $\text{SrTiO}_3$  and  $\text{KTaO}_3$  in the photolysis of water.<sup>19</sup> In these studies, however, no detailed characterization of the platinization was given. In this study, therefore, the effects of platinization on the electrochemical properties of  $\text{TiO}_2$  having the rutile modification were investigated, and the activity of platinized  $\text{TiO}_2$  for the photocatalytic oxidation of cyanide was evaluated on the basis of electrochemical analyses. It was already reported by Frank and Bard<sup>12,20</sup> that cyanide is photocatalytically oxidized on illuminated  $\text{TiO}_2$ .

### **Experimental Section**

A single crystal of TiO<sub>2</sub> was used as the test electrode. It was reduced at 600 °C in a stream of hydrogen to give a high electrical conductivity. The (001) face was chosen as the electrode surface. It was polished with 0.05- $\mu$ m alumina, and then washed in an ultrasonic bath for 30 min, followed by immersion in a mixture of H<sub>2</sub>SO<sub>4</sub> and (N-H<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (1:1) at 220 °C for longer than 30 min. An electrical lead wire was attached to indium deposited on the back of the crystal with silver epoxy, and the crystal was then mounted in a glass tube with epoxy resin to give an electrode. Before use, the electrode was dipped in HNO<sub>3</sub> for 5 min, followed by washing with deionized water.

The platinization was carried out by employing the electrodeposition technique. Prior to electrodeposition, the electrode was cleaned electrochemically in 1 mol·dm<sup>-6</sup> NaOH by repeating cyclic potential sweeps in the potential range between 0 and -1.7 V vs. SCE in such a manner that the sweeps were first carried out under illumination for 20 min and then in the dark for 5 min. By this pretreatment, Pt was deposited on the entire surface in island forms with a fairly homogeneous distribution. The electrolyte used for the deposition was 10<sup>-2</sup> mol·dm<sup>-3</sup> H<sub>2</sub>PtCl<sub>6</sub>, and the deposition potential chosen was -0.29 V vs. SCE. The amount of deposition was controlled by monitoring the charge passed during the electrolysis by means of an electronic coulometer (Nichia Keiki, Model N-CR-404). When electrolysis was performed with a charge equivalent to that required for the deposition of  $4.74 \times 10^{14}/\text{cm}^2$  Pt atoms, the resulting electrode is described here as a monolayer-covered electrode. The surface of the platinized TiO<sub>2</sub> crystal was observed by a scanning electron microscope, SEM (Akashi, Model MSM-7C).

The TiO<sub>2</sub> powder used as the photocatalyst had purity of 99.9% (Mitsuwa Pure Chemicals) and contained about 10% anatase. It was then heat treated in air at 800 °C to convert it completely into the rutile modification. The TiO<sub>2</sub> powder thus prepared had a specific surface area of  $3.84 \text{ m}^2 \text{ g}^{-1}$ , as determined by the BET method. The platinization of the powder was made by mixing it with a known amount of H<sub>2</sub>PtCl<sub>6</sub> in an aqueous suspension, followed by drying under reduced pressure, and finally by heating at 800 °C in air. Afterward, the platinized powder was reduced by hydrogen in the same manner as employed for the reduction of the single crystal. The platinization

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of the powder was also made by employing the photocatalytic deposition method reported by Bard et al.<sup>21</sup>

Polarization curves of  $\text{TiO}_2$  electrodes were measured in a conventional beaker type cell with a quartz window by using a potentiostat (Hokuto Denko, Model HA-101) and a function generator (Hokuto Denko, Model FG-2). In order to investigate the competition of the photosensitized oxidation between cyanide and water, which are given by eq 1 and 2, the rotating ring-disk electrode

$$CN^{-} + 2OH^{-} + 2p^{+} \rightarrow NCO^{-} + H_{2}O \qquad (1)$$

$$2OH^{-} + 2p^{+} \rightarrow \frac{1}{2}O_{2} + H_{2}O$$
 (2)

