JOURNAL OF CATALYSIS 58, 22–27 (1979)

An Electrochemical Study of the Photocatalytic Oxidation of Methanol on Rutile

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Received October 15, 1976; revised August 14, 1978

Photocatalytic oxidation of methanol and 2-propanol by oxygen on illuminated rutile catalysts was analyzed by electrochemical measurements, and the indication was obtained that the Wagner–Traud mechanism prevails in the photocatalytic oxidation of these alcohols; i.e., the oxidation reaction consists of the anodic oxidation of the alcohol and the cathodic reduction of either oxygen or a complex consisting of oxygen and an intermediate of oxidized alcohol.

INTRODUCTION

Vol'kenstein developed an electron theory of catalysis on semiconductors (*1*) and compared his theory with experimental results (*2*). Many other studies also suggest that electronic factors play an important role in catalytic reactions (*3–5*). Morrison and Freund investigated a photocatalytic reaction of formaldehyde in an aqueous solution on ZnO by application of electrochemical measurements (*6*). Later, applicability of electrochemical techniques for investigating catalytic reactions on semiconductors was reviewed by Freund and Gomes (*7*). According to recent investigations on photocatalytic reduction of methylene blue (*8*) and quinones (*9*) dissolved in methanol, which were mainly conducted by electrochemical analyses, it was concluded that these reactions consisted of the anodic oxidation of methanol and the cathodic reduction of methylene blue or quinones. The rutile catalyst provides positive holes to methanol to give formaldehyde, and electrons to methylene blue or quinones to reduce them.

Although the photocatalytic oxidation of alcohols on TiO_2 has been studied quite extensively by a variety of techniques (*10–17*), no electrochemical study has been made on this reaction system. As already demonstrated in the previous studies (*8*, *9*), electrochemical measurements will give valuable information on the charge transfer process if there is an electron transfer between a reactant in solution and a photocatalyst. We have therefore made an electrochemical analysis of the photocatalytic oxidation on a rutile catalyst to obtain information as to whether an electrochemical process is involved in the reaction system or not.

EXPERIMENTAL

The (110) faces of commercial single crystals (6 × 6 × 6 mm) of rutile of different carrier concentrations N_D, were used as the electrodes as well as the catalyst. They were in the form of grown crystals prepared by the Verneuil method and had a gray color. Their N_D values estimated from Mott–Schottky plots were judged

0021-9517/79/070022-06$02.00/0

to be on the order of 10^{19} and $10^{18}/cm^3$, respectively. Preparation of the rutile electrode (catalyst) was the same as reported before (*8*). Before measurements, the electrode (catalyst) was dipped in concentrated nitric acid solution for 1 min, washed with deionized water for more than 30 min, and then dried by hot air.

The solutions used in this study were methanol and 2-propanol containing 0.1 *M* $LiClO_4$ as the supporting electrolyte. The methanol and 2-propanol used were distilled twice with Mg-I_2 (*18*). $LiClO_4$ was dried at 150°C for about 40 hr in vacuum. Purified tank nitrogen or oxygen gas was bubbled into the solution for more than 30 min before measurements.

Rutile was illuminated by a 500-W xenon arc lamp, and the light of wavelength shorter than 350 nm was cut off by setting a convex glass lens in front of a quartz window of a measurement cell. The illumination intensity was adjusted using a standard rutile electrode so as to give an anodic photocurrent of 2.1 mA at 2 V vs SCE. Polarization curves were measured by means of a potentiostat. Potentials were measured against SCE.

For the chemical investigation of the photocatalytic reaction, the same measurement cell and rutile were used as in the electrochemical analysis. In this case, 60 cm^3 of 0.1 *M* $LiClO_4$–methanol was poured into the cell. After introduction of the rutile catalyst into the cell, oxygen was bubbled for 30 min, and then rutile was illuminated with the same photo-intensity as in the electrochemical measurements. During the illumination, 5 cm^3 of the cell solution was sampled intermittently for chemical analysis by interrupting the illumination. After the sampling, oxygen gas was again bubbled for 10 min, and the illumination was then started. Formic acid, formaldehyde, and hydrogen peroxide were detected by colorimetry using mercuric chloride (*19*), phenylhydrazine (*20*), and potassium ferricyanide (*21*), respectively. Absorbancy was measured by a Bausch & Lomb Spectronic 20 spectrophotometer. Detection of methyl formate was made by a gas chromatograph (Shimazu GC-4BPTF) using a column packed with 20% Silicone SE-30 on Uniport B.

