Effect of Solution pH on the Oxidation of Alcohols on an Illuminated Rutile Anode

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In the previous paper, the "current doubling" process on an illuminated rutile anode was reported for the oxidation of methanol, ethanol and 2-propanol, where 0.1 M HCl was dissolved as the supporting electrolyte, and the amount of adsorbed alcohol on the rutile surface was speculated to control the reaction rate¹⁾. In the case of an illuminated CdS anode, the "current doubling" of alcohols and aldehydes was observed in a quite limited high pH region of solutions, and the possible reaction mechanism involving OH^- was proposed²⁾. In the present study, the "current doubling" phenomena on rutile are investigated using various alcohol solutions with different pH values.

1 Experimental

A rutile electrode used was the same as in the previous paper¹⁾. Aqueous buffer solutions containing 50 volume % of methanol or 2-propanol were used as the electrolyte. The buffer solutions were prepared by dissolving either one or two of HCl, KCl, KH_2PO_4 and NaOH³⁾, and pH values of them were checked with a pH meter (Hitachi-Horiba, M-5). There is no assurance for that the hydrogen ion concentration in an aqueous solution is equal to that in the methanolic solution used in the present study even when the indication value of the pH meter is the same between the two kind of the solutions. However, this brings no serious problem in the present study, because only qualitative information on the hydrogen ion concentration was required. The intensity of light incident upon rutile was adjusted so as to give an anodic photo-current of 500 μA on the rutile electrode at 2 V *vs.* S.C.E. in a 0.1 M HCl

aqueous solution without alcohol. Other details such as a light source and an electrochemical cell have already been described¹⁾.

2 Results and Discussion

When the saturated anodic photo-current of water oxidation was measured at 2 V *vs.* S.C.E., the same current value was obtained independently of pH values of solutions. The result is quite reasonable, since the reaction is entirely controlled by supply of photo-generated positive holes to the rutile surface⁴⁾. Although the saturated anodic photo-current is possibly controlled by amount of adsorbed alcohols on the rutile surface¹⁾, the polarization curve measured in a 0.1 M HCl alcohol solution showed almost the same current value in a potential region between 1 and 3 V *vs.* S.C.E. Then, the reactivity of alcohols on the illuminated rutile anode is expressed by the ratio of anodic photo-current measured at 2 V *vs.* S.C.E. in the buffer solutions containing alcohol to that in the corresponding aqueous solutions without alcohol, and is denoted here by i/i_0 .

Fig. 1 Plots of i/i_0 *vs.* pH of buffer aqueous solutions with 50 volume % of alcohol (○) : Methanol, (△) : 2-Propanol

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Figure 1 shows the dependence of i/i_0 on solution pH for the cases of methanol and 2-propanol. It was found that i/i_0 became high with a decrease in pH values of the solutions. Gerischer and Rösler proposed a mechanism of the "current doubling" at CdS anodes, which fitted in their experimental results⁹⁾.

where R_1 and R_2 are H or alkyl groups, and p^+ and e^- denote positive hole and electron, respectively. The results shown in Fig. 1 indicate, however, that this mechanism does not fit in the rutile electrode.

Importance of the degree of dissociation of "current doubling" agents in solutions was reported for the case of the "current doubling" reduction of H_2O_2 and *p*-benzoquinone on illuminated $\text{GaP}^{10,11)}$. Judging from a rather high pK value of methanol of 16.7¹²⁾, almost all methanol seems to be in a molecular form and no noticeable effect of the dissociation is expected in the pH region studied in this experiment. The same situation seems to be true for 2-propanol¹³⁾. Therefore, the pH dependence of the reactivity of alcohols should be brought about by another factor.

The relative position of the energy levels of the band edges at the rutile surface to that of the chemical species in the solution is believed to be fixed even when the solution pH is changed, since the same pH dependency, that is, a decrease of 59 mV *per* an increase in the unit pH, is expected between the flat-band potential of rutile⁹⁾ and the electrode potentials of both the first and second steps of the alcohol oxidation¹⁴⁾:

Hence, the relative energy position of the semiconductor to the chemical species would bring about no variation of the reactivity.