(RRDE) technique was employed,  $2^{2-24}$  where p<sup>+</sup> denotes a positive hole generated by illumination. For this purpose, a Nikko Keisoku RRDE measuring system was used. The potential of the Pt ring (7 mm i.d., 9 mm o.d.) and the TiO<sub>2</sub> disk (5.8 mm diameter) electrodes were independently controlled by a dual potentiogalvanostat (Nikko keisoku, Model DPGS-1). The electrolytic cell configuration was almost the same as that reported by Inoue et al.<sup>22</sup> Before measurements were carried out, the ring-disk electrodes were first dipped in aqua regia for 1 min, followed by washing with deionized water. Afterward, the platinum ring electrode was pretreated electrochemically in 0.2 mol·dm<sup>-3</sup> NaOH which used as the base electrolyte for cyanide solutions; it was cyclically polarized under bubbling nitrogen with a potential sweep method (dE/dt =20 mV·s<sup>-1</sup>) in a potential range between -1.0 and 1.2 V vs. SCE until reproducible voltammograms were obtained, and then it was polarized at a fixed potential of -0.7 V vs. SCE which was chosen for the detection of oxygen. At this potential, it was possible to reduce oxygen under a diffusion-limited condition, but both cyanide and cyanate ions were inactive.<sup>25</sup> Therefore, the flux of oxygen from the TiO<sub>2</sub> disk was selectively detected at the ring electrode. However, the activity of the ring electrode was found to decrease with polarization time at -0.7 V, so that it was necessary to prepolarize the ring electrode for a time long enough to give a constant activity (about 1 h). At this stage, the electrolyte was switched to a test solution, and both disk and ring currents were measured repeatedly under desired conditions. The ring current due to the oxygen flux was determined as the difference in the cathodic current measured under illumination and nonillumination of the disk electrode. The collection efficiency of the ring electrode was determined experimentally in 0.2 mol·dm<sup>-3</sup> NaOH, and the value obtained was applied to all cyanide solutions used.

Photocatalytic experiments were carried out in a small quartz vessel of 10-mL capacity (16 mm diameter, 60 mm height) with a window of ca. 12-mm diameter and a gas inlet. During photocatalytic experiments, which were carried out under bubbling oxygen, the cyanide solution suspended with the catalyst powder was agitated with a magnetic stirrer at such a rate that no appreciable amount of the catalyst stayed on the bottom of the reaction vessel. The vessel was equipped with a small reflux condenser to prevent the cyanide solution from evaporation.

The concentration of cyanide was determined by using a calibrated ion selective electrode (Toa Dempa, Model CN-125). The solutions used reagent grade chemicals and doubly distilled water. Illumination was made by focusing light from a 500-W xenon lamp into ca. 1.0 cm<sup>2</sup> throughout the entire experiments except where RRDE experiments were carried out. For RRDE experiments, illumination was made onto the disk electrode through the bottom of the electrolytic cell. A horizontal light path from the lamp was bent vertically by using a mirror. The illumination



**Figure 1.** Current-potential curves of TiO<sub>2</sub> electrodes covered with different amount of Pt in deaerated 1 mol·dm<sup>-3</sup> NaOH: (a) under illumination, (b) in the dark.  $\theta$  denotes the amount of deposited Pt equivalent to monolayers;  $dE/dt = 20 \text{ mV} \cdot \text{s}^{-1}$ .

intensity on the electrode surface was then decreased roughly to a quarter of that obtained with the horizontally focused light, as judged from the magnitude of the saturated photocurrent at the disk electrode.

#### Results

Electrochemical Behavior of Platinized  $TiO_2$ . Current-potential curves were measured for  $TiO_2$  electrodes deposited with different amount of Pt, i.e., the deposition of 50, 100, and 200 monolayers. Judging from the current-potential curves of the  $TiO_2$  electrode in a solution having the same pH value as the plating bath but containing no platinum at all, we feel that the cathodic current presumably attributable to hydrogen evolution seemed likely to superpose on the Pt deposition current in a ratio not greater than 20%. For this reason, the actual amount of deposited Pt must be less than the value presented in this paper. However, this brings about no serious problem in the present study, because the effects of platinization are compared on a relative scale.

According to SEM observations, the deposition of 50 monolayers covered only a fraction of the electrode surface with small island forms. With an increase in the amount of deposition, the coverage became more perfect, but even if the deposition of 200 monolayers was made, complete coverage was not achieved. Large islands were separated from each other by loops of bare portions with irregular forms and widths. The area of the bare portions was, however, judged to be usually around 10% at most.