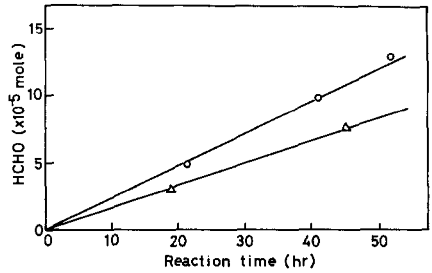

FIG. 1. Quantity of formaldehyde formed as a function of illumination time in 0.1 *M* $LiClO_4$–methanol saturated with oxygen: (○) rutile with low N_D, (△) rutile with high N_D.

The electrochemical and chemical analyses were conducted at 25°C. Other details such as the structure of the cell (*9*), the measurement of a differential capacitance (*22*), and purification of the gas (*9*) were described before.

RESULTS AND DISCUSSION

Chemical Analysis

It was found that the main oxidation product of methanol was formaldehyde. Formic acid, which was the further oxidized product, was produced, but in negligibly small amounts. Methyl formate, a condensed product of methanol and formic acid, was not detected in the reaction products. Figure 1 shows the amount of formaldehyde formed in the solution by the photocatalytic reaction on rutile as a function of the illumination time. The figure shows that the amount of formaldehyde increased linearly with the reaction time. The linear increase of the product with reaction time is reasonable, because the reactants were in great excess compared with the products. A similar relationship was observed by Cundall *et al.* in the oxidation of 2-propanol (*14*). Hydrogen

TABLE 1

Reaction Rates Determined by Chemical and Electrochemical Analysis

Rutile	Rate by chemical analysis ($\mu A/cm^2$)	Rate by electrochemical analysis ($\mu A/cm^2$)
Low N_D	130	140
High N_D	88	52

peroxide was produced in the liquid phase, so the following overall reaction was feasible;

$$CH_3OH + O_2 + h\nu \rightarrow HCHO + H_2O_2. \quad (1)$$

The probability of another reaction was suggested by Bickley *et al.* (*11*) and by Filimonov (*16*):

$$2CH_3OH + O_2 + h\nu \rightarrow 2HCHO + 2H_2O. \quad (2)$$

Our main intention was not to determine precisely the ratio of the products of reaction (1) to those of (2), but to gain information on electronic exchange between the catalyst and the reactants. For this reason, qualitative analysis of H_2O was not conducted.

The reaction rate was estimated from the slope of the line in Fig. 1 on the assumption that production of 1 mol of formaldehyde requires 2 faradays (*23*). Thus estimated reaction rates are summarized in Table 1 together with the results obtained by the electrochemical analysis which is described later.

Detailed discussion about the side reactions is beyond the scope of this paper.

Electrochemical Analysis

Figure 2 shows polarization curves of the rutile electrode of high N_D. Only a small anodic current was observed in the dark because of the paucity of positive holes in the valence band of rutile. Therefore, the anodic polarization curve (a) in Fig. 2, as obtained under illumination without oxygen in the solution, is connected with the oxidation of methanol in which positive holes participate. Cathodic polarization curves obtained in the dark were not influenced by introduction of oxygen, as is observed by comparing curve (e) with (f). This result shows that rutile in the dark is inactive for the reduction of oxygen. Generally, illumination of an n-type rutile electrode has no appreciable effect on cathodic polarization curves. However, the cathodic current was increased by illumination in the oxygen atmosphere. The observation suggests that oxygen adsorbs onto rutile only under illumination, as has already been reported by Bickley and Stone (*24*). The decrease of the anodic photocurrent by introduction of oxygen into the solution should be due to the participation of oxygen reduction. The polarization curve of oxygen reduction on illuminated rutile is, then, estimated by subtracting the current value of curve (b) from that of the (a), and the value of curve (d) from that of curve (c) at respec-

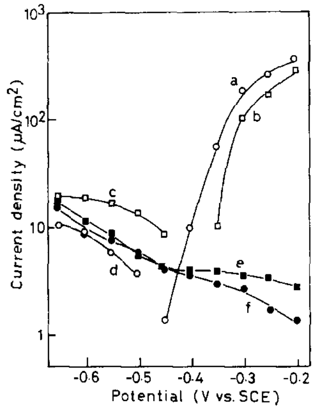

FIG. 2. Polarization curves of the rutile electrode with high N_D in 0.1 *M* $LiClO_4$–methanol: (a) anodic curve under illumination in N_2 atmosphere; (b) anodic curve under illumination in O_2 atmosphere; (c) cathodic curve under illumination in O_2 atmosphere; (d) cathodic curve under illumination in N_2 atmosphere; (e) cathodic curve in the dark in O_2 atmosphere; (f) cathodic curve in the dark in N_2 atmosphere.

tive potentials. The cathodic polarization curve of oxygen obtained in this way is presented in Fig. 3 together with the anodic curve of methanol oxidation. Polarization curves obtained at the rutile electrode of low N_D show close similarities to those in Fig. 2.