In addition, we can expect that the efficiency of the charge injection from the intermediate radical ($R_1R_2 \dot{\text{C}}(\text{OH})$) into the conduction band of rutile is not affected by the solution pH so far as the radical is not extinguished with a pH

dependency in the solution, because the intermediate radical is electronically very unstable and ready to release an electron to form its corresponding stable aldehyde or ketone molecule⁹⁾. If the extinction of the radical intermediate is responsible for the pH dependence of the reactivity, then, we should think that the rate of the extinction is high in a solution with a high pH value. This is not true, however, because Gerischer *et al.* have already found at CdS electrodes that the maximum rate of the injection attained at a high pH value of the solution²⁾.

It is believed that the rutile surface is usually covered with OH as well as water molecules^{10,11)} and that the following dissociation equilibrium is established in an aqueous solution^{9,12)}:

The point of zero charge of rutile, at which the numbers of $-\text{Ti}^+$ sites are equal to those of $-\text{Ti-O}^-$ sites, was reported to lie at pH 6.0 at room temperature¹³⁾, and $-\text{Ti}^+$ sites become abundant with a decrease of pH value of the solution^{9,12)}. In our experimental condition with high anodic polarization, $-\text{Ti}^+$ sites will be occupied with OH^- or H_2O to evolve oxygen if there is no specific adsorbate such as alcohols in aqueous solutions. $-\text{Ti-OH}$ sites may also be oxidized to something like $-\text{Ti=O}$, as is usually believed at metal electrodes in aqueous solutions¹⁴⁾. When alcohols are added into the solutions, they can adsorb on the sites of rutile surface. An alcohol molecule is considered to adsorb on a pair of bare $-\text{Ti}^+$ and $-\text{Ti-O}^-$ site^{10,15)}, and a strong adsorption is suggested on $-\text{Ti}^+$ site of the rutile surface, compared with that on $-\text{Ti-O}^-$ site^{10,13)}. Therefore, it is concluded that the high reactivity of alcohols in a low pH region is considered to be responsible for an increase in the number of active sites ($-\text{Ti}^+$) at the rutile surface.

As already stated, the flat-band potential of rutile was reported to shift to a cathodic direction by 59 mV with an increase of unit pH⁹⁾. When the rutile electrode is polarized at the fixed potential (2 V *vs.* S.C.E.) in the solutions with different pH values, magnitude of the band bending must be different depending on solution pH, and high for high solution pH. If

the adsorption is affected by the electric field of the space charge formed in the electrode, a high amount of adsorption of alcohol should be observed in alkaline solutions. The result in Fig. 1, however, shows an inverse tendency for this prediction. Then, another conclusion is drawn that the difference in the band bending plays a minor role in alcohol adsorption on rutile in a potential region where the saturated photo-current appears.

In the present study, 0.1 M HCl was used as the supporting electrolyte. Gerischer *et al.* reported that such a high concentration of chloride ion was enough to suppress preferential oxidation of HCOO^- on ZnO^{16} . However, when 0.1 M HClO_4 was used as the supporting electrolyte in place of 0.1 M HCl, the same reactivity of methanol was obtained at rutile. A low adsorbability of chloride ion on the rutile surface has already been reported by Bérubé *et al.* who considered that this phenomenon was due to a small tendency of surface titanium ions to form complexes with chloride and oxyanions¹⁷. Their result is qualitatively in good agreement with our present result that chloride ions in the electrolyte did not suppress the oxidation of the alcohols.

Rutile and ZnO are quite resemble with each other in their band gap energies and flat-band potentials¹⁸. However, one can find another example of difference in electrochemical properties between rutile and ZnO. In the case of the "current doubling" oxidation of methanol on illuminated ZnO, such a small concentration of methanol as 2×10^{-2} M was enough to give preferential oxidation of alcohols, *i. e.*, $i/i_0=2$, in 1 M KCl+0.05 M KOH aqueous solutions⁹. On the other hand, as was reported previously, the concentration of more than 15 M of alcohols

were necessary for methanol and 2-propanol to be preferentially oxidized on rutile¹¹. These difference may be connected to the difference in surface conditions between ZnO and rutile. The fact that ZnO is anodically dissolved, while rutile is not, would bring about a completely different surface condition in the anodically polarized electrodes.

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