Figure 1 shows typical current-potential curves of platinized electrodes in deaerated 1 mol·dm<sup>-3</sup> NaOH. The curves shown in this figure did not always reproduce the points of the absolute current value and the shape of current-potential curves itself. Especially noticeable was that a sharp rise in the anodic photocurrent observed at ca. -0.2 V vs. SCE, followed by a current plateau, occasionally became ambiguous, and only an ascending trend of the current with anodic polarization which starts at a much more negative potential was observed. Even so, a general tendency was noticeable that platinization suppressed the anodic photocurrent depending on its degree.

When a cyanide solution was used as the electrolyte, different behaviors were noticed in current-potential curves. Figure 2a shows current-potential curves obtained under illumination in a deaerated cyanide solution. By comparing this figure with Figure 1a, we noticed the fol-



**Figure 2.** Current-potential curves of TiO<sub>2</sub> electrodes with different amount of Pt in 0.1 mol·dm<sup>-3</sup> KCN in 1 mol·dm<sup>-3</sup> KOH: (a) under illumination in the deaerated solution; (b) in the dark in the oxygen-saturated solution;  $\theta$ , the same as in Figure 1; d*E*/d*t* = 20 mV·s<sup>-1</sup>.



**Figure 3.** Current-potential curves of TiO<sub>2</sub> electrodes covered with different amount of Pt in oxygen-saturated 1 mol·dm<sup>-3</sup> KOH containing 0.1 mol·dm<sup>-3</sup> KCN: (a) platinized TiO<sub>2</sub>; (b) a plane Pt electrode;  $dE/dt = 20 \text{ mV} \cdot \text{s}^{-1}$ . Measurements were carried out in the dark.

lowing. In cyanide solution, the anodic photocurrent was observed at potentials positive of ca. -1.0 V vs. SCE, regardless of the amount of Pt deposited, although the magnitude of the photocurrent was affected by the degree of platinization. The onset potential was the same as that observed at the bare TiO<sub>2</sub> electrode in the cyanide-free solution.

Figure 2b shows current-potential curves of  $TiO_2$  electrodes with and without 200 monolayers of Pt in a cyanide solution saturated with oxygen. According to this figure, the onset potential of the oxygen reduction was positively shifted by platinization. The shift depended on the amount of Pt deposited, as Figure 3 shows.

Competition of Photosensitized Oxidation of Cyanide and Water. In order to investigate whether the oxidation of CN<sup>-</sup> competes with that of water, we performed RRDE measurements for the electrode with and without 50 monolayers of Pt. The collection efficiency determined in a variety of runs by using the procedures described in the Experimental Section was scattered to  $\pm 30\%$ . In the data shown below, therefore, an average value of 0.14 was used. This value is quite low as compared to that expected on the basis of the electrode geometry.<sup>26</sup> Figure 4 shows the percentage of the oxidation of cyanide  $\Phi_{CN}$  at the bare TiO<sub>2</sub> electrode as a function of the disk electrode potential.



**Figure 4.** The ratio of the oxidation current of CN<sup>-</sup>,  $\Phi_{CN^-}$ , to the total anodic photocurrent measured in 0.1 mol·dm<sup>-3</sup> KCN in 0.2 mol·dm<sup>-3</sup> NaOH, as a function of the potential of the disk electrode. The potential of the Pt ring electrode was fixed at -0.7 V vs. SCE. The bare TiO<sub>2</sub> electrode was used. The rotation rate was 500 rpm.



**Figure 5.** The ratio of the oxidation current of  $CN^-$  to the total anodic photocurrent as a function of the concentration of  $CN^-$ . Electrolyte: *C* mol·dm<sup>-3</sup> KCN in 0.2 mol·dm<sup>-3</sup> NaOH: (O) the electrode covered with 50 monolayers of Pt; ( $\bullet$ ) the bare TiO<sub>2</sub> electrode. The potential of the disk electrode was set at 0 V vs. SCE. The rotation rate was 500 rpm.