The behavior of the cathodic reduction curve in Fig. 3 is unique in the sense that the cathodic current showed a maximum in the potential region where the anodic oxidation of methanol occurs. The curves in Fig. 3 were reproducible, and the hump in the reduction curve was also observed at the low N_D electrode. At present, we cannot give a definite interpretation to this phenomenon, but either one of the following is plausible: (i) Methanol adsorbs on a pair of Ti and O sites of rutile, while oxygen adsorbs on Ti sites (*12*). If the adsorption of methanol becomes tighter with potentials lower than that giving the cathodic current peak, the oxygen adsorption is prevented with the potential dependency so that the unique behavior of the cathodic polarization curve appears. This mechanism relies on the electrochemical reduction requiring a strong interaction of an oxygen molecule with the electrode surface (*25*) and a neutral molecule showing a potential-dependent adsorption (*26*). (ii) The reduction rate is entirely controlled by the rate of the anodic oxidation; that is, oxygen is not directly reduced by electrons, but a complex formed by an oxygen molecule and an oxidized intermediate of a methanol molecule is reduced. If the reduction of the complex is prevented in the potential region positive to the potential giving the cathodic peak current, then a maximum will appear in the cathodic polarization curve. The prevention will occur due to the fact that electrons available for the reduction become scarce with the increased upward bending of the energy band of rutile, i.e., with increasing anodic potential.

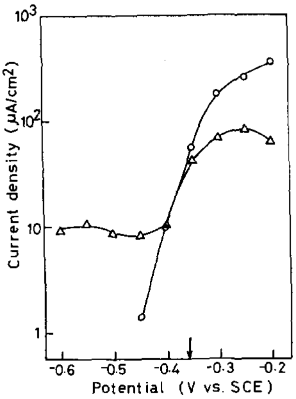

FIG. 3. (○) Oxidation and (△) reduction curves obtained from Fig. 2.

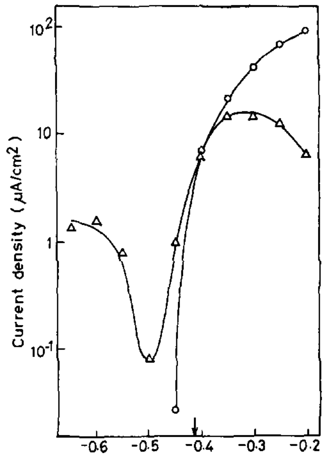

FIG. 4. (○) Oxidation and (△) reduction curves of the rutile electrode with high N_D in 0.1 *M* $LiClO_4$-2-propanol.

Figure 4 shows polarization curves of the same electrode used in Fig. 3 for 2-propanol, which were obtained by employing the same procedures as used to obtain Fig. 3. The polarization curves in this figure show close similarities in their shapes to those in Fig. 3. Therefore, almost the same argument as that applied to methanol seems to be valid for 2-propanol. By comparing the anodic polarization curve in Fig. 4 with that in Fig. 3, it can be noticed that the oxidation current of 2-propanol was smaller than that of methanol at respective potentials. This is possibly brought about by the difference in the amount of adsorbed alcohol, as discussed in another paper (*23*).

The Reaction Rates

When a photocatalytic reaction is proceeding, the catalyst maintains electrical neutrality. This condition corresponds to the intersection point of the oxidation curve of alcohol and the reduction curve of oxygen both in Fig. 3 and in Fig. 4. Therefore, the rate of the photocatalytic reaction should be given by the current value at the intersection point. The validity of this method was proved previously (*8, 9*). However, in the present study, the oxidation and reduction curves in Fig. 3 seem to intersect with each other over a rather wide range. Another method is needed to determine the intersection point. The catalyst must have a fixed potential when the photocatalytic reaction is proceeding under steady-state conditions. This potential was obtained by measuring the open circuit potential of the illuminated rutile catalyst in the methanol solution containing oxygen, and is shown on the potential axis of Fig. 3 with an arrow. The rate of the photocatalytic reaction was then estimated as the current value at this potential.

The reaction rates are summarized in Table 1 together with the result obtained for the other rutile electrode with low N_D. Table 1 also contains the reaction rates obtained by the chemical analysis which was described above. The reaction rates obtained by the chemical analysis roughly coincided with those obtained by electrochemical analysis. This indicates that electrochemical analysis gives valid information on the rate of photocatalytic reaction.

Concluding Remarks

It was already reported that alcohol molecules are electrochemically oxidized through the "current doubling" mechanism at illuminated rutile when the concentrations of alcohols are high (*23*), even under the presence of dissolved oxygen. If methanol as well as 2-propanol molecules are oxidized in the photocatalytic reactions through a chemical process, not by an electrochemical process, then no appreciable oxidation current of the alcohols would appear at the potential at which the reaction is proceeding. The present study showed that this was not the case. Therefore, it seems to be important to include the electrochemical oxidation step of alcohols in the mechanism of photocatalytic oxidation of alcohols.

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