As this figure shows,  $\Phi_{CN^-}$  was not influenced by the electrode potential in the range between -0.5 and 0 V vs. SCE. The values at more negative potentials were not obtained owing to the small disk current. Figure 5 shows that  $\Phi_{CN^{-}}$  is strongly dependent on the concentration of cyanide. In addition, platinization was shown to have a positive effect on  $\Phi_{CN}$ . According to the results shown in this figure, the oxidation of water occurs in preference to that of cyanide as far as the experimental conditions investigated are concerned. The lowest limit for the concentration of cyanide below which its oxidation cannot occur was judged to be  $10^{-5}$  mol·dm<sup>-3</sup> for the bare TiO<sub>2</sub> electrode. In this study, the collection efficiency determined in 0.2 mol·dm<sup>-3</sup> NaOH was applied to all the cyanide solutions used. It may be probable that the collection efficiency is decreased by the presence of cyanide if it specifically adsorbed on the ring electrode to inhibit the adsorption of oxygen. In this sense, the results given in Figures 4 and 5 are believed to show the lowest limit for  $\Phi_{CN^{-1}}$ 

Photocatalytic Oxidation of Cyanide on Single Crystal and Powder Catalysts. Experiments on the single crystal TiO<sub>2</sub> catalyst were carried out by illuminating the entire surface of the crystal with and without 50 monolayers of Pt in the form of an electrode in which the back face of the crystal was covered with epoxy resin. The results obtained are given in Table I. According to Frank and Bard,<sup>12,20</sup> the rate of photocatalytic oxidation of CN<sup>-</sup> does not change with illumination time as long as the solution concentration is higher than 1 mmol·dm<sup>-3</sup>. Since our solution was in this range, the rates can be converted into current values with no ambiguity, and these are also given in the seventh column of the table. As columns 6 and 7

	out
Covered Pt of 50 Monolayers	

	surf. area, reactn cm² time, h	cyanide amount, <sup>a</sup> µmol		reactn rate		total	
catalyst		reactn time, h	initial	final	$\mu mol/(cm^2 \cdot h)$	$\mu A/cm^2$	current, $\mu A/cm^2$
TiO <sub>2</sub> Dt (2 50)//TiO	0.32	17	30	27.6	0.44	24	130
$Pt (\theta = 50)/110_2$	0.26	19	30	22.4	1.95	104	430

<sup>a</sup> 10 mL of  $3 \times 10^{-3}$  mol·dm<sup>-3</sup> KCN in 0.2 mol·dm<sup>-3</sup> NaOH was used.

TABLE II: Effects of Platinization of TiO2 PowderCatalyst on the Rate of PhotocatalyticOxidation of Cyanide<sup>a</sup>

	initial amount		oxidized	reactn rate	
θ	of cya- nide, μmol	reactn time, h	cyanide, µmol	µmol · h <sup>-1</sup>	μA
0	15	2	1.8	0.9	48
5	15	2	2.0	1.0	54
10	15	2	3.0	1.5	80
25	15	2	3.3	1.65	88
50	15	2	3.8	1.9	102

 $^a$  The catalyst loading was 0.1 g for 5 mL of 3  $\times$  10<sup>-3</sup> mol·dm<sup>-3</sup> KCN in 0.2 mol·dm<sup>-3</sup> NaOH.  $^b$  Amount of covered Pt.

TABLE III: Photocatalytic Oxidation of Cyanide onTiO2 Powder Covered with 50 Monolayers of Pt

catalyst	initial amount of cya- nide <sup>a</sup>	al nt a- reactn <sup>a</sup> time	oxidized	oxidation rate		
g g	μmol	h	μmol	$\mu mol \cdot h^{-1}$	μA	
0.05	15	3	2.2	0.73	59	
0.1	15	3	3.8	1.26	102	
0.2	15	3	4.2	1,4	113	
$0.1^{b}$	15	3	28	0.93	75	

<sup>a</sup> 5 mL of  $3 \times 10^{-3}$  mol·dm<sup>-3</sup> KCN in 0.2 mol·dm<sup>-3</sup> NaOH was used. <sup>b</sup> The platinization was made by the photocatalytic deposited method.<sup>21</sup>

show, the rate of photocatalytic reaction was higher for platinized than for nonplatinized  $TiO_2$ .

Table II shows the dependency of the rate of photocatalytic oxidation of cyanide on the amount of Pt deposited onto the TiO<sub>2</sub> powder, and, in Table III, the effects of the amount of catalyst on the reaction rate are given for a coverage of 50 monolayers. From these tables, the following observations are noticed. (1) The platinization to give 50 monolayers of Pt was effective to double the rate achieved at the nonplatinized catalyst. (2) The increase in the amount of the catalyst from 0.1 to 0.2 g enhanced the reaction rate only by 10%. This implies that the reaction rate will not be greatly increased by a further increase in catalyst loading, which is in qualitative agreement with the results obtained by Frank and Bard.<sup>12,20</sup> (3) The activity of the platinized catalyst seemed to be uninfluenced by the method of platinization. The catalyst platinized by photocatalytic deposition<sup>21</sup> showed almost the same activity as that prepared by the thermal decomposition of  $H_2PtCl_6$  mixed with  $TiO_2$  powder.

### Discussion

Effects of Platinization on Photoelectrochemical Properties of  $TiO_2$ . The anodic photocurrent in the cyanide-free solution is due to the photosensitized oxidation of water, which is given by eq 2. According to Figures 1 and 2, the apparent onset potential of this reaction was positively shifted by depositing Pt. This is especially noticeable for the deposition of 200 monolayers. On the other hand, the onset potential of the anodic photocurrent in the cyanide solution did not vary with platinum deposition, and was well in accord with that for the bare  $TiO_2$  electrode in the cyanide-free solution.

It is well known that the onset potential for the anodic photocurrent at n-type semiconductors is usually well in accord with the flat-band potential of the electrode. If we can judge from the results in the cyanide solution, therefore, the flat-band potential must be ca. -1.0 V vs. SCE regardless of whether or not platinum was deposited. The question arises: Why does the onset potential for the photosensitized oxidation of water shift toward a positive direction especially at the TiO<sub>2</sub> electrode with 200 monolayers of Pt? To answer this, the results for the oxygen reduction given in Figure 3, in which positive shifts of the onset potential of the cathodic current are shown, seem to be helpful.

The photosensitized oxidation of water to produce oxygen must occur at potentials positive of ca. -1.0 V vs. SCE even at the TiO<sub>2</sub> electrode with 200 monolayers of Pt, but the oxygen produced can be reduced immediately at potentials negative of the onset potential of oxygen reduction. Active sites for the former process are believed to be the bare portions of the electrode surface, while those for the latter are Pt sites. Therefore, the activities for both processes depend on the Pt coverage. For TiO<sub>2</sub> electrode with 200 monolayers of Pt, the activity for oxygen reduction was very high, so that the oxygen produced can completely be reduced at potentials negative of the onset potential of the oxygen reduction, i.e., -0.2 V vs. SCE, resulting in no appreciable oxidation wave in the corresponding potentials.

The limiting photocurrent for the electrode covered with 200 monolayers of Pt was about 40% that of the bare electrode. It is well established that the limiting photocurrent is proportional to the number of incident photons.<sup>27</sup> Therefore, 40% of the photons which struck the electrode surface must have reached the TiO<sub>2</sub> surface. Considering the fact that the bare portion of the electrode surface was much less than 40% the total area of the electrode surface, a fraction of photons which struck deposited Pt must have been reflected randomly to strike the bare portions and/or penetrated through the Pt to enter into the TiO<sub>2</sub>. Since the photocurrent is controlled by the number of photons and not by the surface area, the limited dimension of the bare portions is judged to have been still large enough to sustain the anodic photocurrent.

Usually, the cathodic current at  $TiO_2$  electrodes in the dark starts to flow at a potential close to the flat-band potential.<sup>28</sup> The positive shift of the onset potential for oxygen reduction with the platinization reflects, therefore, that surface states become abundant with an increase in the amount of Pt deposition by covering a larger fraction of the electrode surface. Direct evidence for surface states formation is a sharp rise in the anodic current observed at ca. +0.6 V vs. SCE which was not affected by illumination. This current seems to be due to electron tunneling from the electrolyte into the conduction band of the



**Figure 6.** Steady-state current-potential curves for TiO<sub>2</sub> electrodes with and without 50 monolayers of Pt in  $3 \times 10^{-3}$  mol·dm<sup>-3</sup> KCN in 0.2 mol·dm<sup>-3</sup> NaOH. The open symbols represent anodic current under illumination in the oxygen-free solution and the filled symbols cathodic current in the dark in oxygen-saturated solution. (a),(c) The bare TiO<sub>2</sub> electrode; (b),(d) the electrode covered with 50 monolayers of Pt.

electrode via surface states.<sup>29</sup>

For electrode with 200 monolayers of Pt, the upward bending of the band is judged to be 0.7 eV at the onset potential for oxygen reduction. Such a high potential barrier is believed to inhibit the electron flow from the conduction band to the electrolyte if there are no surface states. The contribution of surface states will be confirmed from this point of view. The positive shift of the onset potential with platinization may reflect effects of the surface state concentration. According to Figure 3, however, the activity of the electrode with 200 monolayers of Pt was higher than that of the Pt electrode. Then, at least in this case, the rate of the oxygen reduction seems to be determined not by the surface state concentration but by another factor such as the electrocatalytic activity of the electrode surface. The effective area of Pt for this platinized electrode is believed to be larger than that of the plain Pt electrode, and the rate of the oxygen reduction is believed to be controlled by charge-transfer kinetics on the effective sites.

Photocatalytic Oxidation of Cyanide. The photocatalytic oxidation of cyanide can occur on illuminated TiO<sub>2</sub> catalysts with an electrochemical mechanism if the condition is fulfilled<sup>3,10</sup> that the onset potential of the photosensitized oxidation of CN<sup>-</sup> is negative of that for oxygen reduction. Frank and Bard<sup>12,20</sup> speculated that such a situation is realized on several n-type semiconductor photocatalysts. Figure 6 shows current-potential curves for these electrochemical processes at the TiO<sub>2</sub> electrode with and without 50 monolayers of Pt, which were obtained under steady-state conditions. The results shown in this figure satisfy the above-mentioned requirement for the photocatalytic reaction to occur. The oxidation of cyanide is expected to proceed at the potentials given by the intersection points of curves a and c and of curves b and d.<sup>3</sup> Judging from the results for  $\Phi_{CN}$ , however, only a small fraction of the oxidation current at the intersection points concerns the oxidation of cyanide. The poor photocatalytic activity of rutile<sup>20</sup> may be attributable to this effect. As shown in Figure 5, the oxidation of cyanide occurs

As shown in Figure 5, the oxidation of cyanide occurs in competition with the oxidation of water. Therefore, the total oxidation current of the photocatalytic reaction would be estimated by dividing the rate of the oxidation of cyanide expressed in a current value, which is given in the seventh column, by  $\Phi_{CN}$ . The values obtained are given



**Figure 7.** Change in open circuit potential of  $TiO_2$  electrodes in oxygen-saturated 3 × 10<sup>-3</sup> mol·dm<sup>-3</sup> KCN in 0.2 mol·dm<sup>-3</sup> NaOH with illumination time: (a) the bare  $TiO_2$  electrode; (b) the electrode covered with 50 monolayers of Pt.

in the eighth column. By comparing these values with the current values of the intersection points of the polarization curves shown in Figure 6, which are  $20 \ \mu A \cdot cm^{-2}$  for the bare TiO<sub>2</sub> and 340  $\mu A \cdot cm^{-2}$  for the platinized TiO<sub>2</sub>, it is noticed that there is no good correspondence with each other. Since the illumination condition was always fixed, the discrepancies observed are not believed to be attributable to any difference in the illumination intensity. The following two reasons seem to be responsible: (1) errors expected in  $\Phi_{\rm CN}$ , which were already described; and (2) the difference in the method for the determination of the reaction rate.

Let the latter problem be discussed here. The electrochemical analysis based on the polarization measurements is an indirect method. Judging from the manner of analysis, we will obtain an estimated rate under the hypothetical condition that both anodic and cathodic reactions independently occur on the entire surface of the catalyst. In the actual photocatalytic process, a part of the surface sites are used in the photosensitized oxidation reaction and the rest in the cathodic reaction, or vice versa. Furthermore, it was found that the open circuit potential of the catalyst appreciably shifted with illumination time, as shown in Figure 7. As can be easily understood from Figure 6, the change in the open circuit potential must be caused by some change in either the cathodic or the anodic polarization curves, or both. The electrochemical analysis cannot follow the change in the rate of the photocatalytic reaction caused by such a shift of the open circuit potential. Nevertheless, electrochemical analysis gives useful information on an individual electrochemical process which constitutes the photocatalytic reaction.

In the present study, light from the xenon lamp was focused into ca.  $1.0 \text{ cm}^2$ . Hence, the reaction rate per unit surface area of the single crystal, shown in the seventh column of Table I, is the rate which would be obtained when all photons from the xenon lamp strike the single crystal catalyst. Then, comparison of the results shown in Table III with those in Table I is meaningful to obtain the relative activity of the powder compared to that of the single crystal. As a result, we find that the activity was almost the same. By use of a powder catalyst, the surface area of the catalyst is greatly increased. Nevertheless, the activity was not enhanced at the powder. This result seems to suggest that another factor and not the surface area controls the reaction rate at the powder, so that there is no marked difference in the rate of photocatalytic reaction between the single crystal and the powder catalyst.

If we consider that the illumination condition was almost the same between the experiments using the single crystal and the powder, the reaction rate seems to be entirely controlled by the illumination condition. The photosensitized oxidation process as the partial process of the photocatalytic reaction is controlled by the number of photons striking the catalyst surface.<sup>26</sup> Then, in order to achieve a comparable rate of photocatalytic reaction between the single crystal and the powder catalysts as was observed, the rate of oxygen reduction as the other partial process must be roughly the same between the two kinds of catalysts.

The open circuit potential of the electrode with 50 monolayers of Pt in the dark was almost the same as the onset potential of the oxygen reduction which was ca. -0.3V vs. SCE and was positive of the flat-band potential (see Figure 6). By illuminating the electrode, therefore, a photovoltage must arise, resulting in weakening of the band bending. Then, electron transfer from the conduction band to the electrolyte via surface states occurs easily. In this respect, the reduction process is also affected by illumination. Since only the powders onto which photons struck are effective for photocatalytic reaction, the reaction rate will be entirely controlled by the illumination condition if the catalyst loading is more than enough to absorb all the incident photons.

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# Surface Reactions of Oxygen Ions. 4. Oxidation of Alkenes by $O_3^-$ on MgO

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Surface reactions between simple alkenes and  $O_3^-$  ions on MgO were observed at 25 °C. Following the reaction of ethylene or propylene with  $O_3$ ,  $CO_2$  and  $CH_4$  were detected as major products upon heating the sample. The reaction of cis-2-butene with  $O_3^-$  resulted in the formation of butadiene and oxygen-containing organic compounds, as well as  $CO_2$  and  $CH_4$ . Thermal desorption patterns and infrared spectra of surface complexes suggest that carboxylate ions are intermediates in the formation of  $CO_2$  and  $CH_4$  and peroxy radicals are intermediates in the formation of oxygen-containing organic molecules.

Determining the role of oxygen ions remains a fundamental problem in heterogeneous oxidation catalysis. Stoichiometric reactions of  $O^-$  ions on MgO with simple alkanes and alkenes have been reported,<sup>1,2</sup> and the study has been extended to include the catalytic role of O<sup>-</sup> in the oxidative dehydrogenation of ethane over supported molybdenum oxide.<sup>3</sup> Moreover, reactions between  $O_3^-$  ions on MgO with simple alkanes have been described in a recent publication from this laboratory.<sup>4</sup>

In general, experimental evidence suggests that both O<sup>-</sup> and  $O_3^-$  ions on MgO react with hydrocarbons by hydrogen-atom abstraction.<sup>1,2,4</sup> The resulting alkyl or alkenyl radicals then react with surface oxide ions, forming stable intermediates which may be decomposed at elevated temperatures. In this note reactions between O<sub>3</sub><sup>-</sup> on MgO and simple alkenes are described.

The preparation of the MgO samples, as well as the purification of the gases, was the same as previously reported.<sup>4</sup> The ozonide ion,  $O_3^-$ , was formed by irradiation (254 nm) of the MgO sample in the presence of 10-50 torr of  $N_2O$  for 10–60 min at 25 °C. The formation and reaction of  $O_3^-$  was followed by EPR spectroscopy. Stable

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